

Universität  
Rostock



Traditio et Innovatio

# Synthesis and Characterization of new CN-based transition metal complexes

## Dissertation

zur

Erlangung des akademischen Grades  
*doctor rerum naturalium (Dr. rer. nat.)*

der Mathematisch-Naturwissenschaftlichen Fakultät  
der Universität Rostock

vorgelegt von Omar Mowafaq Younis AL-Ramadhani, geb. am 03.08.1976 in Mosul, Iraq  
Rostock, 21.04.2016

Die vorliegende Arbeit wurde in der Zeit von August 2012 bis July 2015 am Institut für Chemie der Universität Rostock am Lehrstuhl für Anorganische Chemie in der Arbeitsgruppe von Prof. Dr. Axel Schulz angefertigt.

**Dekan:** Prof. Dr. Klaus Neymeyr, Mathematisch-Naturwissenschaftliche Fakultät,  
Universität Rostock.

1. Gutachter: Prof. Dr. Axel Schulz, Universität Rostock
2. Gutachter: Prof. Dr. Uwe Rosenthal, Leibniz-Institut für Katalyse (LIKAT), Rostock

Datum der Einreichung: **20 July 2016**

Datum der verteidigung: **29 November 2016**

## **ERKLÄRUNG**

Ich versichere hiermit an Eides statt, dass ich die vorliegende Arbeit selbstständig angefertigt und ohne fremde Hilfe verfasst habe. Dazu habe ich keine außer den von mir angegebenen Hilfsmitteln und Quellen verwendet und die den benutzten Werken inhaltlich und wörtlich entnommenen Stellen habe ich als solche kenntlich gemacht.

Rostock, 21.04.2016

.....  
Omar Younis

***Affectionately Dedicated to***

***The spirit of My Father***

***My Dear Mother***

***My Own Family***

## Acknowledgements

I would like to express my heartfelt gratitude to my supervisor **Prof. Dr. Axel Schulz** for giving me the opportunity to work in this interesting field, I thank him for support, advices and guidance.

I also thank to **Dr. Jörg Harloff** and **Dr. Ronald Wustrack** for their constructive advices, guidance, helpful discussions, encouragement throughout my work and for their help in the arrangement of the thesis.

I am pleased to thank **Mrs Isabel Schicht** and **Dr. Alexander Villinger** for measuring my X-ray crystal structures, especially Dr. Alexander Villinger which knew how to bring the smile on my face when the measured structures were correct.

I also thank to **Prof. Dr. Wolfram Seidel** for his guidance and discussion with me throughout my work.

I moreover thank all the entire analytical department of the Institute of chemistry. Special thanks to **Mrs Brigitte Goronzi** and **Dr. Dirk Michalik** for measuring NMR spectra, **Mrs Angela Weihs** for measuring IR spectra and **Mrs Petra Duncker** for measuring the elemental analysis.

I also thank to **Dr. Fabian Reiß, M.Sc. Jonas Bresien** for measuring Raman spectra, and **Dipl. Chem. Katharina Sievert** for measuring TGA/DSC.

I am grateful to our research group with whom I had the pleasure of working, for their friendship, helpful discussions, and the good co-operative atmosphere.

Unforgettable, I am also thank to Ministry of higher education and scientific research of Iraq and DAAD. With their financial support, I could complete this significant research.

Most of all I thank my parents for understanding and supporting me in all my life decisions and who have stood by me always whatever I did and whatever I am, I owe it to them.

Finally, Lots of thanks to a special persons, my mother, my wife, my children, my sisters, as well as my brother, especially my wife, for their continued moral support, patience and

encouragement. They are the most important people in my life and they have been with me every step of the way.

Sincere thanks to all my friends and family who have given me support and encouragement throughout my life.

*Omar*

## Zusammenfassung

Wegen seiner ambidenten Natur ist Tricyanophosphan ( $\text{P}(\text{CN})_3$ ) ein interessanter Baustein für den Aufbau von höhermolekularen Strukturen. Metalle können entweder am Stickstoff oder/und Phosphor koordinieren, was zu einer 3:1 Donor-Stöchiometrie führt. Mit Blick auf die Koordinationschemie ist ebenfalls Tetracyanopyrrolid ( $\text{TCP}^-$ ) interessant, da es mit fünf Donorzentren ausgestattet ist: zwei Cyanid-Gruppen in 2- und zwei in 3-Position sowie ein Stickstoffatom im Pyrrolidring. Somit ist das  $\text{TCP}^-$ -Anion ein sehr vielseitiger Ligand und sehr gut geeignet, Koordinationspolymere zu bilden. Demzufolge scheint es aus koordinationschemischer Sicht interessant zu sein, das neutrale  $\text{P}(\text{CN})_3$  und anionische  $\text{TCP}^-$  als neue CN-basierte Liganden in der Übergangsmetallchemie zu verwenden.

Im ersten Teil der vorliegenden Arbeit wurde das Koordinationsverhalten von Tricyanophosphin untersucht, um CN-reiche Phosphorverbindungen zu erhalten, ausgehend von Umsetzungen von  $\text{P}(\text{CN})_3$  mit schwachkoordinierenden Anionen (WCAs), Lewis-Basen, Übergangsmetallkomplexen und Raumtemperatur-Ionischen Flüssigkeiten (RT-ILs). Die meisten der erhaltenen Verbindungen waren Polymere, weil sie in den meisten Lösungsmitteln unlöslich waren. Alle präparierten Verbindungen wurden mittels der üblichen Analytik charakterisiert.

Im zweiten Teil dieser Arbeit wurden neue Übergangsmetallkomplexe synthetisiert, die das Tetracyanopyrrolid-Anion  $[\text{C}_4(\text{CN})_4\text{N}]^-$  ( $\text{TCP}^-$ ) ausgehend von Tetracyanopyrrol (HTCP) enthalten. Hervorzuheben ist dabei, dass ein neues 1D-Koordinationspolymer aus der Reaktion von HTCP mit  $\text{Mn}(\text{acac})_3$  isoliert werden konnte. Des Weiteren wurden neue TCP-Salze des Typs  $[\text{R}_3\text{NH}]\text{TCP}$  ( $\text{R} = \text{Me}$  or  $^i\text{Pr}$ ) synthetisiert, ausgehend von der Reaktion von  $[\text{R}_3\text{NH}]\text{Cl}$  mit HTCP in Wasser. Alle neuen Verbindungen wurden mittels Einkristall-Diffraktometrie und anderer Analytik charakterisiert.

## Summary

Due to its ambident nature of tricyanophosphine,  $\text{P}(\text{CN})_3$ , is an interesting building block for the formation of supramolecular architectures. Metals can either coordinate at nitrogen or/and phosphorus leading to a 3:1 donor stoichiometry. With respect to coordination chemistry tetracyanopyrrolide ( $\text{TCP}^-$ ) is also interesting, because it is furnished with five donor centers: two cyanide group in 2- and two in 3- position and one pyrrolide N-ring atom. Therefore, the anion is an extremely versatile ligand with potential to form coordination polymers. Thus from the coordination chemistry view it seems interesting to utilize the neutral  $\text{P}(\text{CN})_3$  and the anionic  $\text{TCP}^-$  as new CN-based ligands in transition metal chemistry.

In the first part of this thesis the coordination behavior for tricyanophosphine was studied, for preparing CN-rich phosphorous compounds from the reaction of tricyanophosphine with weakly coordinating anions (WCAs), Lewis bases, transition metal complexes and room temperature ionic liquids (RT-ILs). Most of these obtained compounds were polymers because they were insoluble in most of the solvents. All prepared compounds were characterized by common analytics.

In the second part of this thesis the new transition metal complexes containing the tetracyanopyrrolide anion  $[\text{C}_4(\text{CN})_4\text{N}]^-$  (TCP) from tetracyanopyrrole (HTCP) were synthesized. Remarkably, a new 1D-coordination polymer from reaction of HTCP with  $\text{Mn}(\text{acac})_3$  could be isolated. Additionally, new TCP- salts of the type  $[\text{R}_3\text{NH}]\text{TCP}$  (R= Me or  $^n\text{Pr}$ ) from reaction  $[\text{R}_3\text{NH}]\text{Cl}$  with HTCP in water were synthesized. All new compounds were characterized by mean of X-ray crystallography and other analytics.

# Table of contents

List of abbreviations.....	XI
Unit conversion.....	XII
1. Objective.....	1
2. Introduction.....	2
2.1 Phosphorus cyanide compounds.....	2
2.2 Tetracyanopyrrolide compounds .....	10
3. Results and discussion.....	20
3.1 Synthesis of tricyanophosphine.....	20
3.2 Reactions of P(CN) <sub>3</sub> with weakly coordinating anions (WCA) <sup>-</sup> and Lewis bases.....	21
3.2.1 General.....	21
3.2.2 Reactions of P(CN) <sub>3</sub> with (WCA) <sup>-</sup> .....	22
3.2.3 Reactions of P(CN) <sub>3</sub> with Lewis bases.....	24
3.2.4 Reaction of P(CN) <sub>3</sub> with triphenylphosphine.....	28
3.3 Reactions of P(CN) <sub>3</sub> with transition metal complexes.....	30
3.3.1 General.....	30
3.3.2 Reaction of P(CN) <sub>3</sub> with dichloro(p-cymene)ruthenium(II) dimer.....	30
3.3.3 Reaction of P(CN) <sub>3</sub> with tetrakis(triphenylphosphine) palladium(0).....	31
3.3.4 Reaction of P(CN) <sub>3</sub> with tris(diphenylphosphinomethyl)ethane nickel(0).....	33
3.3.5 Reaction of P(CN) <sub>3</sub> with hydrido(3,5-dimethylpyrazolyl)borate tricarbonyl tungsten(II) and hexafluorophosphate.....	35
3.3.6 Reaction of P(CN) <sub>3</sub> with tris(propionitrile)tricarbonyl molybdenum(0).....	35
3.4 Reactions of P(CN) <sub>3</sub> with Room Temperature Ionic Liquids .....	36

3.4.1	General.....	36
3.4.2	Reaction of P(CN) <sub>3</sub> with EMIm.N(CN) <sub>2</sub> in dichloromethane.....	36
3.4.3	Reaction of P(CN) <sub>3</sub> with EMIm.N(CN) <sub>2</sub> in tetrahydrofuran.....	37
3.4.4	Reaction of P(CN) <sub>3</sub> with silver dicyanoamide-tris(pentafluorophenyl) borane•diether.....	39
3.5	Reactions of tetracyanopyrrolide.....	40
3.5.1	General.....	40
3.5.2	Synthesis of tetracyano-1,4-dithiin.....	40
3.5.3	Synthesis of tetramethylammoniumtetracyanopyrrolide.....	41
3.5.4	Synthesis of silver tetracyanopyrrolide.....	42
3.5.5	Synthesis of tetracyanopyrrole.....	43
3.5.6	Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis (tetrahydrofuran)copper(II).....	46
3.5.7	Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate.....	48
3.5.8	Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate.....	50
3.5.9	Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II) acetonitrile solvate.....	53
3.5.10	Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II) acetonitrile solvate.....	55
3.5.11	Synthesis of di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese(III).....	57
3.5.12	Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolido chromium(III).....	59
3.5.13	Reaction of HTCP with tri(acetylacetonate)manganese(III).....	61
3.5.14	Synthesis of trimethylammoniumtetracyanopyrrolide.....	63
3.5.15	Synthesis of tripropylammoniumtetracyanopyrrolide.....	66
4.	Summary.....	70

<b>5. Appendix .....</b>	<b>74</b>
<b>5.1 Experimental part .....</b>	<b>74</b>
<b>5.1.1 Working technique.....</b>	<b>74</b>
<b>5.1.2 Analytical methods.....</b>	<b>75</b>
<b>5.1.3 Synthesis of starting materials.....</b>	<b>77</b>
<b>5.1.4 Synthesis of compounds.....</b>	<b>82</b>
<b>5.2 Data on the X-ray structure analysis.....</b>	<b>108</b>
<b>5.3 Selected interatomic distances and angles in the structures.....</b>	<b>113</b>
<b>5.4 List of figures.....</b>	<b>141</b>
<b>5.5 List of schemes.....</b>	<b>143</b>
<b>5.6 List of tables.....</b>	<b>146</b>
<b>6. References.....</b>	<b>147</b>

## List of abbreviations

<b>ATR</b>	<i>Attenuated Total Reflection</i>	<b>NMR</b>	<i>Nuclear Magnetic Resonance</i>
<b>acac</b>	acetylacetonate	<b><i>o</i></b>	<i>ortho</i>
<b>BMI</b>	1-butyl-3-methylimidazolium	<b><i>p</i></b>	<i>para</i>
<b>COD</b>	Cyclooctapentadiene	<b>ppm</b>	<i>parts per million</i>
<b>DFT</b>	<i>density functional theory</i>	<b>1,10-phen</b>	1,10-phenanthroline
<b>DMAP</b>	Dimethylaminopyridine	<b><i>p</i>-cymene</b>	1-methyl-4-(1-methyl ethyl)benzene
<b>DMSO</b>	Dimethylsulfoxide	<b>q</b>	Quartet (NMR)
<b>DSC</b>	<i>Differential Scanning Calometry</i>	<b><i>RT-ILs</i></b>	Room Temperature Ionic Liquids
<b>DAN</b>	1,8-Diaminonaphthalene	<b>r<sub>cov</sub></b>	covalent radius
<b>DMF</b>	<i>N, N</i> -Dimethylformamide	<b><math>\delta</math></b>	Chemical shift (NMR)
<b>EA</b>	Elemental analysis	<b>s</b>	<i>strong</i> (IR), Singulett (NMR)
<b>EI</b>	<i>electron impact</i>	<b>Triphos</b>	1,1,1-tris(diphenylphosphinomethyl)ethane
<b>Et<sub>3</sub>N</b>	Triethylamine	<b>Tp<sup>-</sup></b>	Hydridotris(3,5-dimethylpyrazolyl)borate
<b>EtCN</b>	Propionitrile	<b>TMEDA</b>	Tetramethylethylenediamine
<b>ESI</b>	Electrospray-Ionisation	<b>TCP</b>	Tetracyanopyrrolide
<b>EMIm</b>	1-ethyl-3-methylimidazolium	<b>tcpc</b>	Tricyanopyrrole-2-carboxamide
<b>HTCP</b>	Tetracyanopyrrole	<b>thf</b>	Tetrahydrofuran
<b>HUMO</b>	Highest Unoccupied Molecular Orbital	<b>T<sub>dec</sub></b>	Decomposition temperature
<b>IR</b>	Infrared	<b>TGA</b>	<i>Thermogravimetric analysis</i>
<b>LUMO</b>	Lowest Unoccupied Molecular Orbital	<b>v:v</b>	volume ratio
<b><i>m</i></b>	<i>medium</i> (IR), <i>meta</i> (NMR), multiplett (NMR)	<b>WCA</b>	<i>weakly coordinating anion</i>
		<b>w</b>	<i>weak</i> (IR)

---

## Unit conversion

Quantity	Symbol	Name	Conversion
Frequency	MHz	Megahertz	1 MHz = $10^6 \text{ s}^{-1}$
	Hz	Hertz	1 Hz = $1 \text{ s}^{-1}$
Length	Å	Angstrom	1 Å = $10^{-10} \text{ m}$
	µm	micrometer	1 µm = $10^{-6} \text{ m}$
	nm	nanometer	1 nm = $10^{-9} \text{ m}$
Power	mW	Milliwatt	1 mW = $10^{-3} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-3}$
Temperature	°C	degrees Celsius	$x^\circ\text{C} = (x + 273.15) \text{ K}$
Volume	mL	Milliliter	1 ml = $1 \text{ cm}^3 = 10^{-6} \text{ m}^3$
Heat	kJ	Kilojoule	1 kJ = $10^3 \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2}$
Wavenumber	$\text{cm}^{-1}$	reciprocal centimeter	$1 \text{ cm}^{-1} = 100 \text{ m}^{-1}$
Time	h	hour	1 h = 3600 s
	min	Minute	1 min = 60 s
Pressure	bar	bar	1 bar = 100,000 Pa
	hpa	hectopascal	1 hPa = 100 Pa
Energy	eV	electron-volt	1 eV = $1.6 \times 10^{-19} \text{ J}$

## 1. Objective

The aim of this study was to examine the coordination chemistry of novel donor-acceptor complexes (with new CN linkers) containing anions such as tetracyanopyrrolide (TCP) and neutral phosphorus(III)cyanide. Surprisingly, the knowledge about the general coordination behavior of  $\text{P}(\text{CN})_3$  is very limited yet. Therefore the first coordination experiments for  $\text{P}(\text{CN})_3$  addressed the question of coordination control. Strong  $\pi$ -bases were used to force P-coordination, while first row or late transition metals were expected to bind *via* nitrogen. In addition, the nitrogen position may be blocked by formation of Lewis adducts with  $\text{B}(\text{C}_6\text{F}_5)_3$ . Finally, if  $\text{P}(\text{CN})_3$  shows a similar behavior like  $\text{PF}_3$  in the coordination, indeed, the synthesis of homoleptic complexes was an intriguing synthetic goal.

With respect to coordination chemistry tetracyanopyrrolide is furnished with five donor centers, three of which are of different type: cyanide group in 2- and 3- position and the pyrrolide N-ring atom. Therefore the anion is an extremely versatile ligand with the potential to form coordination polymers. The utilization of tetracyanopyrrolide ions in combination with transition metal ions was investigated and additionally the possibility of  $\pi$ -bonding by the anionic pyrrolide system was tested, because the pyrrolide is considered  $\pi$ -isoelectronically to cyclopentadienide.

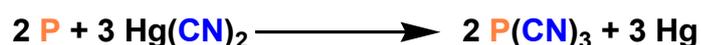
For characterization of all prepared compounds both vibrational spectroscopic methods (Raman and IR spectroscopy), multi-nuclear magnetic resonance spectroscopy ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , INEPT  $^{29}\text{Si}$  and  $^{31}\text{P}$ ) in solution, elemental analysis, thermal analysis (DSC/TGA), mass spectroscopy and X-Ray were applied.

## 2. Introduction

### 2.1 Phosphorus cyanide compounds

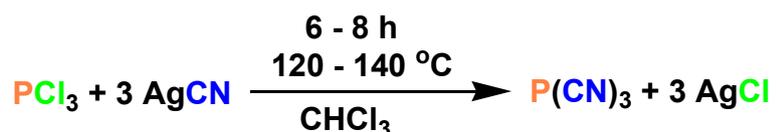
The first supposed connection between the cyanide and phosphorus is based on a publication by *H. Davy* from 1816.<sup>[1]</sup> *H. Davy* described the conversion of mercury cyanide with some elements, including phosphorus, whereby the respective compounds were formed, but were not isolated or characterized.

In 1835 *Cenedella* also described a supposed synthesis of phosphorus cyanide compound.<sup>[2]</sup> Similar to the method by *H. Davy*, elementary phosphorus reacted with  $\text{Hg}(\text{CN})_2$  by carefully heating in a glass tube, but the resulting product had clearly different properties than the later isolated and characterized phosphorus tricyanide. Therefore it was not established as a synthetic method.



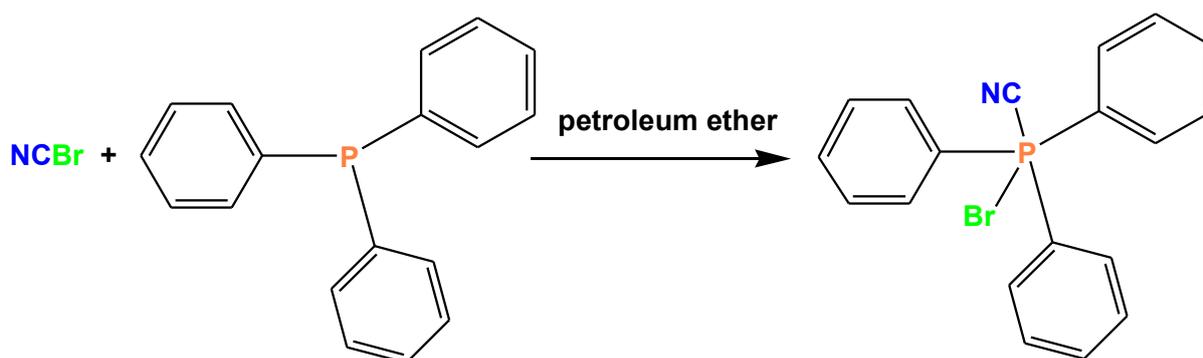
**Scheme 1:** Supposed formation of  $\text{P}(\text{CN})_3$  by *H. Davy* in 1816<sup>[1]</sup> and *Cenedella* 1835.<sup>[2]</sup>

The first proper synthetic method and characterization of  $\text{P}(\text{CN})_3$  was published by *Hübner* and *Wehrhane* in 1863 and 1864.<sup>[3, 4]</sup> They filled  $\text{AgCN}$ , phosphorus and dried chloroform in a sealed vial, which was heated to 120 - 140 °C for 6 - 8 hours.



**Scheme 2:** Preparation of  $\text{P}(\text{CN})_3$  by *Hübner* and *Wehrhane* 1863/64.<sup>[3, 4]</sup>

The first who succeeded in synthesizing a phosphorus<sup>V</sup> cyanide were *Steinkopf* and *Buchheim* in 1921.<sup>[5]</sup> For the synthesis of a pentavalent phosphorus, which contained a cyanide, triphenylphosphine was reacted with cyanogen bromide in petroleum ether, obtaining triphenylphosphine bromide cyanide  $\text{PPh}_3(\text{Br})\text{CN}$ .



**Scheme 3:** Formation of  $\text{PPh}_3\text{Br}(\text{CN})$  by *Steinkopf* and *Buchheim* 1921.<sup>[5]</sup>

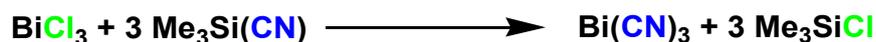
One of the first synthetic methods for  $[\text{PX}_6]^-$  anions by *Lange* and *Müller* was published in 1930.<sup>[6]</sup> Hydrogen fluoride was reacted with phosphorus pentoxide in the presence of ammonia and after recrystallization with ammonia- ammonium hexafluoridophosphate was obtained.



**Scheme 4:** Synthesis method of the first  $\text{P}^{\text{V}}$  salt by *Lange* and *Müller* 1930.<sup>[6]</sup>

A method for the preparation of phosphorus pentacyanide was developed by *Gall* and *Schüppen* in 1930.<sup>[7]</sup> The conversion of phosphorus tricyanide with cyanogen was performed under high pressure and heating in a sealed tube. Recent studies have shown that  $\text{P}(\text{CN})_5$  is formed in oxidizing solvents, but in solvents such as chloroform or dichloromethane it decomposes to  $\text{P}(\text{CN})_3$  and  $(\text{CN})_2$ .<sup>[8]</sup>

In 1958,  $\text{Me}_3\text{SiCN}$  was used by *Bither et al.* as a cyanation reagent for the first time.<sup>[9]</sup> By a substitution reaction proceeding from half-metal-halogen compounds were obtained the half-metal-cyanide compounds. For example, it was possible to synthesize bismuth tricyanide by the reaction of bismuth trichloride with  $\text{Me}_3\text{SiCN}$ .



**Scheme 5:** First cyanation with  $\text{Me}_3\text{SiCN}$  by *Bither et al.* 1958.<sup>[9]</sup>

The salts of  $[\text{PCl}_4]^-$  are based on a publication of *Masaguer* from 1957.<sup>[10]</sup> The reaction of  $\text{PCl}_3$  with sulfuryl chloride has been described, whereby  $[\text{SO}_2\text{Cl}][\text{PCl}_4]$  was obtained .



**Scheme 6:** Synthesis of the first  $\text{P}^{\text{III}}$  - salts of *Masaguer* 1957.<sup>[10]</sup>

Phosphorus tricyanide can be synthesized also by the method of *Bither et al.*<sup>[9]</sup> from reaction of  $\text{PCl}_3$  with  $\text{Me}_3\text{SiCN}$ . A further alternative synthesis method for  $\text{P}(\text{CN})_3$  was developed by *Maier* in 1963.<sup>[11]</sup> The reaction of phosphorus bromide was carried out with silver cyanide in acetonitrile. The synthesis method according to *Maier* for  $\text{P}(\text{CN})_3$  and also to *Dillon* and *Platt*<sup>[12]</sup> is carried out in diethylether .

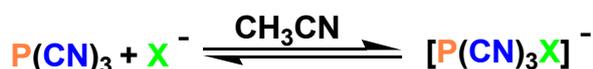


**Scheme 7:** Synthesis of  $\text{P}(\text{CN})_3$ , starting from  $\text{PBr}_3$  by *Maier* 1963.<sup>[11]</sup>

The effectiveness of the method of *Hübner* and *Wehrhane* was increased by *Jones* and *Coskran*.<sup>[13]</sup> They also used dried acetonitrile, but the reaction was carried out in a nitrogen atmosphere. Here, the product could already be obtained with good yield after two hours at room temperature.

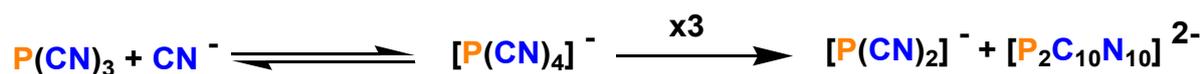
In addition to the mentioned anion  $[\text{P}(\text{CN})_3\text{X}]^-$  also the cation  $[\text{P}(\text{CN})_4]^+$  was found, but only in solution along with other tetrapseudohalogenphosphonium cations.<sup>[8]</sup>

In 1980 *Wilkie et al.* reported the supposed compound potassium tetracyanidophosphate  $\text{K}[\text{P}(\text{CN})_4]$ .<sup>[14]</sup> As described in 1981/82,<sup>[15, 16]</sup> it may be due the Lewis acidity of the phosphorus atom that leads to adduct formation with halides.

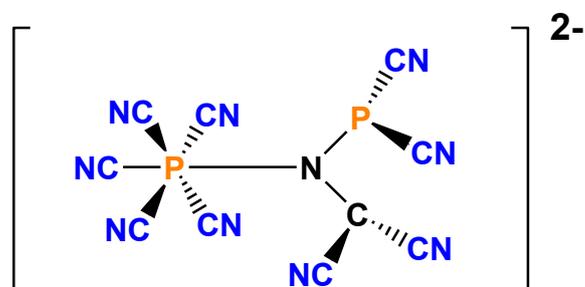


**Scheme 8:** Adduct formation of  $\text{P}(\text{CN})_3$  with halides by *Dillon* 1981/82.<sup>[15, 16]</sup>

Further investigations by *Schmidpeter et al.*<sup>[17]</sup> have shown that the  $[\text{P}(\text{CN})_4]^-$  ion in solution is formed by adding  $\text{CN}^-$  to  $\text{P}(\text{CN})_3$ , but then an intermolecular redox reaction of decomposition took place rapidly. This produced a dicyanophosphide,  $[\text{P}(\text{CN})_2]^-$  and the unusual anion  $[\text{P}_2\text{C}_{10}\text{N}_{10}]^{2-}$  .

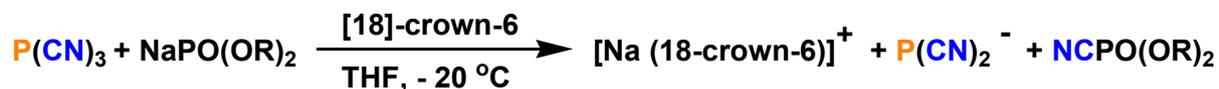


**Scheme 9:** In-situ formation and decay of  $[\text{P}(\text{CN})_4]^-$



**Figure 1:** Schematic structure of the anion  $[\text{P}_2\text{C}_{10}\text{N}_{10}]^{2-}$

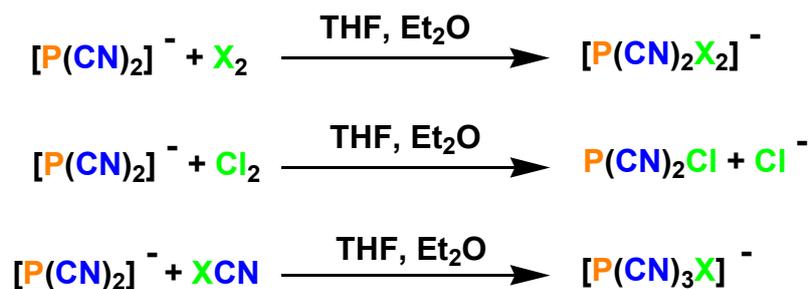
Dicyanophosphide is described for the first time by *Schmidpeter* and *Zwaschka* 1977. The synthesis and properties of this ion were reported.<sup>[18]</sup> It is prepared by reacting  $\text{P}(\text{CN})_3$  with dialkylphosphites,  $\text{NaPO}(\text{OR})_2$ , and [18] crown-6 in THF, under cooling to  $-20^\circ\text{C}$ .



**Scheme 10:** Formation of dicyanophosphide anion.

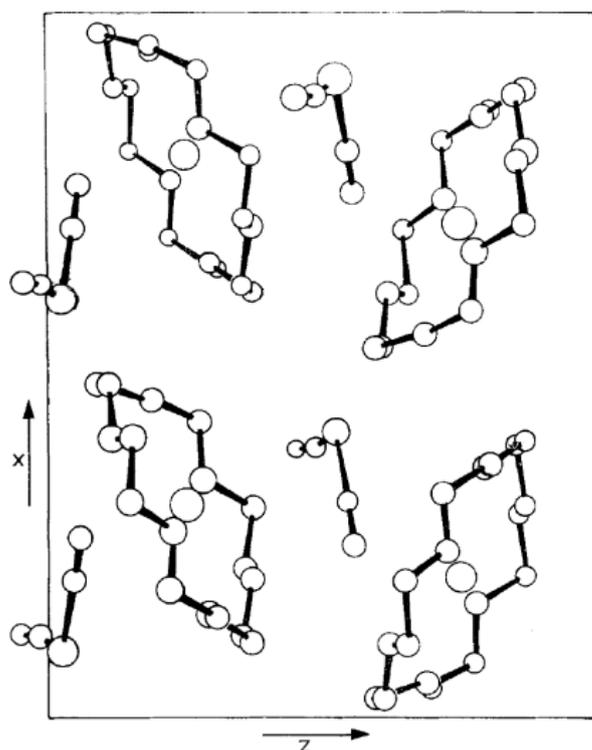
Dicyanophosphide can be considered as a pseudohalide which means that to  $\text{P}(\text{CN})_3$  could be described as inter pseudo halogen compound. This is consistent with the electrophilic transmission of cyano residue on the dialkylphosphate during the above synthesis. Similarly, the addition of a halide to  $[\text{P}(\text{CN})_3\text{X}]^-$  according to scheme 8 is analogous to the formation of  $\text{I}_3^-$  from  $\text{I}_2$  and  $\text{I}^-$ .

Substituting  $[\text{P}(\text{CN})_2]^-$  with  $\text{X}_2$  ( $\text{X} = \text{Br}, \text{I}$ ) by the oxidative addition was gave  $[\text{P}(\text{CN})_2\text{X}_2]^-$  anions also addition  $\text{XCN}$  instead of halogens to  $[\text{P}(\text{CN})_2]^-$  anion was gave  $[\text{P}(\text{CN})_3\text{X}]^-$  ion. By contrast, with  $\text{Cl}_2$  under the same conditions only  $\text{P}(\text{CN})_2\text{Cl}$  is formed.<sup>[19]</sup>



**Scheme 11:** Reactions of  $[\text{P}(\text{CN})_2]^-$  with halogens and cyanogen halides.

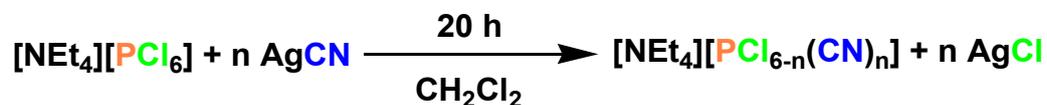
Dicyanophosphide is angled; in the crystal  $[\text{18}] \text{-crown-6-K}[\text{P}(\text{CN})_2]$  the nitrogen of the CN group coordinates to the  $\text{K}^+$  ion, so that zigzag-shaped P-C-N  $\cdots$  K  $\cdots$  N-C-P- chains are observed in crystal structure.<sup>[20]</sup>



**Figure 2:** Crystal structure of  $[\text{18}] \text{-crown-6-K}[\text{P}(\text{CN})_2]$ <sup>[20]</sup> with P-C-N  $\cdots$  K  $\cdots$  N-C-P-chains.

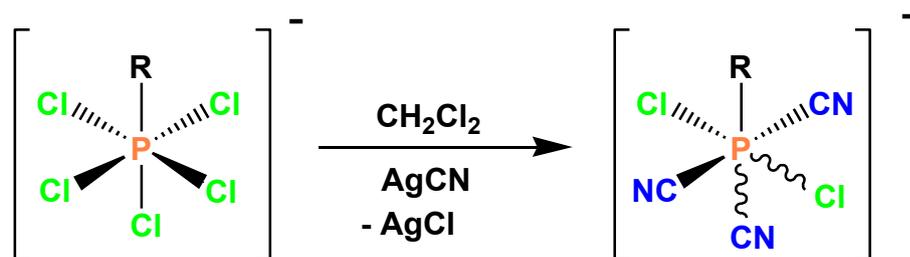
*Dillon* and *Platt* developed in 1982-83 synthetic methods for Phosphor<sup>V</sup>cyanide halide compounds.<sup>[12, 21]</sup> Silver cyanide was at that time the conventional reagent for introducing cyanide. By the reaction of  $[\text{NEt}_4][\text{PCl}_6]$  with  $\text{AgCN}$  in  $\text{CH}_2\text{Cl}_2$  the mono-, di- and tricyanido derivatives were obtained (Scheme 12). The compound  $[\text{PCl}_3(\text{CN})_3]^-$  show at room temperature the greatest stability to hydrolysis in air and further substitutions. The authors

attributed this to the lowering of the free  $T_{2g}$  3d orbitals through the CN groups. Due to this lowering of the orbitals can held  $\pi$  interaction with the lone pairs of chlorine atoms, with the strengthening and stabilizing of the P–Cl bonds.



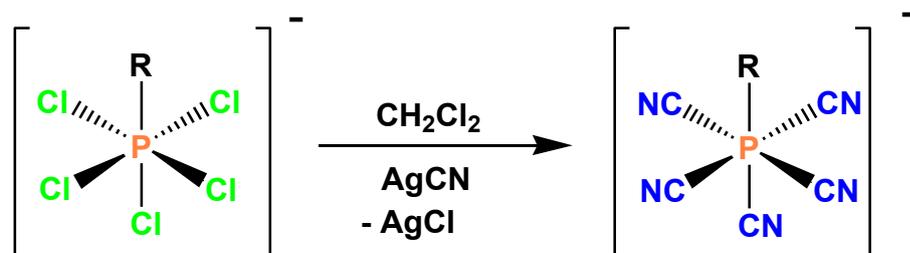
**Scheme 12:** Synthesis of  $[\text{PCl}_{6-n}(\text{CN})_n]^-$  anion ( $n = 1-3$ ) by *Dillon and Platt* 1982/83.<sup>[12, 21]</sup>

*Dillon et al.* investigated in 1986/88 organochloridophosphate (V) anions.<sup>[22, 23]</sup> They discovered that the coordination behavior of  $[\text{PPhCl}_5]^-$  and  $[\text{P}(\text{CCl}_3)\text{Cl}_5]^-$  are not similar to  $[\text{PCl}_6]^-$  towards the cyanation behavior using silver cyanide. The substitution at this two compounds ends also in the stable tricyanido form ( $[\text{PPhCl}_2(\text{CN})_3]^-$  or  $[\text{P}(\text{CCl}_3)\text{Cl}_2(\text{CN})_3]^-$ ).



**Scheme 13:** Cyanation investigation of *Dillon et al.* 1986/88<sup>[22, 23]</sup> only three chlorine atoms are substituted by CN; R=Ph,  $\text{CCl}_3$ .

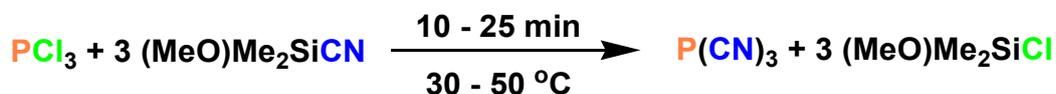
In contrast, the authors found that inserting a small alkyl group, a complete substitution of halogen by cyanide takes place.



**Scheme 14:** Cyanation investigation of *Dillon et al.* 1986/88<sup>[22, 23]</sup> all chlorine atoms are substituted by CN; R = Me, Et.

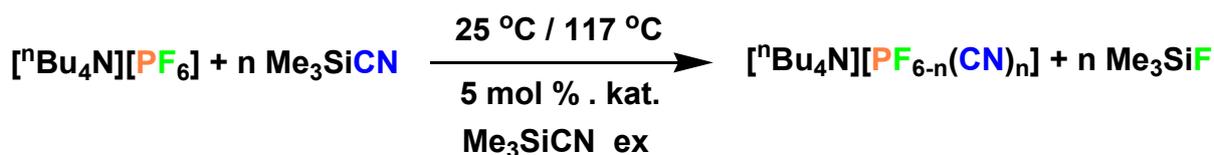
The authors explained these results by the fact that the small alkyl group have a +I-effect that destabilizes the compound and makes the formation of a five-coordinate possible for the transition state, which supports a substitution. Electron-withdrawing substituent, with a –I-effect stabilizes, the hexa- coordinate phosphate anion, so that it is not possible to form a five-coordinate transition state. However, in contradiction to this, is the substitution of  $[\text{P}(\text{C}_6\text{F}_5)\text{Cl}_5]^-$  by means of AgCN for  $[\text{P}(\text{C}_6\text{H}_5)\text{Cl}(\text{CN})_4]^-$ ,<sup>[23]</sup> although the pentafluorophenyl group with a significantly stronger –I-effect exerted as phenyl radical and should, therefore, be theoretically substituted only up to three times. One possible explanation for this is the fact that the pentafluorophenyl group accepts a larger space consumption and facilitates the dissociation of chlorido- ions.

In 1991 *Krolevets et al.* developed one of the most effective methods for the synthesis of phosphortricyanide.<sup>[24]</sup> By reacting phosphorus trichloride with Methoxydimethylsilylcyanide for 10 to 25 minutes at 30 - 50 °C  $\text{P}(\text{CN})_3$  is obtained with a yield of 97% .  $(\text{MeO})\text{Me}_2\text{SiCN}$  is in contrast with  $\text{Me}_3\text{SiCN}$  to a significantly stronger cyanating, by the +M-effect of the other group. The mesomeric effect leads to an increase of the electron density in the system, which in turn promotes a substitution.



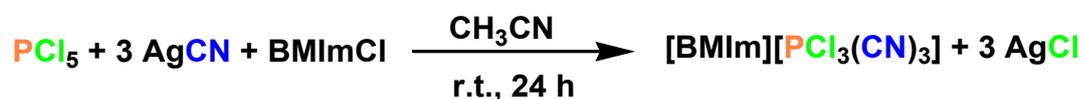
**Scheme 15:** Preparation of  $\text{P}(\text{CN})_3$ , with  $(\text{MeO})\text{Me}_2\text{SiCN}$ .<sup>[24]</sup>

*K. Sievert* and *K. Bläsing* in our group developed methods for catalytic syntheses of phosphorus<sup>V</sup> cyanide compounds.<sup>[25]</sup> As cyanation reagent trimethylsilyl cyanide was used by addition of catalytic amounts of a variety of Lewis acids. This could be achieved at room temperature and in short times. By reaction of  $[\text{nBu}_4\text{N}][\text{PF}_6]$  with  $\text{Me}_3\text{SiCN}$  the mono-, di-, tri- and tetracyanido phosphates are obtained.



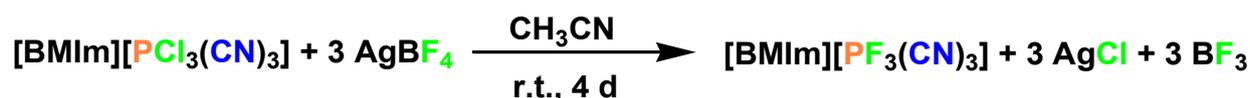
**Scheme 16:** Synthesis of  $[\text{PF}_{6-n}(\text{CN})_n]^-$  anion ( $n = 1-4$ ) by *Sievert* and *Bläsing* 2014.<sup>[25]</sup>

The first use of cyanide phosphate anion in ionic liquids derived from a patent by *The Nippon Synthetic Chemical Industry CO. LTD* from 2012.<sup>[26]</sup> By reacting phosphorus pentachloride, silver cyanide and BMImCl, will obtain the BMIm- salt of trichloridotricyanidophosphates at room temperature.



**Scheme 17:** Synthesis of [BMIm][PCl<sub>3</sub>(CN)<sub>3</sub>].<sup>[26]</sup>

By reacting the product with silver tetrafluoridoborate can also be accessed a to trifluoridotricyanidophosphate analogous anion. The characterization was carried out by mean of <sup>1</sup>H NMR, <sup>31</sup>P NMR, IR spectroscopy and mass spectrometry.



**Scheme 18:** Synthesis of [BMIm][PF<sub>3</sub>(CN)<sub>3</sub>].

In the literature, significantly fewer from known, the compounds can be found to the other elements of group 15. All arsenic, antimony and bismuth compounds so far were only described as tricyanide E(CN)<sub>3</sub>, which can be synthesized similar to the phosphorus trichloride from the element trichloride with a cyanation reagent. The characterization was carried out by mean of melting point and elemental analysis.<sup>[27]</sup> The molecular structure for arsenic tricyanide was published by *K. Emerson and D. Britton* in 1963.<sup>[28]</sup>

## 2.2 Tetracyanopyrrolide compounds

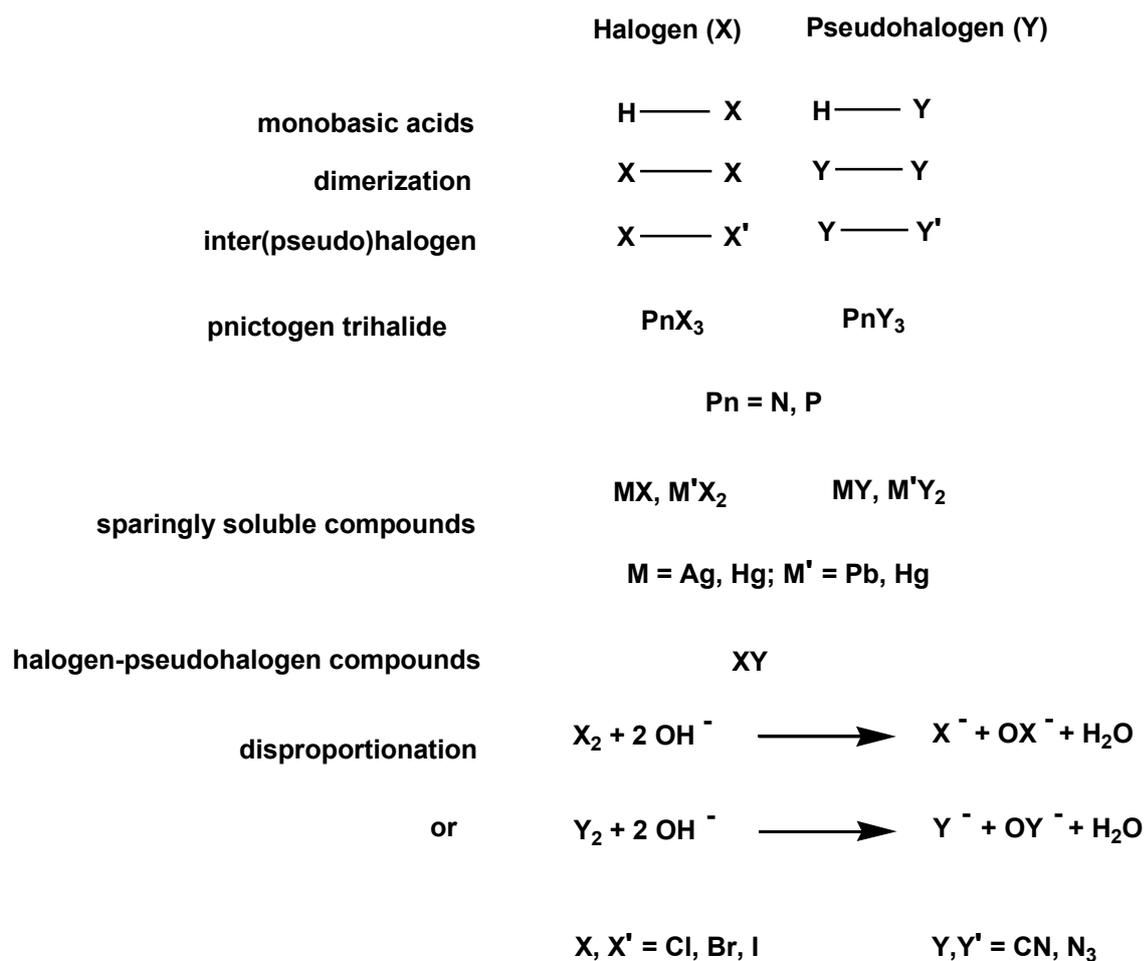
Cyanocarbons are a class of compounds that consist solely of C and N, known as neutral species and as anions. The functionality is mainly dominated by the high number of present cyano groups, which are strongly electron withdrawing groups and participate by resonance with the  $\pi$  system of the underlying carbon ring or chain.

Cyanocarbons are highly electron deficient and are only weakly basic and weakly coordinating.<sup>[29]</sup> Azole ring based on polynitriles<sup>[30]</sup> and cyano-substituted pyrroles<sup>[31]</sup> have been in the focus of theoretical investigations showing the aromaticity, the stability vs. oxidation and decreasing basicity with increasing number of CN groups.

The pentacyanocyclopentadienide anion  $[\text{C}_5(\text{CN})_5]^-$  is a prominent member due to its high symmetry. The coordination chemistry of  $[\text{C}_5(\text{CN})_5]^-$  has received substantial attention during the last years for the preparation of metal-organic coordination polymers.<sup>[32, 33, 34, 35]</sup> In contrast, the chemistry of its congener, in which a nitrogen atom replaces one ring carbon atom, namely the tetracyanopyrrolide anion (TCP) is still scarcely explored. Only some references about tetracyanopyrrolide were reported.<sup>[36, 37, 38]</sup>

The term *pseudohalogen* was introduced in 1925 for strongly bond, linear or planar univalent radicals ( $\text{Y}\cdot$ , e.g.,  $\text{Y} = \text{CN}, \text{OCN}, \text{N}_3, \text{SCSN}_3$ ), which can form anions ( $\text{Y}^-$ ), hydracids ( $\text{H-Y}$ ), and neutral species ( $\text{Y-Y}$ , dipseudohalogens) as well as the inter-pseudohalogens ( $\text{X-Y}$ ,  $\text{X} = \text{halogen or pseudohalogen}$ )<sup>[39, 40, 41]</sup> and has remained a widely used this concept ever since.

An extension of the concept of pseudohalogens means compounds also singly negatively charged ions form and fulfill the characteristics shown in scheme 19. These are molecules that are no longer linear but planar. An important example of pseudohalides is the  $[\text{CS}_2\text{N}_3]^-$  ion.<sup>[42, 43, 44]</sup> Two examples of planar pseudohalides are dicyanamide ( $[\text{N}(\text{CN})_2]^-$ ) and the tricyanmethanide ( $[\text{C}(\text{CN})_3]^-$ ).<sup>[45, 46]</sup>

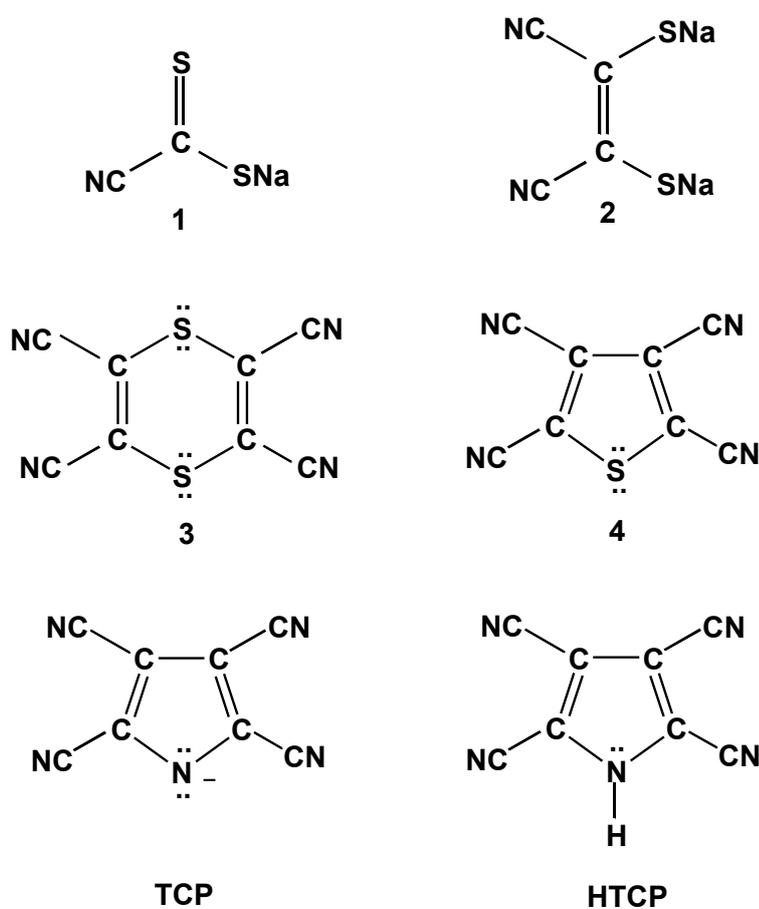


**Scheme 19:** The most important halogen and pseudohalogen compounds compared.

Some other known pseudohalogen acids are isocyanic (HNCO), cyanuric acid C<sub>3</sub>N<sub>3</sub>(OH)<sub>3</sub>, fulminic acid (HCNO) as the thiocyanic (HSCN) and isothiocyanic acid (HNCS). In deprotonated form, they are known as the pseudohalides ago as cyanate (OCN<sup>-</sup>), isocyanate (NCO<sup>-</sup>), thiocyanate (SCN<sup>-</sup>) (also called rhodanide), isothiocyanate (NCS<sup>-</sup>) and fulminate (CNO<sup>-</sup>), all with one negative charge. But selenocyanate (SeCN<sup>-</sup>) or tellurocyanate (TeCN<sup>-</sup>) belong to known pseudohalides. In these examples, already a trend becomes clear how to extend such systems. In the case of cyanide it became a cyanate by the addition of a chalcogen. Here this was varied from oxygen to tellurium. Similarly, it is possible to produce new pseudohalides and to extend the concept of pseudohalogens.<sup>[47, 48, 49]</sup>

The starting materials that are needed for the synthesis of tetracyanopyrrolide are sodium cyanide (NaCN), sodium azide (NaN<sub>3</sub>) and carbon disulfide (CS<sub>2</sub>). Both NaN<sub>3</sub> and NaCN in it are pseudohalogen compounds. Pseudohalogens are compounds which are no halogens, but behave as halogens or have specific properties that have also halogens. In the textbooks of

inorganic chemistry pseudo-elements are discussed.<sup>[50]</sup> The chemistry of thiacyanocarbons (Scheme 20) was developed by *Bähr* and *Schleitzer* as early as 1955-1957.<sup>[51]</sup> They started from CS<sub>2</sub> and NaCN to obtain sodium cyanodithioformate, which dimerizes under oxidizing conditions to give disodium dimercaptomaleodinitrile (**2**) as shown in (Scheme 20). Both **1** or **2** can be oxidized to afford tetracyano-1,4-dithiin (**3**) in high yield.<sup>[51, 52]</sup> The reactive dithiin **3** extrudes sulfur at elevated temperatures to give tetracyanothiophene **4**.



**Scheme 20:** Thiacyanocarbons and tetracyanopyrrolides.

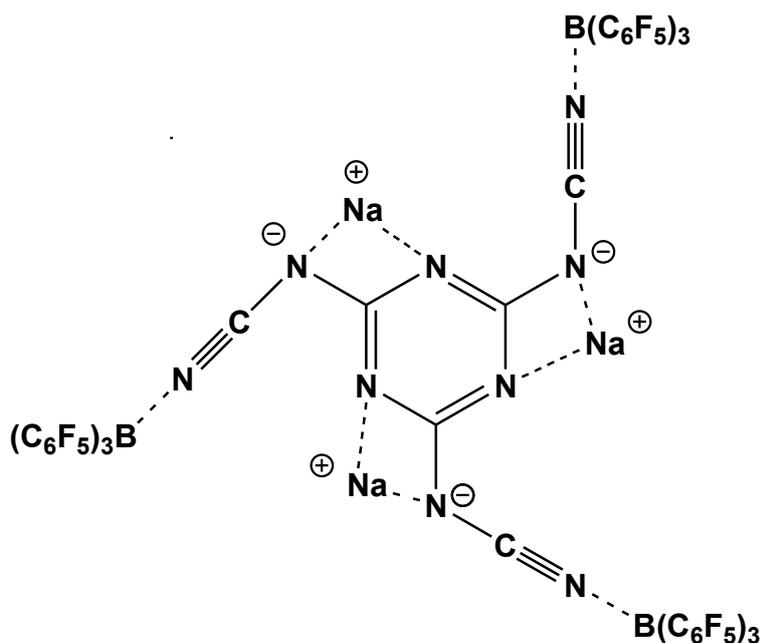
The free acid (HTCP) of the tetracyanopyrrolide (TCP) ion (Scheme 20) is easily obtained by ion exchange utilizing acidic amberlite resin. HTCP, which is a medium strong acid,<sup>[53]</sup> forms salts bearing the TCP anion upon addition of strong bases such as MOH (M = R<sub>4</sub>N, alkali metal) or even ammonia.<sup>[54]</sup>

An other chemical term is binary CN compounds, which also include the tetracyanopyrrolide anion (TCP).<sup>[54,55]</sup> Compared to their hydrogen-containing analogues (amide, methanide, pyrrolide) it was found acceptable from the terms of Bronsted base contrary. While the  $pK_b$  value of the Pyrrolide base is  $-3.51$  and the  $pK_a$  value of the pyrrole at  $17.51$ ,<sup>[56]</sup> the tetracyanopyrrolide shows only a weak basicity of ( $pK_b = 11.29$ ) and the HTCP an acidity of ( $pK_a = 2.71$ ),<sup>[53]</sup> strong delocalization of the negative charge on the CN groups causes the high acidity and the easy deprotonation, respectively.

The tetracyanopyrrolide ion is not only a pseudohalide, but due to the low alkalinity and the associated good distribution of negative charge, it is a weakly coordinating anion (WCA<sup>-</sup> – weakly coordinating anion). Typical representatives of weakly coordinating anion are singly charged complex anions such as  $[BF_4]^-$ ,  $[AlX_4]^-$  ( $X = Cl, Br, I$ ),  $[PnF_6]^-$  ( $Pn = P, As, Sb$ ),  $[XSO_3]^-$  ( $X = F, CF_3$ ) or even  $[ClO_4]^-$ .<sup>[57, 58, 59, 60, 61]</sup>

The halogens can of course also be exchanged for pseudohalogens and obtained, for example,  $[B(CN)_4]^-$  or  $[P(N_3)_6]^-$ .<sup>[62, 63]</sup> Pseudohalogens have the advantage that they are slightly larger and the negative charge can be better delocalized. With the formation of Lewis acid-base adducts the anions (Lewis base) may be greatly magnified by the Lewis acids bonded to them, and thus the concept for the synthesis of WCAs is extended.

*K. Voss et al.* in our group succeeded in the conversion of tricyanmelaminates with  $B(C_6F_5)_3$  to tricyanmelamine-borane adduct ( $[TCMel \cdot 3B]^-$ ).<sup>[64]</sup> Also here, the CN groups as donor groups are involved in the coordination to the borane. From the x-ray crystallographic structure determination of  $Na_3[TCMel \cdot 3B]$  and, however,  $MMIm_3 [TCMel \cdot 3B]$  shows that donor-acceptor interactions between the respective cations and the amidic and aromatic nitrogen atoms in the anion (Figure 3).

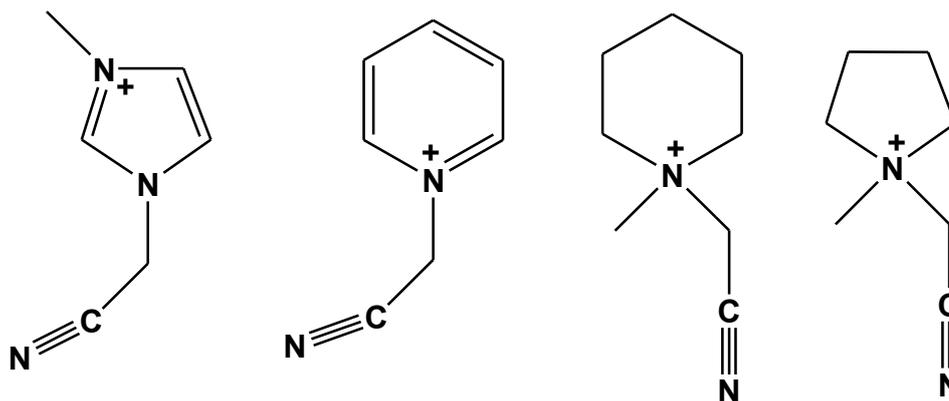


**Figure 3:** Coordination environment at tricyanmelaminato-borane adduct anion in  $\text{Na}_3[\text{TCMeI} \cdot 3\text{B}]$ .<sup>[64]</sup>

The presentation of the first moisture- and air-stable ionic liquids led to a steady increase of interest in this class of compounds.<sup>[65]</sup> Today Ionic liquids (ILs) can be divided into classic ILs, which have a melting point below possess the boiling point of water ( $<100\text{ }^\circ\text{C}$ ) and the more important for many applications Room Temperature ILs (RT-ILs), which are even still liquid at room temperature ( $<25\text{ }^\circ\text{C}$ ). By combination of flow properties of liquids with more interesting properties, such as e.g. electrical conductivity, negligible vapor pressure and high heat capacity, the application is diversified now widely. Ionic Liquids find use as alternative solvents in the so-called "Green Chemistry" (e.g. Cellulose-processing),<sup>[66]</sup> in catalysis,<sup>[67]</sup> as a liquid heat storage media<sup>[68]</sup> and as electrolytes in batteries.<sup>[69]</sup>

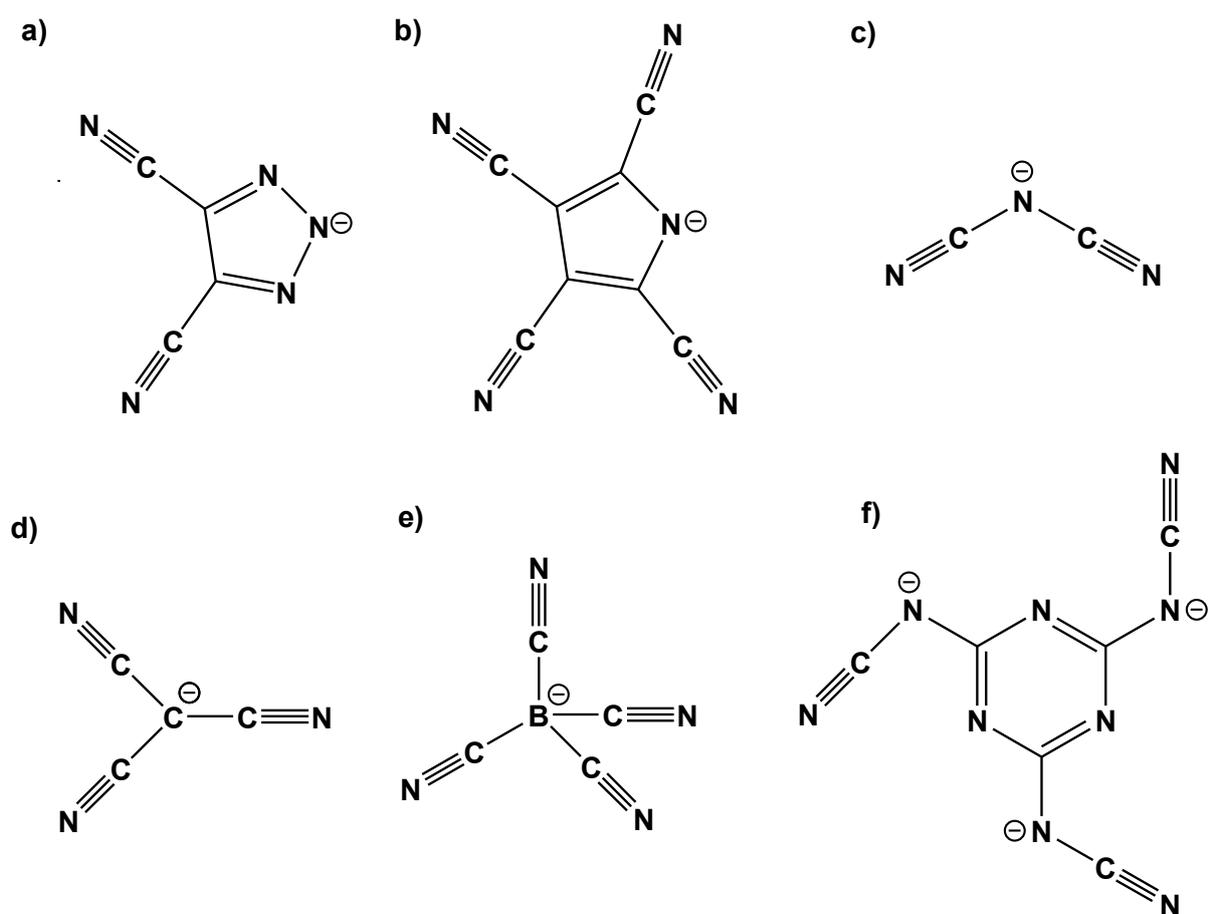
*Paul Walden* presented in 1914 the first RT-IL, the triethylammoniumnitrate, which has a melting point at  $12\text{ }^\circ\text{C}$ .<sup>[70]</sup> A breakthrough was the work of the research group led by *Wilkes* 1992, which succeeded in synthesizing hydrolytically stable RT-ILs.<sup>[71]</sup>

With CN-functionalized imidazolium, pyridinium, piperidinium and pyrrolidinium cations (Figure 4) ionic liquids based on CN-functionalized cations are more common in the literature, while about ionic liquids with CN-functionalized anions are known not so much.



**Figure 4:** Selected examples of CN-functionalized imidazolium, pyridinium, Piperidinium and pyrrolidinium cations.

One application is known, however, ionic liquids that include the CN-containing 4,5-dicyano-triazolate anion (a) (Figure 5). These ionic liquids, which also are called "Armand's ligand", are effective stabilization reagents for the production of contaminant-free, especially chloride free, highly disperse catalysts.<sup>[72]</sup> Besides the already mentioned "Armand's ligand" only few more CN- functionalized anions are known which forming ionic liquids with weakly coordinating cations, such as e.g. tetracyanopyrrolide(b),<sup>[36]</sup> dicyanamide (c),<sup>[73]</sup> tricyanmethanide (d)<sup>[74]</sup> or tetracyanidoborate (e).<sup>[75]</sup> A special feature within the CN-functionalized ILs are the imidazolium-based ionic liquids with the tricyanmelamine (f) as anion.<sup>[64]</sup> To the best knowledge, these are the first ionic liquids with a triply negatively charged anion.

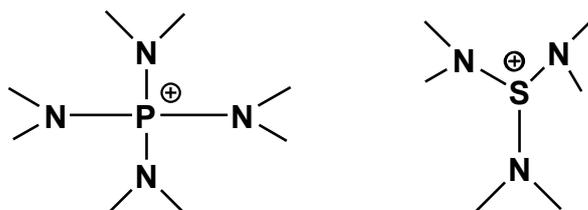


**Figure 5:** For ionic liquids suitable CN-functionalized anions: 4,5-dicyano-triazolate (a), tetracyanopyrrolide (b), dicyanamide (c), tricyanmethanide (d), tetracyanidoborate (e) and tricyanmelaminatate (f).

Ammonium, sulfonium and phosphonium ions are also excellent as weak coordinating cations, if the positive charge is delocalized over a large area and these cations are chemically extremely robust. The first tetraalkylphosphonium compounds are already known since 1871 and were synthesized by *Hofmann*.<sup>[76]</sup>



**R = Me, Et, *i*-Pr, *n*-Bu, Ph**



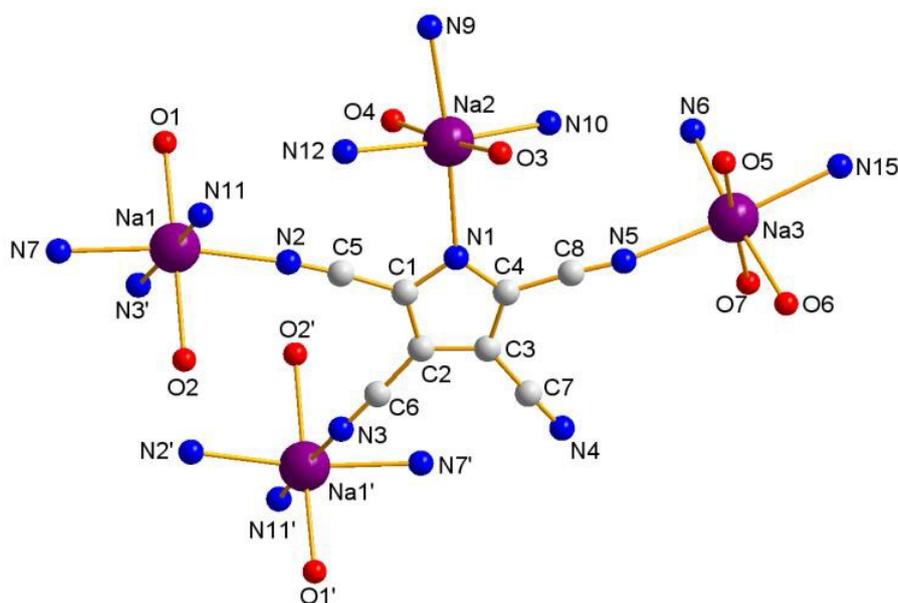
**Scheme 21:** Selected examples of tetraalkylphosphonium, tetraalkylammonium, tetraaminophosphonium and triaminosulfonium cations.

By definition, the coordination polymers are inorganic polymers, in which metal centers and ligands are bridged together by coordinate bonds. The coordination units may extend base their choice in one, two or three dimensions.<sup>[77]</sup> By varying the metal centers and ligands leave interesting build polymeric structures with special chemical and physical properties. In addition to their high thermal stability they have more specific properties, such as for example luminescence, magnetism and porosity. Thus these are suitable coordination polymers used as materials in LEDs (Light-Emitting Diodes), superconductors and molecular storage media.<sup>[78]</sup>

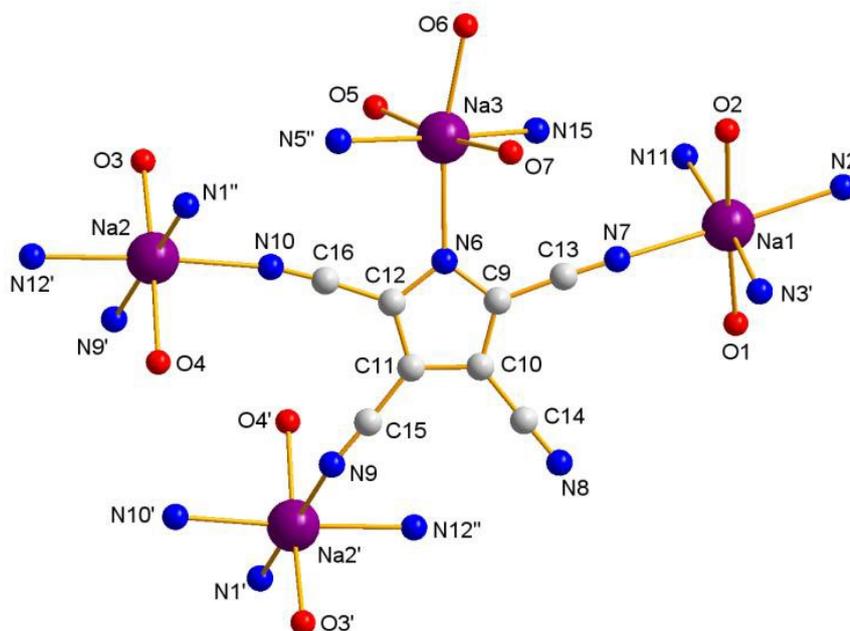
Cyanide-bridged copper centers form coordination polymers, luminescence in it have a broad spectral range, co-ligands influence the frequency of the emitted radiation.<sup>[79]</sup> By bridging of transition metals (eg. nickel, iron, chromium) with cyanides ferromagnetic coordination polymers are could synthesized. Some of these coordination polymers, which also have permanent porosity, can show changes in the magnetic order or the color changing as a function of the load condition with guest molecules, such as in  $\text{Co}^{\text{II}}_3 [\text{Cr}^{\text{III}}(\text{CN})_6]_2$ , was observed.<sup>[80]</sup>

In addition, a large number of coordination polymers are known from the anionic or neutral poly nitrile ligands are built. Among other things, can be found in the literature a set of coordination polymers with dicyanamide<sup>[81]</sup> and tricyanmethanide<sup>[82]</sup> as anionic ligands.

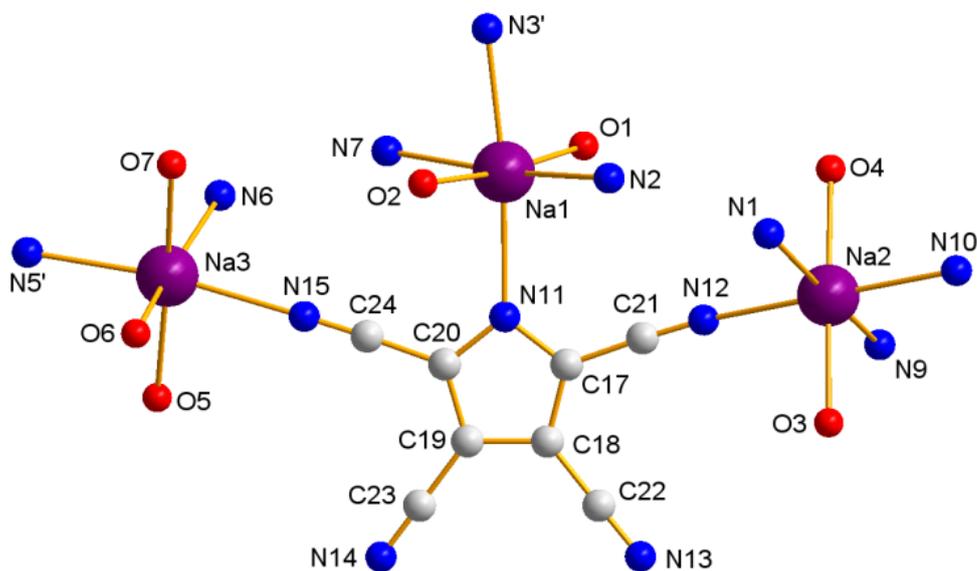
About tetracyanopyrrolide as ligand in coordination polymers, however, is very little known. The first three-dimensional coordination polymer network based on tetracyanopyrrolide was prepared in our group by *T. Jantz* 2012<sup>[83]</sup> from ion-exchange of [Me<sub>4</sub>N][TCP] with sodium cations in acetonitrile, where the solid state indicated the unit cell contains six NaTCP and in addition seven THF solvent molecules, which are linked by numerous interactions. The Na<sup>+</sup> ions have either a 4N + 2O or a 3N + 3O coordination leading to a distorted octahedral environment for all sodium ions. Although, the pyrrolide nitrogen atom always takes part in the Na<sup>+</sup> coordination, either one (Figure 6 and 7) or two CN groups in (Figure 8) remain uncoordinated.



**Figure 6:** Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.



**Figure 7:** Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.

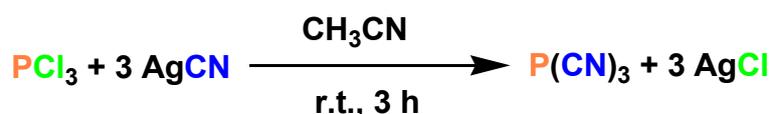


**Figure 8:** Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.

### 3. Results and discussion

#### 3.1 Synthesis of tricyanophosphine

The synthesis of tricyanophosphine was carried out following a literature method.<sup>[13]</sup> Phosphorus trichloride was added to a suspension of silver cyanide in acetonitrile. This immediately gave milky white precipitate, which is attributed to the formation of silver chloride. In order to avoid the formation of elemental silver, the reaction was carried out in absence of light.



**Scheme 22:** Synthesis of tricyanophosphine

After filtering off and washing the precipitate, the filtrate was dried in vacuo. It has arisen that an additional safety flask with a cooling bath is useful, since the  $\text{P(CN)}_3$  starts to sublime under high vacuum at room temperature and in particular is supported from the solution of acetonitrile.

For purification, the crude product was dried initially at room temperature. Later under gentle warming it was sublimated under high vacuum at a bath temperature of 60 °C. Colorless crystals were formed in long white needles.

The **IR-ATR** and **Raman** spectrum of  $\text{P(CN)}_3$  show a distinct CN band at  $2204 \text{ cm}^{-1}$ . This is in agreement with comparative data from the literature.<sup>[13, 84-85]</sup>

**NMR** spectra were recorded in deuterated dichloromethane. In  $^{13}\text{C}$  **NMR** spectrum is the split signal of the CN groups of  $\text{P(CN)}_3$  by coupling with the phosphorus atom to the doublet ( $\delta = 110.7 \text{ ppm}$ ). In  $^{31}\text{P}$  **NMR** spectrum can be observed a singlet for the central phosphorus atom at  $-125.1 \text{ ppm}$ .

The shift of the phosphorus atom to the high field falls here at lower than in acetonitrile ( $\delta = -137.8 \text{ ppm}$ ).<sup>[86]</sup> This is quite plausible, as in acetonitrile a weak coordinative interaction between the CN group of the solvent and the phosphorus atom of  $\text{P(CN)}_3$  can be discussed. In addition mole mass investigations have shown that  $\text{P(CN)}_3$  in acetonitrile solution is present

as a dimer.<sup>[87]</sup> The situation is similar in the solid state, which is also an interaction between the CN groups and the phosphorus center of the  $\text{P}(\text{CN})_3$ .<sup>[88]</sup> According to the isotropic chemical shift of the phosphorus atom in the  $^{31}\text{P}$  MAS-NMR spectrum is ( $\delta = -140.0$  ppm), with which is the effect similar to the acetonitrile solution.<sup>[89]</sup>

The shift of the phosphorus atom in 1-iodopropane is  $-129.7$  ppm<sup>[86]</sup> and is therefore in a similar range to the value determined for dichloromethane. It is thus that  $\text{P}(\text{CN})_3$  is less coordinated, as expected in these solvents.

## 3.2 Reactions of $\text{P}(\text{CN})_3$ with Weakly Coordinating Anions (WCA)<sup>-</sup> and Lewis bases

### 3.2.1 General

Weakly coordinating anions (WCA)<sup>-</sup> have achieved great interest in olefin polymerization, ionic liquids, stabilizing highly reactive intermediates and battery technology. This interest has led to basic research on the physical and chemical properties of anions containing bulky hydrocarbon and fluoro carbon functionalities over the last two decades.<sup>[90]</sup> *F. Reiss et al.* in our group was prepared a series of salts containing the terphenyl-substituted bis(amino)phosphenium cation  $[(\text{TerNH})_2\text{P}]^+$  with different weakly coordinating anions by salt-elimination reactions of  $(\text{TerNH})_2\text{P}-\text{Cl}$  with  $\text{AgWCA}$  ( $\text{WCA}^- = [\text{CF}_3\text{CO}_2]^-$ ,  $[\text{CF}_3\text{SO}_3]^-$ ,  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ ,  $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$  and  $[\text{SbF}_6]^-$  in dry toluene or dichloromethane.<sup>[91]</sup> So the reaction  $\text{P}(\text{CN})_3$  with weakly coordinating anions (WCA)<sup>-</sup> should be investigated.

Phosphines are known as Lewis bases, usually. But *Wilkie and Parry*<sup>[14]</sup> have already shown that  $\text{P}(\text{CN})_3$  do not react with Lewis acids like  $\text{AlCl}_3$  or  $\text{B}_2\text{H}_6$ . On the other hand  $\text{P}(\text{CN})_3$  reacts with  $\text{KCN}$  to give  $\text{K}[\text{P}(\text{CN})_4]$ . That is why reactions from  $\text{P}(\text{CN})_3$  with different Lewis bases should be investigated.

### 3.2.2 Reactions of P(CN)<sub>3</sub> with Weakly Coordinating Anions (WCA)<sup>-</sup>

These reactions were carried out in expectation to the general reaction shown in scheme 23.



WCA<sup>-</sup> = [OOCFF<sub>3</sub>]<sup>-</sup>, [Al(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup> and [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>

**Scheme 23:** General reaction of P(CN)<sub>3</sub> with weakly coordinating anions

A solution of AgWCA was added to a solution of P(CN)<sub>3</sub> in dry tetrahydrofuran or dichloromethane at room temperature. This gave immediately a white precipitate. In order to avoid the formation of elemental silver, the reaction was carried out in absence of light. After filtering off and washing the white precipitate the solvent was removed from the filtrate. The resulting residue was washed two times with tetrahydrofuran or dichloromethane and dried *in vacuo*.

In the reaction of P(CN)<sub>3</sub> with Ag[Al(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>], there are changes in <sup>13</sup>P NMR and IR-ATR spectra compared to the spectra from the starting materials but it was not possible to isolate any product.

With P(CN)<sub>3</sub> and Ag[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]•Et<sub>2</sub>O at room temperature or low temperature (-70 °C), no reaction has occurred. After heating the solution for two hours the <sup>19</sup>F NMR spectrum gave more signals compared to <sup>19</sup>F NMR spectrum of starting material.

The use of heating in this reaction could be led to decomposition of the anion, as well as, the melting point of P(CN)<sub>3</sub> is between 50 – 60 °C and when using the heating at 50 °C or up from this temperature could be led to decomposition of the P(CN)<sub>3</sub>.

In all reactions except the reaction with Ag[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] the presence of a distinct CN band at 2164 cm<sup>-1</sup> in the IR-ATR spectrum of the white precipitate is observed. This agrees well with comparative data of (AgCN)<sub>∞</sub> from the literature.<sup>[92]</sup> Where in the case of the ν(CN) mode, this is readily explained as a consequence of the change in the nature of the vibration when the trimeric units are linked into an infinite chain. The frequency of this mode is partly affected by the ν(MC) mode through coupling of the coordinates involved in these vibrations.<sup>[92]</sup> However, the frequency of the ν(CN) mode also increases as a result of

“stiffening” of the CN bond when the cyano group acts as a  $\sigma$ -donor which gives a band at  $2094\text{ cm}^{-1}$ .<sup>[93]</sup> In the case of the infinite chains, a greater frequency increase occurs relative to the monomer because the CN group is involved in a  $\sigma$ -donor interaction with both of the metal atoms that is bridges.<sup>[92]</sup> Nevertheless it could not be isolated any product which could result from AgCN elimination.

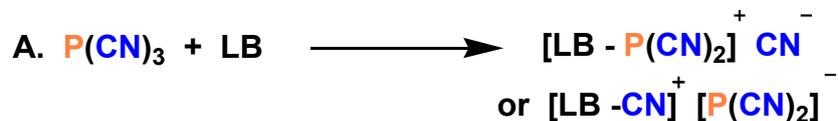
In addition, it is known that the  $[\text{Ag}(\text{CN})_2]^-$  moiety is a versatile rod-shaped building block for the construction of coordination polymers. However, AgCN is hardly used because its insolubility in common solvent presents serious difficulty in preparation and characterization of the intended products.<sup>[94]</sup> So we can see the insolubility in most of common solvents for the resulting residue in all reactions because the presence of the AgCN in the structure.

The resulting residue from the mixture after removal of the solvent for all of these reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as  $\text{CH}_3\text{CN}$  or THF, but it shows a solubility in DMSO, and this confirms to the formation of the polymer.

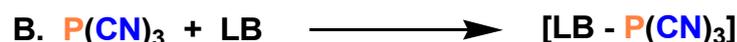
Generally, in all reactions, there are no isolated products, only a mixture from products and starting materials. The crystals obtained from the reaction solutions were characterized always as  $\text{P}(\text{CN})_3$ .

### 3.2.3 Reactions of P(CN)<sub>3</sub> with Lewis bases

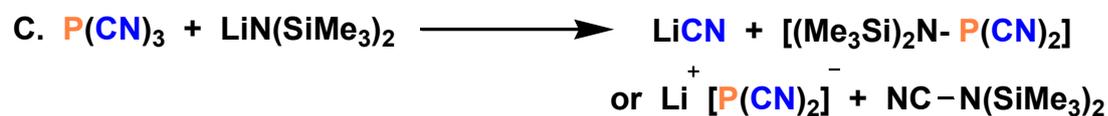
These reactions were carried out in expectation to the general reactions shown in scheme 24.



LB = Et<sub>3</sub>N and TMEDA



LB = 2,2'-bipy, DMAP, S, 1,8-DAN and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>



LB = Et<sub>3</sub>N, PPh<sub>3</sub>      X<sup>-</sup> = [BF<sub>4</sub>]<sup>-</sup>, [B(Ph)<sub>4</sub>]<sup>-</sup>

**Scheme 24:** General reactions of P(CN)<sub>3</sub> with Lewis bases

The general reaction of **A** was carried out according to the following procedure. Lewis bases were added at -70 °C to a solution of P(CN)<sub>3</sub> in dry dichloromethane. The resulting yellow solution was warmed up to ambient temperature. After stirring overnight for the yellow solution at room temperature, resulting in a brown solution. The solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In the reaction of P(CN)<sub>3</sub> with Et<sub>3</sub>N and TMEDA, there is observed a change in <sup>13</sup>P NMR and IR-ATR spectra compared to the starting solution but that it was not possible to isolate any product, as well as, it seems the dicyano phosphide ion [P(CN)<sub>2</sub>]<sup>-</sup> unstable in the solution, and in these reactions may be tricyanophosphine behave as an interpseudoalogen compound, NC-P(CN)<sub>2</sub>, with “positive cyanogen”.<sup>[18]</sup>

The resulting residue from the mixture after removal of the solvent from these reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH<sub>3</sub>CN or THF, but it shows a solubility in DMSO.

The general reaction of **B** was carried out according to the following procedure. A solution of Lewis base was added at room temperature or low temperature to a solution of P(CN)<sub>3</sub> in dry tetrahydrofuran or dichloromethane. After stirring overnight for the solution at room temperature, the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In the reaction of P(CN)<sub>3</sub> with 2,2'-bipyridine and sulfur at room temperature or low temperature (−70 °C), no reaction has occurred, where in <sup>31</sup>P NMR and IR-ATR spectra show the same signal for P(CN)<sub>3</sub> and the same vibration for CN group at P(CN)<sub>3</sub>.

With P(CN)<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, there is observed a change in <sup>11</sup>B NMR spectrum compared to <sup>11</sup>B NMR spectrum of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, but it was not possible to isolate any product.

In the reaction of P(CN)<sub>3</sub> with DMAP (DMAP = 4-dimethylaminopyridine) and 1,8- DAN (DAN = diaminonaphthalene), there are changes in <sup>31</sup>P NMR and IR-ATR spectra at room temperature or low temperature compared to the spectra from the starting materials but that it was not possible to isolate any product.

The resulting residue from the mixture after removal of the solvent in all reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH<sub>3</sub>CN or THF, except the resulting residue from the reaction with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and 1,8-diaminonaphthalene shows a good solubility in polar solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN and THF.

The reaction of **C** was carried out according to the following procedure. A solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> was added at −70 °C to a solution of P(CN)<sub>3</sub> in dry tetrahydrofuran. The resulting yellow solution was warmed up to ambient temperature. After stirring three hours for the yellow solution at room temperature, resulting in a yellow solution. The solvent was removed *in vacuo* and the residue was dried *in vacuo*.

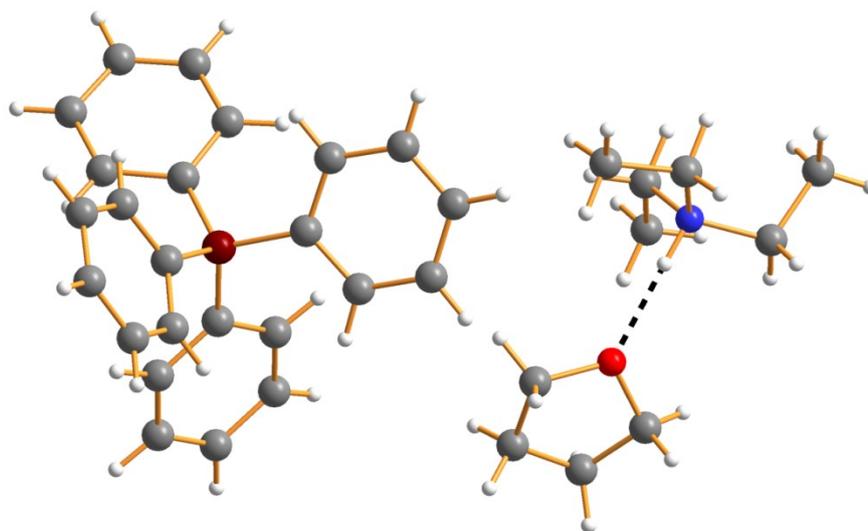
The idea from this reaction was that on the one hand, the interaction of a  $\text{Li}^+$  cation with the one CN group in  $\text{P}(\text{CN})_3$  to formation  $\text{LiCN}$  and on the other hand could generate the reaction of  $(\text{Me}_3\text{Si})_2\text{N}^+$  with  $[\text{P}(\text{CN})_2]^-$  to formation neutral product  $[(\text{Me}_3\text{Si})_2\text{N}-\text{P}(\text{CN})_2]$ .<sup>[95]</sup>

In the  $^{31}\text{P}$  NMR spectrum, there is a major signal at  $-197.50$  ppm was confirmed the formation of  $[\text{P}(\text{CN})_2]^-$  anion<sup>[17]</sup> and in INEPT  $^{29}\text{Si}$  NMR spectrum a signal at  $-11.71$  ppm was confirmed the presence of *Si* in product. In the  $^1\text{H}$  NMR spectrum shows a singlet signal at  $0.3$  ppm due to  $\text{CH}_3$  group in trimethylsilyl. But unfortunately it was not possible to isolate any product.

The general reaction of **D** was carried out according to the following procedure. A solution of Lewis bases was added to a solution of  $\text{P}(\text{CN})_3$  in dry dichloromethane or tetrahydrofuran at  $-70$  °C. After stirring 30 min, a solution of silver tetrafluoroborate or sodium tetraphenylborate in dry dichloromethane or tetrahydrofuran was added at  $-70$  °C. After stirring overnight for the yellow solution at room temperature, the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

The reaction  $\text{P}(\text{CN})_3$  with trimethylamine and sodium tetraphenylborate was achieved as described above. The yellow solution was concentrated and stored at  $-30$  °C for four days resulting colorless crystals.

The isolated colorless crystals belong only to the triethylammoniumsalt of the tetraphenylborate. The proton could come from the solvent.  $[\text{Et}_3\text{NH}\cdot\text{THF}]^+ [\text{B}(\text{Ph})_4]^-$  (Figure 9).



**Figure 9:** Ball and stick representation of  $[\text{Et}_3\text{NH}\cdot\text{THF}]^+ [\text{B}(\text{Ph})_4]^-$  with the color code:  
dark Red –Boron, blue –Nitrogen, red –Oxygen, gray – Carbon, white – Hydrogen.

In the reaction of  $\text{P}(\text{CN})_3$  with  $\text{PPh}_3$  and  $\text{Na}[\text{B}(\text{Ph})_4]$ , there is observed a change in  $^{31}\text{P}$  NMR spectrum compared to the spectra from the starting materials, but that it was not possible to isolate any product.

About the reaction of  $\text{P}(\text{CN})_3$  with  $\text{Et}_3\text{N}$  and  $\text{AgBF}_4$ , there is observed a change in  $^{31}\text{P}$  NMR spectrum, as well as, in the **IR-ATR** spectrum shows a vibration for CN group at  $2164\text{ cm}^{-1}$  was confirmed the formation of  $\text{AgCN}$ , but that it was not possible to isolate any product.

Although the presence of more changes in **NMR** ( $^{31}\text{P}$ ,  $^{19}\text{F}$  and  $^{11}\text{B}$ ) and **IR-ATR** spectra compared to the spectra from the starting materials are observed, but in all reactions, there are no isolated products, only a mixture from products and starting materials.

### 3.2.4 Reaction of P(CN)<sub>3</sub> with triphenylphosphine (5)

It is known that pure P(CN)<sub>3</sub> is associated in solution<sup>[96]</sup> and that in the solid state<sup>[97]</sup> nitrogen atoms are significantly closer to the phosphorus atoms than van der Waals distances. These facts suggest internal acid-base interactions, with phosphorus as the acid center and nitrogen as the base.<sup>[98]</sup>

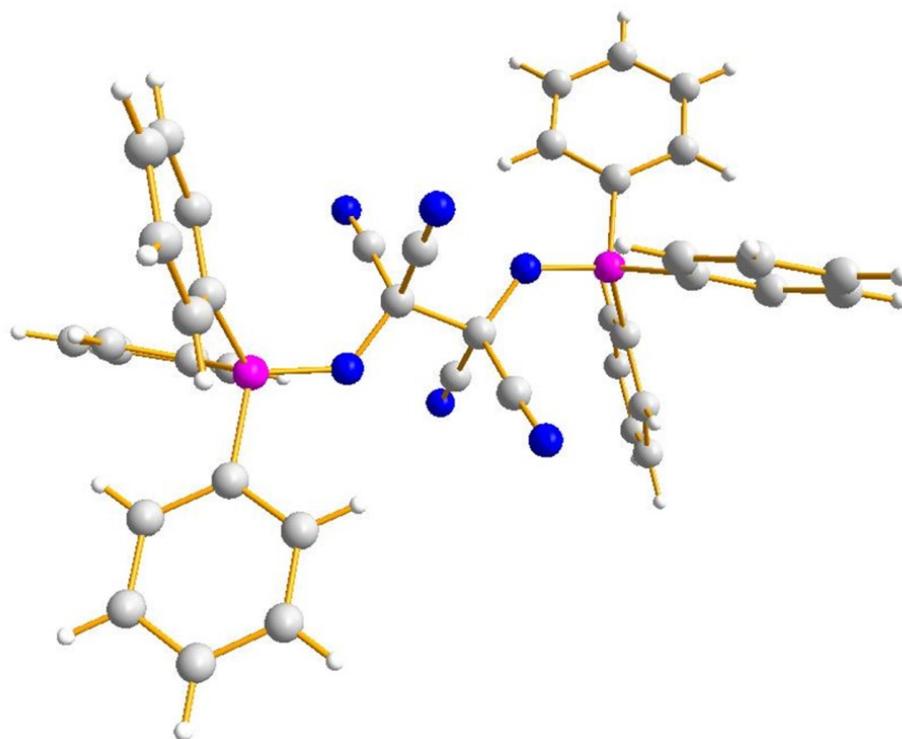
The reaction of P(CN)<sub>3</sub> with triphenylphosphine was carried out according to the following procedure. Triphenylphosphine was added at -40 °C to a solution of P(CN)<sub>3</sub> in dry dichloromethane. After stirring overnight at room temperature, the orange brown solution was concentrated and stored at -30 °C for three days, which results colorless crystals.

Surprisingly, the product for the reaction of PPh<sub>3</sub> with P(CN)<sub>3</sub> in a dichloromethane solution was unexpected and was obtained as colorless crystals of the product [Ph<sub>3</sub>P=N-C(CN)<sub>2</sub>-C(CN)<sub>2</sub>-N=PPh<sub>3</sub>]•2CH<sub>2</sub>Cl<sub>2</sub> (**5**). That means an oxidation from P(III) to P(V) has occurred.

The structure of the tetracyanodiiminophosphorane (**5**) consists of two PPh<sub>3</sub> units linked by a -NC(CN)<sub>2</sub>C(CN)<sub>2</sub>N-bridge (Figure 10). The molecule has center symmetry, with the N-PPh<sub>3</sub> units adopting an anti-configuration along the C1-C1<sup>i</sup> bond. The P1-N1 bond length = 1.576(13) Å is consistent with a P=N double bond, with the P1-N1-C1 bond angle of 129.3(10)° being somewhat larger than the idealized 120° expected for an sp<sup>2</sup> nitrogen atom. The C1-N1 bond length of 1.409(19) Å is typical for a C-N single bond, while the terminal CN bond lengths are consistent with C≡N triple bonds.

*Godfrey et al.*<sup>[99]</sup> prepared dicyano triphenylphosphine from the reaction of PPh<sub>3</sub> with PhSeCN in diethyl ether. They obtained after several weeks crystals from acetone solution for the same reaction, these crystals were characterized as tetracyanodiiminophosphorane by mean of <sup>31</sup>P NMR and IR spectra.

The mechanism for the formation of [Ph<sub>3</sub>P=N-C(CN)<sub>2</sub>-C(CN)<sub>2</sub>-N=PPh<sub>3</sub>] is unclear, but it seems that it forms PPh<sub>3</sub>(CN)<sub>2</sub> in the first step from the reaction and then happened decomposition for this product. The elimination of (CN)<sub>2</sub> from PPh<sub>3</sub>(CN)<sub>2</sub>, followed by attack of PPh<sub>3</sub> at the nitrogen atom is likely to result in the initial formation of unsaturated bridged species, such as Ph<sub>3</sub>P=N-C≡C-N=PPh<sub>3</sub>. This unit would be susceptible to successive addition of (CN)<sub>2</sub> across the unsaturated carbon-carbon bonds, thus resulting finally in [Ph<sub>3</sub>P=N-C(CN)<sub>2</sub>-C(CN)<sub>2</sub>-N=PPh<sub>3</sub>].<sup>[100]</sup>



**Figure 10:** Ball and stick representation of **5** with the color Code: pink – Phosphorus, blue – Nitrogen, gray – Carbon, white – Hydrogen.

NMR spectra were recorded in deuterated dichloromethane. In  $^1\text{H}$  NMR spectrum of the product, the aromatic ring protons appear as a multiplet in the range 7.58–7.23 ppm and  $^{13}\text{C}$  NMR spectrum confirms the presence of the aromatic ring protons.

The  $^{31}\text{P}$  NMR spectrum shows one signal at 27.65 ppm due to triphenyl phosphine,<sup>[99]</sup> a significant down field shift was observed after coordination to the nitrogen atom as compared to free  $\text{P}(\text{CN})_3$  which gives a signal at  $-125.1$  ppm.

In the IR-ATR spectrum, the vibration band at  $2187\text{ cm}^{-1}$  confirms the presence of the CN groups, compared to IR spectrum of  $\text{P}(\text{CN})_3$  which gives a vibration band for CN group at  $2204\text{ cm}^{-1}$ .

## 3.3 Reactions of P(CN)<sub>3</sub> with transition metal complexes

### 3.3.1 General

Phosphines are among the most important ligands in organometallic chemistry, with a wide range of steric and electronic properties. They have found widespread applications in transition metal-catalysed asymmetric syntheses. The catalytic activity of these complexes ranges from hydrogen transfer<sup>[101]</sup> to ring-closing metathesis.<sup>[102]</sup>

So that in a further part the possibility of using P(CN)<sub>3</sub> as a ligand in transition metal chemistry should be investigated.

### 3.3.2 Reaction of P(CN)<sub>3</sub> with dichloro(*p*-cymene)ruthenium(II)dimer

The reaction was carried out according to the following procedure. A solution of dichloro (*p*-cymene) ruthenium(II) dimer in dichloromethane (*p*-cymene=1-methyl-4-(1-methylethyl)benzene) was added to a solution of P(CN)<sub>3</sub> in dichloromethane. After stirring overnight for the red solution at room temperature, diethyl ether was added with stirring after reducing the solvent to about 3 mL, the solvent was removed *in vacuo*.

For purification, the yellow precipitate was washed with dichloromethane two times and was dried *in vacuo*.

**NMR** spectra were recorded in deuterated dimethylsulfoxide. In <sup>1</sup>H **NMR** spectrum of the product, the *p*-cymene signals are well-resolved and exhibit only H–H coupling. The aromatic ring protons appear as a multiplet in the range 7.05–7.10 ppm. The protons of isopropyl group HC(*Me*)<sub>2</sub> signals appear as a doublet at 1.16 ppm.

The <sup>31</sup>P **NMR** spectrum shows one signal at –11.33 ppm due to phosphine ligand, a significant down field shift was observed after coordination to the metal as compared to free P(CN)<sub>3</sub> which gives a signal at –125.1 ppm, as well as, <sup>13</sup>C **NMR** and **mass** spectra confirm the presence of the *p*-cymene ring.

New strong vibration at 2143 cm<sup>-1</sup> in the **IR-ATR** spectrum confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at P(CN)<sub>3</sub> which gives a vibration at 2204 cm<sup>-1</sup>. The stretching frequency of the cyanide band is shifted by about 60 cm<sup>-1</sup>. It is apparent

that the chloride ligands participate to enhance donation of the electron ion pairs from both the atoms in the CN moiety towards the ruthenium metal center, which are in fact anti-bonding with respect to C=N bond. Hence the  $\nu(\text{C}=\text{N})$  frequency increases with increasing donation of these ion pairs.<sup>[103]</sup>

The compound is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as  $\text{CH}_3\text{CN}$  or THF, but it shows a good solubility in DMSO.

Unfortunately it was not possible to isolate crystals.

### 3.3.3 Reaction of $\text{P}(\text{CN})_3$ with tetrakis(triphenylphosphine)palladium(0) (6)

The aim of this synthesis was the preparation of the homoleptic complex  $\text{Pd}\{\text{P}(\text{CN})_3\}_4$ , considering that  $\text{P}(\text{CN})_3$  shows parallels to  $\text{PF}_3$  in the coordination behavior, especially the calculated HOMO-LUMO gap is comparable to  $\text{PF}_3$ , which is a strong  $\pi$ -acceptor.

The reaction was carried out according to this procedure. A solution of  $\text{Pd}(\text{PPh}_3)_4$  in tetrahydrofuran was added at  $-70\text{ }^\circ\text{C}$  to a solution of an excess  $\text{P}(\text{CN})_3$  in tetrahydrofuran. This gave after stirring overnight at room temperature a yellow precipitate, removed by filtration and dissolved in dichloromethane. The yellow solution was concentrated and stored at  $-30\text{ }^\circ\text{C}$  for one day, which results colorless crystals.

The product of the reaction of  $\text{Pd}(\text{PPh}_3)_4$  with  $\text{P}(\text{CN})_3$  in a tetrahydrofuran was the unexpected complex  $[\text{Pd}(\text{PPh}_3)_2(\text{CN})_2]$ . That means an oxidation from Pd(0) to Pd(II) has occurred, as well as, there is no coordination of phosphorous atom to metal ion.

The synthesized compound **6** crystallizes in the orthorhombic unit cell space group *pbca*. The crystal structure of  $[\text{Pd}(\text{PPh}_3)_2(\text{CN})_2]$  contains mononuclear complex with the central metal ion  $\text{Pd}^{2+}$  located in inversion center.

The crystal structure **6** (Figure 11) confirms the trans arrangement of the two triphenyl phosphine donors. The coordination geometry around the palladium atom is slightly distorted square planar where the  $\text{P}-\text{Pd}-\text{P}^i$  angle is  $180.00(8)^\circ$  and the  $\text{C}1-\text{Pd}-\text{C}1^i$  angle is  $180.0(3)^\circ$ . The plane of the CN group is oriented perpendicular to the palladium coordination plane. The

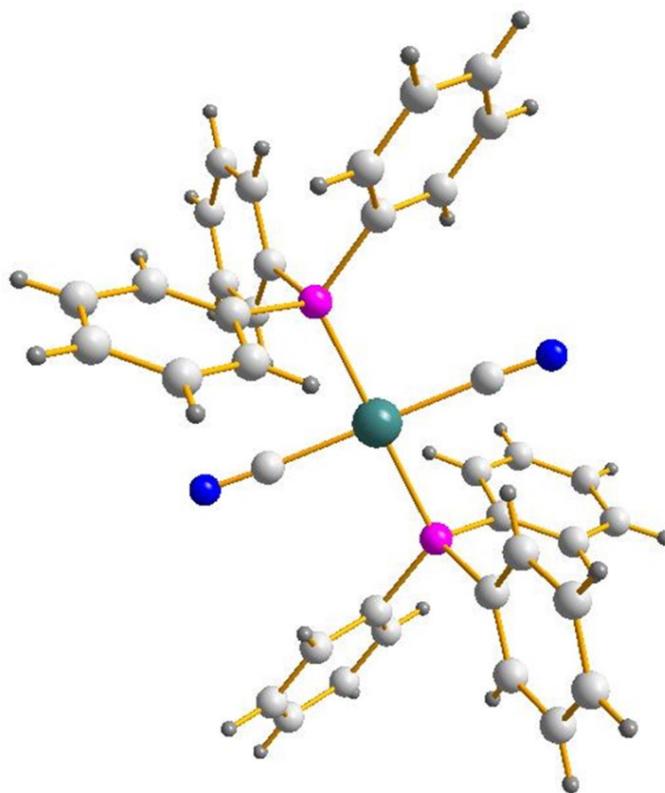
Pd–P bond lengths (2.314(11) Å) and Pd–C1 bond lengths (1.994(5) Å) fall in the range previously observed for the related palladium(II) complexes.<sup>[104]</sup>

**NMR** spectra were recorded in deuterated dichloromethane. In the <sup>1</sup>H **NMR** spectrum, the signal of the aromatic ring protons appears as a multiplet in the range 7.38–7.59 ppm.

The <sup>31</sup>P **NMR** spectrum shows one signal at 23.06 ppm due to triphenyl phosphine,<sup>[105]</sup> a significant down field shift was observed for coordination to the metal as compared to free P(CN)<sub>3</sub> which gives a signal at –125.1 ppm.

The C≡N group can be detected in the **Raman** spectrum, the band appears at 2144 cm<sup>-1</sup>. In the **IR-ATR** spectrum, the band appears at 2131 cm<sup>-1</sup>. These vibrations confirm of the CN groups coordinated to the metal, compared to IR and Raman spectra of P(CN)<sub>3</sub> which give a vibration band for CN group at 2204 cm<sup>-1</sup>.

The compound **6** is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene, but it shows a good solubility in polar solvents such as CH<sub>2</sub>Cl<sub>2</sub> and THF.



**Figure 11:** Ball and stick representation of **6** with the color code: dark green – Palladium, pink – Phosphorus, blue – Nitrogen, White – Carbon, gray – Hydrogen

### 3.3.4 Reaction of P(CN)<sub>3</sub> with 1,1,1-tris(diphenylphosphinomethyl)ethane nickel(0) (7)

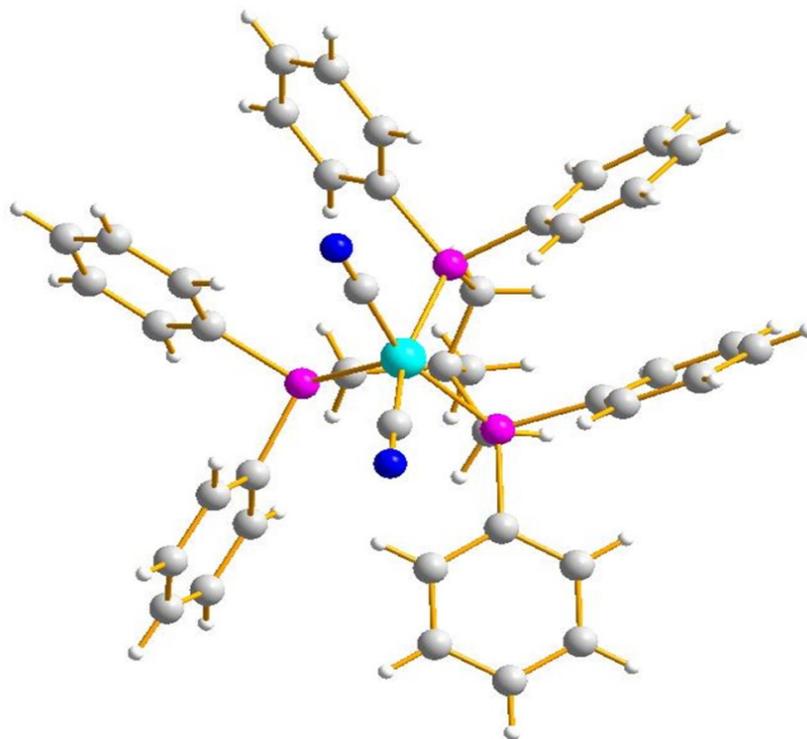
The reaction was carried out according to the following procedure. A solution of 1, 1, 1-tris(diphenylphosphinomethyl)ethane (triphos = CH<sub>3</sub>C(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>) in tetrahydrofuran was added to a solution of Ni(COD)<sub>2</sub> in tetrahydrofuran (COD = cyclooctadiene). After stirring four hours at room temperature, a solution of P(CN)<sub>3</sub> in tetrahydrofuran was added. This gave a brown precipitate after stirring overnight, which was removed by filtration.

To work up, the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane and concentrated, diethyl ether was added dropwise and stored at room temperature for two days resulting red crystals.

The isolated red crystals are not the expected cyanophosphine complex but the mononuclear complex [Ni(triphos)(CN)<sub>2</sub>]. That means an oxidation from Ni(0) to Ni(II) has occurred, as well as, there is no coordination of phosphorous atom to metal ion.

The synthesized compound 7 crystallizes in the monoclinic unit cell space group *P2<sub>1</sub>/C*. The crystal structure of [Ni(triphos)(CN)<sub>2</sub>] contains mononuclear complex with the central metal ion Ni<sup>2+</sup> located in inversion center.

The crystal structure 7 (Figure 12) shows an idealized square-pyramidal coordination of the nickel center with one of phosphorus donors occupying the apical position and with the other two phosphorus donors and the two co-ligands (CN groups) are forming the base of the pyramid. The apical Ni–P2 bond (2.36 (5) Å) was longer than the equatorial Ni–P bonds (2.19–2.20 (4) Å). The P–Ni–P angle are, by virtue of being part of the chelate cage, close to 90°. The C–Ni–C angle spanned by the coordination atoms of the cyano groups is found at 84.97(7)°. The P–Ni–C angles fall in two classes. The angles referring to CN groups which are in an idealized *trans* position to each other show values between 156° and 158°, while angles referring to mutual idealized *cis* positions are in a range between 87°–110°. The deviations from the idealized square-pyramidal geometry are thus substantial.<sup>[106]</sup>



**Figure 12:** Ball and stick representation of **7** with the color code: dark blue– Nickel, pink– Phosphorus, blue–Nitrogen, gray – Carbon, white – Hydrogen.

**NMR** spectra were recorded in deuterated dichloromethane. The  $^1\text{H}$  **NMR** spectrum results confirm the presence of the 1,1,1-tris(diphenylphosphinomethyl)ethane ligand (triphos).

In the  $^{31}\text{P}$  **NMR** spectrum of the compound, the signal for the product was at a major chemical shift of  $\delta = -3.70$  (1.0) ppm due to 1,1,1-tris(diphenylphosphinomethyl)ethane ligand (triphos).

The  $\text{C}\equiv\text{N}$  group can be detected in the **Raman** spectrum, the band appears at  $2123\text{ cm}^{-1}$ . In the **IR-ATR** spectrum, the band appears at  $2116\text{ cm}^{-1}$ . These vibrations confirm of the CN groups coordinated to the metal, compared to IR and Raman spectra of  $\text{P}(\text{CN})_3$  which give a vibration band for CN group at  $2204\text{ cm}^{-1}$ .

The compound **7** is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene, but it shows a good solubility in polar solvents such as  $\text{CH}_2\text{Cl}_2$  and THF.

### 3.3.5 Reaction of P(CN)<sub>3</sub> with [hydridotris(3,5-dimethylpyrazolyl)borate tricarbonyltungsten(II)] and ferroceniumhexafluorophosphate

In this reaction the sevenfold coordinated tungsten(II) hydrotris(3,5-dimethylpyrazolyl)borate tricarbonyl phosphine complex was used. The tris(3,5-dimethylpyrazolyl)borate ligand is especially sterically demanding, with an estimated cone angle of 244°. The label “tetrahedral enforcer” should be used to describe this.<sup>[107]</sup>

The reaction was carried out according to the following procedure. Oxidation of the anionic tungsten (0) tricarbonyl reagent [TpW(CO)<sub>3</sub>]<sup>-</sup> by ferrocenium hexafluorophosphate generates a neutral 17-electron radical tungsten (I). To prepare 7-coordinated phosphine complex after oxidizing the TpW(CO)<sub>3</sub> radical with ferrocenium, presumably a cationic 16-electron tungsten (II) intermediate [Tp<sup>-</sup>W(CO)<sub>3</sub>]<sup>+</sup> is generated, which has solvent coordinated in accord with 18-electron-rule guidelines. Addition of tricyano phosphine may lead to formation of the 7-coordinated cationic complex. The residue was washed two times with diethyl ether to remove ferrocene and the residue was dried *in vacuo*. It was not possible to isolate crystals.

The <sup>19</sup>F NMR spectrum of the residue, a doublet at -73.3 ppm to be detected for the fluorine atoms at the central phosphorus atom in the anion. In <sup>31</sup>P NMR spectrum can be observed a septet at -144.5 ppm belongs to coordinate phosphorus atom of the hexafluorophosphate, as well as, one singlet signal at -65.68 ppm may be attributed to coordinate phosphorus atom with tungsten atom.

In IR-ATR spectrum, three bands appear at 1910, 1960 and 2045 cm<sup>-1</sup> belongs to carbonyl group, as well as, one band at 2228 cm<sup>-1</sup> for CN group, compared to IR spectrum of P(CN)<sub>3</sub> which gives a vibration band for CN group at 2204 cm<sup>-1</sup>.

Surprisingly, mass spectrum (negative ions) shows the highest intensity peak at *m/z* = 144.964687 corresponding to the [PF<sub>6</sub>]<sup>-</sup>, but mass spectrum (positive ions) shows the highest intensity peak at *m/z* = 566.167 corresponding to the TpW(CO)<sub>3</sub>H<sup>+</sup> with other peak at *m/z* = 542.167.

### 3.3.6 Reaction of P(CN)<sub>3</sub> with tris(propionitrile)tricarbonylmolybdenum(0)

The reaction was carried out according to the following procedure. A solution of [Mo(CO)<sub>3</sub>(EtCN)<sub>3</sub>] was added to a solution of P(CN)<sub>3</sub> in dry dichloromethane. After stirring

overnight for a yellow solution at room temperature the brown precipitate was removed by filtration, the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In this reaction, no changes in  $^{31}\text{P}$  NMR and IR-ATR spectra compared to the spectra from the starting materials are observed, while  $^{31}\text{P}$  NMR spectrum for the brown precipitate did not give any signal because it was insoluble in most of the solvents. It was not possible to isolate any product.

### 3.4 Reactions of $\text{P}(\text{CN})_3$ with Room Temperature Ionic Liquids (RT-ILs)

#### 3.4.1 General

Room Temperature Ionic Liquids (RT-ILs) are salts with low melting points composed of an organic cation and either an organic or an inorganic anion.<sup>[108]</sup> In contrast to classical solvents, ionic liquids possess a series of outstanding advantages as electrolytes such as no vapor pressure, high thermal stability, wide range of solubility and wide electrochemical window.<sup>[109]</sup> *Hardacre et al.*<sup>[110]</sup> have shown that addition of N-methylimidazole (NMI) to a solution of  $\text{PCl}_3$  in  $[\text{EMim}]^+ [\text{OTf}]^-$  resulted in the formation of a yellow precipitate, probably of  $[\text{P}(\text{NMI})_3]\text{Cl}_3$  which rapidly hydrolysed when exposed to air.

So reactions from  $\text{P}(\text{CN})_3$  with different room temperature ionic liquids (RT-ILs) should be investigated.

#### 3.4.2 Reaction of $\text{P}(\text{CN})_3$ with 1-ethyl-3-methylimidazolium dicyanamide in dichloromethane

The reaction was carried out according to the following procedure. A solution of 1-ethyl-3-methylimidazolium dicyanamide was added to a solution of  $\text{P}(\text{CN})_3$  in dry dichloromethane at 0 °C. After stirring four hours at room temperature the color changed from yellow to brown. After stirring overnight at room temperature the solvent was removed *in vacuo*.

For purification the brown precipitate was washed two times with acetonitrile and was dried for 6 h *in vacuo*.

NMR spectra were recorded in deuterated acetonitrile. In  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra show the signals belong to EMIm cation.

In the  $^{31}\text{P}$  NMR spectrum of the residue, there is a major chemical shift of  $\delta = -194.82$  ppm (s,  $[\text{P}(\text{CN})_2]^-$ ),<sup>[17]</sup> compared to  $^{31}\text{P}$  NMR spectrum of  $\text{P}(\text{CN})_3$  which gives a signal at  $-142$  ppm.

New vibration at  $2165\text{ cm}^{-1}$  in the IR-ATR spectrum confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at  $\text{P}(\text{CN})_3$  which gives a vibration at  $2204\text{ cm}^{-1}$ . By mean of DSC measurement the decompose temperature at  $305\text{ }^\circ\text{C}$ , at a heating rate of  $10\text{ K / min}$  was determined.

The residue from the mixture after removal of the solvent is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene. It shows very poor solubility in common polar organic solvents such as MeCN or THF. In water, at the same time the residue is unstable and a water hydrolyzation takes place because  $^{31}\text{P}$  NMR spectrum in  $\text{D}_2\text{O}$  shows new signals at  $0.25$  and  $2.65$  ppm and these signals refer to form phosphoroxide or phosphonic acid  $[\text{DPO}(\text{OD})_2]$ .

### 3.4.3 Reaction of $\text{P}(\text{CN})_3$ with 1-ethyl-3-methylimidazolium dicyanamide in tetrahydrofuran

The reaction was carried out according to the following procedure. A solution of 1-ethyl-3-methylimidazolium dicyanamide was added to a solution of  $\text{P}(\text{CN})_3$  in dry tetrahydrofuran at  $0\text{ }^\circ\text{C}$ . After stirring overnight for the deep brown oily solution at room temperature the solvent was removed *in vacuo* and the *deep brown oily precipitate* was dried *in vacuo*.

For purification the deep brown oily precipitate was washed six times with acetonitrile. The *brown precipitate* was separated by filtration and was dried for  $12\text{ h}$  *in vacuo*. From the deep brown solution the solvent was removed *in vacuo* and the *deep brown precipitate* was dried *in vacuo*.

After stirring overnight, new vibration shows at  $2173\text{ cm}^{-1}$  in the IR-ATR spectrum of the *deep brown oily precipitate* confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at  $\text{P}(\text{CN})_3$  which gives a vibration at  $2204\text{ cm}^{-1}$ .

In the  $^{31}\text{P}$  NMR spectrum of the *deep brown oily precipitate* there is a major chemical shift of  $\delta = -194.43$  ppm (s,  $[\text{P}(\text{CN})_2]^-$ ),<sup>[17]</sup> compared to  $^{31}\text{P}$  NMR spectrum of  $\text{P}(\text{CN})_3$  which gives a signal at  $-142$  ppm.

NMR spectra were recorded in deuterated acetonitrile. In  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the *deep brown oily precipitate* show the signals belong to EMIm cation.

After washing with acetonitrile, the  $^{31}\text{P}$  NMR spectrum of the *brown precipitate* was not clear because it was insoluble in deuterated acetonitrile. The  $^1\text{H}$  NMR and mass spectra refer to EMIm cation but the  $^{13}\text{C}$  NMR spectrum was not clear. A new vibration at  $2172\text{ cm}^{-1}$  in the IR-ATR spectrum of the *brown precipitate* confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at  $\text{P}(\text{CN})_3$  which gives a vibration at  $2204\text{ cm}^{-1}$ , but when using high temperature at  $200\text{ }^\circ\text{C}$  for three hours, new vibration for CN group shows at  $2166\text{ cm}^{-1}$ .

For filtrate after washing with acetonitrile and filtration, new vibration shows at  $2170\text{ cm}^{-1}$  in the IR-ATR spectrum of the *deep brown precipitate* confirms the presence of the CN groups. In the  $^{31}\text{P}$  NMR spectrum of the *deep brown precipitate* there is a major chemical shift of  $\delta = -194.43$  ppm (s,  $[\text{P}(\text{CN})_2]^-$ ).<sup>[17]</sup> NMR spectra were recorded in deuterated acetonitrile. In  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra show the signals belong to EMIm cation.

In DSC/TGA results of the *brown precipitate*, it can be seen is comparably stable before being heated to  $257\text{ }^\circ\text{C}$  and evaporation of some solvent in the compound causes the mass loss before  $100\text{ }^\circ\text{C}$ . The obvious mass loss of  $39.5\%$  between  $257$  and  $335\text{ }^\circ\text{C}$ , should be caused the decomposition of compound.

The *brown precipitate* is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene. It shows very poor solubility in common polar organic solvents such as MeCN or THF. In water, at the same time the *brown precipitate* is unstable and reacted under water (hydrolyzation) because  $^{31}\text{P}$  NMR spectrum in  $\text{D}_2\text{O}$  shows new signals at  $0.25$  and  $2.65$  ppm and these signals refer to form phosphoroxide or phosphonic acid  $[\text{DPO}(\text{OD})_2]$ .

### 3.4.4 Reaction of P(CN)<sub>3</sub> with silver dicyanoamide–tris(pentafluorophenyl) Borane•diether

The reaction was carried out according to the following procedure. A solution of Ag[N{CN•B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub>]•2Et<sub>2</sub>O in fluorobenzene was added to a solution of P(CN)<sub>3</sub> in fluorobenzene. After stirring overnight for the yellow solution at room temperature the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In the <sup>31</sup>P NMR spectrum of the residue there is a major chemical shift of δ = 142.88 (1.0) ppm. Furthermore, there are signals at δ = 49.67 (0.2) and 17.39 (0.2) ppm, which are associated to resulting by-products.

The <sup>19</sup>F NMR spectrum of the residue shows resonances shifted to lower frequency compared to B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in starting material, but similarly broad. The <sup>11</sup>B NMR spectrum shows a signal at -13.35 ppm compared to <sup>11</sup>B NMR spectrum of starting material which gives a signal at -12.10 ppm.<sup>[111]</sup>

A new vibration at 2222 cm<sup>-1</sup> in the IR-ATR spectrum of the residue confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at P(CN)<sub>3</sub> which gives a vibration at 2204 cm<sup>-1</sup> and IR-ATR spectrum for CN group at Ag[N{CN•B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub>] which gives a vibration at 2291 cm<sup>-1</sup>.<sup>[111, 112]</sup>

The residue is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene, but it shows a good solubility in polar solvents such as CH<sub>3</sub>CN, that means it is not a polymer.

Unfortunately it was not possible to isolate any products or crystals from all reactions of P(CN)<sub>3</sub> with Room Temperature Ionic Liquids (RT-ILs).

## 3.5 Reactions of tetracyanopyrrolide

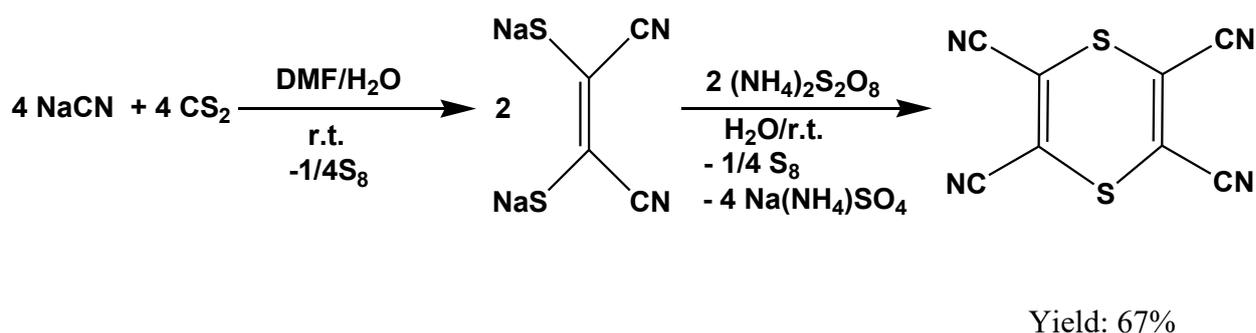
### 3.5.1 General

With respect to the coordination chemistry tetracyanopyrrolide is furnished with five donor centers, three of which are of different type: cyanide group in 2- and 3- position and the pyrrolide N ring atom. Therefore the anion is an extremely versatile ligand with potential to form coordination polymers and finally, the possibility of  $\pi$ -bonding by the anionic pyrrolide system will be tested, because the pyrrolide is considered  $\pi$ -iso electronically to cyclopentadienide.

In the following part the possibility of using the tetracyanopyrrolide anion as a ligand in transition metal chemistry should be investigated.

### 3.5.2 Synthesis of tetracyano-1,4-dithiin ( $C_8N_4S_2$ )

The synthesis of tetracyano-1,4-dithiin was carried out following a literature method.<sup>[51, 54-55]</sup> Carbon disulfide was added dropwise to a suspension of NaCN and DMF with stirring vigorously,  $H_2O$  was added and the mixture was stirred overnight at room temperature. The resulting sulfur was filtered off, under stirring ammonium peroxodisulfate as an oxidizing reagent was added and tetracyano-1,4-dithiin was obtained as product.



**Scheme 25:** Direct conversion of cyanide and carbon disulfide in DMF and subsequent oxidation by ammonium peroxodisulfate in water to dithiin.

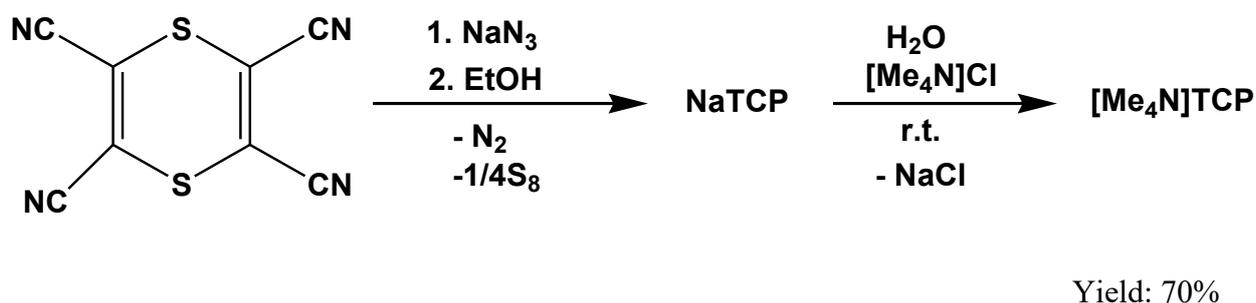
For purification, the crude product was dried at room temperature, several recrystallisations from a saturated dichloroethane solution of tetracyano-1,4-dithiin resulted yellow crystals, which were already isolated and discussed by *Martin Becker* in our group.<sup>[113]</sup>

The C≡N group can be detected in the  $^{13}\text{C}$  NMR spectrum, the signal appears at 125.4 ppm and in the IR-ATR spectrum the band appears at  $2218\text{ cm}^{-1}$ . In the Raman spectrum, the band appears as a very sharp peak at  $2220\text{ cm}^{-1}$ . This vibration in the IR and Raman spectra confirms the presence of the CN groups.

### 3.5.3 Synthesis of tetramethylammoniumtetracyanopyrrolide $[\text{Me}_4\text{N}]\text{TCP}$

The synthesis of tetramethylammoniumtetracyanopyrrolide was carried out following a literature method.<sup>[36]</sup> The dithiine was dissolved in ethanol and added to sodium azide. In addition faster vigorous evolution of gas is observed, since  $\text{N}_2$  escapes. The solution is dark and sulfur deposits can be observed. For work up, the ethanol is removed and the brown residue was dissolved in water. The resulting sulfur was filtered off. To the resulting sodium-tetracyanopyrrolide (NaTCP) resulting from the reaction in byproducts separate, which was dissolved in water and filtrated. Tetramethylammoniumchloride ( $[\text{Me}_4\text{N}]\text{Cl}$ ) as a saturated aqueous solution was added at  $0\text{ }^\circ\text{C}$  and the tetramethylammoniumtetracyanopyrrolide was obtained as product.

For purification, the crude product was dried at room temperature, several recrystallisations from a saturated isopropylalcohol solution pure tetramethylammoniumtetracyanopyrrolide was obtained as colorless crystals, which were already isolated and discussed by *Martin Becker* in our group.<sup>[113]</sup>



**Scheme 26:** Scheme of reaction steps from dithiine to  $[\text{Me}_4\text{N}]\text{TCP}$ .

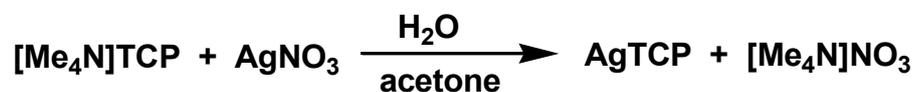
The C≡N group can be detected on the vibration in the Raman spectrum at  $2233\text{ cm}^{-1}$ . In the IR-ATR spectrum, the band appears as a very sharp peak at  $2220\text{ cm}^{-1}$ . This vibration in the

IR and Raman spectra confirms the presence of the CN groups. By **DSC** measurement the melting point at 272 °C and decompose temperature at 324 °C, at a heating rate of 10 K / min were determined.

Characteristic of the TCP anion are the four  $^{13}\text{C}$  **NMR** signals occurring at a shift of 119.7, 114.5, 112.4 and 102.0 ppm. It involves singlet signal as where the methyl group of the cation, which can be found at 54.4 ppm. The NMR spectrum was measured in DMSO- $d_6$ , in which all pyrrolides solve very well, as all precursors. The NMR spectra are thus suitable for a direct signal comparison.

### 3.5.4 Synthesis of Silver tetracyanopyrrolide AgTCP

The synthesis of silver tetracyanopyrrolide was carried out following a literature method.<sup>[36]</sup> A solution of silver nitrate in water was added to a solution of tetramethylammonium tetracyanopyrrolide in mixture ( $\text{H}_2\text{O}$  and acetone). In order to avoid the formation of elemental silver, the reaction was carried out in absence of light. After stirring for 3 h, the precipitate was removed by filtration, washed three times with ethanol and was dried *in vacuo*.



Yield: 75%

#### **Scheme 27:** Synthesis of silver tetracyanopyrrolide

The **NMR** spectrum was recorded in deuterated dimethylsulfoxide. In the  $^{13}\text{C}$  **NMR** spectrum the signals of the  $\text{TCP}^-$  anion appear at 119.8, 114.3, 112.3 and 102.1 ppm.

In the **IR-ATR** spectrum, the band appears as a very sharp peak at  $2233\text{ cm}^{-1}$ . This vibration in the IR spectrum confirms the presence of the CN groups. By **DSC** measurement the melting point at 270 °C and decompose temperature at 313 °C, at a heating rate of 10 K / min were determined.

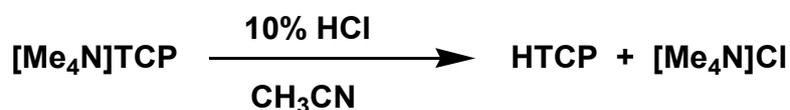
### 3.5.5 Synthesis of tetracyanopyrrole HTCP

#### Procedure 1

*Simmons et al.*<sup>[53,54]</sup> described the possibility of starting from tetramethylammoniumtetracyanopyrrolide to obtain the acidic compound (Scheme 28). A column was charged with Amberlyst 15 ion exchange resin. The column was washed with 10 mol% HCl, de-ionized water, acetone, and acetonitrile. Tetramethylammonium tetracyanopyrrolide was dissolved in acetonitrile and added slowly to the given column. Free pyrrole was eluted with acetonitrile.

For purification, the residue was eluted to column chromatography (Ethyl acetate / heptane (v: v = 3: 1)). After evaporating under reduced pressure, the precipitate was washed two times with dichloromethane under heating, and dried *in vacuo* at room temperature.

*Martin Becker* in our group has also carried out this reaction, the product was obtained by column chromatography and isolated from the water adduct as colorless crystals, which was already discussed.<sup>[113]</sup>



Yield: 45%

**Scheme 28:** Ion exchange in which a  $[\text{Me}_4\text{N}]^+$  ion is exchanged to a  $\text{H}^+$  ion.

A  $^1\text{H}$  NMR spectrum appears a singlet signal at a shift of 11.03 ppm, which is attributed to the NH group in  $\text{CD}_3\text{CN}$ . In  $^{13}\text{C}$  NMR spectrum the typical TCP signals at shifts of 112.1, 108.8, 107.6 and 105.7 ppm in  $\text{CD}_3\text{CN}$  are seen, these signals in the  $^{13}\text{C}$  NMR spectrum confirm the presence of the CN groups.

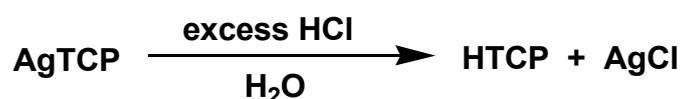
In the IR-ATR spectrum shows as a strong vibration band at  $2243 \text{ cm}^{-1}$  and this confirms the presence of the CN groups.

## Procedure 2

Tetracyanopyrrole free from water was prepared for the first time by *Simmons* in 1962<sup>[53]</sup> and characterized by IR-ATR, elemental analysis and mass spectroscopy but the yield from this reaction was 20%. *Thomas Jantz* in our group in 2012<sup>[83]</sup> prepared tetracyanopyrrole containing two water molecular using ion-exchange column of [Me<sub>4</sub>N]TCP in acetonitrile with full characterization but the yield from this reaction was 54% .

So we decided preparation tetracyanopyrrole free from water in high yield by new procedure as the following: excess hydrochloric acid was added to a suspension of silver tetracyanopyrrolide in water at room temperature. After stirring overnight, the suspension was filtrated and the solvent was removed under reduced pressure.

For purification, the precipitate was washed two times with dichloromethane under heating and was dried *in vacuo* for 6 h at room temperature. Sublimation of the residue at (150 °C) for 6 h gave tetracyanopyrrole as a white crystalline solid. The interesting in this procedure the yield was high 71% .



Yield: 71%

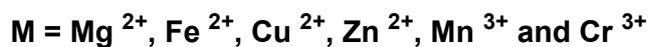
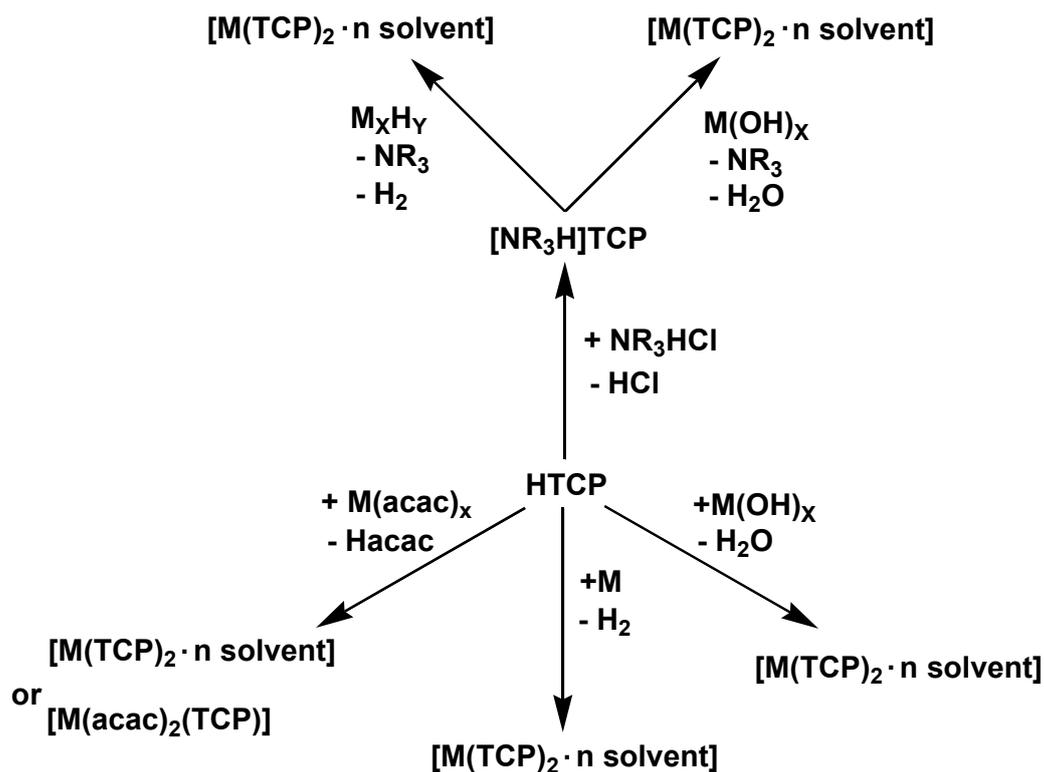
**Scheme 29:** Reaction of AgTCP with HCl in water for HTCP.

The C≡N group can be detected in the **Raman** spectrum, the band appears at 2252 cm<sup>-1</sup>. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2244 cm<sup>-1</sup>. This vibration in the IR and Raman spectra confirms the presence of the CN groups. By **DSC** measurement the melting point at 207 °C and decompose temperature at 237 °C, at a heating rate of 10 K / min were determined.

Characteristic of the TCP anion are the four <sup>13</sup>C **NMR** signals occurring at a shift of 112.1, 108.7, 107.6 and 105.8 ppm in CD<sub>3</sub>CN. These signals in the <sup>13</sup>C **NMR** spectrum confirm the presence of the CN groups. In <sup>1</sup>H **NMR** spectrum shows a singlet signal at a shift of 11.09 ppm, which is attributed to the NH group in CD<sub>3</sub>CN. The cyano groups thus provide a dramatic increase in the acidity of the nitrogen proton, which is also clearly reflected in the

down field shift resonance signal in  $^1\text{H}$  NMR spectrum shows (9.27 in the  $^1\text{H}$  pyrrole <sup>[114]</sup> vs. 11.9 ppm in the tetracyanopyrrole).

So we utilized the tetracyanopyrrole as a ligand to prepare new transition metal complexes shown in scheme 30.

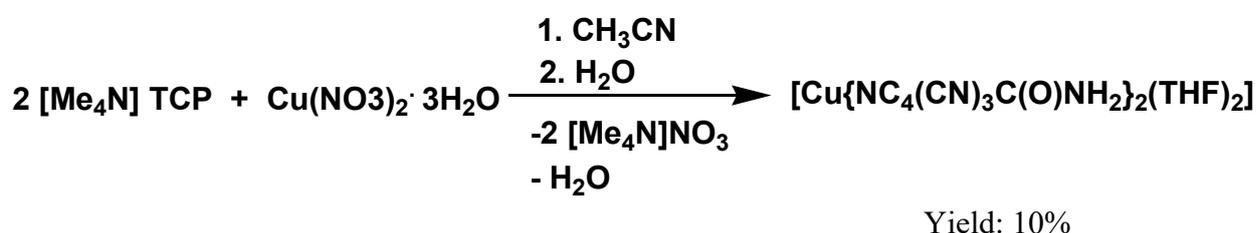


**Scheme 30:** General representation for HTCP reactions.

### 3.5.6 Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran)copper(II) $[\text{Cu}\{\text{NC}_4(\text{CN})_3\text{C}(\text{O})\text{NH}_2\}_2(\text{THF})_2]$ (**8**)

A solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in water was added to a solution of tetramethylammonium-tetracyanopyrrolide in acetonitrile at room temperature. After stirring for 15 min, the acetonitrile was evaporated and the solution was filtered, the filtrate was evaporated to give a greenish yellow precipitate **8** (Scheme 31).

By vapor diffusion of diethyl ether into a tetrahydrofuran solution of a greenish yellow precipitate, crystals could be obtained as a by-product in small amounts.



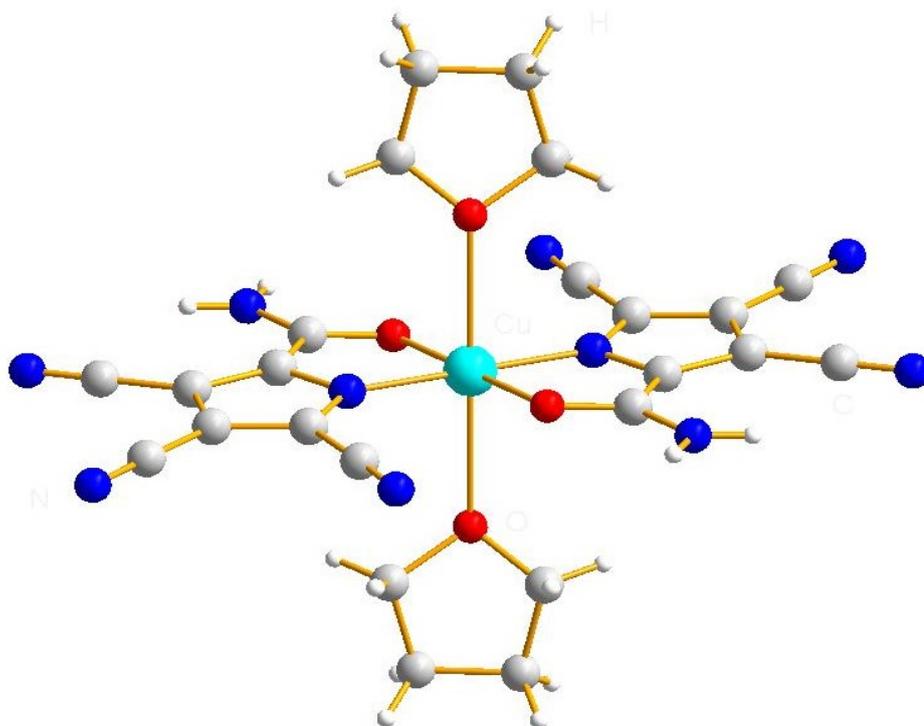
**Scheme 31:** Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran) copper(II).

In the **IR-ATR** spectrum appears a new vibration band for CN group at  $2233 \text{ cm}^{-1}$ , compared to IR spectrum of  $[\text{Me}_4\text{N}]\text{TCP}$  which gives a vibration band for CN group at  $2220 \text{ cm}^{-1}$ .

The compound **8** crystallizes in the monoclinic unit cell space group  $P2_1/c$ . The two CN distances are  $1.13 \text{ \AA}$  and are therefore slightly larger than the sum of the covalent radii ( $\Sigma r_{\text{cov}} \text{C}\equiv\text{N} 1.11 \text{ \AA}$ ).<sup>[115]</sup> The CC distances in the ring differ only in third decimal place and are on average  $1.40 \text{ \AA}$ . This value is between the sums of the covalent radii of a CC single ( $1.54 \text{ \AA}$ ) and a C = C double bond ( $1.34 \text{ \AA}$ ),<sup>[115]</sup> which is closer to a double bond. This also applies to the same size CN distances in five-membered ring ( $1.35 \text{ \AA}$ ).

In the crystal structure of  $[\text{Cu}\{\text{NC}_4(\text{CN})_3\text{C}(\text{O})\text{NH}_2\}_2(\text{THF})_2]$  (**8**), the copper(II) central atom is located in an inversion center and adopts an octahedral coordination (Figure 13). The equatorial positions are occupied by two symmetry related tcpc ligands, forming five-membered chelate rings in one plane, coordinating the metal center via the oxygen atom of the amide group and the N atom of the pyrrole ring. Two trans-positioned tetrahydrofuran

molecules coordinate via their oxygen atoms almost perpendicular to this plane and complete the coordination geometry around the copper central atoms to an elongated octahedron.



**Figure 13:** Ball and stick representation of **8** with the color code: dark blue – Copper, blue – Nitrogen, red – Oxygen, gray – Carbon, white – Hydrogen.

The distance between Cu–N(equat) and Cu–O(equat) was 1.97 Å and 1.99 Å while Cu–O(axial) was 2.47Å, that means clearly the Jahn-Teller effect is present.<sup>[37]</sup>

If water is not strictly excluded, the tetracyanopyrrolide anion can undergo hydrolysis under transformation of one cyano substituent to a carboxamide group, transforming tcp into tricyanopyrrole-2-carboxamide ( $\text{NC}_4(\text{CN})_3\text{C}(\text{O})\text{NH}_2^-$ ) (tcpc).

We observed that this reaction occurs in the presence of  $\text{Cu}^{2+}$  ions and converts tcp after one day at room temperature completely. From THF solutions, the copper(II) complex  $[\text{Cu}\{\text{NC}_4(\text{CN})_3\text{C}(\text{O})\text{NH}_2\}_2(\text{THF})_2]$  could be isolated, which incorporates the mononegative tricyanopyrrole-2-carboxamide as a chelating ligand. This copper(II)-assisted hydrolysis to the corresponding amide under mild conditions is well known.<sup>[116, 117]</sup>

### 3.5.7 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate $[\text{Zn}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$ (**9**)

The reaction was carried out according to this procedure. A powder of zinc was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the unconsumed powder of zinc was removed by filtration, and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 °C for one day resulted colorless crystals of  $[\text{Zn}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  (Scheme 32).



Yield: 44%

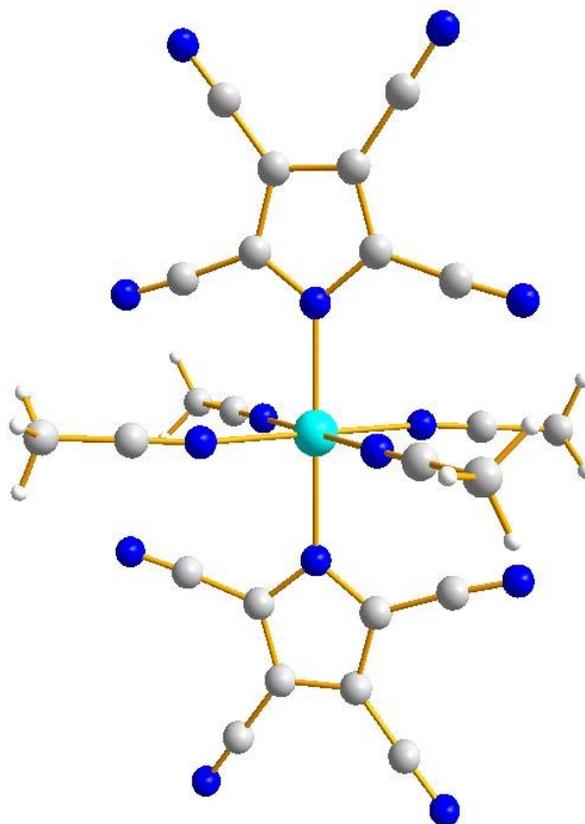
**Scheme 32:** Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate.

The synthesized compound **9** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of  $[\text{Zn}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  contains a mononuclear complex with the central metal ion  $\text{Zn}^{2+}$  located in inversion center. The central metal ion has octahedral six-coordination environment, by two-trans positioned (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 14). A sandwich structure with  $\eta^5$ -pyrrolide ligands as characteristic for bis( $\eta^5$ -pyrrolide)zinc<sup>[37, 118-119]</sup> is not present, which obviously caused by the low electron density in the central  $\text{C}_4\text{N}$  ring due to the strong electron-withdrawing effect of the nitrile substituents.

The carbon-nitrogen bond length in the  $\text{C}\equiv\text{N}$  groups is on average 1.144 (11) Å.<sup>[120]</sup> The distances C1–C2 1.392 (18), C2–C3 1.409 (2) and C3–C4 1.397 (19) Å are also here between the values for a C–C single and double bond ( $\Sigma_{\text{r}_{\text{cov}}}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.361 (18), C4–N1 1.362 (17) Å and the exocyclic C–C bond lengths (1.421–1.432 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>

The average angle M–N–centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the  $\text{C}_4\text{N}$  ring, which expected for a  $\sigma$  bonding situation. The bonds M–N<sub>pyrrole</sub> amount to 2.15 Å, while the bonds M–NCMe in the equatorial planes (average M–N 2.153 (13) Å).

The complex  $[\text{Zn}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  adopt a similar structural arrangement as found for the complex  $[\text{Co}\{\text{C}_5(\text{CN})_5\}_2(\text{H}_2\text{O})_2(\text{THF})_2]$ , ( $\text{C}_5(\text{CN})_5^-$  = pentacyanocyclopentadienide anion), where the  $\text{Co}(\text{II})$  atom is coordinated by the N atoms of nitrile groups of two trans positioned  $\text{C}_5(\text{CN})_5$  ligands.<sup>[33]</sup>



**Figure 14:** Ball and stick representation of **9** with the color code: dark blue – Zinc, blue – Nitrogen, gray – Carbon, white – Hydrogen.

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature rang 50–900 °C. The first mass loss of 8.74 % occurs between 350–475 °C is assigned to the release of the one solvate acetonitrile molecules (calculated weight loss 6.37 %). In the second stage started of decomposition for the compound at 497 °C and this decomposition caused results of low accuracy with the elemental analysis.

The  $\text{C}\equiv\text{N}$  group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at  $2231\text{ cm}^{-1}$ . In the **IR-ATR** spectrum, the band appears as a strong

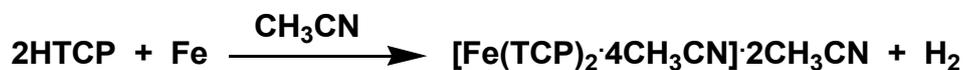
vibration band at  $2232\text{ cm}^{-1}$ , compared to IR spectrum of HTCP which gives a vibration band for CN group at  $2244\text{ cm}^{-1}$  and in Raman spectrum at  $2252\text{ cm}^{-1}$ .

Characteristic of the TCP anion are the four  $^{13}\text{C}$  NMR signals occurring at a shift of 112.8, 108.9, 108.2 and 104.8 ppm in  $\text{CD}_3\text{CN}$ . These signals in the  $^{13}\text{C}$  NMR spectrum confirm the presence of the CN groups.

### 3.5.8 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II)

#### acetonitrile solvate $[\text{Fe}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$ (10)

The reaction was carried out according to the following procedure. A powder of iron was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the unconsumed powder of iron was removed by filtration, and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at  $8\text{ }^\circ\text{C}$  for one day resulted colorless crystals of  $[\text{Fe}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  (Scheme 33).



Yield: 45%

**Scheme 33:** Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate.

The  $\text{C}\equiv\text{N}$  group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at  $2237\text{ cm}^{-1}$ . In the **IR-ATR** spectrum, the band appears as a strong vibration band at  $2227\text{ cm}^{-1}$ , compared to IR spectrum of HTCP which gives a vibration band for CN group at  $2244\text{ cm}^{-1}$  and in Raman spectrum at  $2252\text{ cm}^{-1}$ .

Characteristic of the TCP anion are the four  $^{13}\text{C}$  NMR signals occurring at a shift of 112.9, 108.9, 108.2 and 104.8 ppm in  $\text{CD}_3\text{CN}$ . These signals in the  $^{13}\text{C}$  NMR spectrum confirm the presence of the CN groups.

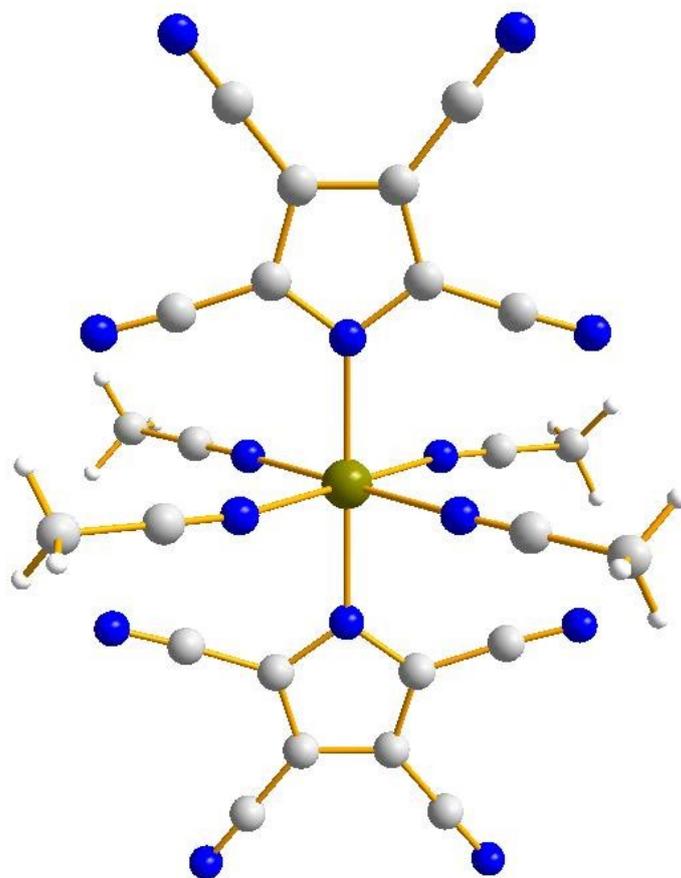
By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature rang  $50\text{--}900\text{ }^\circ\text{C}$ . The first mass loss of 15.29 % occurs between  $110\text{--}130\text{ }^\circ\text{C}$  is assigned to the release of the two solvate acetonitrile molecules

(calculated weight loss 12.94 %). In the second stage started of decomposition for the compound at 360 °C and this decomposition caused results of low accuracy with the elemental analysis.

The synthesized compound **10** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of  $[\text{Fe}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  contains a mononuclear complex with the central metal ion  $\text{Fe}^{2+}$  located in inversion center. The central metal ion has octahedral six-coordination environment, by two axially bond (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 15).

The average angle M–N–centroid (tcp ring) equals  $180^\circ$ , indicating that the metal atoms are essentially in the plane of the  $\text{C}_4\text{N}$  ring and represents a multifunctional binary CN ligand, which is capable of forming classic coordination bonds through the ion pairs of the CN groups or the ring N atom. The bonds M–N<sub>pyrrole</sub> (average 2.178 (8) Å), while the bonds M–NCMe in the equatorial planes (average M–N 2.161 (9) Å).

The carbon-nitrogen bond length in the  $\text{C}\equiv\text{N}$  groups is on average 1.145 (15) Å.<sup>[120]</sup> The distances C1–C2 1.397 (13), C2–C3 1.408 (14) and C3–C4 1.398 (13) Å are also here between the values for a C–C single and double bond ( $\Sigma r_{\text{cov}}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.363 (12), C4–N1 1.363 (12) Å and the exocyclic C–C bond lengths (1.421–1.431 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>



**Figure 15:** Ball and stick representation of **10** with the color code: dark green – Iron, blue – Nitrogen, gray – Carbon, white – Hydrogen.

The tendency for delocalization of the  $\pi$ -electron system towards the peripheral cyano groups is displayed in the exocyclic C–C bond lengths, which are only slightly longer than those within the aromatic ring. The two nitrile substituents in the positions 2 and 5 of the pyrrole ring cause a high sterical demand of this molecule when bond in the  $\eta^1$ -N mode.<sup>[37]</sup>

### 3.5.9 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II) acetonitrile solvate [Mg(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN (11)

The reaction was carried out according to this procedure. A solution of magnesium hydroxide in acetonitrile was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the resulting was filtrated and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 °C for one week resulted colorless crystals of [Mg(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN (Scheme 34).



Yield: 64%

**Scheme 34:** Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II)acetonitrile solvate.

By TGA/DSC measurement, the thermal decomposition of the synthesized compound occurs in three stages in the temperature rang 50–800 °C. The first mass loss of 7.37 % occurs between 78–120 °C is assigned to the release of the one solvate acetonitrile molecules (calculated weight loss 6.81 %). The second mass loss of 16.51 % occuring between 125–152 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 13.62 %). In the third stage started of decomposition for the compound at 248 °C and this decomposition caused results of low accuracy with the elemental analysis.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears at 2235 cm<sup>-1</sup>. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2227 cm<sup>-1</sup>.

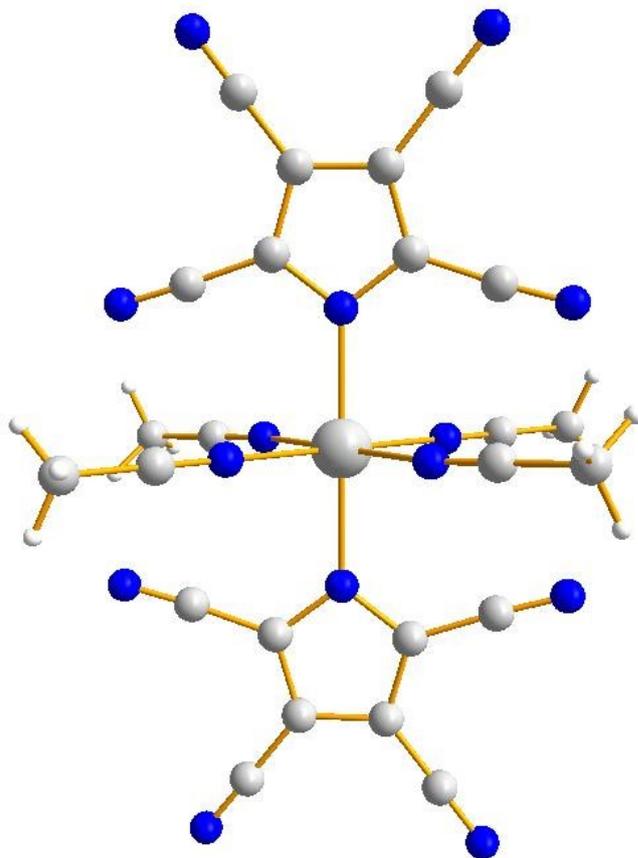
Characteristic of the TCP anion are the four <sup>13</sup>C NMR signals occurring at a shift of 118.1, 112.7, 111.4 and 103.2 ppm in CD<sub>3</sub>CN. These signals in the <sup>13</sup>C NMR spectrum confirm the presence of the CN groups.

The synthesized compound **11** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of [Mg(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN contains a mononuclear complex with the central metal ion Mg<sup>2+</sup> located in inversion centre. In the centrosymmetry for

[Mg(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN, the six coordinate magnesium atom has a regular octahedral geometry, by two trans positioned (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 16).

The average angle M–N–centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the C<sub>4</sub>N ring, the bonds M–N<sub>pyrrole</sub> (average 2.203 (8) Å). The bonds M–NCMe in the equatorial planes (average M–N 2.152 (9) Å).<sup>[121]</sup>

The carbon-nitrogen bond length in the C≡N groups is on average 1.144 (14) Å.<sup>[120]</sup> The distances C1–C2 1.393 (13), C2–C3 1.402 (14) and C3–C4 1.396 (13) Å are also here between the values for a C–C single and double bond ( $\Sigma_{r_{cov}}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.361 (12), C4–N1 1.365 (12) Å and the exocyclic C–C bond lengths (1.422– 1.432 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>



**Figure 16:** Ball and stick representation of **11** with the color code: dark gray – Magnesium, blue – Nitrogen, gray – Carbon, white – Hydrogen

The tendency for delocalization of the  $\pi$ -electron system towards the peripheral cyano groups is displayed in the exocyclic C–C bond lengths, which are only slightly longer than those within the aromatic ring. The two nitrile substituents in the positions 2 and 5 of the pyrrole ring cause a high sterical demand of this molecule when bond in the  $\eta^1$ -N mode.<sup>[37]</sup>

### 3.5.10 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II) acetonitrile solvate [Cu(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN (12)

The reaction was carried out according to the following procedure. A solution of tetracyanopyrrole in acetonitrile was added to a suspension solution of di(acetylacetonate)-copper(II) in acetonitrile at room temperature. After stirring overnight the resulting mixture was filtrated and the solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 °C for one day resulted green crystals of [Cu(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN (Scheme 35).



Yield: 65%

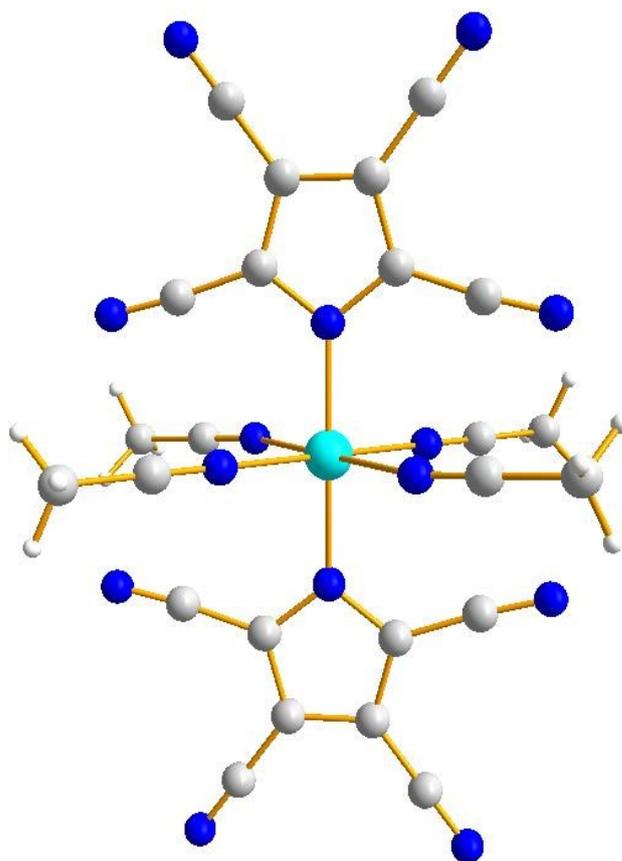
**Scheme 35:** Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II)acetonitrile solvate.

The synthesized compound **12** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of [Cu(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN contains a mononuclear complex with the central metal ion Cu<sup>2+</sup> located in inversion center. The geometry of the complex ion is elongated octahedral coordination (Figure 17) and the equatorial plane is formed by two N atoms of two tetracyanopyrrolide and two N atoms of two acetonitrile. The two other N atoms of two acetonitrile are located at the axial positions at a rather long distance, obviously as a result of Jahn-Teller distortion.<sup>[122]</sup>

The average angle M–N–centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the C<sub>4</sub>N ring, the bonds M–N<sub>pyrrole</sub> (average 2.025 (10) Å).<sup>[123, 124]</sup>

The two bonds M–NCMe in the equatorial plane (average M–N 2.025 (11) Å), while the two bonds M–NCMe in the axial plane (average M–N 2.345 (12) Å).<sup>[122]</sup>

The carbon-nitrogen bond length in the C≡N groups is on average 1.145 (18) Å.<sup>[120]</sup> The distances C1–C2 1.394 (18), C2–C3 1.408 (18) and C3–C4 1.394 (17) Å are also here between the values for a C–C single and double bond ( $\Sigma r_{\text{cov}}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.365 (16), C4–N1 1.363 (16) Å and the exocyclic C–C bond lengths (1.421–1.433 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>



**Figure 17:** Ball and stick representation of **12** with the color code: dark blue – Copper, blue – Nitrogen, gray – Carbon, white – Hydrogen.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at 2239  $\text{cm}^{-1}$ . In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2231  $\text{cm}^{-1}$ .

By TGA/DSC measurement, the thermal decomposition of the synthesized compound occurs in three stages in the temperature range 50–800 °C. The first mass loss of 10.57 % occurs between 59–85 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.78 %). The second mass loss of 12.87 % occurring between 168–200 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.78 %). In the third stage started of decomposition for the compound at 452 °C and this decomposition caused results of low accuracy with the elemental analysis.

### 3.5.11 Synthesis of di(acetylacetonate)-1,5-N- $\mu$ -tetracyanopyrrolido manganese(III) [Mn(acac)<sub>2</sub>TCP] (13)

The reaction was carried out according to this procedure. A solution of tri (acetylacetonate) manganese(III) in acetonitrile was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight, the resulting was filtrated.

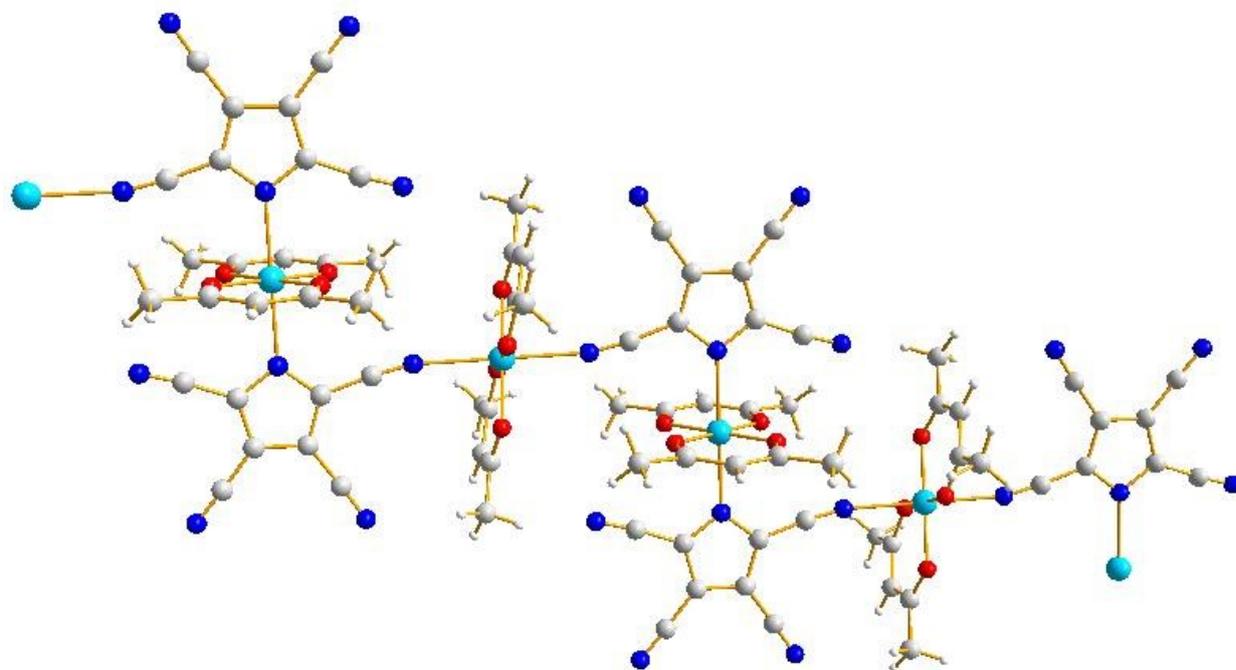
For purification, the yellow-black filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with benzene and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution resulted yellow crystals of [Mn(acac)<sub>2</sub>TCP] (Scheme 36).



Yield: 72%

**Scheme 36:** Synthesis of di(acetylacetonate)-1,5-N- $\mu$ -tetracyanopyrrolidomanganese(III).

The synthesized compound **13** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure gave a 1D-coordination polymer di(acetylacetonate)-1,5-N- $\mu$ -tetracyanopyrrolido manganese(III). The Mn<sup>3+</sup> ions have either a 2N<sub>pyrrolide</sub> + 4O<sub>acetylacetonate</sub> coordination leading to a distorted octahedral environment. Although, the pyrrolide nitrogen atom always takes part in the Mn<sup>3+</sup> coordination, either three CN groups remain uncoordinated (Figure 18).



**Figure 18:** Ball and stick representation of **13** with the color code: dark blue – Manganese, blue – Nitrogen, red – Oxygen, gray – Carbon, white – Hydrogen.

The distances C1–C2 1.395 (2), C2–C3 1.405 (2) and C3–C4 1.397 (2) Å are also here between the values for a C–C single and double bond ( $\Sigma r_{\text{cov}} \text{C}=\text{C}$  1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.356 (2), C4–N1 1.360 (19) Å and the exocyclic C–C bond lengths (1.421–1.433 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>

It is interesting to note that no significant difference in the CN bond lengths is observed depending on the coordination mode (1.141–1.144 Å) and even the uncoordinated cyano groups are within this range ( $\Sigma r_{\text{cov}}(\text{C}\equiv\text{N}) = 1.14$  Å).<sup>[120]</sup> The angle between the CN groups and

the ring are between ( $174.8^{\circ}$ – $178.7^{\circ}$ ), and are almost planar to the ring. The angle between Mn and N<sub>pyrrolide</sub>, Mn and O<sub>acetylacetonate</sub> always equal  $180.0^{\circ}$  and confirm the planarity.

Two different sets of Mn–N bond lengths are found:  $d(\text{Mn–N}_{\text{pyrrolide}}) = 2.29 \text{ \AA}$  and  $d(\text{Mn–N}_{\text{cyano}}) = 2.36 \text{ \AA}$ , this agrees well with comparative data from the literature.<sup>[125, 126]</sup> The bond lengths Mn–O<sub>acetylacetonate</sub> (average  $1.899(8) \text{ \AA}$ ), are in agreement well with the corresponding distance in  $[\text{Mn}(\text{acac})_2(\text{OH}_2)_2\text{ClO}_4] \cdot 2\text{H}_2\text{O}$ .<sup>[127]</sup>

The C≡N groups are confirmed by vibrational spectroscopy methods, **IR-ATR** and **Raman** spectra. In the Raman spectrum, the band appears at  $2232 \text{ cm}^{-1}$ , while in the IR spectrum, there are two bands appear at  $2248$  and  $2232 \text{ cm}^{-1}$ . By **DSC** measurement the melting point at  $56$ – $57 \text{ }^{\circ}\text{C}$  and decompose temperature at  $210 \text{ }^{\circ}\text{C}$ , at a heating rate of  $10 \text{ K / min}$  were determined.

### 3.5.12 Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolido chromium(III) $[\text{Cr}(\text{acac})_2\text{TCP} \cdot \text{CH}_3\text{CN}] \cdot 0.67 \text{ CH}_3\text{CN}$ (14)

The reaction was carried out according to the following procedure. A solution of tri(acetylacetonate)chromium(III) in acetonitrile was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the resulting was filtrated and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at  $8 \text{ }^{\circ}\text{C}$  for one week resulted brown crystals of  $[\text{Cr}(\text{acac})_2\text{TCP} \cdot \text{CH}_3\text{CN}] \cdot 0.67 \text{ CH}_3\text{CN}$  (Scheme 37).



Yield: 38%

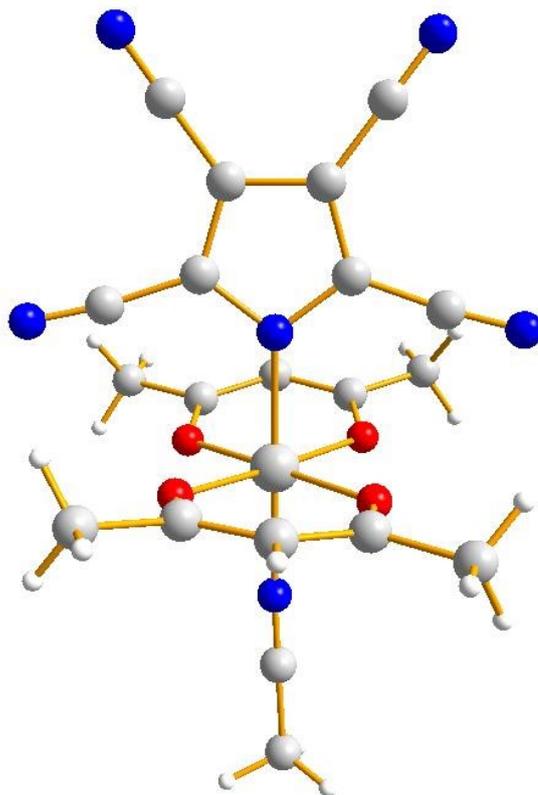
**Scheme 37:** Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolidochromium(III).

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at  $2240 \text{ cm}^{-1}$ . In the **IR-ATR** spectrum, the band appears as a medium band at  $2232 \text{ cm}^{-1}$ .

The synthesized compound **14** crystallizes in the monoclinic unit cell space group  $C2/c$ . The crystal structure gave acetonitrile-di(acetylacetonate)tetracyanopyrrolidochromium (III). The central metal ion  $\text{Cr}^{3+}$  is coordinated by four O atoms of two acetylacetonate ligands in the equatorial plane and one N pyrrolide, one N acetonitrile in trans arrangement, displaying a slightly distorted octahedral geometry (Figure 19).

The carbon-nitrogen bond length in the  $\text{C}\equiv\text{N}$  groups is on average 1.139 (3) Å.<sup>[120]</sup> The distances C1–C2 1.382 (4), C2–C3 1.415 (3) and C3–C4 1.383 (4) Å are also here between the values for a C–C single and double bond ( $\Sigma r_{\text{cov}}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.365 (3), C4–N1 1.364 (3) Å and the exocyclic C–C bond lengths (1.428–1.436 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>

The angle between the CN groups and the ring are between ( $173.6^\circ$ – $178.6^\circ$ ), and are almost planar to the ring. The angle between Cr and  $\text{N}_{\text{pyrrolide}}$ , Cr and  $\text{O}_{\text{acetylacetonate}}$  are between ( $177.1^\circ$ – $180.0^\circ$ ) and confirm the planarity.



**Figure 19:** Ball and stick representation of **14** with the color code: dark gray – Chromium, blue –Nitrogen, red – Oxygen, gray – Carbon, white – Hydrogen

The bond Cr–N<sub>pyrrole</sub> was 2.066 (2) Å), The bond Cr–NCMe in the axial plane was 2.049(2) Å).<sup>[128]</sup> The bond lengths Cr–O<sub>acetylacetonate</sub> (average 1.934 (17) Å), are in good agreement with comparative data from the literature.<sup>[129]</sup>

By TGA/DSC measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature range 50–800 °C. The first mass loss of 14.12 % occurs between 120–180 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 16.93 %). In the second stage started of decomposition for the compound at 247 °C.

### 3.5.13 Reaction of HTCP with tri(acetylacetonate)manganese(III)

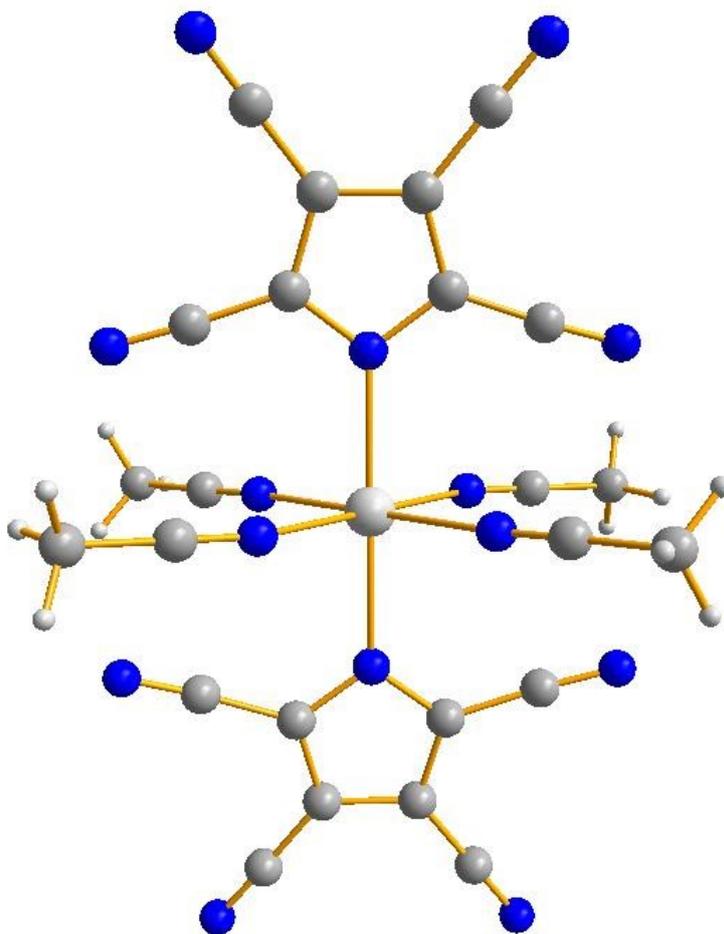
The aim of this synthesis was the preparation of tris(tetracyanopyrrolido)manganese(III), we utilized in this reaction different ratio to get on this product. The reaction was carried out according to this procedure. A solution of tri(acetylacetonate)manganese(III) in acetonitrile was added to a solution of an excess tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the resulting mixture was filtrated and the yellow-black solution was evaporated to dryness to yield a yellow precipitate, washed two times with benzene and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution but the resulting was two crystal structures from solution, first was 1% yellow crystals of [Mn(acac)<sub>2</sub>TCP] (**13**) which already was discussed previously and second was 99% colorless crystals of [Mn(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN (**15**). That means a reduction from Mn(III) to Mn(II) has occurred.

The synthesized compound **15** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of [Mn(TCP)<sub>2</sub>•4CH<sub>3</sub>CN]•2CH<sub>3</sub>CN contains a mononuclear complex with the central metal ion Mn<sup>2+</sup> located in inversion center. The central metal ion has octahedral six-coordination environment, by two axially bond (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 20).

The carbon-nitrogen bond length in the C≡N groups is on average 1.147 (13) Å.<sup>[120]</sup> The distances C1–C2 1.398 (11), C2–C3 1.408 (12) and C3–C4 1.397 (11) Å are also here between the values for a C–C single and double bond ( $\Sigma r_{cov}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.361 (10), C4–N1 1.363 (10) Å and the exocyclic C–C bond lengths

(1.398– 1.429 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>

The average angle M–N–centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the C<sub>4</sub>N ring, the bonds M–N<sub>pyrrole</sub> (average 2.260 (7) Å).<sup>[125]</sup> The bonds M–NCMe in the equatorial plane (average M–N 2.227 (8) Å).<sup>[130]</sup>



**Figure 20:** Ball and stick representation of **15** with the color code: dark gray – Manganese, blue – Nitrogen, gray – Carbon, white – Hydrogen.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at 2236 cm<sup>-1</sup>. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2233 cm<sup>-1</sup>.

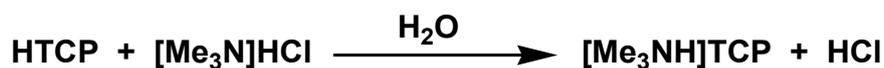
By TGA/DSC measurement, the thermal decomposition of the synthesized compound **15** occurs in two stages in the temperature rang 50–800 °C. The first mass loss of 13.89 % occurs between 50– 65 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.95 %). In the second stage started of decomposition for the compound at 218 °C.

### 3.5.14 Synthesis of trimethylammoniumtetracyanopyrrolide [Me<sub>3</sub>NH]TCP

(16)

The synthesis of this reaction was carried out according to this procedure. A solution of trimethylammoniumchloride in water was added to a solution of tetracyanopyrrole in water at room temperature. After stirring overnight, the resulting was filtrated.

For purification, the yellow filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with dichloromethane and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at room temperature for three days resulted colorless crystals of [Me<sub>3</sub>NH]TCP (Scheme 38).



Yield: 77%

**Scheme 38:** Synthesis of trimethylammoniumtetracyanopyrrolide.

By TGA/DSC measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature rang 50– 800 °C. The first stage gave melting point at 184-185 °C, while in the second stage started the decomposition of the compound at 298 °C.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp at 2235 cm<sup>-1</sup>. In the **IR-ATR** spectrum, there are two bands appear as a medium band at 2234 cm<sup>-1</sup> and very strong band at 2224 cm<sup>-1</sup>.

Characteristic of the TCP anion are the four  $^{13}\text{C}$  NMR signals occurring at a shift of 119.4, 114.3, 112.1 and 102.4 ppm. It involves singlet signal as where the methyl group of the cation, which can be found at 44.6 ppm.

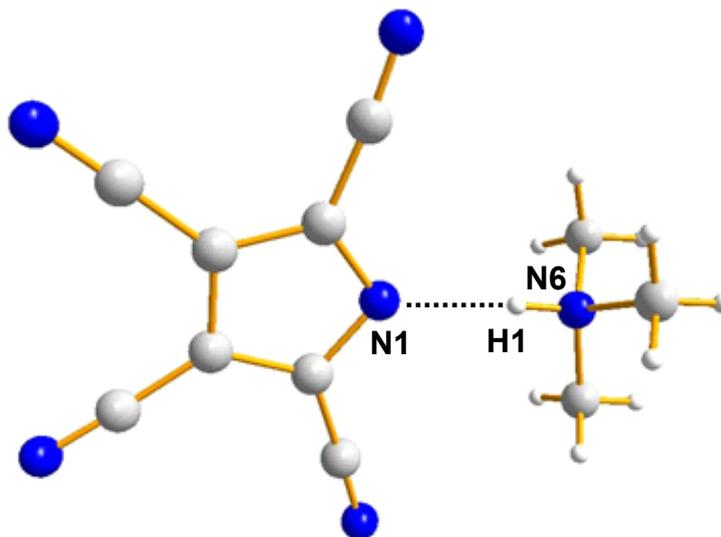
A  $^1\text{H}$  NMR spectrum shows a singlet signal at a shift of 4.41 ppm, which is attributed to the methyl group, and a broad signal at 7.38 ppm, which is attributed to the NH group in  $\text{CD}_3\text{CN}$ .

The synthesized compound **16** crystallizes in the orthorhombic unit cell space group *pnma*. The crystal structure gave trimethylammoniumtetracyanopyrrolide (Figure 21). The carbon-nitrogen bond length in the  $\text{C}\equiv\text{N}$  groups is on average 1.148 (16) Å.<sup>[120]</sup> The distances C1–C2 1.399 (15), C2–C3 1.409 (15) and C3–C4 1.399 (15) Å are also here between the values for a C–C single and double bond ( $\Sigma_{\text{r}_{\text{cov}}}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances C1–N1 1.357 (15), C4–N1 1.357 (13) Å and the exocyclic C–C bond lengths (1.417–1.430 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>

The distance between N6–H1 was 0.915 (18) Å<sup>[32]</sup> and the distance between N1....H1 was 1.955 (18) Å and the solid state structure of  $[\text{Me}_3\text{NH}]\text{TCP}$  consists of ion pairs of the monomer units, which are associated by H-bonding between the H atom of  $[\text{Me}_3\text{NH}]^+$  ion and one of the N atoms of the TCP ion where was the distance between N1....H1–N6 is 2.86 Å (Figure 21).<sup>[36]</sup>

The  $\text{C}_{2v}$  symmetry of the TCP anion is confirmed by the interatomic distances in the same molecule (for example, N1–C1 equal to N1–C4). It shows that the  $\pi$ -electrons thus all the atoms are highly delocalized and connected formal in five-membered ring by a double bond with each other, as in other aromatic systems.

The aromaticity is confirmed by the Hückel rule. The six  $\pi$  electrons satisfy the rule  $4n + 2$  and the molecule is completely planar. All dihedral angles are either  $180^\circ$  or  $0^\circ$  large. From the high symmetry of the anion follows that there can only be very weak interactions with the cation, which is why form layers and no mesh.

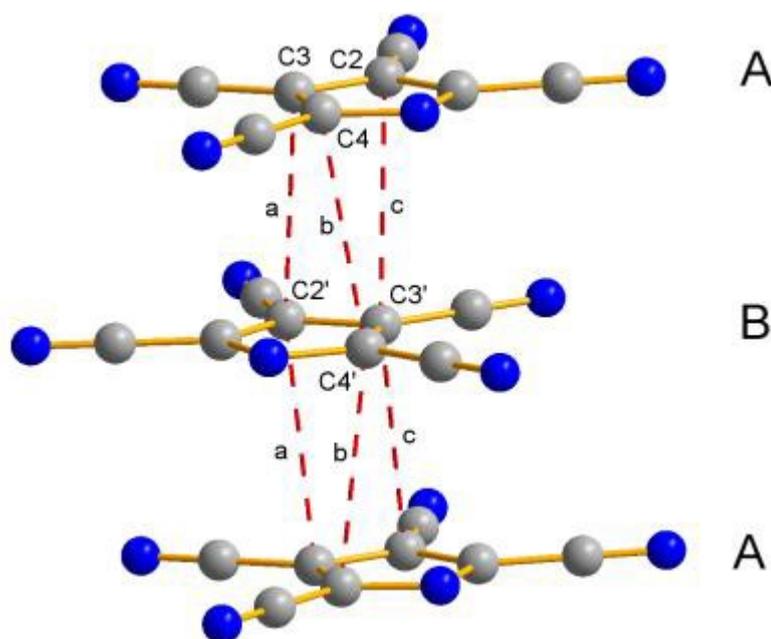


**Figure 21:** Ball and stick representation of **16** with the color code: blue –Nitrogen, gray – Carbon, white – Hydrogen.

There are coordinative interactions between cation and anion are observed. However, as illustrated in Figure 22, anion•••anion  $\pi$ - $\pi$  stacking <sup>[131, 132]</sup> is observed between the TCP layers (3.5–3.6 Å).

The " $\pi$  stacking" describes an interaction of the  $\pi$ -electrons of a compound with other  $\pi$ -electrons. For example, the phenyl rings of a compound can interact with the solvent (benzene, toluene), therefore, the removal of the solvent is difficult.<sup>[83]</sup> The TCP rings show strong intermolecular interactions, as shown here.

As can be seen in Figure 22, the TCP rings are in two orientations (A, B), which then alternately layers one above the other. The red, dashed lines represent the interactions of the  $\pi$ -electron pairs are to each other.

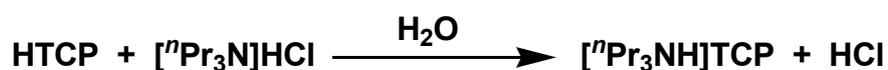


**Figure 22:** Ball and stick representation, wherein the dashed red lines show interaction between of the  $\pi$ -electrons ( $\pi$  stacking) of various levels. Distances [ $\text{\AA}$ ]:  $a = 3.63$ ,  $b = 3.58$ ,  $c = 3.5$ .

### 3.5.15 Synthesis of tripropylammoniumtetracyanopyrrolide [ ${}^n\text{Pr}_3\text{NH}$ ]TCP (17)

The synthesis of this reaction was carried out according to the following procedure. A solution of tripropylammoniumchloride in water was added to a solution of tetracyanopyrrole in water at room temperature. After stirring overnight, the resulting was filtrated.

For purification, the yellow filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with dichloromethane and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at room temperature for three days resulted colorless crystals of [ ${}^n\text{Pr}_3\text{NH}$ ]TCP (Scheme 39).



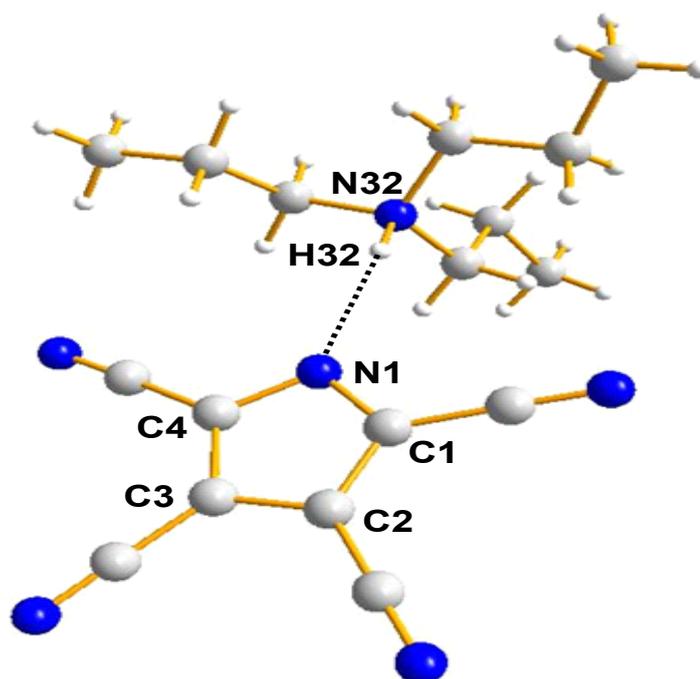
Yield: 63%

**Scheme 39:** Synthesis of tripropylammoniumtetracyanopyrrolide.

The synthesized compound **17** crystallizes in the triclinic unit cell space group  $P-1$ . The crystal structure gave tripropylammoniumtetracyanopyrrolide (Figure 23). The carbon-nitrogen bond length in the  $C\equiv N$  groups is on average 1.145 (2) Å.<sup>[120]</sup> The distances C1–C2 1.398 (2), C2–C3 1.409 (2) and C3–C4 1.397 (2) Å are also here between the values for a C–C single and double bond ( $\Sigma r_{cov}$  C=C 1.34 and C–C 1.54 Å),<sup>[115]</sup> the distances N1–C1 1.353 (2), N1–C4 1.350 (2) Å and the exocyclic C–C bond lengths (1.414–1.430 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.<sup>[36]</sup>

The distance between N32–H32 was 1.000 (13) Å<sup>[32]</sup> and the distance between N1....H32 was 2.100 (13) Å and the solid state structure of  $[{}^nPr_3NH]TCP$  consists of ion pairs of the monomer units, which are associated by H-bonding between the H atom of  $[{}^nPr_3NH]^+$  ion and one of the N atoms of the TCP ion where was the distance between N1.....H32–N32 is 2.97 (18) Å (Figure 23).<sup>[36]</sup>

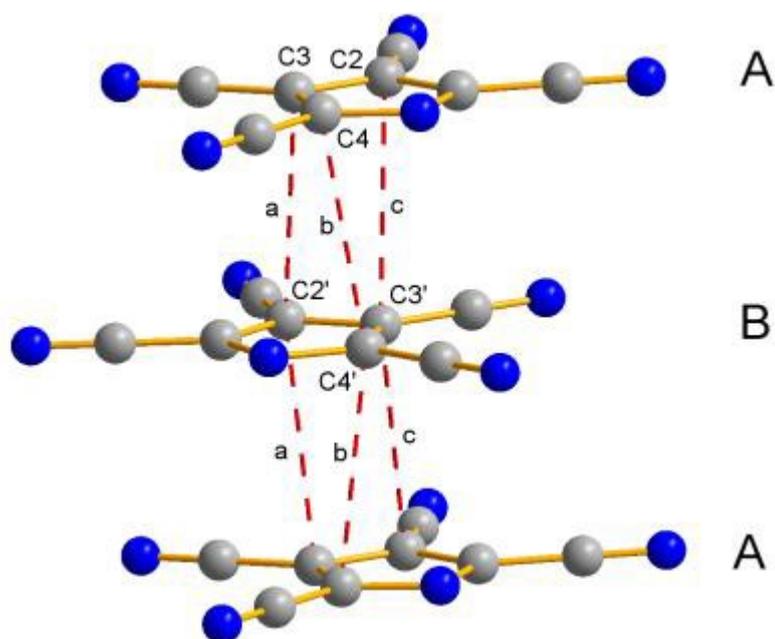
The  $C_{2v}$  symmetry of the TCP anion is confirmed by the interatomic distances in the same molecule (for example, N1–C1 equal to N1–C4). It shows that the  $\pi$ -electrons thus all the atoms are highly delocalized and connected formal in five-membered ring by a double bond with each other, as in other aromatic systems.



**Figure 23:** Ball and stick representation of **17** with the color code: blue –Nitrogen, gray – Carbon, white – Hydrogen.

There are coordinative interactions between cation and anion are observed. However, as illustrated in Figure 24, anion•••anion  $\pi$ - $\pi$  stacking <sup>[131, 132]</sup> is observed between the TCP layers (3.3–3.6 Å).

As can be seen in Figure 24, the TCP rings are in two orientations (A, B), which then alternately layers one above the other. The red, dashed lines represent the interactions of the  $\pi$ -electron pairs are to each other.



**Figure 24:** Ball and stick representation, wherein the dashed red lines show interaction between of the  $\pi$ -electrons ( $\pi$  stacking) of various levels. Distances [ $\text{\AA}$ ]:  $a = 3.65$ ,  $b = 3.35$ ,  $c = 3.61$ .

The  $\text{C}\equiv\text{N}$  group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp at  $2234\text{ cm}^{-1}$ . In the **IR-ATR** spectrum, the band appears as very strong at  $2220\text{ cm}^{-1}$ .

Characteristic of the TCP anion are the four  $^{13}\text{C}$  **NMR** signals occurring at a shift of 119.4, 114.3, 112.2 and 102.4 ppm. It involves singlet signals as where the methyl and ethyl group of the cation, which can be found at 11.36, 17.20 and 53.95 ppm respectively.

A  $^1\text{H}$  **NMR** spectrum appears signals at 1.05, 1.74 and 2.96 ppm, which are attributed to the methyl group and two ethyl groups respectively, and a singlet signal at 9.50 ppm, which is attributed to the NH group in  $\text{CD}_2\text{Cl}_2$ .

By **DSC** measurement the melting point at  $65\text{ }^\circ\text{C}$  and decompose temperature at  $320\text{ }^\circ\text{C}$ , at a heating rate of  $10\text{ K / min}$  were determined.

The aim of the syntheses of these trialkylammoniumtetracyanopyrrolides [ $\text{R}_3\text{NH}$ ]TCP (16:  $\text{R} = \text{Me}$ , 17:  $\text{R} = \text{}^n\text{Pr}$ ) was reactions planed with metal hydroxides  $\text{M}(\text{OH})_x$  and metal hydrides  $\text{M}_x\text{H}_y$  to form new coordination polymers. But there was no more time to carry out these reactions.

## 4. Summary

The aim of this study was to examine the coordination chemistry of novel donor-acceptor complexes (with new CN linkers) containing neutral phosphorus(III)cyanide and anions such as tetracyanopyrrolide (TCP).

In this work the possibility of the reaction  $P(CN)_3$  with weakly coordinating anions (WCA)<sup>-</sup> such as  $Ag(OOCCF_3)$ ,  $Ag[Al(OCH(CF_3)_2)_4]$ ,  $AgBF_4$  and  $Ag[B(C_6F_5)_4] \cdot Et_2O$  was investigated as CN super carrier in a metathesis reaction.

In all reactions except the reaction with  $Ag[B(C_6F_5)_4]$  the presence of a distinct CN band at  $2164\text{ cm}^{-1}$  in the IR-ATR spectrum of the white precipitate was observed. This agrees well with comparative data of  $(AgCN)_\infty$  from the literature.<sup>[92]</sup> Nevertheless it could not be isolated any product which could result from AgCN elimination.

In the reaction of  $P(CN)_3$  with  $Ag(OOCCF_3)$  and  $AgBF_4$ , no changes in <sup>31</sup>P NMR and IR-ATR spectra compared to the spectra from the starting materials were observed.

With  $P(CN)_3$  and  $Ag[Al(OCH(CF_3)_2)_4]$ , changes in <sup>13</sup>P NMR and IR-ATR spectra compared to the spectra from the starting materials were observed.

About the reaction of  $P(CN)_3$  with  $Ag[B(C_6F_5)_4] \cdot Et_2O$  at room temperature or low temperature ( $-70\text{ }^\circ\text{C}$ ), no reaction has occurred. After heating the solution for two hours the <sup>19</sup>F NMR spectrum gave more signals compared to <sup>19</sup>F NMR spectrum of starting material and led to decomposition of the anion because the use of heating.

The resulting residue from the mixture after removal of the solvent for all of these reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as  $CH_3CN$  or THF, but it shows a solubility in DMSO, and this confirms to the formation of the polymer.

Generally, in all reactions, there are no isolated products, only a mixture from products and starting materials. The crystals obtained from the reaction solutions were characterized always as  $P(CN)_3$ .

Reactions from  $P(CN)_3$  as Lewis acid with different Lewis bases were tested. In the reaction of  $P(CN)_3$  with  $Et_3N$  and TMEDA, there is observed a change in <sup>13</sup>P NMR and IR-ATR spectra compared to the starting solution.

With  $\text{P}(\text{CN})_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ , there is observed a change in  $^{11}\text{B}$  NMR spectrum compared to  $^{11}\text{B}$  NMR spectrum of  $\text{B}(\text{C}_6\text{F}_5)_3$

In the reaction of  $\text{P}(\text{CN})_3$  with 2,2'-bipyridine and sulfur at room temperature or low temperature ( $-70\text{ }^\circ\text{C}$ ), no reaction has occurred, where in  $^{31}\text{P}$  NMR and IR-ATR spectra show the same signal for  $\text{P}(\text{CN})_3$  and the same vibration for CN group at  $\text{P}(\text{CN})_3$ .

About the reaction of  $\text{P}(\text{CN})_3$  with DMAP (DMAP = 4-dimethylaminopyridine) and 1,8-DAN (DAN = diamionaphthalene), changes in  $^{31}\text{P}$  NMR and IR-ATR spectra at room temperature or low temperature compared to the spectra from the starting materials were observed.

In the  $^{31}\text{P}$  NMR spectrum for the reaction of  $\text{P}(\text{CN})_3$  with  $\text{LiN}(\text{SiMe}_3)_2$ , a major signal at  $-197.50$  ppm was observed and confirmed the formation of  $[\text{P}(\text{CN})_2]^-$  anion<sup>[17]</sup>.

In the reaction of  $\text{P}(\text{CN})_3$  with trimethylamine and sodium tetraphenylborate the isolated crystals from this reaction were only triethylammoniumsalt of the tetraphenylborate, where the proton could come from the solvent.

About the reaction of  $\text{P}(\text{CN})_3$  with  $\text{Et}_3\text{N}$  and  $\text{AgBF}_4$ , there is observed a change in  $^{31}\text{P}$  NMR spectrum, as well as, in the IR-ATR spectrum shows a vibration for CN group at  $2164\text{ cm}^{-1}$  was confirmed the formation of  $\text{AgCN}$ . Additionally, in the reaction of  $\text{P}(\text{CN})_3$  with  $\text{PPh}_3$  and  $\text{Na}[\text{B}(\text{Ph})_4]$ , there is also observed a change in  $^{31}\text{P}$  NMR spectrum compared to the spectra from the starting materials

The resulting residue from the mixture after removal of the solvent in all reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as  $\text{CH}_3\text{CN}$  or THF, except the resulting residue from the reaction with  $\text{B}(\text{C}_6\text{F}_5)_3$  and 1,8-diamionaphthalene shows a good solubility in polar solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$  and THF.

Although the presence of more changes in NMR ( $^{31}\text{P}$ ,  $^{19}\text{F}$  and  $^{11}\text{B}$ ) and IR-ATR spectra compared to the spectra from the starting materials were observed, but in all reactions, there are no isolated products, only a mixture from products and starting materials.

The product for the reaction of  $\text{PPh}_3$  with  $\text{P}(\text{CN})_3$  in a dichloromethane solution was unexpected and was obtained as colorless crystals of the product  $[\text{Ph}_3\text{P}=\text{N}-\text{C}(\text{CN})_2-\text{C}(\text{CN})_2-\text{N}=\text{PPh}_3] \cdot 2\text{CH}_2\text{Cl}_2$  (**5**). That means an oxidation from P(III) to P(V) has occurred.

The using  $\text{P}(\text{CN})_3$  as a ligand in transition metal chemistry was investigated. In all reactions of  $\text{P}(\text{CN})_3$  with transition metal complexes the formation of a new product were observed except the reaction with  $[\text{Mo}(\text{CO})_3(\text{EtCN})_3]$  was referred always to the presence of  $\text{P}(\text{CN})_3$ .

The product for the reaction of  $\text{P}(\text{CN})_3$  with dichloro(*p*-cymene)ruthenium(II)dimer was insoluble in most of solvents, just in DMSO, so it may be that it is a polymer. The product for the reaction of  $\text{P}(\text{CN})_3$  with palladium and nickel complexes was  $\text{Pd}(\text{CN})_2 \cdot (\text{PPh}_3)_2$  and  $\text{Ni}(\text{CN})_2 \cdot (\text{triphos})$ , respectively and was characterized by mean of X-ray crystallography, that means an oxidation from Pd(0) to Pd(II) in the case Pd complex and an oxidation from Ni(0) to Ni(II) in the case Ni complex has occurred, as well as, there was no coordination of phosphorus atom to metal ion in both reactions, but the product in both reactions was not a polymer because it was soluble in  $\text{CH}_2\text{Cl}_2$ . About the reaction of  $\text{P}(\text{CN})_3$  with tungsten complex, the resulting residue was not a polymer also because it was soluble in  $\text{CH}_2\text{Cl}_2$  but that it was not possible to isolate any crystals.

Finally, reactions from  $\text{P}(\text{CN})_3$  with room temperature ionic liquids (RT-ILs) in  $\text{CH}_2\text{Cl}_2$  and THF solvents were investigated. New signals in  $^{31}\text{P}$  NMR and IR-ATR spectra from the reaction of  $\text{P}(\text{CN})_3$  with EMim $[\text{N}(\text{CN})_2]$  in two different solvents were observed, but the residue for these reactions was almost insoluble in nonpolar or slightly polar organic solvents such as hexane or toluene, but showed a very poor solubility in common polar organic solvents such as MeCN and THF. But that it was not possible to isolate any product.

At the same time, the resulting residue from the reaction of  $\text{P}(\text{CN})_3$  with EMim $[\text{N}(\text{CN})_2]$  was unstable in water and a hydrolyzation took place, because  $^{31}\text{P}$  NMR spectrum in  $\text{D}_2\text{O}$  was gave new signals and referred to form phosphoroxide or phosphonic acid  $[\text{DPO}(\text{OD})_2]$ .

About the reaction of  $\text{P}(\text{CN})_3$  with silver dicyanoamide-tris-(pentafluorophenyl)borane•diether, all results were referred the formation of a new product with a good solubility in MeCN, that means it was not a polymer. But that it was not possible to isolate any product.

In the second part of this thesis, the possibility of using the tetracyanopyrrolide anion as a ligand in transition metal chemistry was investigated. New transition metal complexes containing the tetracyanopyrrolide anion  $[\text{C}_4(\text{CN})_4\text{N}]^-$  (TCP) were synthesized from tetracyanopyrrole (HTCP) and characterized by mean of X-ray crystallography. The complexes showed that, the TCP anion acts as a monodentate ligand towards transition metal ions. Only the  $\eta^1$ -N- $\sigma$  coordination mode via the electron pair of the N atom of the pyrrole ring was found.

The other possible coordination mode, via the N atoms of the nitrile substituents, which was published before from our group for the structure of NaTCP,<sup>[36]</sup> was observed for the product of reaction HTCP with  $\text{Mn}(\text{acac})_3$  in acetonitrile and characterized by mean of X-ray crystallography.

In the reaction of  $[\text{Me}_4\text{N}]\text{TCP}$  with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in acetonitrile/water, the tetracyanopyrrolide anion underwent hydrolysis of one cyano substituent to a carboxamide group, transforming TCP into tricyano-2-pyrrole(carboxamide).

AgTCP was prepared in high yield after isolating from reaction  $[\text{Me}_4\text{N}]\text{TCP}$  with  $\text{AgNO}_3$  in acetone/water and could characterized completely for the first time. Additionally, a new procedure was found for the preparation of tetracyanopyrrole (HTCP) in high yield (71%) from reaction AgTCP with excess HCl in water and HTCP obtained could also be fully characterized.

However, a sandwich structure with  $\eta^5$ -pyrrolide ligands as characteristic for prepared complexes was not observed, which is obviously caused by the low electron density in the central  $\text{C}_4\text{N}$  ring due to the strong electron-withdrawing effect of the nitrile substituents.

New salts bearing the TCP anion were synthesized from reaction  $[\text{R}_3\text{NH}]\text{Cl}$  ( $\text{R} = \text{Me}$  or  $^i\text{Pr}$ ) with HTCP in water and were characterized by mean of X-ray crystallography. The aim of the syntheses of these trialkylammoniumtetracyanopyrrolides  $[\text{R}_3\text{NH}]\text{TCP}$  were the following reactions planed with metal hydroxides  $\text{M}(\text{OH})_x$  and metal hydrides  $\text{M}_x\text{H}_y$  to form new coordination polymers. But there was no more time to carry out these reactions.

## 5. Appendix

### 5.1 Experimental part

#### 5.1.1 Working technique

Unless otherwise indicated, all experiments were carried out under argon atmosphere using Schlenk technique. All glassware was baked out for three times with a hot air blower in a high vacuum and cooled under argon atmosphere. The filling and transfer to hydrolysis substances was carried out under an inert atmosphere in a drybox. Solvents were distilled under argon atmosphere and transferred for the experiments with disposable syringes. The disposable syringes have been previously purged three times with argon.

The solvents used were obtained through the chemical trade and if necessary cleaned and dried by literature methods.<sup>[133]</sup> Dichloromethane  $\text{CH}_2\text{Cl}_2$  was purified analogously to a literature method<sup>[134]</sup> and only about  $\text{P}_4\text{O}_{10}$ , then dried over  $\text{CaH}_2$  and freshly distilled. Tetrahydrofuran (THF), benzene ( $\text{C}_6\text{H}_6$ ) and toluene ( $\text{C}_7\text{H}_8$ ) were dried over Na / benzophenone and freshly distilled. Fluorobenzene (Ar.F) and acetonitrile ( $\text{CH}_3\text{CN}$ ) were dried over  $\text{CaH}_2$  and freshly distilled. Magnesium hydroxide  $\text{Mg}(\text{OH})_2$  was freshly precipitated from an aqueous solution of  $\text{MgCl}_2$  (Merck 99%) with an aqueous solution of sodium hydroxide NaOH (VWR, 98.8%). The solid hydroxide was filtered off and washed three times with water and dried under reduced pressure. Starting materials were either obtained the chemicals trade or produced by known methods from the literature.

**Literature synthesis known:**  $\text{Ag}(\text{OOC}\text{CF}_3)$ ,<sup>[135]</sup>  $\text{Ag}[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$ ,<sup>[136]</sup>  $\text{AgBF}_4$ ,<sup>[137]</sup>  $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{Et}_2\text{O}$ ,<sup>[138]</sup>  $\text{B}(\text{C}_6\text{F}_5)_3$ ,<sup>[138]</sup>  $\text{Et}_3\text{N}$  (Merck, 99%), TMEDA (Aldrich, 99%), 2,2'-bipyridine (Fluka, 99%),  $\text{PPh}_3$  (Fluka, 97%), Sulfur (Riedel-de Haën, 99%),  $\text{Na}[\text{B}(\text{Ph})_4]$  (Fluka, 98%),  $\text{LiN}(\text{SiMe}_3)_2$ ,<sup>[139]</sup> 1,8-diamino naphthalene (Alfa Aesar, 97%), dichloro-(*P*-cymene)ruthenium(II)dimer,<sup>[140]</sup>  $\text{Pd}(\text{PPh}_3)_4$ ,<sup>[141]</sup> 1,1,1-tris[(diphenylphosphino)methyl]ethane,<sup>[142]</sup>  $\text{Fe}(\text{Cp})_2\text{PF}_6$ ,<sup>[143]</sup> [hydridotris(3,5-dimethylpyrazolyl)borate tricarbonyl tungsten(II)],<sup>[144]</sup>  $[\text{Mo}(\text{CO})_3(\text{EtCN})_3]$ ,<sup>[145]</sup>  $\text{Ag}[\text{N}\{\text{CN}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}_2]\cdot\text{Et}_2\text{O}$ ,<sup>[111]</sup>  $\text{Ni}(\text{COD})_2$ ,<sup>[146]</sup>  $\text{EMim}\cdot\text{N}(\text{CN})_2$ ,<sup>[147]</sup>  $\text{BMim}\cdot\text{N}(\text{CN})_2$ ,<sup>[147]</sup> NaCN (Alfa Aesar, 98%),  $\text{CS}_2$  (Aldrich, 99%), DMF (Grüssing, 99%),  $\text{NaN}_3$  (Acros Organics, 99%),  $[\text{Me}_4\text{N}]\text{Cl}$  (Roth, 98%),  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Roth, 99%),  $\text{C}_2\text{H}_4\text{Cl}_2$  (Roth, 99%),  $\text{AgNO}_3$  (Fluka, 99%),  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  (Merck, 99%), zinc powder (Riedel-de

Haën, 99%), iron powder (FerakBerlin, 99.5%), ethanol (Roth, 99%), isopropyl alcohol (Roth, 99%), silver tetracyanopyrrolide AgTCP,<sup>[36]</sup> tetracyano-1,4-dithiinC<sub>8</sub>N<sub>4</sub>S<sub>2</sub>,<sup>[36, 56]</sup> Tetracyanopyrrole HTCP,<sup>[36]</sup> [Me<sub>4</sub>N]TCP,<sup>[36]</sup> trimethylammoniumchloride (Aldrich,98%), Cu(acac)<sub>2</sub>,<sup>[148]</sup> Mn(acac)<sub>3</sub>,<sup>[149]</sup> Cr(acac)<sub>3</sub>,<sup>[150]</sup> tripropylammoniumchloride.<sup>[151]</sup>

## 5.1.2 Analytical methods

### *Single-crystal*

Crystals for X-ray crystal were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods (*SHELXS-97*)<sup>[152]</sup> and refined by full-matrix least squares procedures (*SHELXL-97*).<sup>[153]</sup> Semi-empirical absorption corrections were applied (*SADABS*).<sup>[154]</sup> All non-hydrogen atoms were refined anisotropically, hydrogen atoms were added arithmetically, with two exception found in compounds **16** and **17** where the bridging N6–H1 $\cdots$ N1 in **16** and the bridging N32–H32 $\cdots$ N1 in **17** hydrogen atom are located and refined without constraint.

### *NMR spectroscopy*

NMR: <sup>1</sup>H-, <sup>11</sup>B-, <sup>13</sup>C-, <sup>19</sup>F-, <sup>31</sup>P- and <sup>29</sup>Si-INEPT-NMR spectra were obtained on a Bruker *AVANCE 250* (250 MHz) and *AVANCE 300* (300 MHz) or *AVANCE 500* (500 MHz) spectrometers and were referenced internally to the deuterated solvent (<sup>13</sup>C NMR, CD<sub>3</sub>CN:  $\delta_{\text{Ref}} = 1.3$  and 118.2 ppm, d<sub>6</sub>-DMSO:  $\delta_{\text{Ref}} = 39.5$  ppm, CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_{\text{Ref}} = 54.0$  ppm) or to protic impurities in the deuterated solvent (<sup>1</sup>H, CD<sub>2</sub>H<sub>2</sub>CN:  $\delta_{\text{Ref}} = 1.93$  ppm, d<sub>6</sub>-DMSO:  $\delta_{\text{Ref}} = 2.49$  ppm, CHDCl<sub>2</sub>:  $\delta_{\text{Ref}} = 5.31$  ppm). [D<sub>3</sub>]CD<sub>3</sub>CN, [D<sub>6</sub>]DMSO and [D<sub>2</sub>]CD<sub>2</sub>Cl<sub>2</sub> were dried with molecular sieves (3Å). Extra (<sup>11</sup>B, B(OH)<sub>3</sub>:  $\delta_{\text{Ref}} = 0$  ppm, <sup>19</sup>F, CFCl<sub>3</sub>:  $\delta_{\text{Ref}} = 0$  ppm, <sup>31</sup>P: 85% H<sub>3</sub>PO<sub>4</sub>,  $\delta_{\text{Ref}} = 0$  ppm and <sup>29</sup>Si: SiMe<sub>4</sub>,  $\delta_{\text{Ref}} = 0$  ppm).

### *IR spectroscopy*

For the recording of spectra a Nicolet 380 FT-IR spectrometer with a Smart Orbit ATR unit was used.

### *Raman spectroscopy*

For recording the spectra was either a) Bruker VERTEX 70 FT-IR with RAM II FT-Raman module equipped with a Nd: YAG laser (1064 nm) or a b) Lab RAM HR 800 Horiba Jobin Yvon equipped with a BX40 microscope (focus 1 microns) or an olympus MPLAN 50xNA 0.70 lens. To stimulate an infrared laser (785 nm, 100 mW, air cooled, diode laser), a red laser (633 nm, 17 mW, HeNe-laser); or a blue laser (532 nm, 50 mW, air-cooled, frequency-doubled Nd: YAG solid-state laser) was used.

### *Elemental Analysis*

Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikroanalysator TruSpec-932 from Leco was used.

### *DSC*

DSC 823e from Mettler-Toledo (heating rate 10K/min) was used.

### *TGA measurements*

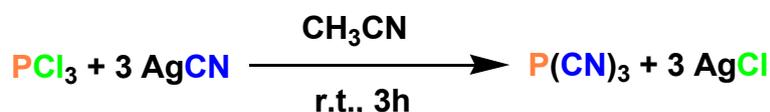
TGA measurements were performed on a Setaram TGA-DSC LapSys 1600 under argon with a heating rate of 5K/min carried out. Mass losses were about the derivation of TG-curve evaluated (DTG curve). The temperatures of the mass losses were on the determined integration of DTG curve. The temperatures indicated correspond to the interpolated intersection of the tangent at the inflection point of the DTG curve with the interpolated baseline of DTG curve. All data were analyzed using the setsoft received 2000 software.

### *Mass spectroscopy*

Finnigan MAT 95-XP from Thermo Electron (ESI-TOF) was used.

## 5.1.3 Synthesis of starting materials

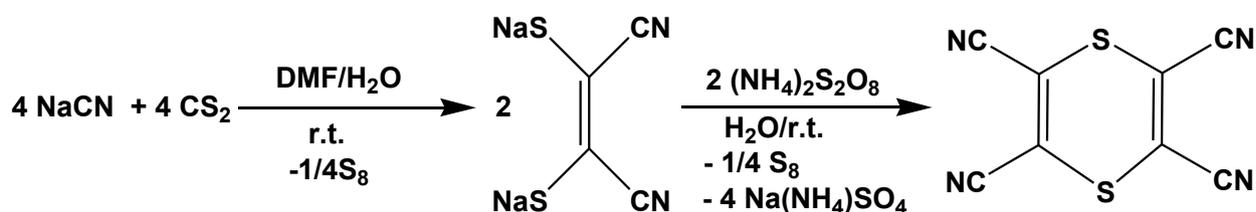
### 5.1.3.1 Synthesis of tricyanophosphine



The synthesis is carried out following a literature method.<sup>[4]</sup> To a suspension solution of AgCN (41.00 g, 306.2 mmol) in acetonitrile (150 mL), a trichlorophosphine (11.5 g, 83.74 mmol) was added with stirring at ambient temperature. The suspension obtained was stirred for 3 hours as the exclusion of light and then filtered off the excess AgCN through a G4 frit. The filter residue was washed twice with CH<sub>3</sub>CN and the filtrate carefully was dried in a vacuum. It should be ensured that P(CN)<sub>3</sub> already sublimated under high vacuum at room temperature; it should be also ensured by additional cooling that only the solvent was evaporated. The white-yellowish solid obtained was purified by sublimation at 1x10<sup>-3</sup> mbar and possibly gentle heating to 60 °C. This gave 8.08 g P(CN)<sub>3</sub> (74.11 mmol) in colorless needles, yield 88%

**EA%** calc. (found) C 33.05 (32.39); N 38.54 (37.76). <sup>13</sup>C NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 110.74 (d, 3C, CN). <sup>31</sup>P NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -125.2 (s, P(CN)<sub>3</sub>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2204 (m), 1241 (w), 622 (s), 593 (vs), 570 (vs). **Raman** (25 °C, 65 mW, 24 scans, cm<sup>-1</sup>): 2209 (5), 2204 (8), 627 (1), 599 (1), 571 (2), 465 (3), 145 (4), 117 (10).

### 5.1.3.2 Synthesis of tetracyano-1,4-dithiin (C<sub>8</sub>N<sub>4</sub>S<sub>2</sub>)

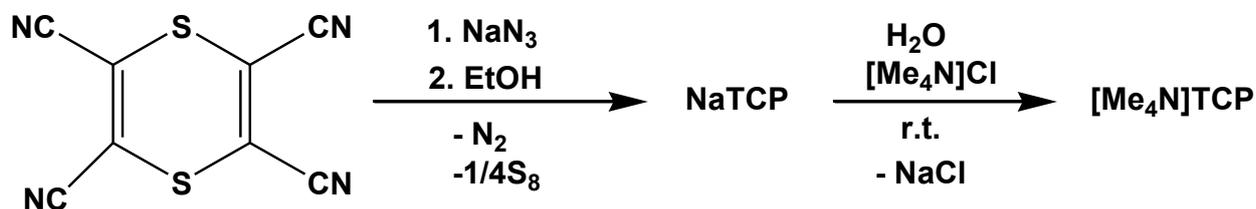


A suspension of NaCN (30.0 g, 612 mmol) and DMF (185mL) was stirred vigorously and CS<sub>2</sub> (46.6 g, 612 mmol) was added dropwise over 40min. H<sub>2</sub>O (dest. 1.5 L) was added and the mixture was stirred overnight at ambient temperature. The precipitate (sulfur) was removed

by filtration. A solution of H<sub>2</sub>O (dest. 305mL) and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (139.7 g, 216 mmol) was added to the filtrate dropwise over an hour, the mixture was stirred over 40min, and the raw product was collected by filtration. Several recrystallisations from a saturated dichloroethane solution of tetracyano-1,4-dithiin resulted yellow crystals. Yield 22 g (67 %, 102 mmol) tetracyano-1,4-dithiin.

**C/H/N/S analysis** % calc. (found): C 44.43 (44.21); H 0.0 (0.0); N 25.91 (25.35); S 29.66 (29.61). <sup>13</sup>C NMR (300 K, d<sub>6</sub>-DMSO, 250.13 MHz): δ = 125.4 (s, 4C, CN), 112.4 (s, 4C, C<sub>quat</sub>). IR (25 °C, ATR, 32 scans cm<sup>-1</sup>): 2242 (w), 2229 (w), 2218 (w), 1558 (w), 1519 (vs), 1176 (m), 1157 (m), 1054 (w), 1011 (s), 972 (s), 933 (m), 873 (m), 811 (w), 645 (m), 619 (w). Raman (25 °C, 65 mW, 3 scans, cm<sup>-1</sup>): 2243 (5), 2229 (10), 2220 (10), 1562 (7), 1522 (1), 1158 (1), 1130 (1), 646 (2), 621 (2), 524 (2), 516 (1), 506 (3), 472 (4), 351 (2), 341 (2), 312 (1).

### 5.1.3.3 Synthesis of tetramethylammoniumtetracyanopyrrolide [Me<sub>4</sub>N]TCP

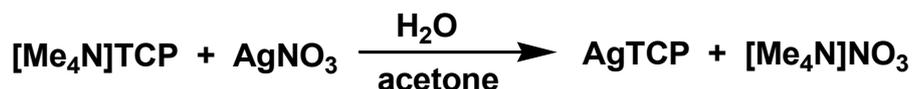


Tetracyano-1,4-dithiin (10.8 g, 50 mmol), sodium azide (3.25 g, 50 mmol), and (200 mL) of ethanol was mixed and stirred overnight, and nitrogen slowly evolved. The dark red reaction mixture was filtered to remove elemental sulfur, and the filtrate was evaporated to dryness under reduced pressure. Water (dest. 200mL) was added, and a brown solid that contained appreciable amounts of elemental sulfur was removed by filtration. The aqueous filtrate was decolorized with (Darco) and stirred at 0 °C, tetramethylammoniumchloride (11g, 100 mmol) was added as a saturated aqueous solution. Reddish brown tetramethylammoniumtetracyanopyrrolide 8.4 g (70 %, 35 mmol) was removed by filtration, washed with water, and dried under reduced pressure.

Several recrystallisations from a saturated isopropylalcohol solution of tetramethylammonium tetracyanopyrrolide resulted colorless crystals.

**DSC:** m.p. 272 °C,  $T_{\text{dec}} = 324$  °C. **C/H/N analysis** % calc. (found): C 59.99 (59.14); H 5.03 (5.56); N 34.98 (33.86).  **$^1\text{H}$  NMR** (300 K,  $d_6$ -DMSO, 250.13 MHz):  $\delta = 3.09$  (s, 12H,  $\text{CH}_3$ ).  **$^{13}\text{C}$  NMR** (300 K,  $d_6$ -DMSO, 250.13 MHz):  $\delta = 119.7$  (s, 2C,  $\text{C}_{\text{quat}}$ ), 114.5 (s, 2C,  $\text{C}_{\text{quat}}$ ), 112.4 (s, 2C,  $\text{C}_{\text{quat}}$ ), 102.0 (s, 2C,  $\text{C}_{\text{quat}}$ ), 54.4 (s, 4C,  $\text{CH}_3$ ). **IR** (25 °C, ATR, 32 scans  $\text{cm}^{-1}$ ): 3041 (w), 2982 (w), 2759 (w), 2720 (w), 2221 (vs), 1543 (w), 1485 (vs), 1475 (s), 1450 (s), 1383 (m), 1330 (m), 1290 (m), 1271 (m), 1204 (w), 1183 (w), 1133 (w), 1074 (m), 948 (vs), 788 (w), 676 (w), 557 (w). **Raman** (25 °C, 65 mW, 30 scans,  $\text{cm}^{-1}$ ): 2233 (6), 1474 (3), 1415 (4), 1308 (2), 751 (4), 540 (3). **MS (ESI-TOF):** calcu.(found): cation 74.0964 (74.0971), anion 166.0159 (166.0160).

#### 5.1.3.4 Synthesis of Silver tetracyanopyrrolide AgTCP



To a stirred solution of tetramethylammoniumtetracyanopyrrolide (2.4 g, 10 mmol) in water (dest. / acetone 10 mL: 100 mL), a solution of silver nitrate  $\text{AgNO}_3$  (2.2 g, 13 mmol) in water (dest., 30 mL) was added at ambient temperature. After stirring for 3h as the exclusion of light, the tan silver salt was collected by filtration, washed three times with ethanol (20 mL), and dried under reduced pressure; Yield 2.05 g (75% , 7.48 mmol).

**DSC:** m.p. 270 °C,  $T_{\text{dec}} = 313$  °C. **C/H/N analysis** % calc. (found) for **AgTCP $\cdot$ 0.5H $_2$ O**: C 33.95 (33.40); H 0.36 (0.09); N 24.75 (23.34).  **$^{13}\text{C}$  NMR** (298.2 K,  $d_6$ -DMSO, 300.13 MHz):  $\delta = 119.8$  (s, 2C,  $\text{C}_{\text{quat}}$ ), 114.3 (s, 2C,  $\text{C}_{\text{quat}}$ ), 112.3 (s, 2C,  $\text{C}_{\text{quat}}$ ), 102.1 (s, 2C,  $\text{C}_{\text{quat}}$ ). **IR** (25 °C, ATR, 32 scans  $\text{cm}^{-1}$ ): 3560 (w), 2973 (w), 2935 (w), 2899 (w), 2798 (w), 2741 (w), 2650 (w), 2260 (m), 2233 (vs), 2031 (w), 1981 (w), 1614 (w), 1481 (s), 1420 (s), 1325 (m), 1240 (w), 1092 (m), 1036(w), 951 (w), 903 (w), 876 (w), 844 (w), 810 (w), 714 (w), 696 (m), 683 (m), 611 (w), 557 (w), 534 (w). **MS (ESI-TOF):** calcu. (found) cation 106.9045 (106.9047), anion 166.0159 (166.0160).

### 5.1.3.5 Synthesis of tetracyanopyrrole HTCP

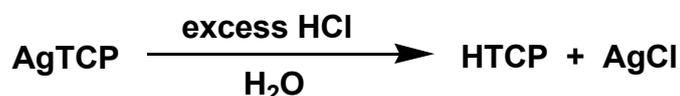
#### Procedure 1



A column containing Amberlyst 15 ion-exchange resin (200g) was thoroughly washed with 10 mol 10% HCl, deionized water, acetone, and acetonitrile. A solution of tetramethylammoniumtetracyanopyrrolide (2.4g, 10 mmol) in acetonitrile (30 mL) was slowly added to the top of the column. The free pyrrole was eluted with acetonitrile and the eluent evaporated to dryness under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column. The column was eluted with ethylacetate/*n*-heptane (v:v = 3:1). The resulting purified fractions were combined and evaporated under reduced pressure. The precipitate was washed two times with dichloromethane (15 mL) under heating, and dried *in vacuo* at room temperature; Yield 0.75 g (45 %, 4.5 mmol).

**C/H/N analysis** % calc. (found): C 57.49 (57.04); H 0.60 (0.47); N 41.90 (41.28). **<sup>1</sup>H NMR** (300 K, CD<sub>3</sub>CN, 250.13 MHz): δ = 11.03 (s, 1H, *NH*). **<sup>13</sup>C NMR** (298 K, CD<sub>3</sub>CN, 250.13 MHz): δ = 112.1 (s, 2C, C<sub>quat</sub>), 108.8 (s, 2C, C<sub>quat</sub>), 107.6 (s, 2C, C<sub>quat</sub>), 105.7 (s, 2C, C<sub>quat</sub>). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3543 (vw), 3168 (s), 3101 (s), 3001 (m), 2902 (w), 2819 (w), 2708 (w), 2291 (vw), 2260 (m), 2243 (vs), 1596 (w), 1494 (m), 1452 (s), 1347 (w), 1256 (s), 1224 (m), 1190 (m), 1018 (w), 962 (w), 936 (vw), 837 (w), 745 (vs), 685 (vs), 673 (s).

#### Procedure 2



To a stirred suspension of silver tetracyanopyrrolide (1.5 g, 5.47 mmol) in water (dest., 65 mL), hydrochloric acid (0.39 g, 10.68 mmol) was added at ambient temperature. The resulting suspension was allowed to stir overnight. The resulting suspension was filtered, and the resulting yellow filtrate was evaporated to dryness to yield a yellow precipitate. The precipitate was washed two times with dichloromethane (15 mL) under heating, and dried *in vacuo* at room temperature for 6 h. Sublimation of the yellow residue at (150 °C) for 6 h gave 0.65 g (71%, 3.89 mmol) of tetracyanopyrrole as a white crystalline solid.

**DSC:** m.p. 207 °C,  $T_{\text{dec}} = 237$  °C. **C/H/N analysis** % calc. (found): C 57.49 (57.24); H 0.60 (0.41); N 41.90 (41.28).  **$^1\text{H}$  NMR** (298 K,  $\text{CD}_3\text{CN}$ , 300.13 MHz):  $\delta = 11.09$  (s, 1H, NH).  **$^{13}\text{C}$  NMR** (298 K,  $\text{CD}_3\text{CN}$ , 300.13 MHz):  $\delta = 112.1$  (s, 2C,  $C_{\text{quat}}$ ), 108.7 (s, 2C,  $C_{\text{quat}}$ ), 107.6 (s, 2C,  $C_{\text{quat}}$ ), 105.8 (s, 2C,  $C_{\text{quat}}$ ). **IR** (25 °C, ATR, 32 scans  $\text{cm}^{-1}$ ): 3170(m), 3100 (m), 2999 (m), 2962 (m), 2902 (w), 2818 (w), 2706 (w), 2291 (vw), 2260 (m), 2244 (s), 2198 (w), 1678 (w), 1602 (w), 1566 (w), 1493 (m), 1452 (m), 1348(w), 1258 (vs), 1224 (m), 1204(w), 1190 (w), 1087 (s), 1017 (s), 937 (w), 865 (w), 837 (m), 796 (vs), 744 (vs), 685 (vs), 673 (s). **Raman** (25 °C, 12 mW, 8 scans,  $\text{cm}^{-1}$ ): 3048 (1), 2252 (10), 1597 (0.3), 1496 (3), 1446 (5), 1348 (1), 1086 (1), 685 (1), 518 (2), 138 (2). **MS**  $m/z$  (%) = 167 (100) [M]. **HRMS (ESI):** calcu. for  $\text{C}_8\text{N}_5^-$  166.01592; found 166.01578

## 5.1.4 Synthesis of compounds

### 5.1.4.1 Reactions of tricyanophosphine

#### 5.1.4.1.1 Reaction of P(CN)<sub>3</sub> with Ag(OOCCF<sub>3</sub>)

To a stirred solution of P(CN)<sub>3</sub> (0.028 g, 0.26 mmol) in tetrahydrofuran (6 mL), a solution of silver trifluoroacetate (0.055 g, 0.25 mmol) in tetrahydrofuran (6 mL) was added dropwise at ambient temperature. The white suspension solution was allowed to stir overnight as the exclusion of light, resulting in precipitation of white precipitate. The white precipitate was removed by filtration and was washed with tetrahydrofuran, the solvent was removed *in vacuo*. The resulting residue was washed two times with tetrahydrofuran and was dried *in vacuo*.

#### *Analytical data for white precipitate:*

**C/H/N analysis %** found C 9.88; H 0.89; N 9.37; F 1.99; P 3.63. **<sup>19</sup>F NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -76.15 to -76.17 (m, 1.0), -76.85 (s, 0.2). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 3.46 (s). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2943 (w), 2860 (w), 2162 (vs), 1238 (m), 1182 (m), 1122 (m), 999 (s), 984 (s), 744 (m), 621 (m).

#### *Analytical data for resulting residue:*

**C/H/N analysis %** found C 29.42; H 1.28; N 21.91; F 11.21. **<sup>13</sup>C NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 106.80 (d, 3C, CN). **<sup>19</sup>F NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -76.80 (s, 1.0), -76.34 (s, 0.3). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -142.14 (s, P(CN)<sub>3</sub>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2958 (vw), 2929 (vw), 2873 (vw), 2204 (m), 1783 (w), 1267 (w), 1223 (w), 1165 (w), 1039 (w), 926 (w), 829 (w), 775 (w), 621 (s), 594 (vs), 575 (vs). **MS (ESI-TOF)**: cation 241.813 (8), 282.839 (2), 415.747 (3), 591.681 (2), 724.589 (2), anion 119.986 (5), 158.912 (10) Ag(CN)<sub>2</sub>, 293.820 (4), 426.729 (2).

#### 5.1.4.1.2 Reaction of P(CN)<sub>3</sub> with Ag[Al(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]

To a stirred solution of P(CN)<sub>3</sub> (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a solution of Ag[Al(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] (0.20 g, 0.25 mmol) in dichloromethane (5 mL) was added dropwise at ambient temperature. The white suspension solution was allowed to stir two days as the exclusion of light, resulting in precipitation of white precipitate. The white precipitate was removed by filtration and was washed with dichloromethane, the solvent was removed *in vacuo*. The resulting residue was washed two times with dichloromethane and was dried *in vacuo*.

##### *Analytical data for white precipitate:*

**C/H/N analysis %** found C 9.25; H 0.57; N 9.59; F 6.30; P 1.72. **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2166 (m), 1373 (w), 1300 (m), 1229 (vs), 1200 (vs), 1105 (vs), 982 (vs), 897 (m), 806 (m), 744 (m), 687 (s), 665 (m), 638 (s), 627 (s), 554 (m).

##### *Analytical data for resulting residue:*

**C/H/N analysis %** found C 20.67; H 0.62; N 9.81; F 16.06; P 10.79. **<sup>1</sup>H NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 4.40 (m, 4H, CH). **<sup>19</sup>F NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -77.35 (s, 1.0), -76.06 (s, 2.5), -74.48 (t, 3.0, ), -73.33 (s, 1.2). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 29.65 (s, 1.0), 129.35 (s, 0.2), 139.77 (s, 0.2). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2958 (w), 2928 (w), 2858 (vw), 2193 (vw), 2168 (vw), 1371 (m), 1292 (m), 1192 (vs), 1095 (vs), 987 (m), 874 (s), 858 (s), 733 (m), 687 (vs). **Raman** (25 °C, 65 mW, 4 scans, cm<sup>-1</sup>): 3015 (0.8), 2970 (1), 2953 (1), 2921 (1), 2898 (0.8), 2210 (0.2), 1496 (0.3), 1460 (0.6), 1382 (1), 1299 (0.7), 1260 (0.5), 1207 (1), 1101 (1), 1084 (0.5), 999 (0.3), 928 (3), 858 (10), 776 (2), 719 (2), 702 (2), 690 (1), 576 (2), 539 (1), 526 (1), 335 (5), 302 (2), 203 (2).

#### 5.1.4.1.3 Reaction of P(CN)<sub>3</sub> with AgBF<sub>4</sub>

To a stirred solution of P(CN)<sub>3</sub> (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a solution of silver tetrafluoridoborate (0.048 g, 0.25 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The white suspension solution was allowed to stir two days as the exclusion of light, resulting in precipitation of white precipitate. The white precipitate was removed by filtration and was washed with dichloromethane, the solvent was removed *in vacuo*. The resulting residue was washed two times with dichloromethane and was dried *in vacuo*.

***Analytical data for white precipitate:***

**C/H/N analysis** % found C 8.75; H 0.11; N 10.44; F 0.0; P 1.47. **IR** (ATR, 25 °C, 32 scans,  $\text{cm}^{-1}$ ): 2918 (w), 2850 (w), 2164 (vs), 1124 (m), 1059 (m), 849 (m), 822 (m), 623 (w), 542 (w).

***Analytical data for resulting residue:***

**C/H/N analysis** % found C 30.05; H 0.66; N 29.88; P 17.97.  **$^{19}\text{F}$  NMR** (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = -156.09$  (s, 1.0),  $-149.60$  (s, 0.4),  $-35.90$  (s, 0.05),  $-30.95$  (s, 0.05).  **$^{11}\text{B}$  NMR** (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 96.3 MHz):  $\delta = -0.03$  (s).  **$^{31}\text{P}$  NMR** (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = -125.1$  (s,  $\text{P}(\text{CN})_3$ ). **IR** (ATR, 25 °C, 32 scans,  $\text{cm}^{-1}$ ): 3213 (w), 2924 (w), 2852 (w), 2658 (w), 2488 (w), 2370 (w), 2281 (w), 2204 (m), 2094 (m), 1614 (m), 1466 (m), 1014 (s), 845 (vs), 621 (s), 573 (vs).

#### **5.1.4.1.4 Reaction of $\text{P}(\text{CN})_3$ with $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4] \cdot \text{Et}_2\text{O}$**

##### **Procedure 1**

To a stirred solution of  $\text{P}(\text{CN})_3$  (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a suspension solution of  $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4] \cdot \text{Et}_2\text{O}$  (0.22 g, 0.25 mmol) in dichloromethane (10 mL) was added dropwise at  $-70$  °C over a period of five minutes. The resulting suspension solution was allowed to warm up to ambient temperature and was stirred three days as the exclusion of light and then filtrated. The solvent was removed *in vacuo*, and the residue was washed two times with dichloromethane and was dried *in vacuo*.

**$^{31}\text{P}$  NMR** (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = -125.2$  (s,  $\text{P}(\text{CN})_3$ ).  **$^{19}\text{F}$  NMR** (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = -133.13$  (s, *o*-F),  $-163.64$  (t, *p*-F),  $-167.56$  (s, *m*-F).  **$^{11}\text{B}$  NMR** (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 96.3 MHz):  $\delta = -16.65$  (s).

##### **Procedure 2**

To a stirred solution of  $\text{P}(\text{CN})_3$  (0.055 g, 0.50 mmol) in toluene (10 mL), a solution of  $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4] \cdot \text{Et}_2\text{O}$  (0.43 g, 0.50 mmol) in toluene (10 mL) was added dropwise at ambient temperature. The colorless solution was allowed to stir overnight as the exclusion of light and

then filtered. The resulting solution was heated for four hours at 50 °C with stirring. The solvent was removed *in vacuo*, and the oil residue was dissolved in dichloromethane and concentrated, the solvent was removed *in vacuo* and the oil residue was dried *in vacuo*.

***Analytical data for colorless solution after stirring overnight:***

<sup>31</sup>P NMR (298.2 K, Toluene-d<sub>8</sub>, 300.13 MHz):  $\delta = -131.72$  (s, P(CN)<sub>3</sub>). <sup>19</sup>F NMR (298.2 K, Toluene-d<sub>8</sub>, 300.13 MHz):  $\delta = -132.22$  (s, *o*-F),  $-163.11$  (d, *p*-F),  $-167.09$  (d, *m*-F). <sup>11</sup>B NMR (298.2 K, Toluene-d<sub>8</sub>, 96.3 MHz):  $\delta = -16.23$  (s).

***Analytical data for colorless solution after heating:***

<sup>31</sup>P NMR (298.2 K, Toluene-d<sub>8</sub>, 300.13 MHz):  $\delta = -131.70$  (s, 1.0, P(CN)<sub>3</sub>),  $-99.62$  (s, 0.3). <sup>19</sup>F NMR (298.2 K, Toluene-d<sub>8</sub>, 300.13 MHz):  $\delta = -131.85$  to  $-133.67$  (m),  $-139.08$  to  $-139.16$  (m),  $-157.99$  to  $-158.18$  (m),  $-162.33$  to  $-162.51$  (m),  $-164.50$  to  $-164.99$  (m),  $-166.40$  (s). <sup>11</sup>B NMR (298.2 K, Toluene-d<sub>8</sub>, 96.3 MHz):  $\delta = -15.98$  (s).

***Analytical data for solution after dissolving in CH<sub>2</sub>Cl<sub>2</sub> and concentrated:***

<sup>31</sup>P NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = 36.68$  to  $37.73$  (m, 1.0),  $41.61$  (s, 0.1). <sup>19</sup>F NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = -132.99$  to  $-133.42$  (m),  $-139.16$  (s),  $-159.10$  to  $-159.41$  (m),  $-165.53$  to  $-165.97$  (m). <sup>11</sup>B NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 96.3 MHz):  $\delta = -12.00$  (s),  $-16.62$  (s),  $-21.85$  (s).

#### **5.1.4.1.5 Reaction of P(CN)<sub>3</sub> with triethylamine**

To a stirred colorless solution of P(CN)<sub>3</sub> (0.055 g, 0.50 mmol) in dichloromethane (10 mL), triethylamine (0.051 g, 0.50 mmol) was added dropwise at  $-70$  °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting in an orange brown solution. The solvent was removed *in vacuo*, and the brown oil residue was washed two times with dichloromethane and was dried *in vacuo*.

<sup>31</sup>P NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to [P(CN)<sub>2</sub>]<sup>-</sup>) for a yellow solution:  $\delta = -9.15$  (s, 0.2),  $-35.55$  (s, 0.3),  $-195.52$  (s, 1.0, [P(CN)<sub>2</sub>]<sup>-</sup>). <sup>31</sup>P NMR (298.2 K,

CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to [P(CN)<sub>2</sub>]<sup>-</sup>) for an orange-brown solution:  $\delta = -8.98$  (s, 4.0),  $-33.69$  (s, 2.2),  $-35.27$  (s, 3.8),  $-194.87$  (s, 1.0, [P(CN)<sub>2</sub>]<sup>-</sup>).

***Analytical data for resulting residue after drying:***

**C/H/N analysis %** found C 37.26; H 6.22; N 13.26. **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3369 (m), 2987 (m), 2951 (m), 2885 (w), 2685 (m), 2497 (m), 2361 (w), 2200 (w), 2128 (w), 1651 (m), 1475 (m), 1454 (m), 1396 (m), 1362 (m), 1282 (s), 1223 (s), 1159 (s), 1132 (s), 1093 (vs), 1063 (s), 1038 (s), 1012 (s), 951 (s), 837 (s), 804 (s), 714 (s), 608 (vs).

#### **5.1.4.1.6 Reaction of P(CN)<sub>3</sub> with tetramethylethylenediamine**

To a stirred colorless solution of P(CN)<sub>3</sub> (0.055 g, 0.50 mmol) in dichloromethane (10 mL), tetramethylethylene diamine (0.058 g, 0.50 mmol) was added dropwise at  $-70$  °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting in an orange brown solution. The solvent was removed *in vacuo*, and the brown oil residue was washed two times with dichloromethane and was dried *in vacuo*.

<sup>31</sup>P NMR (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to [P(CN)<sub>2</sub>]<sup>-</sup>) for a yellow solution:  $\delta = -22.5$  (s, 0.8),  $-162.81$  (s, 5.0),  $-194.73$  (s, 1.0, [P(CN)<sub>2</sub>]<sup>-</sup>). <sup>31</sup>P NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz integration normalized to [P(CN)<sub>2</sub>]<sup>-</sup>) for an orange-brown solution:  $\delta = -22.31$  (s, 1.4),  $-34.37$  (s, 1.1),  $-45.05$  (s, 0.5),  $-50.53$  (s, 0.9),  $-168.68$  (s, 4.4),  $-194.34$  (s, 1.0, [P(CN)<sub>2</sub>]<sup>-</sup>).

***Analytical data for resulting residue after drying:***

**C/H/N analysis %** found C 34.97; H 7.73; N 15.64. **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3375 (vw), 3018 (m), 2958 (m), 2920 (m), 2781 (w), 2569 (s), 2526 (m), 2455 (s), 2428 (s), 2220 (w), 2197 (w), 2106 (w), 2077 (m), 1470 (s), 1412 (m), 1288 (vs), 1240 (s), 1155 (m), 1095 (s), 1022 (s), 1003 (vs), 984 (vs), 943 (vs), 903 (vs), 797 (m), 743 (m), 650 (m), 608 (s).

### 5.1.4.1.7 Reaction of P(CN)<sub>3</sub> with 2, 2' –bipyridine

#### Procedure 1

To a stirred colorless solution of P(CN)<sub>3</sub> (0.028 g, 0.25 mmol) in tetrahydrofuran (10 mL), a solution of 2, 2'-bipyridine (0.039 g, 0.25 mmol) in tetrahydrofuran (10 mL) was added dropwise at -70 °C over a period of five minutes. The resulting colorless solution was allowed to warm up to ambient temperature and was stirred overnight. The solvent was removed in *vacuo*, and the yellow oil residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

<sup>31</sup>P NMR (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to P(CN)<sub>3</sub>) for colorless solution: δ = -21.10 (s, 0.01), -35.14 (s, 0.01), -50.86 (s, 0.1), -99.76 (s, 0.01), -142.19 (s, 1.0, P(CN)<sub>3</sub>). IR (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3055 (w), 2924 (w), 2852 (w), 2200 (w), 2164 (vw), 2077 (w), 1618 (w), 1583 (m), 1529 (m), 1473 (w), 1458 (m), 1421 (m), 1300 (m), 1277 (m), 1221 (m), 1173 (w), 1148 (m), 1090 (m), 1074 (m), 1038 (m), 991 (s), 941 (m), 893 (m), 808 (m), 758 (vs), 725 (m), 619 (s), 588 (s).

#### Procedure 2

To a stirred colorless solution of P(CN)<sub>3</sub> (0.028 g, 0.25 mmol) in dichloromethane (10 mL), a solution of 2,2'-bipyridine (0.039 g, 0.25 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting colorless solution was allowed to stir overnight at ambient temperature, resulting a yellow solution. The solvent was removed in *vacuo*, and the pale yellow residue was washed two times with dichloromethane and was dried in *vacuo*.

C/H/N analysis % found C 58.94; H 3.92; N 21.22; P 11.35. <sup>31</sup>P NMR (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to P(CN)<sub>3</sub>) for a yellow solution: δ = 14.48 (s, 0.2), -126.56 (s, 1.0, P(CN)<sub>3</sub>). IR (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3076 (w), 3055 (w), 3016 (w), 2200 (w), 2079 (w), 2004 (vw), 1963 (vw), 1927 (vw), 1898 (vw), 1859 (vw), 1616 (w), 1583 (m), 1556 (m), 1529 (m), 1458 (m), 1421 (m), 1300 (m), 1277 (m), 1250 (m), 1173 (w), 1148 (m), 1094 (m), 1074 (m), 1038 (m), 991 (s), 962 (m), 808 (m), 758 (vs), 725 (m), 654 (w), 619 (s), 557 (s).

#### 5.1.4.1.8 Reaction of P(CN)<sub>3</sub> with sulfur

To a stirred colorless solution of P(CN)<sub>3</sub> (0.11 g, 1.1 mmol) in tetrahydrofuran (10 mL), a solution of sulfur (0.032 g, 1 mmol) in tetrahydrofuran (10 mL) was added dropwise at -70 °C over a period of five minutes. The resulting colorless solution was allowed to warm up to ambient temperature and was stirred overnight. The solvent was removed in *vacuo*, and the pale yellow residue was dried in *vacuo*.

<sup>31</sup>P NMR (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to P(CN)<sub>3</sub>) for colorless solution:  $\delta = -63.7$  (s, 0.04),  $-142.2$  (s, 1.0, P(CN)<sub>3</sub>). IR (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2926 (vw), 2858 (vw), 2204 (w), 1256 (w), 1014 (w), 914 (w), 748 (w), 579 (vs)

#### 5.1.4.1.9 Reaction of P(CN)<sub>3</sub> with 4-dimethylaminopyridine

##### Procedure 1

To a stirred colorless solution of P(CN)<sub>3</sub> (0.055 g, 0.50 mmol) in tetrahydrofuran (10 mL), a solution of 4-dimethylaminopyridine (0.061 g, 0.50 mmol) in tetrahydrofuran (10 mL) was added dropwise at -70 °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting a yellow solution. The solvent was removed in *vacuo*, and the brown oil residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

C/H/N analysis % found C 48.35; H 5.41; N 23.14; P 29.25. <sup>31</sup>P NMR (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to P(CN)<sub>3</sub>) for a yellow solution:  $\delta = -33.27$  (s, 0.03),  $-150.6$  (s, 1.0, P(CN)<sub>3</sub>). IR (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3078 (w), 2930 (w), 2202 (w), 2081 (w), 1643 (vs), 1560 (s), 1441 (m), 1400 (s), 1317 (m), 1211 (s), 1121 (s), 1059 (vs), 1028 (s), 941 (s), 814 (s), 743 (s), 604 (s).

##### Procedure 2

To a stirred colorless solution of P(CN)<sub>3</sub> (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a solution of 4-dimethylaminopyridine (0.061 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting yellow solution was allowed to stir

overnight, resulting a brown solution. The solvent was removed in *vacuo*, and the brown oil residue was washed two times with dichloromethane and was dried in *vacuo*.

**C/H/N analysis %** found C 46.73; H 4.76; N 22.67; P 14.62. **<sup>31</sup>P NMR** (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz) for a brown solution:  $\delta = -16.08$  (s, 0.01),  $-32.02$  (s, 0.02),  $-170.66$  (s, 1.0). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3390 (w), 3225 (w), 3072 (w), 2924 (m), 2852 (m), 2677 (w), 2355 (w), 2206 (w), 2104 (w), 2081 (w), 1963 (w), 1641 (vs), 1603 (m), 1556 (s), 1443 (m), 1400 (m), 1259 (m), 1209 (s), 1063 (vs), 1028 (s), 978 (vs), 939 (vs), 806 (vs), 771 (s), 743 (s), 602 (s). **HRMS (EI)**: calcu. for DMAP 122.08; found 121 (10)

#### 5.1.4.1.10 Reaction of P(CN)<sub>3</sub> with 1,8-diaminonaphthalene

To a stirred solution of P(CN)<sub>3</sub> (0.050 g, 0.45 mmol) in dichloromethane (10 mL), a solution of 1,8-diaminonaphthalene (0.071 g, 0.45 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting yellow solution was allowed to stir overnight. The solvent was removed in *vacuo*, and the yellow residue was dried in *vacuo*.

**C/H/N analysis %** found C 53.59; H 4.12; N 12.67; P 14.67. **<sup>1</sup>H NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = 7.31$  (m, 4H, *m*-CH), 6.68 (d, 2H, *o*-CH), 3.66 (s, 2H, NH). **<sup>13</sup>C NMR** (300 K, CD<sub>2</sub>Cl<sub>2</sub>, 250.13 MHz):  $\delta = 136.46$  to 136.09 (m, 1C, C=C), 126.94 (s, 2C, CH), 122.23 (s, 2C, CH), 111.69 (s, 2C, CH). **<sup>31</sup>P NMR** (298.4 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = 18.77$  (s, 1.0),  $-12.37$  (s, 0.2). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3361 (m), 3306 (m), 3055 (m), 2162 (w), 1909 (w), 1738 (w), 1620 (vw), 1595 (s), 1487 (w), 1462 (m), 1410 (w), 1358 (m), 1300 (m), 1257 (m), 1182 (m), 1161 (m), 1119 (w), 1057 (m), 1034 (m), 970 (m), 912 (m), 878 (m), 814 (s), 789 (m), 752 (vs), 679 (m), 635 (m), 619 (m), 555 (m). **MS (ESI-TOF)**: cation 159.09222 (10), anion 112.98591 (2), 339.23369 (10).

#### 5.1.4.1.11 Reaction of P(CN)<sub>3</sub> with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

To a stirred solution of P(CN)<sub>3</sub> (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.26 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The colorless solution was allowed to stir overnight. The solvent was removed in *vacuo*, and the pale yellow residue was dried in *vacuo*.

**C/H/N analysis** % found C 38.26; H 0.34; N 5.46; P 5.25; F 45.89. **<sup>19</sup>F NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = -133.71$  (d, *o*-F),  $-154.99$  (s, *p*-F),  $-163.39$  to  $-163.57$  (m, *m*-F). **<sup>11</sup>B NMR** (298.2 k, CD<sub>2</sub>Cl<sub>2</sub>, 96.3 MHz):  $\delta = -4.18$  (s, 1.0),  $-21.7$  (s, 0.2). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to P(CN)<sub>3</sub>):  $\delta = 11.14$  (s, 0.08),  $-125.64$  (s, 1.0, P(CN)<sub>3</sub>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3566 (vw), 3246 (w), 2200 (w), 1647 (m), 1518 (s), 1460 (vs), 1385 (m), 1288 (m), 1182 (w), 1101 (s), 972 (vs), 860 (m), 795 (m), 773 (s), 739 (s), 681 (s), 617 (m), 577 (m). **Raman** (25 °C, 65 mW, 6 scans, cm<sup>-1</sup>): 2276 (0.1), 2204 (0.3), 1649 (1), 1393 (1), 859 (0.5), 796 (1), 685 (0.6), 624 (0.6), 583 (10), 493 (9), 447 (10), 391 (7), 357 (0.3), 285 (0.6), 232 (2), 158 (1).

#### 5.1.4.1.12 Reaction of P(CN)<sub>3</sub> with 3B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

To a stirred solution of P(CN)<sub>3</sub> (0.028 g, 0.25 mmol) in dichloromethane (10 mL), a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.42 g, 0.82 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The colorless solution was allowed to stir two days. The solvent was removed in *vacuo*, and the pale yellow residue was dried in *vacuo*.

**C/H/N analysis** % found C 40.10; H 0.23; N 1.91; P 1.81; F 43.41. **<sup>13</sup>C NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = 150.20$  (s), 146.95 to 146.79 (m, *o*-C), 139.59 to 139.32 (m, *p*-C), 136.46 to 136.03 (m, *m*-C). **<sup>19</sup>F NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = -130.64$  (s, *o*-F),  $-148.65$  (s, *p*-F),  $-161.94$  to  $-162.05$  (m, *m*-F). **<sup>11</sup>B NMR** (298.2 k, CD<sub>2</sub>Cl<sub>2</sub>, 96.3 MHz):  $\delta = 31.03$  (br, 1.0),  $-21.80$  (s, 0.4). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to P(CN)<sub>3</sub>):  $\delta = 5.40$  (s, 0.3),  $-25.99$  (s, 0.05),  $-52.10$  (s, 0.08),  $-129.18$  (s, 1.0, P(CN)<sub>3</sub>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3689 (vw), 3562 (vw), 3495 (vw), 3246 (vw), 2200 (vw), 1647 (m), 1608 (w), 1518 (s), 1458 (vs), 1379 (s), 1319 (w), 1288 (m), 1159 (w), 1101 (s), 1016 (m), 966 (vs), 860 (m), 796 (m), 773 (s), 739 (m), 681 (s), 621 (m), 575 (m). **Raman** (25 °C, 65 mW, 8 scans, cm<sup>-1</sup>): 2279 (0.3), 2199 (0.2), 1645 (4), 1392 (3), 1382 (3), 1310 (0.5), 1299 (0.6), 852 (5), 791 (0.5), 728 (0.6), 654 (1), 580 (8), 494 (9), 469 (3), 440 (10), 390 (7), 380 (7), 279 (1), 233 (2), 155 (2).

#### 5.1.4.1.13 Reaction of P(CN)<sub>3</sub> with Lithium bis(trimethylsilyl)amide

To a stirred colorless solution of P(CN)<sub>3</sub> (0.028 g, 0.26 mmol) in tetrahydrofuran (5 mL), a solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.043 g, 0.26 mmol) in tetrahydrofuran (5 mL) was added dropwise at -70 °C over a period of five minutes. The colorless solution was stirred at this temperature for 30 min. The resulting colorless solution was allowed to warm up to ambient temperature and was stirred for three hours, resulting in a yellow solution. The solvent was removed in *vacuo*, and the yellow residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

##### *Analytical data for yellow solution:*

<sup>1</sup>H NMR (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 0.30 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P NMR (298.4 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -197.50 (s, [P(CN)<sub>2</sub>]<sup>-</sup>). <sup>29</sup>Si-INEPT-NMR (298.7 K, CD<sub>2</sub>Cl<sub>2</sub>, 59.6 MHz): δ = -11.71 (s, (CH<sub>3</sub>)<sub>3</sub>Si).

##### *Analytical data for resulting residue after drying:*

C/H/N analysis % found C 30.63; H 4.18; N 19.92. IR (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3223 (m), 2957 (w), 2926 (w), 2845 (w), 2370 (w), 2193 (w), 2039 (vw), 1633 (w), 1456 (vw), 1134 (s), 1080 (s), 933 (m), 841 (s), 754 (m).

#### 5.1.4.1.14 Reaction of P(CN)<sub>3</sub> with triethylamine and silver tetrafluoridoborate

To a stirred colorless solution of P(CN)<sub>3</sub> (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a triethylamine (0.051 g, 0.50 mmol) was added dropwise at -70 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for one hour. To this a yellow solution, a solution of silver tetrafluoridoborate (0.098 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at -70 °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight as the exclusion of light, resulting in precipitation of silver cyanide. The precipitate was removed by filtration and the solvent was removed in *vacuo*. The resulting yellow residue was dried in *vacuo*.

C/H/N analysis % calc. (found) for AgCN: C 8.97 (8.56); H 0.0 (0.0); N 10.46 (9.52). IR (ATR, 25 °C, 32 scans, cm<sup>-1</sup>) for AgCN: 2164 (vs), 1306 (vw), 1237 (m), 1126 (s), 1059

(s), 820 (m), 805 (m).  $^{31}\text{P}$  NMR (299.1 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz) for a yellow solution:  $\delta = -35.92$  (s, 0.5),  $-51.64$  (s, 1.0).  $^{31}\text{P}$  NMR (299.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz, after drying):  $\delta = -35.67$  (s).  $^{19}\text{F}$  NMR (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = -151.47$  (s).  $^{11}\text{B}$  NMR (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 96.3 MHz):  $\delta = -1.11$  (s)

#### 5.1.4.1.15 Reaction of $\text{P}(\text{CN})_3$ with trimethylamine and sodium tetraphenyl borate

To a stirred colorless solution of  $\text{P}(\text{CN})_3$  (0.028 g, 0.25 mmol) in tetrahydrofuran (10 mL), triethylamine (0.025 g, 0.25 mmol) was added dropwise at  $-70\text{ }^\circ\text{C}$  over a period of five minutes. The resulting yellow solution was stirred at this temperature for 30 min. To this a yellow solution, a solution of  $\text{Na}[\text{B}(\text{Ph})_4]$  (0.085 g, 0.25 mmol) in tetrahydrofuran (10 mL) was added dropwise at  $-70\text{ }^\circ\text{C}$  over a period five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight. This solution was concentrated and stored at  $-30\text{ }^\circ\text{C}$  for four days, which results in the deposition of colorless crystals.

$^{11}\text{B}$  NMR (298.3 K,  $\text{CD}_2\text{Cl}_2$ , 96.3 MHz):  $\delta = -6.61$  (s).  $^{31}\text{P}$  NMR (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz, integration normalized to  $\text{P}(\text{CN})_3$ ) for a yellow solution:  $\delta = -75.48$  (s, 0.06),  $-142.80$  (s, 1.0,  $\text{P}(\text{CN})_3$ ),  $-195.74$  (s, 0.08,  $[\text{P}(\text{CN})_2]^-$ ).

#### 5.1.4.1.16 Reaction of $\text{P}(\text{CN})_3$ with triphenylphosphine and sodium phenyl borate

To a stirred colorless solution of  $\text{P}(\text{CN})_3$  (0.028 g, 0.25 mmol) in tetrahydrofuran (5 mL), a solution of  $\text{PPh}_3$  (0.65 g, 0.25 mmol) in tetrahydrofuran (5 mL) was added dropwise at  $-70\text{ }^\circ\text{C}$  over a period of five minutes. The resulting yellow solution was stirred at this temperature for 30 min. To this a yellow solution, a solution of  $\text{Na}[\text{B}(\text{Ph})_4]$  (0.085 g, 0.25 mmol) in tetrahydrofuran (10 mL) was added dropwise at  $-70\text{ }^\circ\text{C}$  over a period of five minutes. The resulting pale yellow solution was allowed to warm up to ambient temperature and was stirred for three days. The solvent was removed *in vacuo*, and the pale yellow residue was dried *in vacuo*.

**<sup>11</sup>B NMR** (298.4 K, CD<sub>2</sub>Cl<sub>2</sub>, 96.3 MHz):  $\delta = -12.16$  (s). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz, integration normalized to P(CN)<sub>3</sub>):  $\delta = 26.23$  (s),  $-5.57$  (s, PPh<sub>3</sub>),  $-142.26$  (s, P(CN)<sub>3</sub>).

#### 5.1.4.1.17 Reaction of P(CN)<sub>3</sub> with triphenylphosphine (5)

To a stirred colorless solution of P(CN)<sub>3</sub> (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a solution of PPh<sub>3</sub> (0.13 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at  $-40$  °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting in an orange brown solution. This solution was concentrated and stored at  $-30$  °C for three days, which results in the deposition of colorless crystals.

**<sup>31</sup>P NMR** (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz) for a yellow solution:  $\delta = 62.46$  (m, 0.1), 27.39 (s, 1.0),  $-44.71$  (m, 0.1),  $-50.89$  (s, 0.01),  $-190.47$  (s, 0.01, [P(CN)<sub>2</sub>]<sup>-</sup>). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz) for an orange-brown solution:  $\delta = 62.57$  (s, 0.02), 41.16 (s, 0.2), 37.49 (s, 0.3), 30.50 (s, 1.0),  $-5.47$  (s, 0.4, PPh<sub>3</sub>),  $-137.75$  (s, 0.1),  $-186.63$  (s, 0.2),  $-190.30$  (s, 0.3, [P(CN)<sub>2</sub>]<sup>-</sup>).

#### *Analytical data for colorless crystals:*

**C/H/N analysis** % calc. (found) for [Ph<sub>3</sub>P=N-C(CN)<sub>2</sub>-C(CN)<sub>2</sub>-N=PPh<sub>3</sub>] $\cdot$ 2CH<sub>2</sub>Cl<sub>2</sub>  
C 62.13 (64.75); H 4.03 (4.77); N 9.88 (6.69). **<sup>1</sup>H NMR** (298.8 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = 7.58$  to 7.23 (m, 30 H, Ph). **<sup>13</sup>C NMR** (300.3 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = 137.64$  (d, 2C, N-C(CN)<sub>2</sub>-C(CN)<sub>2</sub>), 134.07 to 133.93 (d, 3C, C-P), 132.70 to 132.20 (m, 6C, CH), 129.11 to 128.79 (m, 9C, CH). **<sup>31</sup>P NMR** (296 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta = 27.65$  (s). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3055 (w), 2351 (w), 2187 (w), 1981 (w), 1700 (vw), 1817 (vw), 1578 (m), 1556 (m), 1481 (m), 1435 (s), 1310 (m), 1178 (m), 1157 (m), 1115 (s), 1068 (m), 1026 (m), 995 (s), 928 (s), 851 (m), 743 (s), 719 (vs), 689 (vs), 617 (m). **HRMS (EI)**: calcu. for PPh<sub>3</sub>P=N 276.29; found 277.0 (10)

#### 5.1.4.1.18 Reaction of P(CN)<sub>3</sub> with dichloro (*p*-cymene)ruthenium(II) dimer

To a stirred solution of P(CN)<sub>3</sub> (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a solution of dichloro-(*p*-cymene)ruthenium(II)dimer (0.16 g, 0.26 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting red solution was allowed to stir overnight. The solvent was reduced to about 3 ml, and addition of excess diethyl ether (10 mL) with vigorous stirring gave the yellow precipitate. The solvent was removed *in vacuo*, and the yellow residue was washed two times with dichloromethane and was dried *in vacuo*.

**C/H/N analysis** % calc. (found) for [(*p*-cymene)RuCl<sub>2</sub>•P(CN)<sub>3</sub>•CH<sub>2</sub>Cl<sub>2</sub>] C 33.62 (35.23); H 3.22 (3.94); N 8.40 (7.57). **<sup>1</sup>H NMR** (300 K, d<sub>6</sub>-DMSO, 250.13 MHz): δ = 1.16 (d, 6H, HC(CH<sub>3</sub>)<sub>2</sub>), 2.23 (s, 3H, CH<sub>3</sub>), 7.10 to 7.05 (m, 5H, Ph). **<sup>13</sup>C NMR** (300 K, d<sub>6</sub>-DMSO, 500.13 MHz): δ = 20.53 (s, HC-CH<sub>3</sub>), 23.95 (s, HC-(CH<sub>3</sub>)<sub>2</sub>), 32.95 (s, HC-(CH<sub>3</sub>)<sub>2</sub>), 126.05 (s, CH-Ph), 128.77 (s, CH), 134.52 (s, CH), 145.28 (s, CH). **<sup>31</sup>P NMR** (300 K, d<sub>6</sub>-DMSO, 250.13 MHz): δ = -11.33 (s). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3063 (w), 2964 (m), 2930 (m), 2872 (m), 2143 (s), 1504 (m), 1466 (m), 1387 (m), 1279 (m), 1198 (m), 1161 (m), 1088 (m), 1057 (m), 1034 (m), 926 (m), 862 (s), 802 (m), 594 (s). **HRMS (EI)**: calcu. for *p*-cymene 134.21; found 134 (9)

#### 5.1.4.1.19 Reaction of P(CN)<sub>3</sub> with tetrakis(triphenylphosphine) palladium(0) (6)

To a stirred solution of excess P(CN)<sub>3</sub> (0.065 g, 0.6 mmol) in tetrahydrofuran (10 mL), a solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.1 mmol) in tetrahydrofuran (10 mL) was added directly at -70 °C. The resulting yellow solution was stirred at this temperature for 30 min. The resulting yellow solution after stirring for 3h was changed to a pale yellow solution at ambient temperature. This pale yellow solution was allowed to stir overnight. The yellow precipitate was removed by filtration and dissolved in dichloromethane. This solution was concentrated and stored at -30 °C for one day, which results in the deposition of colorless crystals.

**C/H/N analysis** % calc. (found) for [Pd(PPh<sub>3</sub>)<sub>2</sub>(CN)<sub>2</sub>]•2CH<sub>2</sub>Cl<sub>2</sub>•5THF C 59.39 (60.81); H 6.15 (6.61); N 2.31 (2.40). **<sup>1</sup>H NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 7.59 to 7.38 (m, 30H, Ph). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 23.06 (s). **IR** (ATR, 25 °C,

32 scans,  $\text{cm}^{-1}$ ): 3047 (w), 2943 (w), 2864 (w), 2804 (w), 2131 (w), 1479 (m), 1433 (m), 1371 (w), 1331 (w), 1310 (w), 1279 (w), 1180 (w), 1159 (w), 1094 (s), 1072 (w), 1026 (m), 997 (m), 845 (w), 748 (s), 727 (m), 708 (m), 689 (vs), 617 (w). **Raman** (25 °C, 12 mW, 6 scans,  $\text{cm}^{-1}$ ): 3169 (0.2), 3144 (0.2), 3056 (2), 2957 (0.1), 2144 (3), 1584 (7), 1480 (0.3), 1436 (0.3), 1329 (0.2), 1309 (0.2), 1182 (0.8), 1157 (0.6), 1091 (4), 1023(4), 996 (10), 915 (0.2), 846 (0.2), 750 (0.3), 705 (1), 685 (0.8), 613 (1), 530 (5), 500 (0.2), 492 (0.2), 439 (2), 411 (2), 358 (0.7), 283 (0.6), 251 (2), 220 (0.7), 196 (2).

#### 5.1.4.1.20 Reaction of $\text{P}(\text{CN})_3$ with 1, 1, 1- tris(diphenylphosphinomethyl) ethane nickel(0) (7)

To a stirred yellow solution of  $\text{Ni}(\text{COD})_2$  (0.054 g, 0.20 mmol) in tetrahydrofuran (10 mL), a solution of 1,1,1-tris(diphenylphosphinomethyl)ethane (0.124 g, 0.20 mmol) in tetrahydrofuran (10 mL) was added directly. The resulting red solution was stirred at ambient temperature for 4h. To this a red solution, a solution of  $\text{P}(\text{CN})_3$  (0.021 g, 0.20 mmol) in tetrahydrofuran (10 mL) was added dropwise at ambient temperature over a period of five minutes. The resulting deep brown solution was allowed to stir overnight. The brown precipitate was removed by filtration, resulting in a deep brown solution. The solvent was removed *in vacuo*, and a brown residue was dissolved in dichloromethane and concentrated, diethyl ether was added dropwise to this solution and stored at ambient temperature for two days, which results in the deposition of red crystals.

$^1\text{H NMR}$  (298.2 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = 7.37$  to  $7.00$  (m, 30H, Ph – H), 2.45 (br, 6H, *triphos* –  $\text{CH}_2$ ), 1.07 (t, 3H, *triphos*–  $\text{CH}_3$ ).  $^{31}\text{P NMR}$  (299 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = 26.40$  (s, 0.05), 8.18 (m, 0.1),  $-1.05$  (d, 1.0),  $-3.74$  (s, 3.3),  $-57.46$  (s, 0.5). **IR** (ATR, 25 °C, 32 scans,  $\text{cm}^{-1}$ ): 3053 (w), 2922 (w), 2852 (w), 2116 (w), 1666 (w), 1587 (w), 1483 (w), 1435 (m), 1308 (w), 1236 (m), 1180 (s), 1155 (s), 1117 (s), 1095 (s), 984 (s), 802 (m), 739 (s), 714 (s), 690 (vs), 617 (m), 565 (s). **Raman** (25 °C, 65 mW, 6 scans,  $\text{cm}^{-1}$ ): 3055 (0.2), 2123 (0.1), 1585 (2), 1572 (0.6), 1482 (0.2), 1434 (0.2), 1186 (0.7), 1158 (0.8), 1096 (1), 1027 (3), 998 (10), 840 (0.1), 688 (1), 615 (2), 574 (0.1), 425 (0.3), 323 (0.3), 254 (0.6).

#### 5.1.4.1.21 Reaction of P(CN)<sub>3</sub> with [hydrido tris(3,5-dimethylpyrazolyl) borate tricarbonyltungsten(II)] and ferroceniumhexafluoro hexafluorophosphate

To a stirred yellow solution of [hydrido tris(3,5-dimethylpyrazolyl)boratetricarbonyltungsten] (0.21g, 0.36 mmol) in dichloromethane (15 mL), a powder of ferroceniumhexafluorophosphate (0.12 g, 0.36 mmol) was added directly. The resulting deep green solution was stirred at ambient temperature for 30 min. To this a deep green solution, a solution of P(CN)<sub>3</sub> (0.04 g, 0.36 mmol) in dichloromethane (15 mL) was added dropwise at ambient temperature. The resulting deep brown solution was allowed to stir overnight, resulting in a deep brown solution. The solvent was removed *in vacuo*, and the deep brown residue was washed two times with diethyl ether and was dried *in vacuo*.

**C/H/N analysis** % found C 37.45; H 3.63; N 13.68; P 5.41. **<sup>1</sup>H NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 6.0 (s, 3H, Tp - CH), 4.14 (s, 9H, Tp - CH<sub>3</sub>), 2.40 (m, 9H, Tp - CH<sub>3</sub>). **<sup>19</sup>F NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -73.3 (d, 6F, PF<sub>6</sub><sup>-</sup>). **<sup>31</sup>P NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -65.68 (s), -144.51 (spilet, [PF<sub>6</sub>]<sup>-</sup>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3394 (vw), 2962 (vw), 2933 (w), 2875 (w), 2553 (vw), 2231 (vw), 2183 (vw), 2098 (w), 2081 (vw), 1932 (m), 1815 (m), 1543 (m), 1448 (m), 1416 (m), 1365 (m), 1257 (w), 1202 (m), 1107 (m), 1067 (m), 951 (m), 876 (m), 837 (vs), 822 (s), 741 (m), 692 (m), 642 (m), 586 (m). **MS (ESI-TOF)**: calcu. (found): cation 566.167 (566.143) (TpW(CO)<sub>3</sub>H)<sup>+</sup>, 542.167 (2), anion 144.96473 (144.96467). **HRMS (EI)**: calcu. for Fe(Cp)<sub>2</sub> 186.04; found 186 (10)

#### 5.1.4.1.22 Reaction of P(CN)<sub>3</sub> with tris(propionitrile)tricarbonylmolybdenum(0)

To a stirred colorless solution of P(CN)<sub>3</sub> (0.044 g, 0.4 mmol) in dichloromethane (10 mL), a solution of [Mo(CO)<sub>3</sub>(EtCN)<sub>3</sub>] (0.035 g, 0.1 mmol) in dichloromethane (10 mL) was added directly. The resulting brown suspension solution was allowed to stir overnight. The dark brown precipitate was removed by filtration, resulting in a yellow solution. The solvent was removed *in vacuo*, and the brown residue was dried *in vacuo*.

***Analytical data for yellow solution:***

**<sup>1</sup>H NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 1.22 (m, 9H, CH<sub>3</sub>), 2.24 (m, 9H, CH<sub>2</sub>). **<sup>13</sup>C NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 92.06 (s), 16.35 (s, 3C, CH<sub>2</sub>), 10.72 (s, 3C, CH<sub>3</sub>). **<sup>31</sup>P NMR** (298.5 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = -125.36 (s, 1.0, P(CN)<sub>3</sub>).

***Analytical data for brown residue:***

**IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2959 (w), 2928 (w), 2858 (w), 2205 (w), 2183 (vw), 2070 (w), 1949 (m), 1724 (w), 1599 (w), 1580 (w), 1489 (w), 1462 (w), 1380 (w), 1270 (m), 1124 (m), 1073 (m), 1039 (w), 978 (w), 742 (w), 621 (s), 594 (vs), 575 (vs).

**5.1.4.1.23 Reaction of P(CN)<sub>3</sub> with 1-ethyl-3-methylimidazolium dicyanamide in dichloromethane**

To a stirred solution of P(CN)<sub>3</sub> (0.3 g, 2.75 mmol) in dichloromethane (20 mL), a solution of 1-ethyl-3-methylimidazolium dicyanamide (0.5 g, 2.82 mmol) was added dropwise at 0 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for 2 h. The resulting yellow solution after stirring for 4 h was changed to a brown solution at ambient temperature. This brown solution was allowed to stir overnight. The solvent was removed in *vacuo*, and the brown residue was washed two times with acetonitrile and was dried in *vacuo*.

**DSC:**  $T_{dec} = 305$  °C. **C/H/N analysis %** found C 41.39; H 4.33; N 36.32; P 11.61. **<sup>1</sup>H NMR** (298.2 K, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz): δ = 9.05 (s, 1H, NCHN), 7.40 (m, 1H, MeNCH), 7.36 (m, 1H, EtNCH), 4.32 (q, 2H, NCH<sub>2</sub>), 4.00 (s, 3H, NCH<sub>3</sub>), 1.56 (t, 3H, -CH<sub>3</sub>). **<sup>13</sup>C NMR** (273 K, CD<sub>2</sub>Cl<sub>2</sub>, 500.13 MHz): δ = 135.3 (s, 1C, NCHN), 123.0 (s, 1C, MeNCH), 121.4 (s, 1C, EtNCH), 118.8 (s, 1C, CN), 44.8 (s, 2C, NCH<sub>2</sub>), 35.9 (s, 1C, NCH<sub>3</sub>), 14.5 (s, 1C, NCH<sub>2</sub>-CH<sub>3</sub>). **<sup>31</sup>P NMR** (272.9 K, CD<sub>2</sub>Cl<sub>2</sub>, 500.13 MHz) for a yellow solution: δ = -25 (s, 0.05), -154.2 (s, 1.0), -165.2 (s, 0.002). **<sup>31</sup>P NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz) for a brown precipitate: δ = -194.38 (s, [P(CN)<sub>2</sub>]<sup>-</sup>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3146 (w), 3093 (m), 2981 (w), 2165 (m), 2133 (m), 2081 (w), 1445 (s), 1381 (s), 1308 (s), 1163 (vs), 1058 (s), 1021 (s), 977 (s), 831 (s), 742 (s), 700 (s), 645 (s), 619 (vs), 593 (vs).

#### 5.1.4.1.24 Reaction of P(CN)<sub>3</sub> with 1-ethyl-3-methylimidazolium dicyanamide in tetrahydrofuran

To a stirred solution of P(CN)<sub>3</sub> (0.3 g, 2.75 mmol) in tetrahydrofuran (10 mL), a solution of 1-ethyl-3-methylimidazolium dicyanamide (0.5 g, 2.82 mmol) was added dropwise at 0 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for 2h. The resulting yellow solution was allowed at ambient temperature to stir overnight, resulting a deep brown oil solution. The solvent was removed in *vacuo*, and the resulting deep brown oil precipitate was washed six times with acetonitrile. The resulting brown precipitate was removed by filtration and was dried for 12 h in *vacuo*. The resulting deep brown solution, the solvent was removed in *vacuo*, and the deep brown residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

##### *Analytical data for deep brown oil precipitate after stirring overnight:*

**C/H/N analysis %** found C 44.72; H 5.03; N 34.82; P 11.28. **<sup>1</sup>H NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz): δ = 8.61 (s, 1H, NCHN), 7.33 (m, 1H, MeNCH), 7.29 (m, 1H, EtNCH), 4.11 (q, 2H, NCH<sub>2</sub>), 3.77 (s, 3H, NCH<sub>3</sub>), 1.35 (t, 3H, -CH<sub>3</sub>). **<sup>13</sup>C NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz): δ = 135.71 (s, 1C, NCHN), 123.37 (s, 1C, MeNCH), 121.62 (s, 1C, EtNCH), 118.8 (s, 1C, CN), 44.60 (s, 2C, NCH<sub>2</sub>), 35.80 (s, 1C, NCH<sub>3</sub>), 14.38 (s, 1C, NCH<sub>2</sub>-CH<sub>3</sub>). **<sup>31</sup>P NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz) for a deep brown oil precipitate: δ = -194.43 (s, [P(CN)<sub>2</sub>]<sup>-</sup>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3147 (m), 3095 (m), 2982 (m), 2873 (m), 2173 (s), 2133 (m), 1520 (s), 1447 (s), 1383 (s), 1333 (s), 1224 (vs), 1163 (vs), 1058 (s), 1021 (s), 958 (s), 875 (s), 833 (s), 742 (vs), 700 (s), 645 (s), 619 (vs).

##### *Analytical data for brown precipitate after washing with acetonitrile:*

**TGA/DSC:**  $T_{\text{dec}} = 333$  °C. **C/H/N analysis %** found C 42.95; H 4.81; N 34.97; P 12.86. **<sup>1</sup>H NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz): δ = 8.59 (s, 1H, NCHN), 7.36 (m, 1H, MeNCH), 7.32 (m, 1H, EtNCH), 4.20 (q, 2H, NCH<sub>2</sub>), 3.85 (s, 3H, NCH<sub>3</sub>), 1.48 (m, 3H, -CH<sub>3</sub>). **<sup>13</sup>C NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz): δ = 135.49 (s, 1C, NCHN), 122.79 (s, 1C, MeNCH), 121.08 (s, 1C, EtNCH), 118.8 (s, 1C, CN), 44.03 (s, 2C, NCH<sub>2</sub>), 35.09 (s, 1C, NCH<sub>3</sub>), 13.82 (s, 1C, NCH<sub>2</sub>-CH<sub>3</sub>). **<sup>31</sup>P NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz) for a brown precipitate: δ = -194.38 (s, [P(CN)<sub>2</sub>]<sup>-</sup>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3149 (m), 3102 (m), 2984 (m), 2172 (m), 1495 (s), 1464 (s), 1446 (s), 1382 (s), 1219 (s), 1164 (vs), 1058 (s), 1030 (s), 958 (s), 834 (s),

742 (s), 700 (s), 645 (s), 619 (vs). **MS (ESI-TOF):** calcu. (found): cation 111.0916 (111.0918), anion 110.9759(9), 234.8954 (5), 293.1779 (2).

***Analytical data for deep brown precipitate after removal the solvent:***

**C/H/N analysis %** found C 40.64; H 5.21; N 25.35; P 9.79. **<sup>1</sup>H NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz):  $\delta$  = 8.78 (s, 1H, NCHN), 7.40 (m, 1H, MeNCH), 7.35 (m, 1H, EtNCH), 4.22 (q, 2H, NCH<sub>2</sub>), 3.87 (s, 3H, NCH<sub>3</sub>), 1.47 (t, 3H, -CH<sub>3</sub>). **<sup>13</sup>C NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz):  $\delta$  = 135.49 (s, 1C, NCHN), 122.79 (s, 1C, MeNCH), 121.08 (s, 1C, EtNCH), 118.8 (s, 1C, CN), 44.03 (s, 2C, NCH<sub>2</sub>), 35.09 (s, 1C, NCH<sub>3</sub>), 13.82 (s, 1C, NCH<sub>2</sub>-CH<sub>3</sub>). **<sup>31</sup>P NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz) for a brown solution:  $\delta$  = -194.30 (s, [P(CN)<sub>2</sub>]<sup>-</sup>). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 3357 (w), 3147 (m), 3094 (m), 2984 (m), 2170 (m), 2136 (m), 1563 (s), 1504 (s), 1465 (s), 1448 (s), 1382 (s), 1333 (s), 1222 (s), 1165 (vs), 1060 (s), 1031 (s), 958 (s), 838 (s), 745 (s), 700 (s), 646 (s), 620 (vs), 593 (vs).

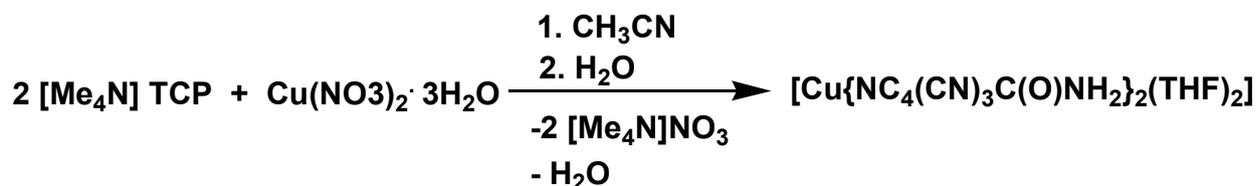
#### **5.1.4.1.25 Reaction of P(CN)<sub>3</sub> with silver dicyanoamide–tris-(pentafluorophenyl)borane·diether**

To a stirred colorless solution of P(CN)<sub>3</sub> (0.015 g, 0.14 mmol) in fluorobenzene (10 mL), a solution of Ag[N{CN.B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub>].2Et<sub>2</sub>O (0.19 g, 0.14 mmol) in fluorobenzene (10 mL) was added dropwise at ambient temperature. The resulting yellow solution after stirring 40 min was allowed to stir overnight, resulting a yellow solution. The solvent was removed in *vacuo*, and the yellow residue was dried in *vacuo*.

**C/H/N analysis %** found C 40.06; H 2.35; N 6.35; P 3.44. **<sup>19</sup>F NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz):  $\delta$  = -113.72 (s, Ph.F), -133.75 (m, 10F, *o*-F), -159.54 (t, 10F, *p*-F), -165.73 (m, 10F, *m*-F). **<sup>11</sup>B NMR** (298.2 K, CD<sub>3</sub>CN, 96.3 MHz):  $\delta$  = -13.35 (s). **<sup>31</sup>P NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz):  $\delta$  = 142.88 (s, 1.0), 49.67 (s, 0.28), 17.39 (s, 0.22). **IR** (ATR, 25 °C, 32 scans, cm<sup>-1</sup>): 2997 (w), 2222 (w), 2160 (vw), 1533 (m), 1516 (s), 1462 (vs), 1379 (m), 1283 (m), 1178 (m), 1144 (m), 1095 (s), 1070 (m), 1022 (m), 974 (vs), 893 (s), 843 (m), 804 (s), 773 (m), 731 (m), 717 (m), 683 (s), 609 (m).

## 5.1.4.2 Reactions of tetracyanopyrrolide

### 5.1.4.2.1 Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran)copper(II) [Cu{NC<sub>4</sub>(CN)<sub>3</sub>C(O)NH<sub>2</sub>}<sub>2</sub>(THF)<sub>2</sub>] (8)



To a stirred solution of tetramethyltetracyanopyrrolide (0.048 g, 0.2 mmol) in acetonitrile (10 mL), a solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.029 g, 0.1 mmol) in water (dest., 10 mL) was added at ambient temperature. The acetonitrile was evaporated, and the solution was filtered. The filtrate was evaporated to dryness to yield 6 mg (10%, 0.010 mmol) as a greenish yellow precipitate of **8**. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of diethyl ether into a tetrahydrofuran solution of **8**

**C/H/N analysis** % calc. (found): C 50.04 (48.93); H 3.50 (4.41); N 24.32 (22.65). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3393 (m), 3342 (m), 3250 (w), 3170 (m), 2985 (m), 2879 (m), 2723 (w), 2644 (w), 2233 (s), 1981 (vw), 1664 (vs), 1578 (s), 1529 (s), 1477 (m), 1450 (vs), 1387 (m), 1364 (m), 1325 (m), 1246 (m), 1213 (m), 1192 (m), 1128 (w), 1099 (s), 1069 (m), 1034 (s), 948 (w), 937(w), 889 (s), 829 (m), 778 (m), 743 (s), 729 (s), 699 (m), 660 (s), 604 (s).

### 5.1.4.2.2 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate [Zn(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]·2CH<sub>3</sub>CN (9)

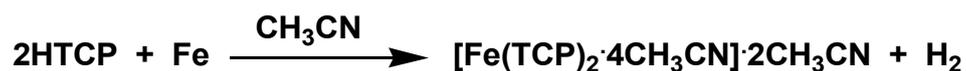


To a stirred solution of tetracyanopyrrole (0.3 g, 1.79 mmol) in acetonitrile (10 mL), a powder of zinc (0.078 g, 1.19 mmol) was added in one portion at ambient temperature. The resulting suspension was allowed to stir overnight. The unconsumed powder of zinc was removed by

filtration, and the resulting solution was concentrated *in vacuo* to a volume of approximately 4 mL. Storage at 8 °C for one day resulted colorless crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.25 g (44 %, 0.39 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II)acetonitrile solvate (**9**) as a white crystalline solid were obtained.

**TGA/DSC** (5 K/min): 475 °C loss of one equivalent of acetonitrile, 497 °C start of decomposition. **C/H/N analysis** % calc. (found) for [Zn(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]: C 51.31 (47.05); H 2.15 (2.56); N 34.90 (32.50). **<sup>13</sup>C NMR** (300 K, CD<sub>3</sub>CN, 500.13 MHz): δ =112.8 (s, 2C, C<sub>quat</sub>), 108.9 (s, 2C, C<sub>quat</sub>), 108.2 (s, 2C, C<sub>quat</sub>), 104.8 (s, 2C, C<sub>quat</sub>). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3381 (m), 3007 (w), 2938 (w), 2749 (w), 2351 (vw), 2316 (w), 2232 (s), 1632 (m), 1484 (m), 1425 (m), 1308 (m), 1231 (vs), 1203 (s), 1149 (vs), 1102 (vs), 982 (s), 806 (m), 744 (m), 702 (s), 690 (s), 639 (s), 554 (s). **Raman** (25 °C, 23 mW, 6 scans, cm<sup>-1</sup>): 2937 (1), 2926 (1), 2231 (10), 1476 (2), 1416 (2), 1313 (1), 1091 (0.3).

#### 5.1.4.2.3 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate [Fe(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]·2CH<sub>3</sub>CN (**10**)



To a stirred solution of tetracyanopyrrole (0.26 g, 1.55 mmol) in acetonitrile (10 mL), a powder of iron (0.054 g, 0.96 mmol) was added in one portion at ambient temperature. The resulting suspension was allowed to stir overnight. The uncosumed powder of iron was removed by filtration, and the resulting solution was concentrated *in vacuo* to a volume of approximately 4 mL. Storage at 8 °C for one day resulted colorless crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.22 g (45 %, 0.35 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II)acetonitrile solvate (**10**) as a white crystalline solid were obtained.

**TGA/DSC** (5 K/min): 110-130 °C loss of two equivalents of acetonitrile, 360 °C start of decomposition. **C/H/N analysis** % calc. (found) for [Fe(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]: C 52.19 (50.27); H 2.19 (2.73); N 35.51 (33.56). **<sup>13</sup>C NMR** (298.2 K, CD<sub>3</sub>CN, 300.13 MHz): δ = 112.8 (s, 2C, C<sub>quat</sub>), 108.9 (s, 2C, C<sub>quat</sub>), 108.2 (s, 2C, C<sub>quat</sub>), 104.7 (s, 2C, C<sub>quat</sub>). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3366 (m), 3247 (w), 3200 (w), 2934 (w), 2795 (w), 2739 (w), 2310 (w), 2281 (m), 2227(vs), 2167 (w), 1639 (m), 1481 (s), 1422 (m), 1367 (m), 1334 (m), 1239 (w), 1201 (w), 1096 (m), 1033 (m), 977 (w), 939 (m), 902 (w), 837 (w), 785 (w), 692 (s), 665 (m), 654 (m), 624 (m), 600 (m), 564 (m). **Raman** (25 °C, 23 mW, 6 scans, cm<sup>-1</sup>): 2934 (1), 2237 (10), 1483 (3), 1423 (3), 1317 (2).

#### 5.1.4.2.4 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium

##### (II) acetonitrile solvate [Mg(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]·2CH<sub>3</sub>CN (11)



To a stirred solution of tetracyanopyrrole (0.36 g, 2.2 mmol) in acetonitrile (10 mL), a solution of magnesium hydroxide Mg(OH)<sub>2</sub> (0.07 g, 1.20 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting solution was allowed to stir overnight. The resulting was filtered, and the filtrate was concentrated *in vacuo* to a volume of approximately 5 mL. Storage at 8 °C for one week resulted colorless crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.41 g (64 %, 0.68 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II)acetonitrile solvate (11) as a white crystalline solid were obtained.

**TGA/DSC** (5 K/min): 73-120 °C loss of three equivalents of acetonitrile, 248 °C start of decomposition. **C/H/N analysis** % calc. (found) for [Mg(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]: C 55.35 (52.67); H 2.32 (1.94); N 37.66 (36.84). **<sup>13</sup>C NMR** (298.4 K, CD<sub>3</sub>CN, 300.13 MHz): δ = 118.1 (s, 2C, C<sub>quat</sub>), 112.7 (s, 2C, C<sub>quat</sub>), 111.4 (s, 2C, C<sub>quat</sub>), 103.2 (s, 2C, C<sub>quat</sub>). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3406 (m), 3182 (m), 3104 (m), 3003 (m), 2941 (w), 2732 (w), 2313 (w), 2285 (m), 2227(vs), 1650 (m), 1479 (m), 1454 (m), 1417 (m), 1369 (m), 1336 (m), 1259 (w),

1095 (m), 1085 (m), 1033 (m), 941 (w), 837 (w), 694 (s), 686 (s). **Raman** (25 °C, 65 mW, 20 scans, cm<sup>-1</sup>): 2937 (0.3), 2235 (7), 1571 (1), 1483 (5), 1421 (10), 1311 (10), 883 (2), 530 (3), 109 (3).

#### 5.1.4.2.5 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II) acetonitrile solvate [Cu(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]·2CH<sub>3</sub>CN (12)



To a suspension solution of di(acetylacetonate)copper(II) Cu(acac)<sub>2</sub> (0.195 g, 0.74 mmol) in acetonitrile (10 mL), a solution of tetracyanopyrrole (0.25 g, 1.49 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting dark green solution was allowed to stir overnight, was filtered, and the resulting filtrate was concentrated *in vacuo* to a volume of approximately 5 mL. Storage at 8 °C for one day resulted green crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.31 g (65 %, 0.48 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II)acetonitrile solvate (12) as a green crystalline solid were obtained.

**TGA/DSC** (5 K/min): 59-168 °C loss of three equivalents of acetonitrile, 452 °C start of decomposition. **C/H/N analysis** % calc. (found) for [Cu(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]: C 51.48 (47.59); H 2.16 (1.56); N 35.02 (32.55). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3000 (w), 2937 (w), 2815 (vw), 2757 (w), 2659 (w), 2323 (m), 2268 (m), 2267(m), 2231 (vs), 1581 (w), 1519 (w), 1479 (s), 1425 (s), 1367 (s), 1348 (s), 1108 (m), 1029 (m), 946 (m), 931 (m), 715 (m), 692 (m), 597 (w), 528 (w). **Raman** (25 °C, 12 mW, 5 scans, cm<sup>-1</sup>): 2933 (1), 2239 (10), 1484 (3), 1426 (2), 1327 (2), 805 (3), 743 (2), 528 (1), 308 (2).

#### 5.1.4.2.6 Synthesis of di(acetylacetonate)-1,5-N- $\mu$ -tetracyanopyrrolido manganese (III) [Mn(acac)<sub>2</sub>TCP] (13)



To a stirred solution of tetracyanopyrrole (0.2 g, 1.19 mmol) in acetonitrile (10 mL), a solution of tri(acetylacetonate)manganese(III) Mn(acac)<sub>3</sub> (0.419 g, 1.19 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting yellow-black solution was allowed to stir overnight, was filtered, and the resulting yellow-black filtrate was evaporated to dryness to yield a yellow precipitate of **13**, washed two times with benzene (10 mL) and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution of **13**. Yield 0.36 g (72%, 0.86 mmol) of di(acetylacetonate)-1,5-N- $\mu$ -tetracyanopyrrolido manganese(III) as a yellow crystalline solid were obtained.

**DSC:** m.p. 56-57 °C.  $T_{\text{dec}} = 210$  °C. **C/H/N analysis** % calc. (found): C 51.56 (51.73); H 3.37 (3.70); N 16.70 (15.09). **IR** (25 °C, ATR, 32 scans  $\text{cm}^{-1}$ ): 3108 (w), 3005(w), 2925 (w), 2740 (w), 2655 (vw), 2248(w), 2232 (m), 1512 (vs), 1476(s), 1420 (s), 1361 (m), 1334 (vs), 1285 (s), 1185 (m), 1095 (m), 1032(s), 1019 (s), 938 (s), 836(w), 801 (s), 689(s), 659 (m), 636 (s), 533 (w). **Raman** (25 °C, 12 mW, 20 scans,  $\text{cm}^{-1}$ ): 2923 (0.5), 2232 (6), 1565 (2), 1477 (2), 1421 (1), 1322 (2), 1032 (2), 991 (9), 686 (2), 456 (10), 217 (10). **MS (ESI-TOF):** calcu. (found): cation 253.0267 (253.0265), anion 166.01592 (166.01595).

#### 5.1.4.2.7 Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolido Chromium (III) [Cr(acac)<sub>2</sub>TCP·CH<sub>3</sub>CN]·0.67CH<sub>3</sub>CN (14)



To a stirred solution of tetracyanopyrrole (0.2 g, 1.19 mmol) in acetonitrile (10 mL), a solution of tri(acetylacetonate)chromium(III) Cr(acac)<sub>3</sub> (0.42 g, 1.19 mmol) in acetonitrile (10 mL) was added at ambient temperature. The red solution was allowed to stir overnight, was filtered, and the resulting red filtrate was concentrated *in vacuo* to a volume of approximately

5 mL. Storage at 8 °C for one week resulted brown crystals. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.22 g (38 %, 0.45 mmol) of acetonitrile-di(acetylacetonate)tetracyanopyrrolidochromium(III) (**14**) as a brown crystalline solid were obtained.

**TGA/DSC** (5 K/min): 153 °C loss of two equivalents of acetonitrile, 247 °C start of decomposition. **C/H/N analysis** % calc. (found) for **14**·CH<sub>3</sub>CN: C 53.29 (53.14); H 4.22 (3.26); N 20.43 (21.17). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3000 (w), 2937 (w), 2326 (w), 2300 (w), 2232 (m), 1616 (w), 1542 (s), 1519 (vs), 1481 (s), 1423 (s), 1349 (vs), 1282 (s), 1187 (m), 1108 (m), 1025 (s), 935 (m), 777 (m), 717 (m), 684 (s), 657 (m), 618 (m). **Raman** (25 °C, 12 mW, 10 scans, cm<sup>-1</sup>): 2926 (1), 2240 (10), 1483 (2), 1425 (2), 1365 (1), 1333 (1), 1284 (1), 1189 (0.3), 1111 (0.3), 947 (1), 686 (0.5), 524 (0.5), 457 (3). **MS (ESI-TOF)**: calcu. (found): cation 250.02918 (250.02905), anion 166.01592 (166.01593).

#### 5.1.4.2.8 Reaction of HTCP with tri(acetylacetonate)manganese(III)

To a stirred solution of tetracyanopyrrole (0.25 g, 1.50 mmol) in acetonitrile (10 mL), a solution of tri(acetylacetonate)manganese(III) Mn(acac)<sub>3</sub> (0.1 g, 0.28 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting yellow-black solution was allowed to stir overnight, was filtered, and the resulting yellow-black filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with benzene (10 mL) and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution of 1% di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese(III) as a yellow crystalline solid (**13**) and 99% tetraacetonitrile-bis(tetracyanopyrrolido)manganese(II)acetonitrile solvate (**15**) as a colorless crystalline solid were obtained.

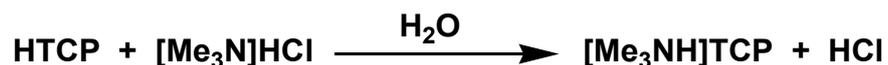
#### *Analytical data for colorless crystals 15:*

**TGA/DSC** (5 K/min): 50-65 °C loss of two equivalents of acetonitrile, 218 °C start of decomposition. **C/H/N analysis** % calc. (found) for [Mn(TCP)<sub>2</sub>·4CH<sub>3</sub>CN]: C 52.28 (52.99); H 2.19 (1.80); N 35.56 (33.70). **IR** (25 °C, ATR, 32 scans cm<sup>-1</sup>): 3559 (m), 3498 (m), 3232 (w), 3051(w), 2942 (w), 2792 (w), 2701 (w), 2559 (w), 2325 (w), 2232 (vs), 2166 (vw), 1651 (vw), 1644 (vw), 1537 (m), 1516 (m), 1470 (m), 1421 (m), 1337 (s), 1285 (s), 1192 (w), 1094 (m), 1032(m), 1020 (m), 899 (m), 837 (m), 801 (w), 691 (s), 674 (s), 636 (s). **Raman** (25 °C,

12 mW, 20 scans,  $\text{cm}^{-1}$ ): 2935 (0.2), 2236 (8), 1483 (3), 1422 (3), 1316 (3), 1095 (1), 939 (0.3), 699 (0.7), 533 (1) 467 (0.6), 396 (0.7), 214 (0.5), 117 (8).

#### 5.1.4.2.9 Synthesis of trimethylammoniumtetracyanopyrrolide

##### [Me<sub>3</sub>NH]TCP (16)

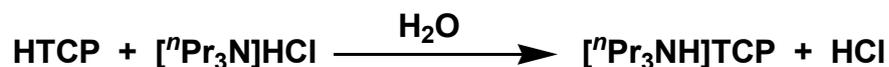


To a stirred solution of tetracyanopyrrole (0.2 g, 1.19 mmol) in water (dest., 10 mL), a solution of trimethylammoniumchloride [Me<sub>3</sub>NH]Cl (0.114 g, 1.19 mmol) in water (dest. 10 mL) was added at ambient temperature. The mixture was allowed to stir overnight. The resulting solution was filtered, and the filtrate was evaporated to dryness to yield a yellow precipitate of **16**, washed two times with dichloromethane (10 mL), and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution of **16** in acetonitrile. Yield 0.21 g (77%, 0.92 mmol) of trimethylammoniumtetracyanopyrrolide as a colorless crystalline solid were obtained.

**TGA/ DSC:** m.p. 184-185 °C, 298 °C start of decomposition. **C/H/N analysis** % calc. (found) for **16**·CH<sub>3</sub>CN: C 58.42 (56.57); H 4.90 (4.33); N 36.68 (35.74). **<sup>1</sup>H NMR** (298 K, CD<sub>3</sub>CN, 300.13 MHz):  $\delta$ = 4.41 (s, 9H, CH<sub>3</sub>), 7.38 (br, 1H, NH). **<sup>13</sup>C NMR** (298 K, CD<sub>3</sub>CN, 300.13 MHz):  $\delta$  = 119.4 (s, 2C, C<sub>quat</sub>), 114.3 (s, 2C, C<sub>quat</sub>), 112.1 (s, 2C, C<sub>quat</sub>), 102.4 (s, 2C, C<sub>quat</sub>), 44.6 (s, 3C, CH<sub>3</sub>). **IR** (25 °C, ATR, 32 scans  $\text{cm}^{-1}$ ): 3381 (vw), 3051(m), 3028 (m), 2982 (w), 2730 (s), 2558(w), 2528 (m), 2480 (m), 2253(w), 2234 (m), 2224 (vs), 1682 (w), 1633 (w), 1475 (vs), 1452(s), 1420 (m), 1371 (w), 1329 (m), 1246 (m), 1088 (m), 1059 (w), 979 (s), 940 (w), 811 (w), 683 (m). **Raman** (25 °C, 12 mW, 20 scans,  $\text{cm}^{-1}$ ): 2972 (0.4), 2235 (10), 1476 (2), 1418 (1), 1317 (1), 1088 (0.2), 529 (0.3), 513 (0.3), 121 (1). **MS (ESI-TOF):** calcu. (found): cation 60.08078 (60.08103), anion 166.01592 (166.01629).

#### 5.1.4.2.10 Synthesis of tripropylammoniumtetracyanopyrrolide

##### $[{}^n\text{Pr}_3\text{NH}]\text{TCP}$ (**17**)



To a stirred solution of tetracyanopyrrole (0.22 g, 1.32 mmol) in water (dest. 10 mL), a solution of tripropylammoniumchloride  $[{}^n\text{Pr}_3\text{NH}]\text{Cl}$  (0.24 g, 1.33 mmol) in water (dest., 10 mL) was added at ambient temperature. The mixture was allowed to stir overnight. The resulting solution was filtered, and the filtrate was evaporated to dryness to yield a yellow precipitate of **17**, washed two times with dichloromethane (10 mL), and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution of **17** in acetonitrile. Yield 0.26 g (63%, 0.84 mmol) of tripropylammoniumtetracyanopyrrolide as a colorless crystalline solid were obtained.

**DSC:** m.p. 65 °C.  $T_{\text{dec}} = 320$  °C. **C/H/N analysis** % calc. (found) for **17**: C 65.78 (64.85); H 7.14 (7.19); N 27.08 (26.40).  **${}^1\text{H}$  NMR** (298 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = 1.05$  (m, 9H,  $\text{CH}_3$ ), 1.74 (m, 6H,  $\text{CH}_2$ ), 2.96 (m, 6H,  $\text{CH}_2$ ), 9.5 (s, 1H, NH).  **${}^{13}\text{C}$  NMR** (298 K,  $\text{CD}_2\text{Cl}_2$ , 300.13 MHz):  $\delta = 119.4$  (s, 2C,  $\text{C}_{\text{quat}}$ ), 114.3 (s, 2C,  $\text{C}_{\text{quat}}$ ), 112.1 (s, 2C,  $\text{C}_{\text{quat}}$ ), 102.4 (s, 2C,  $\text{C}_{\text{quat}}$ ), 11.36 (s, 3C,  $\text{CH}_3$ ), 17.20 (s, 3C,  $\text{CH}_2$ ), 53.95 (s, 3C,  $\text{CH}_2$ ). **IR** (25 °C, ATR, 32 scans  $\text{cm}^{-1}$ ): 3537 (vw), 3112 (m), 3036 (w), 2974 (m), 2942 (m), 2883 (m), 2790 (w), 2718 (w), 2675 (w), 2535 (w), 2220 (vs), 1471 (s), 1459 (m), 1414 (m), 1381 (m), 1327 (m), 1263 (w), 1238 (w), 1075 (m), 1042 (w), 983 (m), 943 (w), 916 (w), 900 (w), 756 (m), 682 (m), 585 (vw), 556(vw). **Raman** (25 °C, 12 mW, 20 scans,  $\text{cm}^{-1}$ ): 2973 (0.5), 2946 (1.0), 2882 (0.8), 2234 (10), 1476 (4.0), 1415 (2.0), 1311 (2.0), 1074 (0.7), 1037 (0.3), 678 (0.5), 514 (0.3), 485 (0.4), 308 (0.2), 123 (1.0).

## 5.2 Data on the X-ray structure analysis

**Table S1.** Crystallographic details of **5**, **6** and **7**

	<b>5</b>	<b>6</b>	<b>7</b>
Chem. Formula	C <sub>42</sub> H <sub>30</sub> N <sub>6</sub> P <sub>2</sub> ·2(CH <sub>2</sub> Cl <sub>2</sub> )	C <sub>38</sub> H <sub>30</sub> N <sub>2</sub> PdP <sub>2</sub> ·2(CH <sub>2</sub> Cl <sub>2</sub> )	C <sub>43</sub> H <sub>39</sub> N <sub>2</sub> NiP <sub>3</sub> ·2(CH <sub>2</sub> Cl <sub>2</sub> )
Form. Wght.[g mol <sup>-1</sup> ]	850.51	852.83	905.23
Color	block, colorless	block, colorless	Block, red
Cryst. System	monoclinic	orthorhombic	monoclinic
Space Group	<i>P2<sub>1</sub>/n</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> [Å]	9.5445(3)	20.5853(19)	15.0113(5)
<i>b</i> [Å]	15.0102(5)	7.8698(7)	15.3108(5)
<i>c</i> [Å]	15.1053(5)	23.149(2)	19.2747(6)
$\alpha$ [°]	90	90	90
$\beta$ [°]	91.891(2)	90	99.602(2)
$\gamma$ [°]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	2162.9(12)	3750.1(6)	4367.9(2)
<i>Z</i>	2	4	4
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.306	1.509	1.377
$\mu$ [mm <sup>-1</sup> ]	0.39	0.90	0.83
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	173	173	173
Measured reflections	5835	46647	77740
Independent reflections	30921	5454	15706
Reflections with $I > 2\sigma(I)$	4327	2682	11493
<i>R</i> <sub>int</sub>	0.096	0.164	0.043
<i>F</i> (000)	876	1728	1872
<i>R</i> 1 ( <i>R</i> [ $F^2 > 2\sigma(F^2)$ ])	0.043	0.056	0.043
w <i>R</i> <sub>2</sub> ( $F^2$ )	0.113	0.126	0.114
GooF	1.01	1.01	1.01
Parameter	286	223	556
CCDC #	–	–	–

**Table S2.** Crystallographic details of **8**, **9** and **10**

	<b>8</b>	<b>9</b>	<b>10</b>
Chem. Formula	C <sub>24</sub> H <sub>20</sub> CuN <sub>10</sub> O <sub>4</sub>	C <sub>24</sub> H <sub>12</sub> N <sub>14</sub> Zn·2(C <sub>2</sub> H <sub>3</sub> N)	C <sub>24</sub> H <sub>12</sub> N <sub>14</sub> Fe·2(C <sub>2</sub> H <sub>3</sub> N)
Form. Wght.[g mol <sup>-1</sup> ]	576.04	643.95	634.43
Color	colorless	colorless	colorless
Cryst. System	monoclinic	triclinic	triclinic
Space Group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	6.5689(6)	7.8924 (2)	7.9176 (3)
<i>b</i> [Å]	18.9107(16)	9.9655 (2)	10.0034 (4)
<i>c</i> [Å]	10.2306(8)	10.5178 (3)	10.5107 (4)
$\alpha$ [°]	90	96.241 (1)	83.719 (2)
$\beta$ [°]	99.729(5)	102.190 (1)	77.806 (2)
$\gamma$ [°]	90	90.050 (1)	89.997 (2)
<i>V</i> [Å <sup>3</sup> ]	1252.59(18)	803.56 (3)	808.58 (5)
<i>Z</i>	2	1	1
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.527	1.331	1.303
$\mu$ [mm <sup>-1</sup> ]	0.93	0.81	0.51
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	173	173	173
Measured reflections	11421	26442	26868
Independent reflections	2449	5770	5805
Reflections with $I > 2\sigma(I)$	1551	4270	4967
<i>R</i> <sub>int</sub>	0.083	0.052	0.046
<i>F</i> (000)	590	328	324
<i>R</i> 1 ( $R [F^2 > 2\sigma(F^2)]$ )	0.051	0.041	0.033
w <i>R</i> <sub>2</sub> ( $F^2$ )	0.142	0.092	0.085
GooF	1.04	1.02	1.05
Parameter	178	208	209
CCDC #	–	–	–

**Table S3.** Crystallographic details of **11**, **12** and **13**

	<b>11</b>	<b>12</b>	<b>13</b>
Chem. Formula	C <sub>24</sub> H <sub>12</sub> N <sub>14</sub> Mg·2(C <sub>2</sub> H <sub>3</sub> N)	C <sub>24</sub> H <sub>12</sub> N <sub>14</sub> Cu·2(C <sub>2</sub> H <sub>3</sub> N)	C <sub>18</sub> H <sub>14</sub> MnN <sub>5</sub> O <sub>4</sub>
Form. Wght.[g mol <sup>-1</sup> ]	602.89	642.28	419.28
Color	colorless	block, green	block, yellow
Cryst. System	triclinic	triclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	7.9203(3)	7.9992(5)	9.0254 (4)
<i>b</i> [Å]	10.0077(4)	9.8401(5)	10.4561 (4)
<i>c</i> [Å]	10.4993(4)	10.4333(6)	11.3113 (5)
$\alpha$ [°]	83.738(2)	95.531(3)	105.321 (2)
$\beta$ [°]	77.828(2)	103.644(3)	102.991 (2)
$\gamma$ [°]	89.900(2)	90.829(3)	101.330 (2)
<i>V</i> [Å <sup>3</sup> ]	808.46(5)	793.76(8)	965.27 (7)
<i>Z</i>	1	1	2
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.238	1.343	1.443
$\mu$ [mm <sup>-1</sup> ]	0.10	0.73	0.72
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	173	123	173
Measured reflections	26901	25680	14755
Independent reflections	5806	5717	5553
Reflections with $I > 2\sigma(I)$	4392	4641	4444
<i>R</i> <sub>int</sub>	0.042	0.032	0.032
<i>F</i> (000)	310	327	428
<i>R</i> 1 ( $R [F^2 > 2\sigma(F^2)]$ )	0.043	0.038	0.037
w <i>R</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> )	0.121	0.083	0.101
GooF	1.04	1.03	1.02
Parameter	208	208	260
CCDC #	–	–	–

**Table S4.** Crystallographic details of **14** and **15**

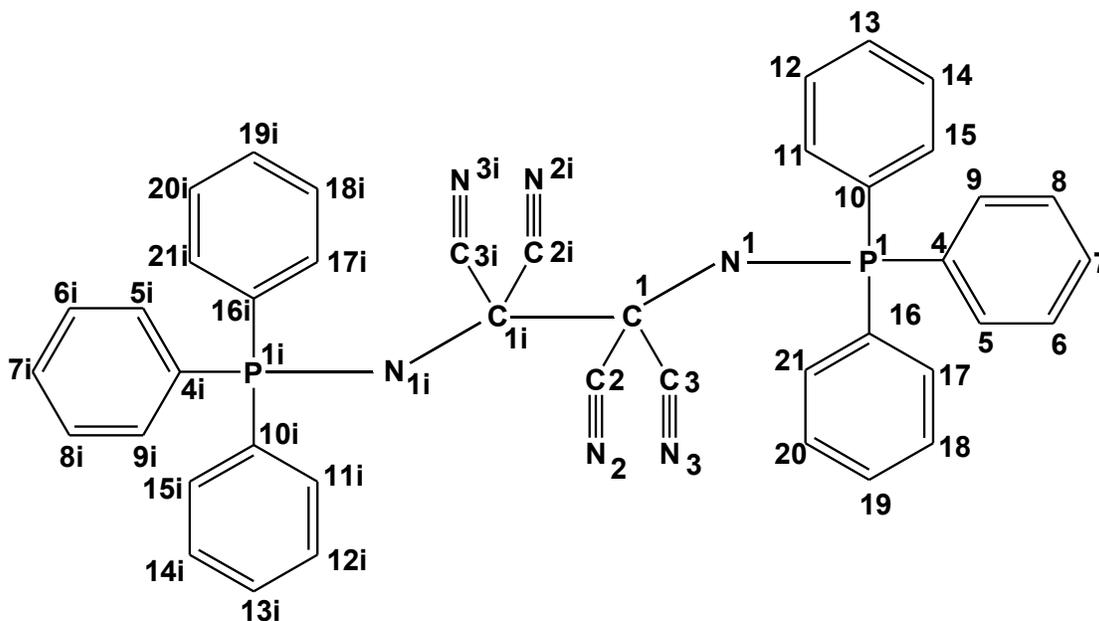
	<b>14</b>	<b>15</b>
Chem. Formula	C <sub>20</sub> H <sub>17</sub> CrN <sub>6</sub> O <sub>4</sub> ·0.67(C <sub>2</sub> H <sub>3</sub> N)	C <sub>24</sub> H <sub>12</sub> N <sub>14</sub> Mn·2(C <sub>2</sub> H <sub>3</sub> N)
Form. Wght.[g mol <sup>-1</sup> ]	484.76	633.52
Color	block, brown	block, colorless
Cryst. System	monoclinic	triclinic
Space Group	<i>C2/c</i>	<i>P</i> -1
<i>a</i> [Å]	28.3609 (13)	7.9176(3)
<i>b</i> [Å]	17.2005 (7)	10.0167(4)
<i>c</i> [Å]	15.1665 (6)	10.4982(4)
$\alpha$ [°]	90	96.522(2)
$\beta$ [°]	101.244(2)	102.882(2)
$\gamma$ [°]	90	90.642(2)
<i>V</i> [Å <sup>3</sup> ]	7256.5(5)	805.81(5)
<i>Z</i>	12	1
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.331	1.306
$\mu$ [mm <sup>-1</sup> ]	0.51	0.45
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073
<i>T</i> [K]	123	123
Measured reflections	51374	26410
Independent reflections	10541	5583
Reflections with $I > 2\sigma(I)$	5642	4641
<i>R</i> <sub>int</sub>	0.105	0.033
<i>F</i> (000)	2996	323
<i>R</i> <sub>1</sub> ( <i>R</i> [ $F^2 > 2\sigma(F^2)$ ])	0.054	0.038
w <i>R</i> <sub>2</sub> ( $F^2$ )	0.127	0.083
GooF	1.01	1.04
Parameter	458	208
CCDC #	–	–

**Table S5.** Crystallographic details of **16** and **17**

	<b>16</b>	<b>17</b>
Chem. Formula	$C_3H_{10}N^+ \cdot C_8N_5^-$	$C_9H_{22}N^+ \cdot C_8N_5^-$
Form. Wght.[g mol <sup>-1</sup> ]	226.25	310.40
Color	block, colorless	block, colorless
Cryst. System	orthorhombic	triclinic
Space Group	<i>pnma</i>	<i>P</i> -1
<i>a</i> [Å]	18.6039(5)	14.0557(3)
<i>b</i> [Å]	6.6761(2)	15.0423(3)
<i>c</i> [Å]	9.7709(3)	27.4242(6)
$\alpha$ [°]	90	78.144(10)
$\beta$ [°]	90	79.978(10)
$\gamma$ [°]	90	75.436(10)
<i>V</i> [Å <sup>3</sup> ]	1213.56(6)	5446.2(2)
<i>Z</i>	4	12
$\rho_{\text{calc.}}$ [g cm <sup>-3</sup> ]	1.238	1.136
$\mu$ [mm <sup>-1</sup> ]	0.08	0.07
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073
<i>T</i> [K]	123	173
Measured reflections	20462	128321
Independent reflections	2351	26266
Reflections with $I > 2\sigma(I)$	1866	15918
$R_{\text{int.}}$	0.032	0.034
<i>F</i> (000)	472	1992
$R_1$ ( $R [F^2 > 2\sigma(F^2)]$ )	0.040	0.058
$wR_2 (F^2)$	0.110	0.164
GooF	1.05	1.02
Parameter	105	1381
CCDC #	–	–

### 5.3 Selected interatomic distances and angles in the structures

**Scheme S1.** Numbering scheme of tetracyanodiiminophosphorane  $[\text{Ph}_3\text{P}=\text{N}-\text{C}(\text{CN})_2-\text{C}(\text{CN})_2-\text{N}=\text{PPh}_3]$  (5)



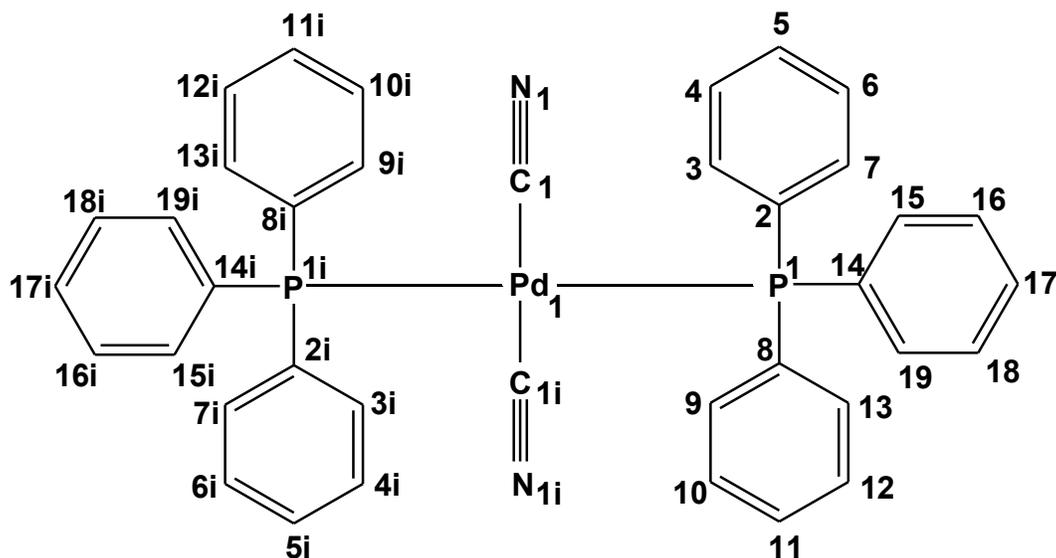
**Table S6.** Selected bond lengths (Å) angles (°) and torsion angles (°) of 5.

P1—N1	1.5765(13)	C9 —C4—P1	118.09(13)
P1 — C10	1.7987(15)	C6 —C5—C4	119.99(18)
P1 — C16	1.8018(16)	C13 —C14—C15	120.18(17)
P1 — C4	1.8026(16)	C10 —C15—C14	119.88(16)
N1—C1	1.4090(19)	C21 —C16—C17	119.09(15)
N2—C2	1.140(2)	C21 —C16—P1	120.42(12)
N3—C3	1.138(2)	C17 —C16—P1	120.18(12)
C1 —C2	1.498(2)	C18 —C17—C16	120.19(17)
C1 —C3	1.499(2)	C19 —C18—C17	120.14(18)
C1 —C1 <sup>1</sup>	1.596(2)	C20 —C19—C18	119.94(17)
C4 —C5	1.392(2)	C10 —P1—N1—C1	160.52(13)
C4 —C9	1.393(2)	C16 —P1—N1—C1	41.83(16)
C5 —C6	1.386(3)	C4 —P1—N1—C1	-81.55(15)
C6 —C7	1.376(3)	P1 —N1—C1—C2	54.76(19)
C7 —C8	1.377(3)	P1 —N1—C1—C3	-70.45(17)

<b>C14 —C15</b>	1.391(2)	<b>P1 —N1—C1—C1<sup>1</sup></b>	172.51(12)
<b>C16 —C17</b>	1.394(2)	<b>N1 —C1—C2—N2</b>	14(3)
<b>C17—C18</b>	1.384(3)	<b>C3 —C1—C2—N2</b>	142(3)
<b>C18—C19</b>	1.381(3)	<b>C16 —P1—C10—C15</b>	-76.42(14)
<b>C19—C20</b>	1.374(3)	<b>C4 —P1—C10—C15</b>	37.99(15)
<b>C20—C21</b>	1.383(2)	<b>N1 —P1—C10—C11</b>	-21.80(15)
<b>C8—C9</b>	1.390(2)	<b>C16 —P1—C10—C11</b>	102.05(14)
<b>C10 —C15</b>	1.390(2)	<b>C4 —P1—C10—C11</b>	-143.54(14)
<b>C16 —C21</b>	1.390(2)	<b>C15 —C10—C11—C12</b>	0.3(3)
<b>C10 —C11</b>	1.391(2)	<b>P1 —C10—C11—C12</b>	-178.15(14)
<b>C11 —C12</b>	1.389(2)	<b>C10 —C11—C12—C13</b>	- 0.8(3)
<b>C12 —C13</b>	1.374(3)	<b>N1 —P1—C4—C9</b>	-16.54(15)
<b>C13 —C14</b>	1.379(3)	<b>C10 —P1—C4—C9</b>	99.53(13)
<b>N1 —P1—C10</b>	104.88(7)	<b>C16 —P1—C4—C9</b>	-144.95(13)
<b>N1 —P1—C16</b>	115.69(7)	<b>C1<sup>1</sup>—C1—C2—N2</b>	-106(3)
<b>C10 —P1—C16</b>	107.86(7)	<b>N1 —C1—C3—N3</b>	-14(2)
<b>N1 —P1—C4</b>	113.80(8)	<b>C2 —C1—C3—N3</b>	-144(2)
<b>C10 —P1—C4</b>	108.10(7)	<b>C1<sup>1</sup>—C1—C3—N3</b>	104(2)
<b>C16 —P1—C4</b>	106.18(7)	<b>N1 —P1—C4—C5</b>	166.29(13)
<b>C1 —N1—P1</b>	129.29(10)	<b>P1 —C10—C15—C14</b>	178.70(13)
<b>N1 —C1—C2</b>	116.62(13)	<b>N1 —P1—C16—C21</b>	93.45(15)
<b>N1 —C1—C3</b>	113.83(12)	<b>C4 —P1—C16—C21</b>	-139.26(14)
<b>C2 —C1—C3</b>	106.89(12)	<b>N1 —P1—C16—C17</b>	-80.15(16)
<b>N1 —C1—C1<sup>1</sup></b>	107.81(14)	<b>C4 —P1—C16—C17</b>	47.13(16)
<b>C2 —C1—C1<sup>1</sup></b>	105.03(14)	<b>P1 —C16—C17—C18</b>	173.85(16)
<b>C3 —C1—C1<sup>1</sup></b>	105.81(14)	<b>P1 —C16—C21—C20</b>	-174.02(14)
<b>C5 —C4—P1</b>	122.41(13)		

Symmetry code: (i)  $-x+1, -y+2, -z$ .

**Scheme S2.** Numbering scheme of bis(triphenylphosphine) dicyanopalladium (II)



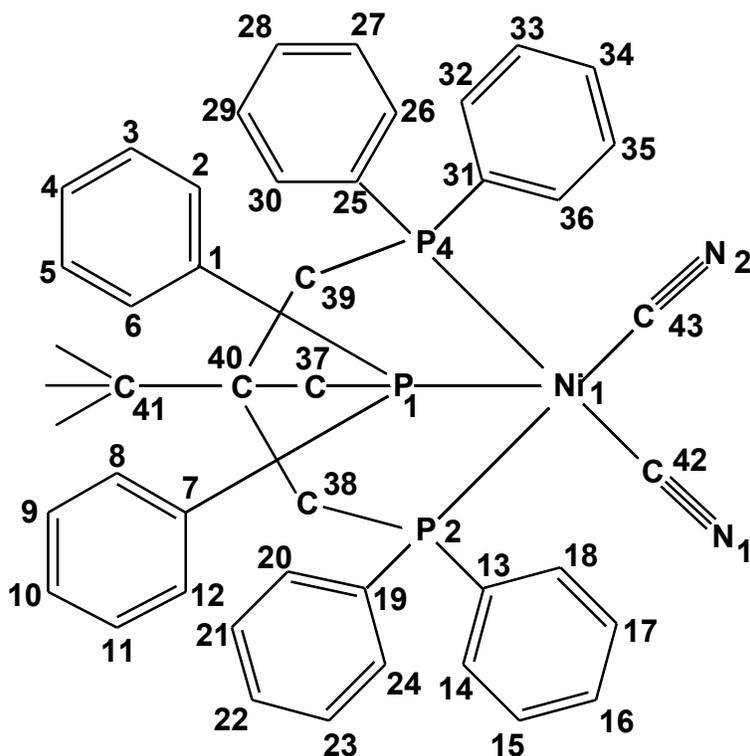
**Table S7.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **6**.

Pd1—C1	1.994(5)	P1 <sup>i</sup> —Pd1—P1—C14	96(100)
Pd1—C1 <sup>i</sup>	1.994(5)	C1—Pd1—P1—C8	108.36(19)
Pd1—P1 <sup>i</sup>	2.3140(11)	C1 <sup>i</sup> —Pd1—P1—C8	-71.64(19)
Pd1—P1	2.3140(11)	P1 <sup>i</sup> —Pd1—P1—C8	-24(100)
P1—C14	1.804(4)	C1—Pd1—P1—C2	-12.7(2)
P1—C8	1.810(4)	C1 <sup>i</sup> —Pd1—P1—C2	167.3(2)
P1—C2	1.813(4)	P1 <sup>i</sup> —Pd1—P1—C2	-145(100)
C11—C20	1.755(6)	C14—P1—C8—C9	-100.2(4)
C12—C20	1.736(6)	C2—P1—C8—C9	149.2(4)
C8—C9	1.386(6)	Pd1—P1—C8—C9	20.0(4)
C8—C13	1.395(6)	C14—P1—C8—C13	79.6(4)
N1—C1	1.133(6)	Pd1—P1—C8—C13	-160.2(3)
C3—C4	1.386(6)	C14—P1—C2—C7	2.9(4)
C3—C2	1.389(6)	C12—C20—C11	112.6(3)
C2—C7	1.385(6)	C2—P1—C14—C15	-80.1(4)
C15—C16	1.373(6)	Pd1—P1—C14—C15	47.8(4)
C17—C18	1.377(7)	P1—C14—C19—C18	178.3(3)
C11—C12	1.368(7)	P1—C14—C15—C16	179.9(4)

C4—C5	1.377(7)	P1—C8—C13—C12	179.6(4)
C5—C6	1.368(7)	C1 <sup>i</sup> —Pd1—C1—N1	-167(12)
C14—C19	1.370(6)	P1 <sup>i</sup> —Pd1—C1—N1	-14(9)
C19—C18	1.389(6)	P1—Pd1—C1—N1	166(9)
C1—Pd1—C1 <sup>i</sup>	180.0(3)	C14—C19—C18—C17	1.7(7)
C1—Pd1—P1 <sup>i</sup>	86.37(12)	C2—C3—C4—C5	0.3(7)
C1 <sup>i</sup> —Pd1—P1 <sup>i</sup>	93.63(12)	Pd1—P1—C2—C7	-119.1(4)
C1—Pd1—P1	93.63(12)	Pd1—P1—C2—C3	-177.0(4)
C1 <sup>i</sup> —Pd1—P1	86.37(12)	C8—P1—C14—C19	61.0(4)
P1 <sup>i</sup> —Pd1—P1	180.00(8)	Pd1—P1—C14—C19	-8.5(4)
C14—P1—C8	107.7(2)	C2—C3—C7—C6	-130.4(4)
C14—P1—C2	104.7(2)	Pd1—P1—C14—C15	0.7(7)
C8—P1—C2	103.85(19)	C4—C5—C6—C7	0.1(8)
C14—P1—Pd1	109.25(14)	C2—C7—C6—C5	-0.4(8)
C8—P1—Pd1	112.09(15)		
C2—P1—Pd1	118.59(15)		
C9—C8—P1	121.1(3)		
C4—C3—C2	120.4(4)		
C7—C2—P1	122.5(4)		
N1—C1—Pd1	177.3(4)		
C17—C18—C19	120.2(5)		
C6—C7—C2	121.3(5)		
C15—C14—P1	117.7(3)		
C1—Pd1—P1—C14	-132.37(19)		
C1 <sup>i</sup> —Pd1—P1—C14	47.63(19)		

Symmetry code: (i)  $-x, -y, -z$ .

**Scheme S3.** Numbering scheme of 1, 1, 1-tris(diphenylphosphinomethyl)ethanedicyano Nickel(II) 1,1,1-tris((Ph<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>)CCH<sub>3</sub>•Ni(CN)<sub>2</sub> (7)

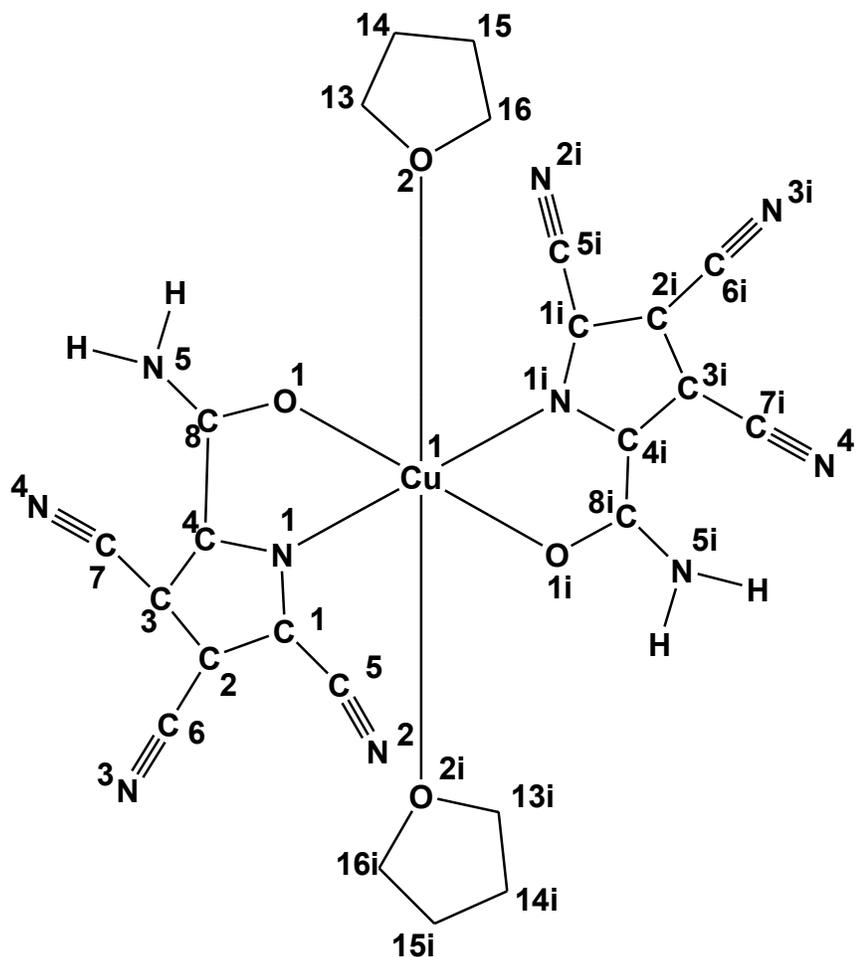


**Table S8.** Selected bond lengths (Å) angles (°) and torsion angles (°) of 7.

Ni1—C43	1.8757(17)	C42—Ni1—P2	109.61(5)
Ni1—C42	1.8828(16)	P4—Ni1—P2	94.199(16)
Ni1—P4	2.1963(4)	P1—Ni1—P2	90.609(17)
Ni1—P1	2.2016(4)	C1—P1—C7	100.49(8)
Ni1—P2	2.3656(5)	C1—P1—C37	104.58(7)
P1—C1	1.8167(17)	C7—P1—C37	104.40(8)
P1—C7	1.8322(18)	C1—P1—Ni1	115.63(5)
P1—C37	1.8529(16)	C7—P1—Ni1	117.46(6)
P2—C19	1.8364(17)	C37—P1—Ni1	112.63(5)
P2—C13	1.8367(18)	C19—P2—C13	99.21(8)
P2—C38	1.8603(17)	C19—P2—C38	105.56(8)

P4—C31	1.8177(16)	C13—P2—C38	102.53(8)
P4—C25	1.8312(15)	C19—P2—Ni1	118.14(6)
P4—C39	1.8350(16)	C13—P2—Ni1	120.13(6)
N1—C42	1.147(2)	C38—P2—Ni1	109.31(6)
N2—C43	1.148(2)	C31—P4—C25	101.94(7)
C1—C6	1.387(2)	C31—P4—C39	108.19(8)
C1—C2	1.398(2)	C25—P4—C39	100.64(7)
C2—C3	1.385(3)	C31—P4—Ni1	111.87(5)
C3—C4	1.382(3)	C25—P4—Ni1	121.08(5)
C4—C5	1.384(3)	C39—P4—Ni1	111.85(6)
C5—C6	1.392(2)	C2—C1—P1	119.43(13)
C7—C8	1.395(3)	C27—C28—C29	120.40(16)
C7—C12	1.400(3)	C36—C31—P4	116.15(13)
C8—C9	1.394(3)	C12—C7—P1	118.54(16)
C25—C30	1.392(2)	C40—C37—P1	117.44(11)
C25—C26	1.399(2)	C40—C38—P2	118.12(11)
C26—C27	1.394(2)	C39—C40—C38	111.52(14)
C28—C29	1.386(2)	C14—C13—P2	121.57(14)
C31—C36	1.397(2)	C24—C19—P2	115.53(13)
C35—C36	1.392(2)	N1—C42—Ni1	177.87(16)
C37—C40	1.544(2)	N2—C43—Ni1	177.21(15)
C38—C40	1.553(2)	C43—Ni1—P1—C1	7.02(16)
C39—C40	1.540(2)	C42—Ni1—P1—C1	76.30(8)
C9—C10	1.387(4)	P4—Ni1—P1—C1	-79.90(6)
C14—C15	1.392(3)	P2—Ni1—P1—C1	-174.10(6)
C19—C24	1.400(3)	C43—Ni1—P1—C7	-111.47(16)
C23—C24	1.387(3)	C42—Ni1—P1—C7	-42.19(9)
C42—Ni1—P4	156.03(5)	P4—Ni1—P1—C7	161.61(8)
C43—Ni1—P1	158.73(5)	P2—Ni1—P1—C7	67.42(8)
C42—Ni1—P1	87.50(5)	P1—Ni1—P2—C19	161.85(7)
P4—Ni1—P1	89.571(16)	P4—Ni1—P2—C13	-166.40(7)
C43—Ni1—P2	110.66(5)	C42—Ni1—P2—C38	128.77(8)
P1—Ni1—P2—C38	41.20(7)	Ni1—P1—C1—C2	162.30(12)
C16—C17—C18—C13	-0.2(3)	C27—C28—C29—C30	1.5(3)
Ni1—P2—C19—C20	-124.66(16)	C25—P4—C31—C32	114.55(15)
Ni1—P2—C19—C24	57.10(15)	Ni1—P1—C37—C40	14.96(14)
C31—P4—C25—C30	154.62(13)	P1—C7—C12—C11	178.66(18)
C39—P4—C25—C26	80.84(14)	Ni1—P2—C13—C18	-19.02(18)
C42—Ni1—P4—C31	-19.22(14)	Ni1—P4—C39—C40	22.56(14)
P2—Ni1—P4—C31	154.23(6)	C43—Ni1—C42—N1	17(4)
P1—Ni1—P4—C25	-176.19(6)	C42—Ni1—C43—N2	-36(3)
C43—Ni1—P4—C39	143.34(8)	P2—Ni1—C43—N2	-145(3)
P2—Ni1—P4—C39	32.67(6)		

**Scheme S4.** Numbering scheme of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran)copper(II)  $[\text{Cu}\{\text{NC}_4(\text{CN})_3\text{C}(\text{O})\text{NH}_2\}_2(\text{THF})_2]$  (**8**)



**Table S9.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **8**.

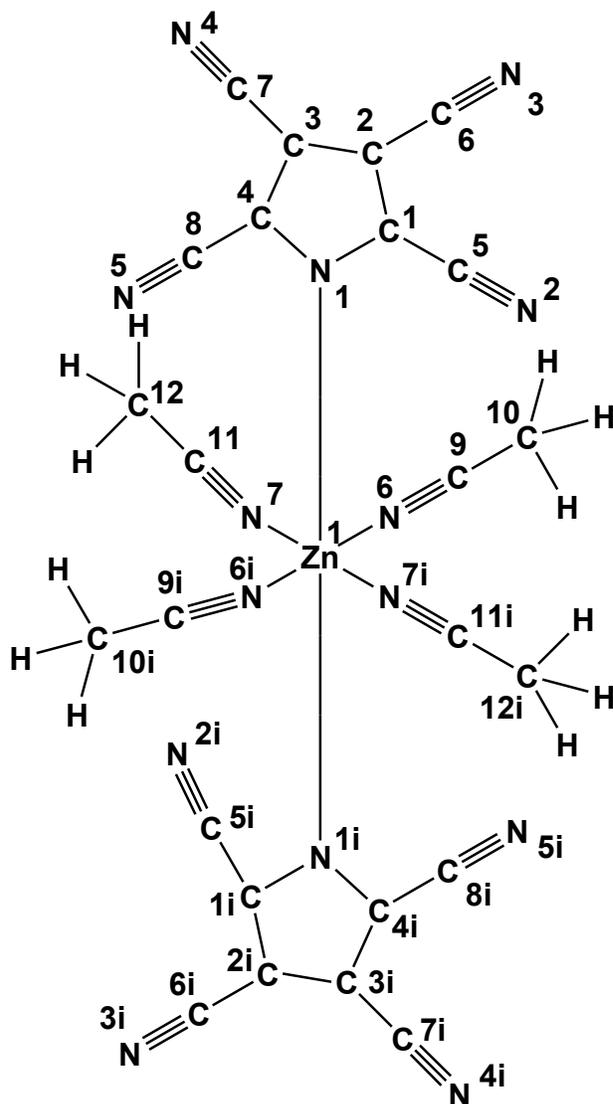
<b>Cu1 – N1<sup>1</sup></b>	1.975 (3)	<b>N1—C1—C2</b>	110.7 (4)
<b>Cu1 – N1</b>	1.975 (3)	<b>N1—C1—C5</b>	124.7 (3)
<b>Cu1 – O1<sup>1</sup></b>	1.998 (3)	<b>C2—C1—C5</b>	124.5 (4)
<b>Cu1 – O1</b>	1.998 (3)	<b>N2—C5—C1</b>	177.0 (5)
<b>Cu1 – O2</b>	2.476 (27)	<b>N3—C6—C2</b>	177.7 (6)
<b>Cu1 – O2<sup>1</sup></b>	2.476 (27)	<b>N4—C7—C3</b>	177.8 (5)
<b>O1 – C8</b>	1.263 (4)	<b>O1—C8—N5</b>	121.7 (4)
<b>N4 – C7</b>	1.133 (5)	<b>O1—C8—C4</b>	116.6 (3)
<b>C4 – N1</b>	1.356 (5)	<b>N5—C8—C4</b>	121.5 (3)

C4 – C3	1.403 (5)	C13—O2—C16	101.6 (3)
C4 – C8	1.460 (6)	O2—C13—C14	107.0 (4)
N1 – C1	1.342 (5)	C13—C14—C15	103.7 (4)
N3 – C6	1.136 (6)	C16—C15—C14	104.2 (4)
C3 – C2	1.403 (6)	O2—C16—C15	104.6 (4)
C3 – C7	1.445 (5)	N1 <sup>i</sup> —Cu1—O1—C8	– 174.7 (3)
N5 – C8	1.319 (5)	N1—Cu1—O1—C8	5.3 (3)
N2 – C5	1.129 (5)	O1 <sup>i</sup> —Cu1—O1—C8	– 14.0 (100)
C2 – C1	1.405 (5)	C3—C4—N1—C1	– 0.2 (5)
C2 – C6	1.433 (6)	C8—C4—N1—C1	– 175.3 (3)
C1 – C5	1.431 (6)	C3—C4—N1—Cu1	– 176.3 (3)
O2 – C13	1.431 (4)	C8—C4—N1—Cu1	1.2 (4)
O2 – C16	1.461 (5)	N1 <sup>i</sup> —Cu1—N1—C1	– 127.0 (100)
C13 – C14	1.481 (6)	O1 <sup>i</sup> —Cu1—N1—C1	– 8.5 (4)
C14 – C15	1.522 (6)	O1—Cu1—N1—C1	171.5 (4)
C15 – C16	1.484 (7)	N1 <sup>i</sup> —Cu1—N1—C4	59.0 (100)
N1 <sup>i</sup> —Cu1—N1	180.00 (17)	O1 <sup>i</sup> —Cu1—N1—C4	176.7 (3)
N1 <sup>i</sup> —Cu1—O1 <sup>i</sup>	81.95 (12)	O1—Cu1—N1—C4	– 3.3 (3)
N1—Cu1—O1 <sup>i</sup>	98.05 (12)	N1—C4—C3—C2	0.3 (5)
N1 <sup>i</sup> —Cu1—O1	98.05 (12)	C8—C4—C3—C2	174.0 (4)
N1—Cu1—O1	81.95 (12)	N1—C4—C3—C7	– 177.4 (4)
O1 <sup>i</sup> —Cu1—O1	180.00 (2)	C8—C4—C3—C7	– 3.7 (8)
C8—O1—Cu1	113.9 (3)	C4—C3—C2—C1	– 0.2 (5)
N1—C4—C3	109.5 (4)	C7—C3—C2—C1	177.6 (4)
N1—C4—C8	115.0 (3)	C4—C3—C2—C6	180.0 (4)
C3—C4—C8	135.2 (4)	C7—C3—C2—C6	– 2.3 (7)
C1—N1—C4	107.7 (3)	C4—N1—C1—C2	0.1 (5)
C1—N1—Cu1	140.1 (2)	Cu1—N1—C1—C2	– 174.9 (3)
C4—N1—Cu1	112.1 (3)	C4—C3—C7—N4	153.0 (12)
C2—C3—C4	106.7 (3)	Cu1—O1—C8—N5	174.6 (3)
C2—C3—C7	124.8 (4)	Cu1—O1—C8—C4	– 6.1 (5)
C4—C3—C7	128.5 (4)	N1—C4—C8—O1	3.4 (6)
C3—C2—C1	105.4 (4)	C3—C4—C8—O1	– 170.1 (4)
C3—C2—C6	127.0 (3)	C13—C14—C15—C16	4.2 (6)
C1—C2—C6	127.6 (4)	C13—O2—C16—C15	42.8 (6)
N1—C4—C8—N5	– 177.3 (4)	C14—C15—C16—O2	– 28.8 (7)
C3—C4—C8—N5	9.2 (7)		
C16—O2—C13—C14	– 40.6 (5)		
O2—C13—C14—C15	22.6 (6)		

Symmetry code: (i) 1-x, 1-y, -z.

**Scheme S5.** Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II)

acetonitrile solvate  $[\text{Zn}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  (**9**)



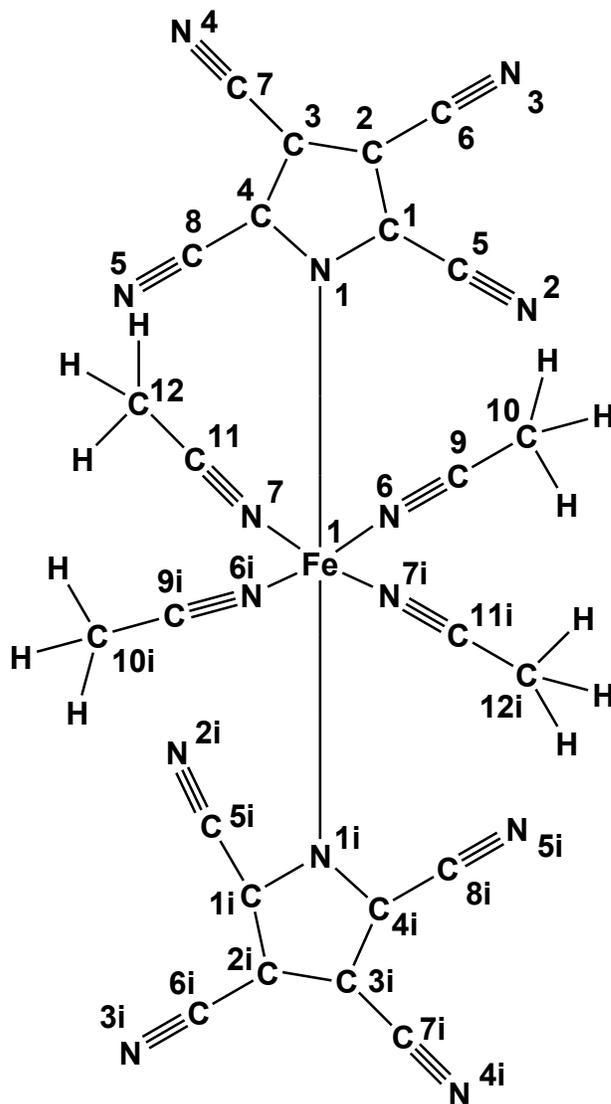
**Table S10.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **9**.

C1 – N1	1.3615 (17)	N4—C7—C3	178.44 (18)
C1 – C2	1.3926 (18)	N5—C8—C4	175.96 (15)
C1 – C5	1.432 (2)	N6—C9—C10	177.62 (16)
C2 – C3	1.409 (2)	N7—C11—C12	178.87 (17)
C2 – C6	1.421 (2)	N8—C13—C14	178.6 (2)
C3 – C4	1.3973 (19)	C1—N1—C4	105.17 (11)

C3 – C7	1.423 (2)	C1—N1—Zn1	127.68 (9)
C4 – N1	1.3624 (17)	C4—N1—Zn1	127.10 (9)
C4 – C8	1.427 (2)	C9—N6—Zn1	163.84 (12)
C5 – N2	1.146 (2)	C11—N7—Zn1	174.52 (12)
C6 – N3	1.1456 (19)	N6—Zn1—N6 <sup>i</sup>	180.00
C7 – N4	1.140 (2)	N6—Zn1—N1 <sup>i</sup>	90.22 (4)
C8 – N5	1.1438 (19)	N6 <sup>i</sup> —Zn1—N1 <sup>i</sup>	89.78 (4)
C9 – N6	1.1380 (18)	N6—Zn1—N1	89.78 (4)
C9 – C10	1.455 (2)	N6 <sup>i</sup> —Zn1—N1	90.22 (4)
C11 – N7	1.1376 (19)	N1 <sup>i</sup> —Zn1—N1	180.00
C11 – C12	1.449 (2)	N6—Zn1—N7	89.32 (5)
C13 – N8	1.127 (2)	N6 <sup>i</sup> —Zn1—N7	90.68 (5)
C13 – C14	1.454 (3)	N1 <sup>i</sup> —Zn1—N7	90.36 (4)
N1 – Zn1	2.1528 (11)	N1—Zn1—N7	89.64 (4)
N6 – Zn1	2.1513 (12)	N6—Zn1—N7 <sup>i</sup>	90.68 (5)
N7 – Zn1	2.1567 (13)	N6 <sup>i</sup> —Zn1—N7 <sup>i</sup>	89.32 (5)
Zn1 – N6 <sup>i</sup>	2.1513 (12)	N1 <sup>i</sup> —Zn1—N7 <sup>i</sup>	89.64 (4)
Zn1 – N1 <sup>i</sup>	2.1528 (11)	N1—Zn1—N7 <sup>i</sup>	90.36 (4)
Zn1 – N7 <sup>i</sup>	2.1567 (13)	N7—Zn1—N7 <sup>i</sup>	180.00 (3)
N1—C1—C2	111.93 (12)	N1—C1—C2—C3	– 0.25 (16)
N1—C1—C5	123.70 (12)	C5—C1—C2—C3	178.39 (14)
C2—C1—C5	124.35 (13)	N1—C1—C2—C6	178.04 (13)
C1—C2—C3	105.59 (12)	C5—C1—C2—C6	– 3.3 (2)
C1—C2—C6	127.37 (13)	C1—C2—C3—C4	0.24 (15)
C3—C2—C6	127.01 (13)	C6—C2—C3—C4	– 178.05 (14)
C4—C3—C2	105.77 (12)	C1—C2—C3—C7	178.89 (14)
C4—C3—C7	126.52 (14)	C6—C2—C3—C7	0.6 (2)
C2—C3—C7	127.69 (13)	C2—C3—C4—N1	– 0.17 (16)
N1—C4—C3	111.54 (12)	C7—C3—C4—N1	– 178.84 (13)
N1—C4—C8	124.67 (12)	C2—C3—C4—C8	179.21 (13)
C3—C4—C8	123.78 (12)	C7—C3—C4—C8	0.5 (2)
N2—C5—C1	176.63 (17)	C2—C1—N1—C4	0.14 (16)
N3—C6—C2	178.98 (16)	C5—C1—N1—C4	– 178.50 (13)
C2—C1—N1—Zn1	– 177.34 (9)		
C5—C1—N1—Zn1	4.0 (2)		
C3—C4—N1—C1	0.02 (16)		
C8—C4—N1—C1	– 179.36 (13)		
C3—C4—N1—Zn1	177.52 (9)		
C8—C4—N1—Zn1	– 1.86 (19)		

Symmetry code: (i) 1-x, 1-y, -z.

**Scheme S6.** Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate  $[\text{Fe}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  (**10**)



**Table S11.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **10**.

C1 — N1	1.3632 (12)	N7—Fe1—N7 <sup>i</sup>	180.00
C1 — C2	1.3971 (13)	N6—Fe1—N1	89.78 (3)
C1 — C5	1.4314 (14)	N6 <sup>i</sup> —Fe1—N1	90.22 (3)
C2 — C3	1.4082 (14)	N7—Fe1—N1	89.54 (3)
C2 — C6	1.4218 (14)	N7 <sup>i</sup> —Fe1—N1	90.46 (3)

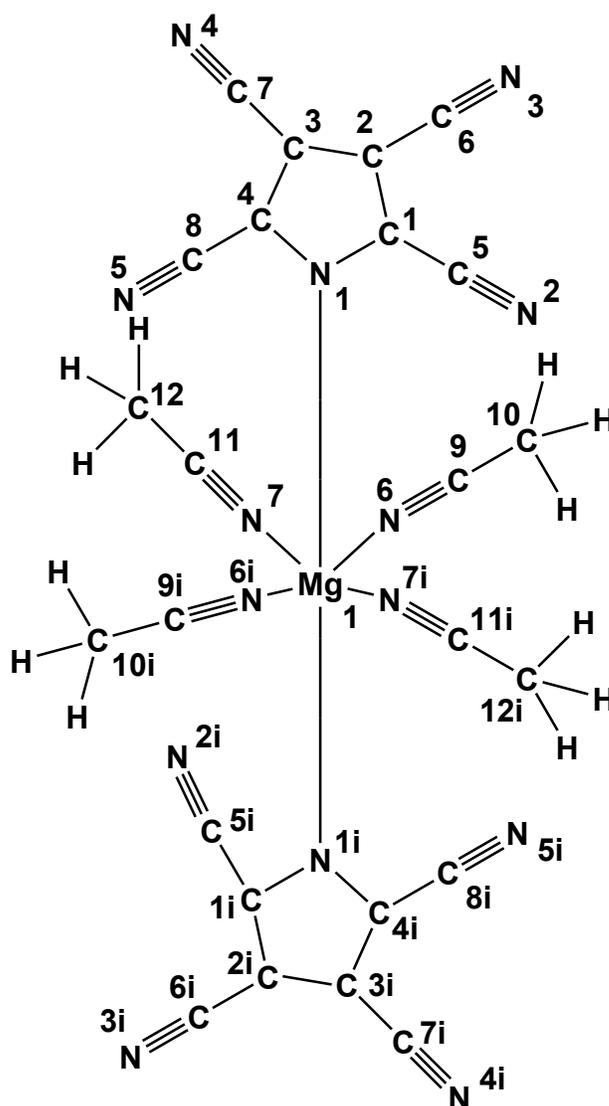
C3 — C4	1.3980 (13)	N6—Fe1—N1 <sup>i</sup>	90.22 (3)
C3 — C7	1.4213 (14)	N6 <sup>i</sup> —Fe1—N1 <sup>i</sup>	89.78 (3)
C4 — N1	1.3635 (12)	N7—Fe1—N1 <sup>i</sup>	90.46 (3)
C4 — C8	1.4275 (14)	N7 <sup>i</sup> —Fe1—N1 <sup>i</sup>	89.54 (3)
C5 — N2	1.1447 (15)	N1—Fe1—N1 <sup>i</sup>	180.00
C6 — N3	1.1466 (14)	N1—C1—C2—C3	− 0.27 (11)
C7 — N4	1.1452 (15)	C5—C1—C2—C3	178.27 (10)
C8 — N5	1.1480 (14)	N1—C1—C2—C6	177.89 (9)
C9 — N6	1.1406 (13)	C5—C1—C2—C6	− 3.57 (17)
C11 —N7	1.1385 (13)	C1—C2—C3—C4	0.19 (11)
C11 — C12	1.4529 (15)	C6—C2—C3—C4	−177.97 (10)
C13 —N8	1.1283 (18)	C1—C2—C3—C7	178.64 (10)
C13 —C14	1.4481 (19)	C6—C2—C3—C7	0.47 (18)
N1 — Fe1	2.1920 (8)	C2—C3—C4—N1	− 0.05 (11)
N6 — Fe1	2.1588 (9)	C7—C3—C4—N1	− 178.53 (10)
C9 — C10	1.4519 (14)	C2—C3—C4—C8	179.30 (9)
N1 — Fe1	2.1659 (9)	C7—C3—C4—C8	0.83 (17)
Fe1 — N6 <sup>i</sup>	2.1589 (9)	C2—C1—N1—C4	0.24 (11)
Fe1 — N7 <sup>i</sup>	2.1659 (9)	C5—C1—N1—C4	− 178.32 (10)
Fe1 — N1 <sup>i</sup>	2.1920 (8)	C2—C1—N1—Fe1	− 177.37 (6)
N1—C1—C2	111.77 (9)	C3—C1—N1—Fe1	4.07 (14)
N1—C1—C5	123.49 (9)	C3—C4—N1—C1	− 0.11 (11)
C2—C1—C5	124.73 (9)	C8—C4—N1—C1	− 179.46 (9)
C1—C2—C3	105.62 (8)	C3—C4—N1—Fe1	177.51 (6)
C1—C2—C6	127.21 (10)	C8—C4—N1—Fe1	− 1.84 (14)
C3—C2—C6	127.14 (9)		
C4—C3—C2	105.84 (8)		
C4—C3—C7	126.44 (10)		
C2—C3—C7	127.69 (9)		
N1—C4—C3	111.56 (8)		
N1—C4—C8	124.21 (9)		
C3—C4—C8	124.23 (9)		
N2—C5—C1	176.97 (12)		
N3—C6—C2	179.24 (12)		
N4—C7—C3	178.93 (14)		
N5—C8—C4	176.12 (11)		
N6—C9—C10	177.47 (11)		
N7—C11—C12	178.83 (13)		
N8—C13—C14	178.67 (17)		
C1—N1—C4	105.20 (8)		
C1—N1—Fe1	127.60 (6)		
C4—N1—Fe1	127.15 (6)		
C9—N6—Fe1	164.01 (8)		
C11—N7—Fe1	173.84 (9)		
N6—Fe1—N6 <sup>i</sup>	180.00		

N6—Fe1—N7	89.01 (3)		
N6 <sup>i</sup> —Fe1—N7	90.99 (3)		
N6—Fe1—N7 <sup>i</sup>	90.99 (3)		
N6 <sup>i</sup> —Fe1—N7 <sup>i</sup>	89.01 (3)		

Symmetry code: (i)  $-x, -y, -z$ .

**Scheme S7.** Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II)

acetonitrile solvate  $[\text{Mg}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  (**11**)

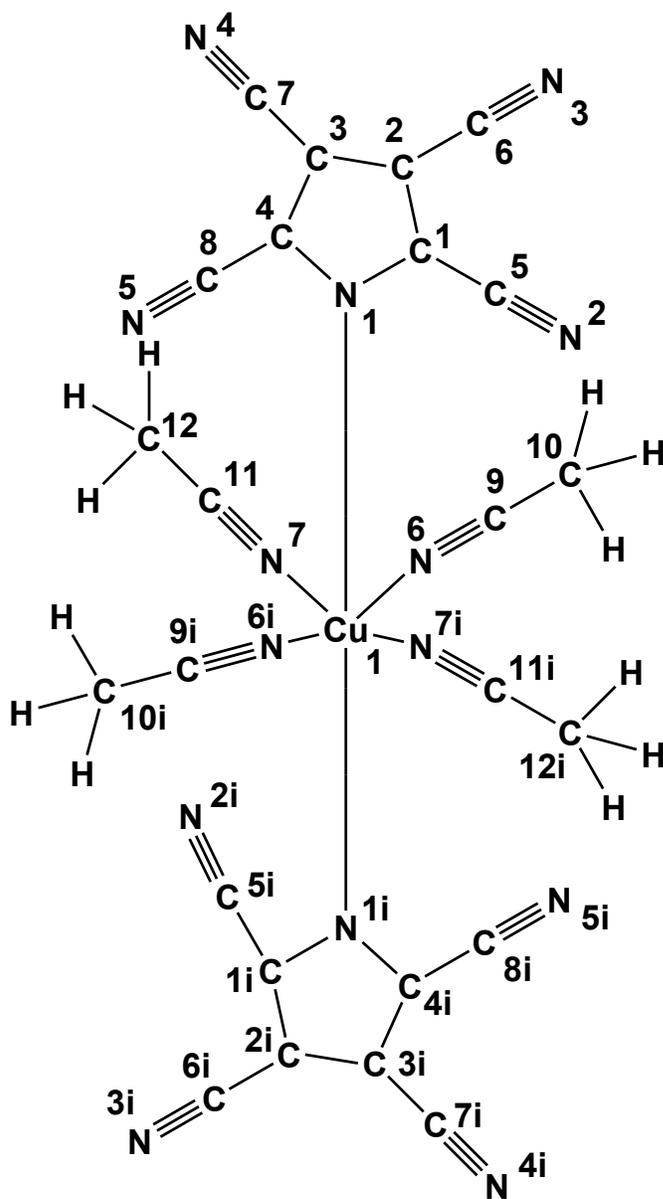


**Table S12.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **11**.

Mg1 — N6	2.1488 (9)	N7—C11—C12	178.82 (13)
Mg1 — N6 <sup>i</sup>	2.1488 (9)	N8—C13—C14	178.78 (16)
Mg1 — N7 <sup>i</sup>	2.1561 (9)	C1—N1—C4	104.83 (8)
Mg1 — N7	2.1562 (9)	C1—N1—Mg1	127.50 (6)
Mg1 — N1 <sup>i</sup>	2.2031 (8)	C4—N1—Mg1	127.62 (6)
Mg1 — N1	2.2031 (8)	C9—N6—Mg1	165.02 (8)
N1 — C1	1.3616 (12)	C11—N7—Mg1	174.48 (9)
N1 — C4	1.3658 (12)	N6—Mg1—N6 <sup>i</sup>	180.00 (4)
N2 — C5	1.1458 (13)	N6—Mg1—N7	89.83 (3)
N3 — C6	1.1411 (15)	N6 <sup>i</sup> —Mg1—N7	90.17 (3)
N4 — C7	1.1453 (14)	N6—Mg1—N7 <sup>i</sup>	90.17 (3)
N5 — C8	1.1471 (14)	N6 <sup>i</sup> —Mg1—N7 <sup>i</sup>	89.83 (3)
N6 — C9	1.1419 (13)	N7 <sup>i</sup> —Mg1—N7	180.00
N7 — C11	1.1394 (13)	N6—Mg1—N1	89.91 (3)
C1 — C2	1.3933 (13)	N6 <sup>i</sup> —Mg1—N1	90.09 (3)
C1 — C5	1.4320 (13)	N7—Mg1—N1	89.52 (3)
C2 — C3	1.4022 (14)	N7 <sup>i</sup> —Mg1—N1	90.48 (3)
C2 — C6	1.4263 (14)	N6—Mg1—N1 <sup>i</sup>	90.09 (3)
C3 — C4	1.3968 (13)	N6 <sup>i</sup> —Mg1—N1 <sup>i</sup>	89.91 (3)
C3 — C7	1.4225 (13)	N7—Mg1—N1 <sup>i</sup>	90.48 (3)
C4 — C8	1.4290 (14)	N7 <sup>i</sup> —Mg1—N1 <sup>i</sup>	89.52 (3)
C9 — C10	1.4465 (15)	N1 <sup>i</sup> —Mg1—N1	180.00
C11 — C12	1.4513 (15)	N1—C1—C2—C3	0.05 (11)
N8 — C13	1.1279 (18)	C5—C1—C2—C3	− 179.16 (9)
C13 — C14	1.448 (2)	N1—C1—C2—C6	178.48 (9)
N1—C1—C2	111.88 (8)	C5—C1—C2—C6	− 0.73 (16)
N1—C1—C5	123.95 (8)	C1—C2—C3—C4	− 0.30 (11)
C2—C1—C5	124.17 (9)	C6—C2—C3—C4	−178.7 (1)
C1—C2—C3	105.90 (8)	C1—C2—C3—C7	178.15 (10)
C1—C2—C6	126.34 (9)	C6—C2—C3—C7	− 0.25 (17)
C3—C2—C6	127.74 (9)	C2—C3—C4—N1	0.47 (11)
C4—C3—C2	105.67 (8)	C7—C3—C4—N1	− 177.99 (9)
C4—C3—C7	127.04 (9)	C2—C3—C4—C8	178.35 (10)
C2—C3—C7	127.26 (9)	C7—C3—C4—C8	3.19 (17)
N1—C4—C3	111.71 (9)	C1—N1—C4—C3	− 0.43 (11)
N1—C4—C8	123.49 (9)	C1—N1—C4—C8	178.41 (9)
C3—C4—C8	124.79 (9)	Mg1—N1—C1—C2	− 177.36 (6)
N2—C5—C1	176.17 (10)	Mg1—N1—C1—C5	1.85 (14)
N3—C6—C2	179.04 (13)	C4—N1—C1—C2	0.23 (11)
N4—C7—C3	179.14 (12)	C4—N1—C1—C5	179.44 (9)
N5—C8—C4	177.14 (12)	Mg1—N1—C4—C3	177.15 (6)
N6—C9—C10	177.47 (11)	Mg1—N1—C4—C8	− 4.01 (14)

Symmetry code: (i) 1−x, 1−y, 1−z.

**Scheme S8.** Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II) acetonitrile solvate  $[\text{Cu}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  (**12**)



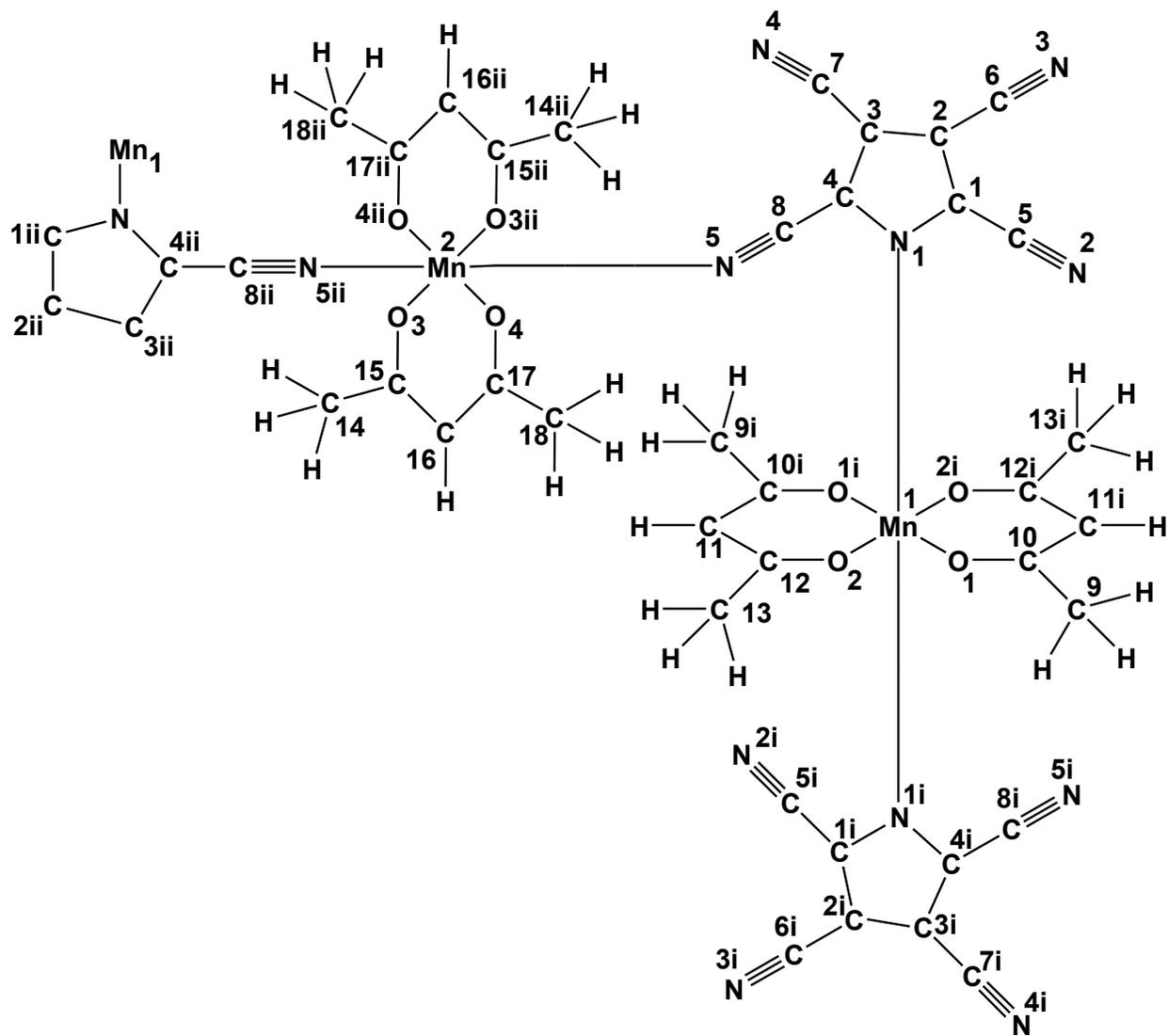
**Table S13.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **12**.

<b>Cu1 — N1<sup>i</sup></b>	2.0258 (10)	<b>N7—Cu1—N7<sup>i</sup></b>	180.000
<b>Cu1 — N1</b>	2.0258 (10)	<b>C4—N1—C1</b>	105.41 (10)
<b>Cu1 — N6</b>	2.0251 (11)	<b>C4—N1—Cu1</b>	127.35 (8)
<b>Cu1 — N6<sup>i</sup></b>	2.0251 (11)	<b>C1—N1—Cu1</b>	127.21 (9)
<b>Cu1 — N7</b>	2.3451 (12)	<b>C9—N6—Cu1</b>	176.94 (11)

<b>Cu1 — N7<sup>i</sup></b>	2.3451 (12)	<b>C11—N7—Cu1</b>	156.50 (11)
<b>N1 — C4</b>	1.3639 (16)	<b>N1—C1—C2</b>	111.39 (11)
<b>N1 — C1</b>	1.3659 (16)	<b>N1—C1—C5</b>	124.63 (12)
<b>N2 — C5</b>	1.1484 (18)	<b>C2—C1—C5</b>	123.98 (12)
<b>N3 — C6</b>	1.1463 (18)	<b>C1—C2—C3</b>	105.87 (11)
<b>N4 — C7</b>	1.1447 (19)	<b>C2—C1—C5</b>	123.98 (12)
<b>N5 — C8</b>	1.1447 (18)	<b>C1—C2—C6</b>	126.73 (12)
<b>N6 — C9</b>	1.1397 (18)	<b>C3—C2—C6</b>	127.37 (12)
<b>N7 — C11</b>	1.1399 (18)	<b>C4—C3—C2</b>	105.88 (11)
<b>C1 — C2</b>	1.3949 (18)	<b>C4—C3—C7</b>	126.50 (12)
<b>C1 — C5</b>	1.4303 (19)	<b>C2—C3—C7</b>	127.59 (12)
<b>C2 — C3</b>	1.4086 (18)	<b>N1—C4—C3</b>	111.45 (11)
<b>C2 — C6</b>	1.4219 (18)	<b>N1—C4—C8</b>	125.12 (11)
<b>C3 — C4</b>	1.3949 (17)	<b>C3—C4—C8</b>	123.43 (12)
<b>C3 — C7</b>	1.4228 (19)	<b>N2—C5—C1</b>	175.52 (14)
<b>C4 — C8</b>	1.4332 (18)	<b>N3—C6—C2</b>	179.04 (15)
<b>C9 — C10</b>	1.450 (2)	<b>N4—C7—C3</b>	178.75 (16)
<b>C11 — C12</b>	1.4507 (19)	<b>N5—C8—C4</b>	174.73 (14)
<b>C13 —N8</b>	1.134 (2)	<b>N6—C9—C10</b>	178.24 (15)
<b>C13 — C14</b>	1.454 (2)	<b>N7—C11—C12</b>	177.54 (15)
<b>N1<sup>i</sup>—Cu1—N1</b>	180.00 (6)	<b>N8—C13—C14</b>	178.9 (2)
<b>N1<sup>i</sup>—Cu1—N6</b>	89.80 (4)	<b>C4—N1—C1—C2</b>	- 0.20 (14)
<b>N1—Cu1—N6</b>	90.20 (4)	<b>Cu1—N1—C1—C2</b>	178.30 (9)
<b>N1<sup>i</sup>—Cu1—N6<sup>i</sup></b>	90.20 (4)	<b>C4—N1—C1—C5</b>	179.29 (12)
<b>N1—Cu1—N6<sup>i</sup></b>	89.80 (4)	<b>Cu1—N1—C1—C5</b>	- 2.21 (19)
<b>N6—Cu1—N6<sup>i</sup></b>	180.000	<b>N1—C1—C2—C3</b>	0.24 (15)
<b>N1<sup>i</sup>—Cu1—N7</b>	89.62 (4)	<b>C5—C1—C2—C3</b>	- 179.26 (12)
<b>N1—Cu1—N7</b>	90.38 (4)	<b>N1—C1—C2—C6</b>	- 177.90 (12)
<b>N6—Cu1—N7</b>	87.24 (4)	<b>C5—C1—C2—C6</b>	2.6 (2)
<b>N6<sup>i</sup>—Cu1—N7</b>	92.76 (4)	<b>C1—C2—C3—C4</b>	- 0.18 (14)
<b>N1<sup>i</sup>—Cu1—N7<sup>i</sup></b>	90.38 (4)	<b>C6—C2—C3—C4</b>	177.95 (13)
<b>N1—Cu1—N7<sup>i</sup></b>	89.62 (4)	<b>C1—C2—C3—C7</b>	178.36 (13)
<b>N6—Cu1—N7<sup>i</sup></b>	92.76 (4)	<b>C6—C2—C3—C7</b>	- 0.2 (2)
<b>N6<sup>i</sup>—Cu1—N7<sup>i</sup></b>	87.24 (4)	<b>C1—N1—C4—C3</b>	0.08 (14)
<b>Cu1—N1—C4—C3</b>	- 178.42 (8)	<b>C7—C3—C4—N1</b>	178.27 (12)
<b>C1—N1—C4—C8</b>	179.94 (12)	<b>C2—C3—C4—C8</b>	- 179.80 (12)
<b>Cu1—N1—C4—C8</b>	1.44 (18)	<b>C7—C3—C4—C8</b>	- 1.6 (2)
<b>C2—C3—C4—N1</b>	0.06 (15)		

Symmetry code: (i)  $-x, -y, 1-z$ .

**Scheme S9.** Numbering scheme of di(acetylacetonate)-1,5-N- $\mu$ -tetracyanopyrrolido manganese (III) [Mn(acac)<sub>2</sub>TCP] (**13**)



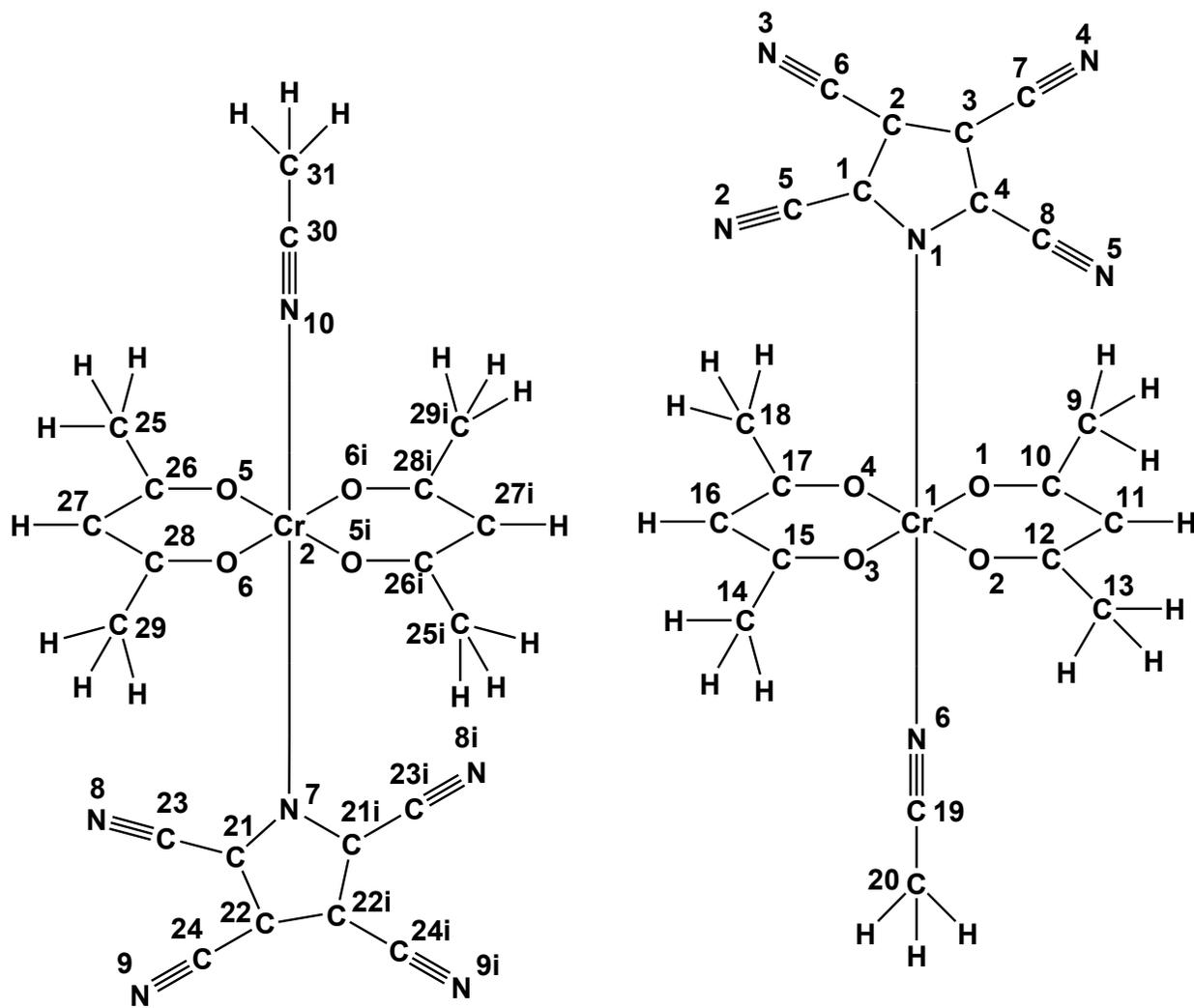
**Table S14.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **13**.

<b>Mn1 — O1</b>	1.890 (1)	<b>C11 — C10 — C9</b>	121.79 (15)
<b>Mn1 — O1<sup>i</sup></b>	1.8901 (10)	<b>O4<sup>ii</sup> — Mn2 — O3<sup>ii</sup></b>	91.70 (5)
<b>Mn1 — O2</b>	1.9092 (11)	<b>O4 — Mn2 — O3<sup>ii</sup></b>	88.30 (5)
<b>Mn1 — O2<sup>i</sup></b>	1.9092 (11)	<b>O3 — Mn2 — O3<sup>ii</sup></b>	180.000
<b>Mn1 — N1<sup>i</sup></b>	2.2994 (13)	<b>O4<sup>ii</sup> — Mn2 — N5<sup>ii</sup></b>	94.76 (5)
<b>Mn1 — N1</b>	2.2994 (13)	<b>O4 — Mn2 — N5<sup>ii</sup></b>	85.24 (5)
<b>C1 — N1</b>	1.356 (2)	<b>O3 — Mn2 — N5<sup>ii</sup></b>	90.35 (5)
<b>C1 — C2</b>	1.395 (2)	<b>O3<sup>ii</sup> — Mn2 — N5<sup>ii</sup></b>	89.65 (5)
<b>C1 — C5</b>	1.430 (2)	<b>O4<sup>ii</sup> — Mn2 — N5</b>	85.24 (5)
<b>N1 — C4</b>	1.3604 (19)	<b>O4 — Mn2 — N5</b>	94.76 (5)
<b>O1 — C10</b>	1.2821 (19)	<b>O3 — Mn2 — N5</b>	89.65 (5)
<b>Mn2 — O4<sup>ii</sup></b>	1.8993 (11)	<b>O3<sup>ii</sup> — Mn2 — N5</b>	90.35 (5)
<b>Mn2 — O4</b>	1.8993 (11)	<b>N5<sup>ii</sup> — Mn2 — N5</b>	180.000
<b>Mn2 — O3</b>	1.9024 (11)	<b>C1 — C2 — C3</b>	105.53 (14)
<b>Mn2 — O3<sup>ii</sup></b>	1.9024 (11)	<b>C1 — C2 — C6</b>	126.91 (14)
<b>Mn2 — N5<sup>ii</sup></b>	2.3618 (14)	<b>C3 — C2 — C6</b>	127.50 (15)
<b>Mn2 — N5</b>	2.3619 (13)	<b>C12 — O2 — Mn1</b>	127.24 (10)
<b>C2 — C3</b>	1.405 (2)	<b>C4 — C3 — C2</b>	105.70 (13)
<b>C2 — C6</b>	1.421 (2)	<b>C4 — C3 — C7</b>	128.57 (15)
<b>N2 — C5</b>	1.142 (2)	<b>C2 — C3 — C7</b>	125.73 (16)
<b>O2 — C12</b>	1.277 (2)	<b>C15 — O3 — Mn2</b>	127.04 (11)
<b>C3 — C4</b>	1.397 (2)	<b>N1 — C4 — C3</b>	111.67 (13)
<b>C3 — C7</b>	1.426 (2)	<b>N1 — C4 — C8</b>	123.14 (14)
<b>N3 — C6</b>	1.144 (2)	<b>C3 — C4 — C8</b>	125.19 (14)
<b>O3 — C15</b>	1.2897 (19)	<b>N5 — C8 — C4</b>	174.80 (17)
<b>C4 — C8</b>	1.433 (2)	<b>O4 — C17 — C16</b>	124.29 (16)
<b>N4 — C7</b>	1.141 (2)	<b>O4 — C17 — C18</b>	114.66 (15)
<b>O4 — C17</b>	1.286 (2)	<b>C16 — C17 — C18</b>	121.06 (16)
<b>N5 — C8</b>	1.141 (2)	<b>C15 — C16 — C17</b>	123.65 (16)
<b>C13 — C12</b>	1.500 (2)	<b>O3 — C15 — C16</b>	124.48 (16)
<b>C12 — C11</b>	1.391 (2)	<b>O3 — C15 — C14</b>	114.44 (15)
<b>C11 — C10</b>	1.387 (3)	<b>C16 — C15 — C14</b>	121.08 (16)
<b>C10 — C9</b>	1.494 (2)	<b>C2 — C1 — N1 — C4</b>	0.12 (19)
<b>C18 — C17</b>	1.494 (2)	<b>C5 — C1 — N1 — C4</b>	-179.40 (15)
<b>C17 — C16</b>	1.390 (2)	<b>C2 — C1 — N1 — Mn1</b>	179.89 (10)
<b>C16 — C15</b>	1.386 (2)	<b>C5 — C1 — N1 — Mn1</b>	0.4 (2)
<b>C15 — C14</b>	1.499 (2)	<b>O2 — Mn1 — O1 — C10</b>	-4.91 (14)
<b>O1 — Mn1 — O1<sup>i</sup></b>	180.00 (7)	<b>O2 — Mn1 — O1 — C10</b>	175.09 (14)
<b>O1 — Mn1 — O2</b>	91.77 (5)	<b>N1 — Mn1 — O1 — C10</b>	-96.59 (13)
<b>O1<sup>i</sup> — Mn1 — O2</b>	88.23 (5)	<b>N1 — Mn1 — O1 — C10</b>	83.41 (13)
<b>O1 — Mn1 — O2<sup>i</sup></b>	88.23 (5)	<b>N1 — C1 — C2 — C3</b>	-0.33 (19)
<b>O1<sup>i</sup> — Mn1 — O2<sup>i</sup></b>	91.77 (5)	<b>C5 — C1 — C2 — C3</b>	179.18 (16)
<b>O2 — Mn1 — O2<sup>i</sup></b>	180.000	<b>N1 — C1 — C2 — C6</b>	-177.49 (16)

<b>O1 — Mn1 — N1<sup>i</sup></b>	88.70 (5)	<b>C5 — C1 — C2 — C6</b>	2.0 (3)
<b>O1<sup>i</sup> — Mn1 — N1<sup>i</sup></b>	91.30 (5)	<b>C1 — C2 — C3 — C4</b>	0.39 (17)
<b>O2 — Mn1 — N1<sup>i</sup></b>	91.71 (5)	<b>C6 — C2 — C3 — C4</b>	177.54 (16)
<b>O2<sup>i</sup> — Mn1 — N1<sup>i</sup></b>	88.29 (5)	<b>C1 — C2 — C3 — C7</b>	179.69 (16)
<b>O1 — Mn1 — N1</b>	91.30 (5)	<b>C6 — C2 — C3 — C7</b>	- 3.2 (3)
<b>O1<sup>i</sup> — Mn1 — N1</b>	88.70 (5)	<b>C1 — N1 — C4 — C3</b>	0.15 (18)
<b>O2 — Mn1 — N1</b>	88.29 (5)	<b>Mn1 — N1 — C4 — C3</b>	- 179.62 (10)
<b>O2<sup>i</sup> — Mn1 — N1</b>	91.71 (5)	<b>C1 — N1 — C4 — C8</b>	179.96 (15)
<b>O1 — Mn1 — N1<sup>i</sup></b>	180.000	<b>Mn1 — N1 — C4 — C8</b>	0.2 (2)
<b>N1 — C1 — C2</b>	112.00 (13)	<b>C2 — C3 — C4 — N1</b>	- 0.35 (18)
<b>N1 — C1 — C5</b>	123.21 (15)	<b>C7 — C3 — C4 — N1</b>	- 179.62 (16)
<b>C2 — C1 — C5</b>	124.79 (15)	<b>O3 — Mn2 — O4 — C17</b>	13.67 (13)
<b>C1 — N1 — C4</b>	105.11 (13)	<b>O3 — Mn2 — O4 — C17</b>	- 166.33 (13)
<b>C1 — N1 — Mn1</b>	125.71 (10)	<b>N5 — Mn2 — O4 — C17</b>	- 76.54 (13)
<b>C4 — N1 — Mn1</b>	129.18 (10)	<b>N5 — Mn2 — O4 — C17</b>	103.46 (13)
<b>C10 — O1 — Mn1</b>	128.2 (1)	<b>Mn1 — O2 — C12 — C11</b>	- 3.4 (3)
<b>O4<sup>ii</sup> — Mn2 — O4</b>	180.000	<b>Mn1 — O2 — C12 — C13</b>	176.58 (12)
<b>O4<sup>ii</sup> — Mn2 — O3</b>	88.30 (5)	<b>O2 — C12 — C11 — C10</b>	- 3.0 (3)
<b>O4 — Mn2 — O3</b>	91.70 (5)	<b>C13 — C12 — C11 — C10</b>	177.04 (18)
<b>C17 — O4 — Mn2</b>	127.17 (11)	<b>Mn1 — O1 — C10 — C11</b>	0.8 (2)
<b>N2 — C5 — C1</b>	175.1 (2)	<b>Mn1 — O1 — C10 — C9</b>	- 179.72 (11)
<b>C8 — N5 — Mn2</b>	167.56 (14)	<b>C12 — C11 — C10 — O1</b>	4.4 (3)
<b>N3 — C6 — C2</b>	178.75 (19)	<b>C12 — C11 — C10 — C9</b>	- 175.02 (17)
<b>N4 — C7 — C3</b>	177.9 (2)	<b>Mn2 — O4 — C17 — C16</b>	- 9.2 (2)
<b>O2 — C12 — C11</b>	124.61 (16)	<b>Mn2 — O4 — C17 — C18</b>	170.96 (10)
<b>O2 — C12 — C13</b>	114.21 (15)	<b>O4 — C17 — C16 — C15</b>	- 2.7 (3)
<b>C11 — C12 — C13</b>	121.17 (16)	<b>C18 — C17 — C16 — C15</b>	177.12 (15)
<b>C10 — C11 — C12</b>	123.72 (16)	<b>Mn2 — O3 — C15 — C16</b>	4.6 (2)
<b>O1 — C10 — C11</b>	124.05 (14)	<b>Mn2 — O3 — C15 — C14</b>	- 175.86 (11)

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-1-x, -y, -1-z$ .

**Scheme S10.** Numbering scheme of acetonitrile-di(acetylacetonate)tetracyanopyrrolido chromium(III)  $[\text{Cr}(\text{acac})_2\text{TCP}\cdot\text{CH}_3\text{CN}]\cdot 0.67\text{CH}_3\text{CN}$  (**14**)



**Table S15.** Selected bond lengths (Å) angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) of **14**.

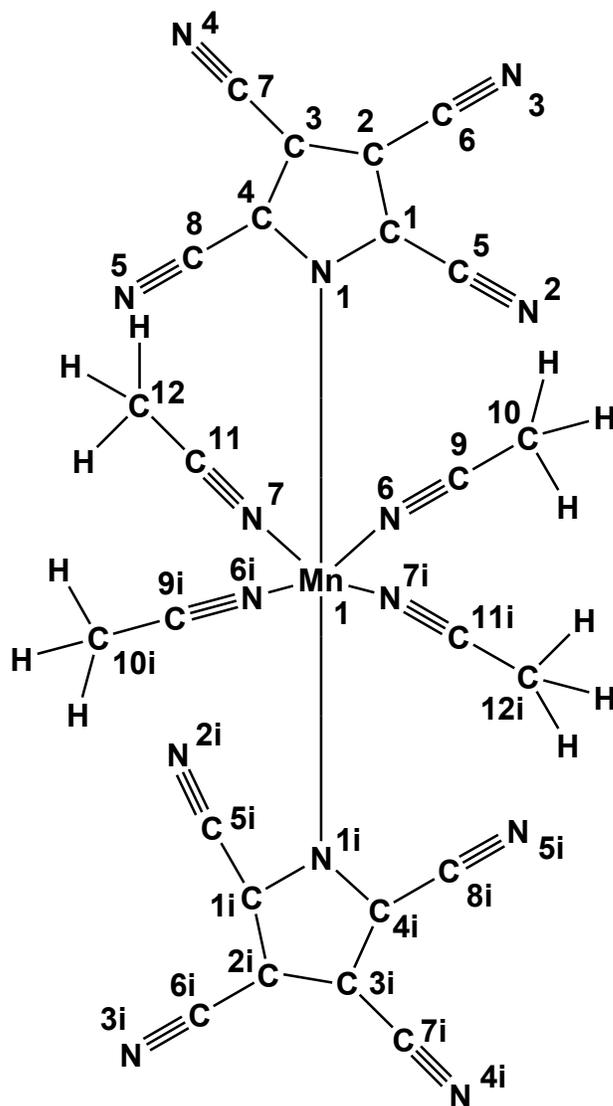
Cr1 – O3	1.9297 (18)	N6 – C19 – C20	179.5 (4)
Cr1 – O2	1.9328 (16)	O6 – Cr2 – O6 <sup>i</sup>	177.58 (11)
Cr1 – O4	1.9364 (16)	O6 – Cr2 – O5	90.76 (7)
Cr1 – O1	1.9420 (18)	O6 <sup>i</sup> – Cr2 – O5	89.26 (7)
Cr1 – N6	2.049 (2)	O6 – Cr2 – O5 <sup>i</sup>	89.26 (7)
Cr1 – N1	2.066 (2)	O6 <sup>i</sup> – Cr2 – O5 <sup>i</sup>	90.76 (7)
N1 – C4	1.364 (3)	O5 – Cr2 – O5 <sup>i</sup>	179.34 (11)

<b>N1 – C1</b>	1.365 (3)	<b>O6 – Cr2 – N10</b>	91.21 (6)
<b>C1 – C2</b>	1.382 (4)	<b>O6<sup>i</sup> – Cr2 – N10</b>	91.21 (6)
<b>C1 – C5</b>	1.436 (3)	<b>O5 – Cr2 – N10</b>	89.67 (6)
<b>C2 – C3</b>	1.415 (3)	<b>O5<sup>i</sup> – Cr2 – N10</b>	89.67 (6)
<b>C2 – C6</b>	1.428 (4)	<b>O6 – Cr2 – N7</b>	88.79 (6)
<b>C3 – C4</b>	1.383 (4)	<b>O6<sup>i</sup> – Cr2 – N7</b>	88.79 (6)
<b>C3 – C7</b>	1.430 (4)	<b>O5 – Cr2 – N7</b>	90.33 (6)
<b>C4 – C8</b>	1.435 (3)	<b>O5<sup>i</sup> – Cr2 – N7</b>	90.33 (6)
<b>C5 – N2</b>	1.142 (3)	<b>C2 – C3 – C7</b>	126.6 (2)
<b>C6 – N3</b>	1.142 (3)	<b>N1 – C4 – C3</b>	111.4 (2)
<b>C7 – N4</b>	1.133 (3)	<b>N1 – C4 – C8</b>	123.9 (2)
<b>C8 – N5</b>	1.140 (3)	<b>C3 – C4 – C8</b>	124.5 (2)
<b>O1 – C10</b>	1.280 (3)	<b>N2 – C5 – C1</b>	173.6 (3)
<b>O2 – C12</b>	1.285 (3)	<b>N3 – C6 – C2</b>	178.6 (3)
<b>C9 – C10</b>	1.496 (4)	<b>N4 – C7 – C3</b>	178.6 (3)
<b>C10 – C11</b>	1.394 (3)	<b>N5 – C8 – C4</b>	173.8 (3)
<b>C11 – C12</b>	1.389 (4)	<b>C10 – O1 – Cr1</b>	126.54 (16)
<b>C12 – C13</b>	1.498 (3)	<b>C12 – O2 – Cr1</b>	126.50 (16)
<b>N6 – C19</b>	1.135 (3)	<b>O1 – C10 – C11</b>	123.9 (2)
<b>C19 – C20</b>	1.450 (4)	<b>O1 – C10 – C9</b>	115.2 (2)
<b>Cr2 – O6</b>	1.9379 (17)	<b>C11 – C10 – C9</b>	121.0 (3)
<b>Cr2 – O6<sup>i</sup></b>	1.9379 (17)	<b>C12 – C11 – C10</b>	125.1 (3)
<b>Cr2 – O5</b>	1.9389 (16)	<b>O2 – C12 – C11</b>	123.8 (2)
<b>Cr2 – O5<sup>i</sup></b>	1.9389 (16)	<b>O2 – C12 – C13</b>	115.3 (3)
<b>Cr2 – N10</b>	2.040 (3)	<b>C11 – C12 – C13</b>	120.9 (3)
<b>Cr2 – N7</b>	2.067 (3)	<b>N10 – Cr2 – N7</b>	180.000
<b>N7 – C21</b>	1.370 (3)	<b>C21 – N7 – C21<sup>i</sup></b>	105.3 (3)
<b>N7 – C21<sup>i</sup></b>	1.370 (3)	<b>C21 – N7 – Cr2</b>	127.34 (15)
<b>C21 – C22</b>	1.386 (4)	<b>C21<sup>i</sup> – N7 – Cr2</b>	127.34 (15)
<b>C21 – C23</b>	1.430 (3)	<b>N7 – C21 – C22</b>	111.3 (2)
<b>C22 – C22<sup>i</sup></b>	1.412 (5)	<b>N7 – C21 – C23</b>	124.3 (3)
<b>C22 – C24</b>	1.424 (4)	<b>C22 – C21 – C23</b>	124.3 (3)
<b>C23 – N8</b>	1.142 (3)	<b>C21 – C22 – C21<sup>i</sup></b>	106.04 (13)
<b>C24 – N9</b>	1.136 (3)	<b>C21 – C22 – C24</b>	126.7 (2)
<b>O5 – C26</b>	1.278 (3)	<b>C22<sup>i</sup> – C22 – C24</b>	127.12 (15)
<b>O6 – C28</b>	1.279 (3)	<b>N8 – C23 – C21</b>	172.4 (3)
<b>C25 – C26</b>	1.505 (3)	<b>N9 – C24 – C22</b>	178.4 (3)
<b>C26 – C27</b>	1.396 (3)	<b>C26 – O5 – Cr2</b>	127.86 (15)
<b>C27 – C28</b>	1.391 (4)	<b>C28 – O6 – Cr2</b>	127.86 (15)
<b>C28 – C29</b>	1.501 (3)	<b>O5 – C26 – C27</b>	124.4 (2)
<b>O3 – C15</b>	1.277 (3)	<b>O5 – C26 – C25</b>	115.2 (2)
<b>O4 – C17</b>	1.279 (3)	<b>C27 – C26 – C25</b>	120.4 (3)
<b>C14 – C15</b>	1.500 (4)	<b>C28 – C27 – C26</b>	124.4 (3)
<b>C15 – C16</b>	1.392 (3)	<b>O6 – C28 – C27</b>	124.4 (2)
<b>C16 – C17</b>	1.391 (4)	<b>C15 – O3 – Cr1</b>	127.55 (16)

<b>C17 – C18</b>	1.498 (3)	<b>C17 – O4 – Cr1</b>	126.85 (15)
<b>C30 – N10</b>	1.137 (5)	<b>N10 – C30 – C31</b>	180.000
<b>C30 – C31</b>	1.453 (6)	<b>C30 – N10 – Cr2</b>	180.000
<b>N11 – C32</b>	1.126 (5)	<b>N11 – C32 – C33</b>	178.6 (5)
<b>C32 – C33</b>	1.454 (5)	<b>C4 – N1 – C1 – C2</b>	0.4 (3)
<b>O3 – Cr1 – O2</b>	88.27 (7)	<b>Cr1 – N1 – C1 – C2</b>	- 172.81 (17)
<b>O3 – Cr1 – O4</b>	91.65 (7)	<b>Cr1 – N1 – C1 – C5</b>	7.7 (4)
<b>O2 – Cr1 – O4</b>	177.12 (8)	<b>N1 – C1 – C2 – C3</b>	0.1 (3)
<b>O3 – Cr1 – O1</b>	178.06 (8)	<b>C5 – C1 – C2 – C3</b>	179.5 (3)
<b>O2 – Cr1 – O1</b>	90.72 (7)	<b>C1 – C2 – C3 – C4</b>	- 0.5 (3)
<b>O4 – Cr1 – O1</b>	89.46 (7)	<b>C6 – C2 – C3 – C4</b>	176.5 (3)
<b>O3 – Cr1 – N6</b>	87.75 (8)	<b>C1 – N1 – C4 – C3</b>	- 0.8 (3)
<b>O2 – Cr1 – N6</b>	92.58 (8)	<b>Cr1 – N1 – C4 – C3</b>	172.49 (17)
<b>O4 – Cr1 – N6</b>	90.29 (8)	<b>C1 – N1 – C4 – C8</b>	174.1 (2)
<b>O1 – Cr1 – N6</b>	90.66 (8)	<b>Cr1 – N1 – C4 – C8</b>	- 12.6 (4)
<b>O3 – Cr1 – N1</b>	91.74 (8)	<b>C2 – C3 – C4 – N1</b>	0.9 (3)
<b>O2 – Cr1 – N1</b>	87.88 (8)	<b>C7 – C3 – C4 – C8</b>	6.4 (4)
<b>O4 – Cr1 – N1</b>	89.24 (7)	<b>Cr1 – O1 – C10 – C11</b>	9.4 (4)
<b>O1 – Cr1 – N1</b>	89.86 (8)	<b>Cr1 – O1 – C10 – C9</b>	- 170.84 (17)
<b>N6 – Cr1 – N1</b>	179.30 (9)	<b>Cr1 – O2 – C12 – C11</b>	- 12.6 (4)
<b>C4 – N1 – C1</b>	105.5 (2)	<b>Cr1 – O2 – C12 – C13</b>	168.80 (18)
<b>C4 – N1 – Cr1</b>	126.80 (16)	<b>Cr1 – O3 – C15 – C16</b>	- 2.3 (4)
<b>C1 – N1 – Cr1</b>	127.31 (17)	<b>Cr1 – O3 – C15 – C14</b>	177.89 (19)
<b>N1 – C1 – C2</b>	111.3 (2)	<b>Cr1 – O4 – C17 – C16</b>	- 7.5 (4)
<b>N1 – C1 – C5</b>	124.4 (2)	<b>Cr1 – O4 – C17 – C18</b>	171.55 (17)
<b>C2 – C1 – C5</b>	124.3 (2)	<b>C21 – N7 – C21 – C22</b>	- 0.50 (15)
<b>C1 – C2 – C3</b>	106.0 (2)	<b>Cr2 – N7 – C21 – C22</b>	179.50 (15)
<b>C1 – C2 – C6</b>	127.4 (4)	<b>C21 – N7 – C21 – C23</b>	176.9 (3)
<b>C3 – C2 – C6</b>	126.5 (2)	<b>Cr2 – N7 – C21 – C23</b>	-3.1 (3)
<b>C4 – C3 – C2</b>	105.8 (2)	<b>N7 – C21 – C22 – C22<sup>1</sup></b>	1.3 (4)
<b>C4 – C3 – C7</b>	127.6 (2)	<b>N7 – C21 – C22 – C24</b>	- 175.1 (2)
<b>C19 – N6 – Cr1</b>	174.9 (2)	<b>Cr2 – O5 – C26 – C27</b>	- 1.6 (4)
<b>Cr2 – O5 – C26 – C25</b>	178.05 (17)	<b>Cr2 – O6 – C28 – C29</b>	171.71 (18)
<b>Cr2 – O6 – C28 – C27</b>	-7.4 (4)	<b>C26 – C27 – C28 – C29</b>	- 178.3 (3)

Symmetry code: (i)  $-x, -y, 0.5-z$ .

**Scheme S11.** Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)manganese(II) acetonitrile solvate  $[\text{Mn}(\text{TCP})_2 \cdot 4\text{CH}_3\text{CN}] \cdot 2\text{CH}_3\text{CN}$  (**15**)



**Table S16.** Selected bond lengths (Å) angles (°) and torsion angles (°) of **15**.

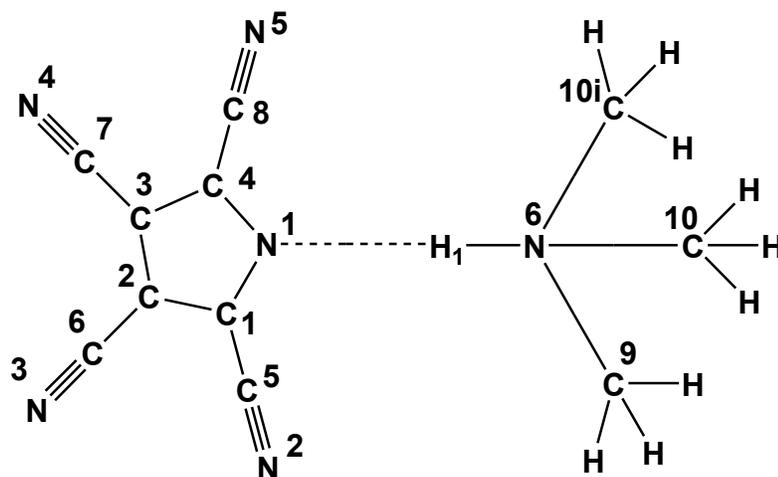
<b>Mn1—N7<sup>i</sup></b>	2.2249(8)	<b>C9—N6—Mn1</b>	174.48(7)
<b>Mn1—N7</b>	2.2250(8)	<b>C11—N7—Mn1</b>	161.51(7)
<b>Mn1—N6</b>	2.2299(8)	<b>N1—C1—C2</b>	111.68(7)
<b>Mn1—N6<sup>i</sup></b>	2.2300(8)	<b>N1—C1—C5</b>	123.94(7)
<b>Mn1—N1<sup>i</sup></b>	2.2600(7)	<b>C2—C1—C5</b>	124.37(7)

<b>Mn1—N1</b>	2.2600(7)	<b>C1—C2—C3</b>	105.78(7)
<b>N1—C1</b>	1.361(1)	<b>C1—C2—C6</b>	126.20(8)
<b>N1—C4</b>	1.3635(10)	<b>C3—C2—C6</b>	128.00(8)
<b>N2—C5</b>	1.1499(12)	<b>C4—C3—C2</b>	105.57(7)
<b>N3—C6</b>	1.1451(13)	<b>C4—C3—C7</b>	127.06(8)
<b>N4—C7</b>	1.1466(12)	<b>C2—C3—C7</b>	127.35(8)
<b>N5—C8</b>	1.1500(13)	<b>N1—C4—C3</b>	111.78(7)
<b>N6—C9</b>	1.1416(12)	<b>N1—C4—C8</b>	123.25(7)
<b>N7—C11</b>	1.1420(11)	<b>C3—C4—C8</b>	124.96(8)
<b>C1—C2</b>	1.3987(11)	<b>N2—C5—C1</b>	176.49(9)
<b>C1—C5</b>	1.4292(12)	<b>N3—C6—C2</b>	178.64(11)
<b>C2—C3</b>	1.4087(12)	<b>N4—C7—C3</b>	179.23(10)
<b>C2—C6</b>	1.4215(12)	<b>N5—C8—C4</b>	177.57(10)
<b>C3—C4</b>	1.3979(11)	<b>N6—C9—C10</b>	179.23(10)
<b>C3—C7</b>	1.4228(12)	<b>N7—C11—C12</b>	177.85(10)
<b>C4—C8</b>	1.4299(12)	<b>N8—C13—C14</b>	178.86(13)
<b>C9—C10</b>	1.4524(13)	<b>C4—N1—C1—C2</b>	-0.19(9)
<b>C11—C12</b>	1.4511(12)	<b>Mn1—N1—C1—C2</b>	177.39(5)
<b>N8—C13</b>	1.1359(15)	<b>C4—N1—C1—C5</b>	-179.45(8)
<b>C13—C14</b>	1.4526(16)	<b>Mn1—N1—C1—C5</b>	-1.87(12)
<b>N7<sup>i</sup>—Mn1—N7</b>	180.000	<b>N1—C1—C2—C3</b>	0.01(10)
<b>N7<sup>i</sup>—Mn1—N6</b>	90.32(3)	<b>C5—C1—C2—C3</b>	179.27(8)
<b>N7—Mn1—N6</b>	89.68(3)	<b>N1—C1—C2—C6</b>	-178.54(8)
<b>N7<sup>i</sup>—Mn1—N6<sup>i</sup></b>	89.68(3)	<b>C5—C1—C2—C6</b>	0.71(14)
<b>N7—Mn1—N6<sup>i</sup></b>	90.32(3)	<b>C1—C2—C3—C4</b>	0.17(9)
<b>N6—Mn1—N6<sup>i</sup></b>	180.000	<b>C6—C2—C3—C4</b>	178.69(9)
<b>N7<sup>i</sup>—Mn1—N1<sup>i</sup></b>	89.60(3)	<b>C1—C2—C3—C7</b>	-178.32(8)
<b>N7—Mn1—N1<sup>i</sup></b>	90.40(3)	<b>C6—C2—C3—C7</b>	0.20(15)
<b>N6—Mn1—N1<sup>i</sup></b>	90.59(3)	<b>C1—N1—C4—C3</b>	0.31(9)
<b>N6<sup>i</sup>—Mn1—N1<sup>i</sup></b>	89.41(3)	<b>Mn1—N1—C4—C3</b>	-177.26(5)
<b>N7<sup>i</sup>—Mn1—N1</b>	90.39(3)	<b>C1—N1—C4—C8</b>	-178.35(8)
<b>N7—Mn1—N1</b>	89.60(3)	<b>Mn1—N1—C4—C8</b>	4.09(12)
<b>N6—Mn1—N1</b>	89.41(3)	<b>C2—C3—C4—N1</b>	-0.3(1)
<b>N6<sup>i</sup>—Mn1—N1</b>	90.59(3)	<b>C7—C3—C4—N1</b>	178.19(8)
<b>N1<sup>i</sup>—Mn1—N1</b>	180.000	<b>C2—C3—C4—C8</b>	178.33(8)
<b>C1—N1—C4</b>	105.19(7)	<b>C7—C3—C4—C8</b>	-3.18(14)
<b>C1—N1—Mn1</b>	127.10(5)		
<b>C4—N1—Mn1</b>	127.66(6)		

Symmetry code: (i) 1-x, 1-y, 2-z.

**Scheme S12.** Numbering scheme of trimethylammoniumtetracyanopyrrolide

[Me<sub>3</sub>NH]TCP (16)



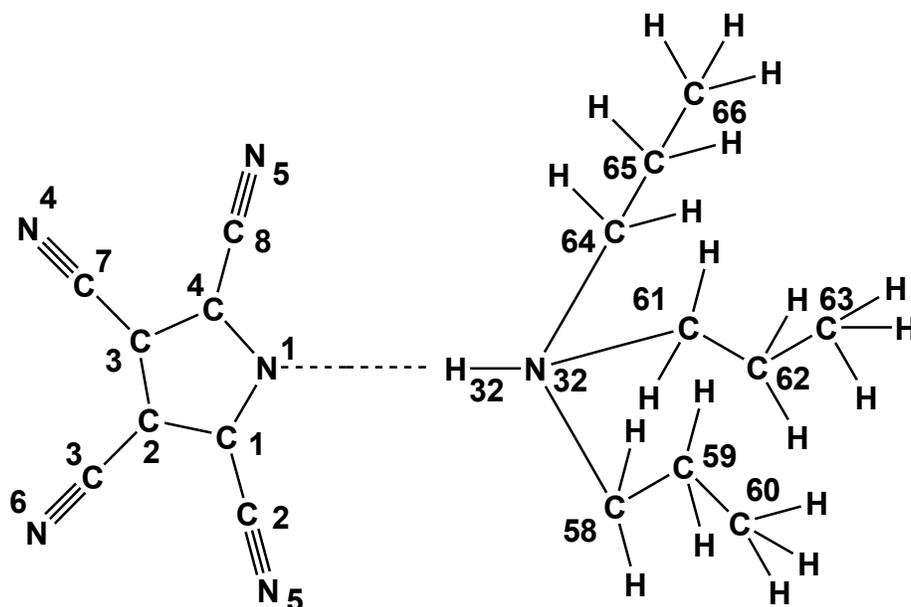
**Table S17.** Selected bond lengths (Å) angles (°) and torsion angles (°) of 16.

N1 – C1	1.3567 (15)	N1 – C1 – C5	122.25 (10)
N1 – C4	1.3574 (13)	C2 – C1 – C5	125.51 (11)
N2 – C5	1.1470 (16)	C1 – C2 – C3	105.19 (10)
N3 – C6	1.1485 (17)	C1 – C2 – C6	128.81 (10)
N4 – C7	1.1495 (14)	C3 – C2 – C6	125.99 (10)
N5 – C8	1.1488 (17)	C4 – C3 – C2	105.63 (9)
C1 – C2	1.3996 (15)	C4 – C3 – C7	127.93 (10)
C1 – C5	1.4299 (15)	C2 – C3 – C7	126.44 (10)
C2 – C3	1.4094 (15)	N1 – C4 – C3	111.93(10)
C2 – C6	1.4171 (17)	N1 – C4 – C8	123.37 (10)
C3 – C4	1.3995 (15)	C3 – C4 – C8	124.69 (9)
C3 – C7	1.4184 (15)	N2 – C5 – C1	178.32 (14)
C4 – C8	1.4305 (16)	N3 – C6 – C2	177.88 (12)
N6 – H1	<b>0.915 (18)</b>	N4 – C7 – C3	179.31 (13)
N1 – H1	<b>1.955(180)</b>	N5 – C8 – C4	175.51 (12)
N6 – C10 <sup>i</sup>	1.4876 (11)	C10 <sup>i</sup> – N6 – C10	111.17 (10)
N6 – C10	1.4877 (11)	C10 <sup>i</sup> – N6 – C9	111.46 (6)

<b>N6 – C9</b>	1.4879 (15)	<b>C10 – N6 – C9</b>	111.46 (6)
<b>C1– N1 – C4</b>	105.00 (9)	<b>C1 – C2 – C3 – C7</b>	180.000
<b>N1– C1 – C2</b>	112.24 (9)	<b>C6 – C2 – C3 – C7</b>	0.000
<b>C4 – N1 – C1 – C2</b>	0.000	<b>C1 – N1 – C4 – C3</b>	0.000
<b>C4 – N1 – C1 – C5</b>	180.000	<b>C1 – N1 – C4 – C8</b>	180.000
<b>N1 – C1 – C2 – C3</b>	0.000	<b>C2 – C3 – C4 – N1</b>	0.000
<b>C5 – C1 – C2 – C3</b>	180.000	<b>C7 – C3 – C4 – N1</b>	180.000
<b>N1 – C1 – C2 – C6</b>	180.000	<b>C2 – C3 – C4 – C8</b>	180.000
<b>C5 – C1 – C2 – C6</b>	0.000	<b>C7 – C3 – C4 – C8</b>	0.000
<b>C1 – C2 – C3 – C4</b>	0.000		
<b>C6 – C2 – C3 – C4</b>	180.000		

Symmetry code: (i)  $x, 0.5-y, z$ .

**Scheme S13.** Numbering scheme of tripropylammoniumtetracyanopyrrolide



**Table S18.** Selected bond lengths (Å) angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) of 17.

N1 – C4	1.349 (2)	N32 – C61 – C62	112.93 (14)
N1 – C1	1.353 (2)	C64 – C65 – C66	110.01 (17)
N2 – C5	1.147 (3)	N32 – C64 – C65	114.67 (14)
N3 – C6	1.149 (2)	C61 – C62 – C63	110.12 (17)
N4 – C7	1.141 (2)	C4 – N1 – C1 – C2	-0.1 (2)
N5 – C8	1.145 (2)	C4 – N1 – C1 – C5	177.74 (18)
C1 – C2	1.398 (2)	N1 – C1 – C2 – C3	0.5 (2)
C1 – C5	1.430 (3)	C5 – C1 – C2 – C3	-177.21 (18)
C2 – C3	1.409 (2)	N1 – C1 – C2 – C6	179.99 (18)
C2 – C6	1.418 (2)	C5 – C1 – C2 – C6	2.3 (3)
C3 – C4	1.397 (2)	C1 – C2 – C3 – C4	-0.70 (19)
C3 – C7	1.414 (3)	C6 – C2 – C3 – C4	179.82 (17)
C4 – C8	1.429 (2)	C1 – C2 – C3 – C7	179.49 (18)
N32 – H32	<b>1.0000 (13)</b>	C6 – C2 – C3 – C7	0.0 (3)
N1 – H32	<b>2.1005 (13)</b>	C1 – N1 – C4 – C3	-0.4 (2)

<b>N32 – C58</b>	1.501 (2)	<b>C1 – N1 – C4 – C8</b>	- 179.50 (16)
<b>N32 – C64</b>	1.505 (2)	<b>C2 – C3 – C4 – N1</b>	0.7 (2)
<b>N32 – C61</b>	1.507 (2)	<b>C7 – C3 – C4 – N1</b>	-179.48 (17)
<b>C58 – C59</b>	1.508 (3)	<b>C2 – C3 – C4 – C8</b>	179.79 (16)
<b>C59 – C60</b>	1.514 (3)	<b>C7 – C3 – C4 – C8</b>	- 0.4 (3)
<b>C61 – C62</b>	1.512 (3)	<b>C64– N32– C58– C59</b>	- 50.99 (19)
<b>C62 – C63</b>	1.516 (3)	<b>C61– N32– C58– C59</b>	- 178.34 (14)
<b>C64 – C65</b>	1.509 (3)	<b>N32– C58– C59– C60</b>	-169.92 (15)
<b>C65 – C66</b>	1.520 (3)	<b>C58– N32– C61– C62</b>	- 63.47 (18)
<b>C4 – N1 – C1</b>	104.27 (14)	<b>C64– N32– C61– C62</b>	168.14 (14)
<b>N1 – C1 – C2</b>	112.67 (15)	<b>N32– C61– C62– C63</b>	- 176.46 (15)
<b>N1 – C1 – C5</b>	121.72 (17)	<b>C58– N32– C64– C65</b>	- 59.4 (2)
<b>C2 – C1 – C5</b>	125.56 (16)	<b>C61– N32– C64– C65</b>	68.0 (2)
<b>C1 – C2 – C3</b>	105.11 (15)	<b>N32– C64– C65– C66</b>	- 177.15 (17)
<b>C1 – C2 – C6</b>	127.98 (16)		
<b>C3 – C2 – C6</b>	126.91 (16)		
<b>C4 – C3 – C2</b>	104.94 (15)		
<b>C4 – C3 – C7</b>	127.22 (16)		
<b>C2 – C3 – C7</b>	127.84 (16)		
<b>N1 – C4 – C3</b>	113.00 (15)		
<b>N1 – C4 – C8</b>	121.97 (16)		
<b>N2 – C5 – C1</b>	177.7 (2)		
<b>N3 – C6 – C2</b>	179.9 (2)		
<b>N4 – C7 – C4</b>	179.4 (2)		
<b>N5 – C8 – C4</b>	177.3 (2)		
<b>C58 – N32 – C64</b>	113.59 (13)		
<b>C58 – N32 – C61</b>	111.70 (13)		
<b>C64 – N32 – C61</b>	111.63 (13)		
<b>N32 – C58 – C59</b>	114.67 (14)		

## 5.4 List of figures

<b>Figure 1:</b> Schematic structure of the anion $[P_2C_{10}N_{10}]^{2-}$ .....	5
<b>Figure 2:</b> Crystal structure of [18]-crown-6- $K[P(CN)_2]$ with P-C-N $\cdots$ K $\cdots$ N-C-P -chains.....	6
<b>Figure 3:</b> Coordination environment at tricyanmelaminato-borane adduct anion in $Na_3[TCMeI \cdot 3B]$ .....	14
<b>Figure 4:</b> Selected examples of CN-functionalized imidazolium, pyridinium, piperidinium and pyrrolidinium cations.....	15
<b>Figure 5:</b> For ionic liquids suitable CN-functionalized anions: 4,5-dicyanotriazolate(a), tetracyanopyrrolide(b), dicyanamide(c), tricyanmethanide(d), tetracyanidoborate(e) and tricyanmelaminato (f).....	16
<b>Figure 6:</b> Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.....	18
<b>Figure 7:</b> Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.....	19
<b>Figure 8:</b> Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.....	19
<b>Figure 9:</b> Ball and stick representation of $[Et_3NH \cdot THF]^+ [B(Ph)_4]^-$ with the color code: dark Red – Boron, blue – Nitrogen, red – Oxygen, gray – Carbon, white – Hydrogen.....	27
<b>Figure 10:</b> Ball and stick representation of <b>5</b> with the color Code : pink – Phosphorus, blue – Nitrogen, gray – Carbon, white – Hydrogen.....	29
<b>Figure 11:</b> Ball and stick representation of <b>6</b> with the color code: green – Palladium, pink – Phosphorus, blue – Nitrogen, White – Carbon, gray – Hydrogen.....	32
<b>Figure 12:</b> Ball and stick representation of <b>7</b> with the color code: pale blue –Nickel, pink – Phosphorus, blue – Nitrogen, gray – Carbon, white – Hydrogen.....	34
<b>Figure 13:</b> Ball and stick representation of <b>8</b> with the color code: pale blue – Copper, blue – Nitrogen, red – Oxygen, gray – Carbon, white – Hydrogen.....	47
<b>Figure 14:</b> Ball and stick representation of <b>9</b> with the color code: pale blue – Zinc, blue – Nitrogen, gray – Carbon, white – Hydrogen.....	49
<b>Figure 15:</b> Ball and stick representation of <b>10</b> with the color code: green – Iron, blue – Nitrogen , gray – Carbon, white – Hydrogen.....	52

<b>Figure 16:</b> Ball and stick representation of <b>11</b> with the color code: dark gray –magnesium, blue – Nitrogen, gray – Carbon, white – Hydrogen.....	<b>54</b>
<b>Figure 17:</b> Ball and stick representation of <b>12</b> with the color code: pale blue – Copper, blue –Nitrogen, gray – Carbon, white – Hydrogen.....	<b>56</b>
<b>Figure 18:</b> Ball and stick representation of <b>13</b> with the color code: pale blue – Manganese, blue –Nitrogen, red – Oxygen, gray – Carbon, white – Hydrogen.....	<b>58</b>
<b>Figure 19:</b> Ball and stick representation of <b>14</b> with the color code: dark gray – Chromium, blue –Nitrogen, red – Oxygen, gray –carbon, white –Hydrogen.....	<b>60</b>
<b>Figure 20:</b> Ball and stick representation of <b>15</b> with the color code: gray – Manganese, blue –Nitrogen, gray – Carbon, white – Hydrogen.....	<b>62</b>
<b>Figure 21:</b> Ball and stick representation of <b>16</b> with the color code: blue –Nitrogen, gray – carbon, white – Hydrogen.....	<b>65</b>
<b>Figure 22:</b> Ball and stick representation, wherein the dashed red lines show interaction between the $\pi$ -electrons ( $\pi$ stacking) of various levels. Distances [ $\text{\AA}$ ] : a = 3.63, b = 3.58, c = 3.58 .....	<b>66</b>
<b>Figure 23:</b> Ball and stick representation of <b>17</b> with the color code: blue –Nitrogen, gray – carbon, white – Hydrogen.....	<b>68</b>
<b>Figure 24:</b> Ball and stick representation, wherein the dashed red lines show interaction between the $\pi$ -electrons ( $\pi$ stacking) of various levels. Distances [ $\text{\AA}$ ] : a = 3.65, b = 3.35, c = 3.61.....	<b>69</b>

## 5.5 List of schemes

<b>Scheme 1:</b>	Supposed formation of $P(CN)_3$ by H. Davy in 1816 and Cenedella 1835.....	2
<b>Scheme 2:</b>	Preparation of $P(CN)_3$ by Hübner and Wehrhane 1863/64.....	2
<b>Scheme 3:</b>	Formation of $PPh_3Br(CN)$ by Steinkopf and Buchheim 1921.....	3
<b>Scheme 4:</b>	Synthesis method of the first $P^V$ salt by Lange and Müller 1930.....	3
<b>Scheme 5:</b>	First cyanation with $TMSCN$ by Bither et al. 1958.....	3
<b>Scheme 6:</b>	Synthesis of the first $P^{III}$ - salts of Masaguer 1957.....	4
<b>Scheme 7:</b>	Synthesis of $P(CN)_3$ , starting from $PBr_3$ by Maier 1963.....	4
<b>Scheme 8:</b>	Adduct formation of $P(CN)_3$ with halides by Dillon 1981/82.....	4
<b>Scheme 9:</b>	In-situ formation and decay of $[P(CN)_4]^-$ .....	5
<b>Scheme 10:</b>	Formation of Dicyanophosphide anion.....	5
<b>Scheme 11:</b>	Reactions of $[P(CN)_2]^-$ with halogens and cyanogen halides.....	6
<b>Scheme 12:</b>	Synthesis of $[PCl_{6-n}(CN)_n]^-$ anion ( $n = 1-3$ ) by Dillon and Platt 1982/83.....	7
<b>Scheme 13:</b>	Cyanation investigation of Dillon et al. 1986/88 only three chlorine atoms are Substituted by CN; $R=Ph, CCl_3$ .....	7
<b>Scheme 14:</b>	Cyanation investigation of Dillon et al. 1986/88 all chlorine atoms are substituted by CN; $R= Me, Et$ .....	7
<b>Scheme 15:</b>	Preparation of $P(CN)_3$ , with $(MeO)Me_2SiCN$ .....	8
<b>Scheme 16:</b>	Synthesis of $[PF_{6-n}(CN)_n]^-$ anion ( $n = 1-4$ ) by Sievert and Bläsing 2014.....	8
<b>Scheme 17:</b>	Synthesis of $[BMIm][PCl_3(CN)_3]$ .....	9
<b>Scheme 18:</b>	Synthesis of $[BMIm][PF_3(CN)_3]$ .....	9
<b>Scheme 19:</b>	The most important halogen and pseudohalogen compounds compared.....	11
<b>Scheme 20:</b>	Thiacyanocarbons and tetracyanopyrrolides.....	12
<b>Scheme 21:</b>	Selected examples of tetraalkylphosphonium, tetraalkylammonium, tetraamino- phosphonium and triaminosulfonium cations.....	17
<b>Scheme 22:</b>	Synthesis of tricyanophosphine.....	19
<b>Scheme 23:</b>	General reaction of $P(CN)_3$ with $(WCA)^-$ .....	22
<b>Scheme 24:</b>	General reactions of $P(CN)_3$ with Lewis bases.....	24
<b>Scheme 25:</b>	Direct conversion of cyanide and carbon disulfide in DMF and subsequent oxidation by ammonium peroxodisulfate in water to dithiin.....	40

<b>Scheme 26 :</b> Scheme of reaction steps from dithiin to[Me <sub>4</sub> N]TCP.....	<b>41</b>
<b>Scheme 27:</b> Synthesis of silver tetracyanopyrrolide.....	<b>42</b>
<b>Scheme 28:</b> Ion exchange in which a [Me <sub>4</sub> N] <sup>+</sup> ion is exchanged to a H <sup>+</sup> ion.....	<b>43</b>
<b>Scheme 29:</b> Reaction of AgTCP with HCl in water for HTCP.....	<b>44</b>
<b>Scheme 30:</b> General representation for HTCP reactions.....	<b>45</b>
<b>Scheme 31:</b> Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran) copper(II).....	<b>46</b>
<b>Scheme 32:</b> Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate.....	<b>48</b>
<b>Scheme 33:</b> Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate.....	<b>50</b>
<b>Scheme 34:</b> Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II)acetonitrile solvate.....	<b>53</b>
<b>Scheme 35:</b> Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II)acetonitrile solvate. ....	<b>55</b>
<b>Scheme 36:</b> Synthesis of di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese (III).....	<b>57</b>
<b>Scheme 37:</b> Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolido chromium(III). ....	<b>59</b>
<b>Scheme 38:</b> Synthesis of trimethylammoniumtetracyanopyrrolide.....	<b>63</b>
<b>Scheme 39:</b> Synthesis of tripropylammoniumtetracyanopyrrolide.....	<b>66</b>
<b>Scheme S1.</b> Numbering scheme of tetracyanodiiminophosphorane [Ph <sub>3</sub> P=N- C(CN) <sub>2</sub> - C(CN) <sub>2</sub> - N=PPh <sub>3</sub> ] (5).....	<b>113</b>
<b>Scheme S2.</b> Numbering scheme of bis(triphenylphosphine) dicyanopalladium (II) [(Ph <sub>3</sub> P) <sub>2</sub> Pd(CN) <sub>2</sub> ] (6).....	<b>115</b>

<b>Scheme S3.</b> Numbering scheme of 1, 1, 1-tris[(diphenylphosphino)methyl]ethane dicyano nickel(II) tris [1,1,1-(Ph <sub>3</sub> ) <sub>2</sub> P-CH <sub>3</sub> ]CH <sub>3</sub> CH <sub>2</sub> •Ni(CN) <sub>2</sub> (7).....	<b>117</b>
<b>Scheme S4.</b> Numbering scheme of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran)copper(II) [Cu{NC <sub>4</sub> (CN) <sub>3</sub> C(O)NH <sub>2</sub> } <sub>2</sub> (THF) <sub>2</sub> ] (8).....	<b>119</b>
<b>Scheme S5.</b> Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate [Zn(TCP) <sub>2</sub> •4CH <sub>3</sub> CN]•2CH <sub>3</sub> CN (9) .....	<b>121</b>
<b>Scheme S6.</b> Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate [Fe(TCP) <sub>2</sub> •4CH <sub>3</sub> CN]•2CH <sub>3</sub> CN (10) .....	<b>123</b>
<b>Scheme S7.</b> Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II)acetonitrile solvate [Mg(TCP) <sub>2</sub> •4CH <sub>3</sub> CN]•2CH <sub>3</sub> CN (11) .....	<b>125</b>
<b>Scheme S8.</b> Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II)acetonitrile solvate [Cu(TCP) <sub>2</sub> •4CH <sub>3</sub> CN]•2CH <sub>3</sub> CN (12).....	<b>127</b>
<b>Scheme S9.</b> Numbering scheme of di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese (III) [Mn(acac) <sub>2</sub> TCP] (13) .....	<b>129</b>
<b>Scheme S10.</b> Numbering scheme of acetonitrile-di(acetylacetonate)tetracyanopyrrolido chromium(III) [Cr(acac) <sub>2</sub> TCP•CH <sub>3</sub> CN] (14).....	<b>132</b>
<b>Scheme S11.</b> Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)manganese(II) acetonitrile solvate [Mn(TCP) <sub>2</sub> •4CH <sub>3</sub> CN]•2CH <sub>3</sub> CN (15).....	<b>135</b>
<b>Scheme S12.</b> Numbering scheme of trimethylammoniumtetracyanopyrrolide [Me <sub>3</sub> NH]TCP (16).....	<b>137</b>
<b>Scheme S13.</b> Numbering scheme of tripropylammoniumtetracyanopyrrolide [ <sup>n</sup> Pr <sub>3</sub> NH]TCP (17).....	<b>139</b>

## 5.6 List of tables

<b>Table S1.</b>	Crystallographic details of <b>5, 6</b> and <b>7</b> .....	<b>108</b>
<b>Table S2.</b>	Crystallographic details of <b>8, 9</b> and <b>10</b> .....	<b>109</b>
<b>Table S3.</b>	Crystallographic details of <b>11, 12</b> and <b>13</b> .....	<b>110</b>
<b>Table S4.</b>	Crystallographic details of <b>14</b> and <b>15</b> .....	<b>111</b>
<b>Table S5.</b>	Crystallographic details of <b>16</b> and <b>17</b> .....	<b>112</b>
<b>Table S6.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>5</b> . .....	<b>113</b>
<b>Table S7.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>6</b> .....	<b>115</b>
<b>Table S8.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>7</b> . .....	<b>117</b>
<b>Table S9.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>8</b> .....	<b>119</b>
<b>Table S10.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>9</b> . .....	<b>121</b>
<b>Table S11.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>10</b> . .....	<b>123</b>
<b>Table S12.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>11</b> . .....	<b>126</b>
<b>Table S13.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>12</b> . .....	<b>127</b>
<b>Table S14.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>13</b> . .....	<b>130</b>
<b>Table S15.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>14</b> . .....	<b>132</b>
<b>Table S16.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>15</b> . .....	<b>135</b>
<b>Table S17.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>16</b> . .....	<b>137</b>
<b>Table S18.</b>	Selected bond lengths (Å) angles (°) and torsion angles (°) of <b>17</b> .....	<b>139</b>

## 6. References

- [1] H. Davy, *Annalen der Physik* **1816**, *54*, 383-385.
- [2] Cenedella, *Journal de Pharmacie* **1835**, *21*, 683-684.
- [3] H. Hübner, G. Wehrhane, *Liebigs Ann. Chem.* **1863**, *128*, 254-256.
- [4] H. Hübner, G. Wehrhane, *Liebigs Ann. Chem.* **1864**, *132*, 277-289.
- [5] W. Steinkopf, K. Buchheim, *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 1024-1035.
- [6] W. Lange, E. Müller, *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 1058-1070.
- [7] H. Gall, J. Schüppen, *Chem. Ber.* **1930**, *32*, 482-487.
- [8] K. B. Dillon, W. G. Platt, *Polyhedron* **1983**, *2*, 641-643.
- [9] T. Bither, W. Knoth, R. Lindsey, W. Sharkey, *J. Am. Chem. Soc.* **1958**, *80*, 4151-4153.
- [10] J. R. Masaguer, *Anales de la Real Sociedad Española de Física y Química* **1957**, *53*, 509-517.
- [11] L. Maier, *Helv. Chim. Acta* **1963**, *46*, 2667-2676.
- [12] K. Dillon, A. Platt, *J. Chem. Soc., Dalton Trans.* **1982**, 1199-1204.
- [13] C. E. Jones, K. J. Coskran, *Inorg. Chem.* **1971**, *10*, 1536-1537.
- [14] C. A. Wilkie, R. W. Parry, *Inorg. Chem.* **1980**, *19*, 1499-1502.
- [15] K. B. Dillon, A. W. G. Platt, T. C. Waddington, *Inorganic and Nuclear Chemistry Letters* **1981**, *17*, 201-205.
- [16] K. B. Dillon, W. G. Platt, A. Schmidpeter, F. Zwaschka, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **1982**, *488*, 7-26.
- [17] A. Schmidpeter, F. Zwaschka, W. S. Sheldrick, *Chem. Ber.* **1985**, *118*, 1078-1085.
- [18] (a) A. Schmidpeter, F. Zwaschka, *Angew. Chem.* **1977**, *89*, 747., (b) *Angew Chem. Int. Ed.* **1977**, *16*, 704-705.
- [19] A. Schmidpeter, F. Zwaschka, *Angew. Chem.* **1979**, *91*, 441-442.

- [20] A. Schmidpeter, G. Burget, F. Zwaschka, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **1985**, 527, 17-32.
- [21] K. B. Dillon, A. W. G. Platt, *J. Chem. Soc., Chem. Commun.* **1983**, 780, 1089-1090.
- [22] R. M. K. Deng, K. B. Dillon, *J. Chem. Soc., Dalton Trans.* **1986**, 1843-1847.
- [23] R. Ali, K. B. Dillon, *J. Chem. Soc., Dalton Trans.* **1988**, 2077-2081.
- [24] A. A. Krolevets, V. V. Antipova, I. V. Martynov, *Bulletin of the Academy of Science of the USSR, Division of chemical science* **1991**, 12, 2847-2850.
- [25] K. Bläsing, *Bachelor thesis*, University of Rostock, Germany, **2014**.
- [26] The Nippon Synthetic Chemical Industry Co. Ltd., *Patent EP2410601A1*, **2012**.
- [27] T. A. Bither, W. H. Knoth, R. V. Lindsey Jr., W. H. Sharkey, *J. Am. Chem. Soc.* **1958**, 80, 4151-4153.
- [28] K. Emerson, D. Britton, *Acta Cryst.* **1963**, 16, 113-119.
- [29] O. W. Webster, *J. Polymer Sci.* **2002**, 40, 210-221.
- [30] P. Johansson, H. Nilsson, P. Jacobsson, M. Armand, *Phys. Chem. Phys.* **2004**, 6, 895-899.
- [31] J. Rimarcik, V. Lukes, E. Klein, M. Griesser, A. -M. Kelterer, *Chem. Phys.* **2008**, 353, 177-184.
- [32] R. J. Less, M. McPartlin, J. M. Rawson, P. T. Wood, D. S. Wright, *Chem. Eur. J.* **2010**, 16, 13723-13728.
- [33] R. J. Less, T. C. Wilson, M. McPartlin, P. T. Wood, D. S. Wright, *Chem. Commun.* **2011**, 47, 10007-10009.
- [34] R. J. Less, B. Guan, N. M. Muresan, M. McPartlin, E. Reisner, T. C. Wilson, D. S. Wright, *Dalton. Trans.* **2012**, 41, 5919-5924.
- [35] R. J. Less, T. C. Wilson, B. Guan, M. McPartlin, A. Steiner, P. T. Wood, D. S. Wright, *Eur. J. Inorg. Chem.* **2013**, 7, 1161-1169.

- [36] M. Becker, J. Harloff, T. Jantz, A. Schulz, A. Villinger, *Eur. J. Inorg. Chem.* **2012**, *34*, 5658-5667.
- [37] B. Szafranowska, J. Beck, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1960-1964.
- [38] B. Szafranowska, C. Landvogt, J. Beck, *Z. Anorg. Allg. Chem.* **2015**, *641*, 176-179.
- [39] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, **1984**, 336.
- [40] M. Kaftory, In *The Chemistry of Halides, Pseudohalides and Azides*, Suppl.D. Part 2, Patai, S. Rappoport, Z. Eds., Wiley, New York, **1983**, Chapter 24, 1229-1264.
- [41] L. Birkenbach, K. Kellermann, *Ber. Dtsch. Chem. Ges.* **1925**, *58B*, 786-794.
- [42] A. W. Browne, A. B. Hoel, *J. Am. Chem. Soc.* **1922**, *44*, 2106-2116.
- [43] E. Lieber, E. Offentdahl, C. N. R. Rao, *J. Org. Chem.* **1957**, *22*, 1750-1751.
- [44] F. Sommer, *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 1833-1841.
- [45] W. Madelung, E. Kern, *Liebigs Ann. Chem.* **1922**, *427*, 1-26.
- [46] a) H. Schmidtmann, *Ber.* **1896**, *29*, 1168-1175; b) E. Cox, A. Fontaine, *Bull. Soc. Chim.Fr.* **1954**, 948-950; c) W. J. Middleton, V. A. Engelhardt, *J. Am. Chem. Soc.* **1958**, *80*, 2788-2795; d) W. J. Middleton, E. L. Little, D. D. Coffman, V. A. Engelhardt, *J. Am. Chem. Soc.* **1958**, *80*, 2795-2806; e) S. Trofimenko, E. Little, H. Mower, *J. Org. Chem.* **1962**, *27*, 433-438.
- [47] A. M. Golub, H. Köhler, *Chemie der Pseudohalogenide*, VEB Deutscher Verlag der Wissenschaften, Berlin, **1979**.
- [48] a) A. Schulz, Habilitationsschrift, LMU München, **2001**; b) A. M. Golub, H. Köhler, V. V. Stopenko, *Chemistry of Pseudohalides*, Elsevier, Amsterdam, **1986**.
- [49] W. Beck, *Organomet. Chem.*, Reviews A, **1971**, *7*, 159-190.
- [50] Holleman Wiberg, *Lehrbuch der Anorganischen Chemie*, 102. Aufl., Walter de Gruyter, Berlin, **2007**, 684-685.
- [51] G. Bähr, G. Schleitzer, *Chem. Ber.* **1955**, *88*, 1771-1777.
- [52] D. C. Blomstrom, S. W. Channing, Du Pont, US3008967 A, **1961**.
- [53] H. E. Simmons, Du Pont de Nemours & Co. patent, US3221024 A, **1962**.

- [54] H. E. Simmons, R. D. Vest, S. A. Vladuchick, O. W. Webster, *J. Org. Chem.* **1980**, *45*, 5113-5121.
- [55] a) H. E. Simmons, D. C. Blomstrom, R. D. Vest, J. R. Roland, T. L. Cairns, *J. Am. Chem. Soc.* **1962**, *84*, 4746-4756; b) H. E. Simmons, D. C. Blomstrom, R. D. Vest, *J. Am. Chem. Soc.* **1962**, *84*, 4756-4771; c) H. E. Simmons, D. C. Blomstrom, R. D. Vest, *J. Am. Chem. Soc.* **1962**, *84*, 4772-4781; d) H. E. Simmons, D. C. Blomstrom, R. D. Vest, *J. Am. Chem. Soc.* **1962**, *84*, 4782-4789.
- [56] I. Heldt, U. Behrens, *Z. Anorg. Allg. Chem.* **2005**, *631*, 749-758.
- [57] a) I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116-2142 and cited literature; b) *Int. Ed.* **2004**, *43*, 2066-2090.
- [58] a) J. Dupont, J. Spencer, *Angew. Chem.* **2004**, *116*, 5408-5409; b) *Int. Ed.* **2004**, *43*, 5296-5297.
- [59] K. Binnemans, *Chem. Rev.* **2005**, *205*, 4148-4204.
- [60] P. Wasserscheid, *Chemie in unserer Zeit* **2003**, *37*, 52-63.
- [61] J. H. Davis, Jr., P. A. Fox, *Chem. Commun.* **2003**, 1209-1212.
- [62] K. E. Bernhardt, G. Henkel, H. Willner, *Z. Anorg. Allg. Chem.* **2000**, *626*, 560-568.
- [63] (a) H. W. Roseky, *Angew. Chem.* **1967**, *79*, 316; (b) *Angew. Chem. Int. Ed.* **1967**, *6*, 363.
- [64] K. Voss, M. Becker, A. Villinger, V. N. Emelyanenko, R. Hellmann, B. Kirchner, F. Uhlig, S. P. Verevkin, A. Schulz, *Chem. Eur. J.* **2011**, *17*, 13526-13537.
- [65] J. S. Wilkes, *Green Chemistry* **2002**, *4*, 73-80.
- [66] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974-4975.
- [67] D. Zhao, M. Wu, Y. Kou, E. Min, *Catal. Today* **2002**, *74*, 157-189.
- [68] a) M. E. Van Valkenburg, R. L. Vaughn, M. Williams, J. S. Wilkes, *Thermochim. Acta* **2005**, *425*, 181-188; b) M. Zhang, R. G. Reddy, *ECS Trans.* **2007**, *2*, 27-34.
- [69] N. Madriaa, T. A. Arunkumar, N. G. Nair, A. Vadapalli, Y.-W. Huangc, S. C. Jones, V. P. Reddy, *J. Power Sources* **2013**, *234*, 277-284.
- [70] P. Walden, *Bull. Acad. Sci. St. Petersburg* **1914**, 405-422.

- [71] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc. Commun.* **1992**, 965-967.
- [72] H. Bönemann, R. Brinkmann, S. Kinge, T. O. Ely, M. Armand, *Fuell Cells* **2004**, *4*, 289-296.
- [73] D. R. MacFarlane, S. A. Forsyth, J. Golding, G. B. Deacon, *Green Chemistry* **2002**, *4*, 444-448.
- [74] C. Täschler, C. Zur Täschler, A. Breuer, F. Previdoli, *WO 2006/021390 A1* **2006**.
- [75] U. Welz-Biermann, N. Ignatjev, E. Bernhardt, M. Finze, H. Willner, *German Pat. DE 10306617/A1* **2004**.
- [76] a) A. W. Hofmann, *Chem. Ber.* **1871**, *4*, 205-209; b) A. Cahours, A. W. Hofmann, *Liebigs Ann. Chem.* **1857**, *104*, 1-39; c) A. W. Hofmann, *Liebigs Ann. Chem.* **1861**, *Suppl. 1*, 26-36.
- [77] S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh, J. Reedijk, *Pure Appl. Chem.* **2013**, *85*, 1715-1724.
- [78] a) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E. B. Lobkovsky, *Adv. Mater.* **2007**, *19*, 1693-1696; b) S. M. Holmes, G. S. Girolami, *J. Am. Chem. Soc.* **1999**, *121*, 5593-5594; c) V. Niel, J. M. Martinez-Agudo, M. C. Muñoz, A. B. Gaspar, J. A. Real, *Inorg. Chem.* **2001**, *40*, 3838-3839; d) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388-2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334-2375.
- [79] M. D. Dembo, L. E. Dunaway, J. S. Jones, E. A. Lepekhina, S. M. McCullough, J. L. Mig, X. Li, F. Baril-Robert, H. H. Patterson, C. A. Bayse, R. D. Pike, *Inorg. Chim. Acta* **2010**, *364*, 102-114.
- [80] a) Y. Sato, S. Ohkoshi, K. Arai, M. Tozawa, K. Hashimoto, *J. Am. Chem. Soc.* **2003**, *125*, 14590-14595; b) S. Ohkoshi, K. Arai, Y. Sato, K. Hashimoto, *Nat. Mater.* **2004**, *3*, 857-861; c) B. Nowicka, M. Rams, K. Stadnicka, B. Sieklucka, *Inorg. Chem.* **2007**, *46*, 8123-8125.
- [81] a) S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray, R. Robson, *Chem. Commun.* **1998**, 439-440; b) P. Jensen, S. R. Batten, G. D. Fallon, B. Moubaraki, K. S. Murray, D. J. Price, *Chem. Commun.* **1999**, 177-178; c) S. R. Marshall, C. D. Incarvito, J. L. Manson, A. L. Rheingold, J. S. Miller, *Inorg. Chem.* **2000**, *39*, 1969-1973; d) Z.-M. Wang, B.-W. Sun, J. Luo, S. Gao, C.-S. Liao, C.-H. Yan, Y. Li, *Inorg. Chim. Acta* **2002**, *332*, 127-134.

- [82] a) S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray, R. Robson, *J. Chem. Soc., Dalton Trans.* **1999**, 2977-2986; b) P. Jensen, D. J. Price, S. R. Batten, B. Moubaraki, K. S. Murray, *Chem. Eur. J.* **2000**, *6*, 3186-3195.
- [83] T. Jantz, *Diploma thesis*, University of Rostock, Germany, **2012**.
- [84] J. Goubeau, H. Haeberle, H. Ulmer, *Z. Anorg. Allg. Chem.* **1961**, *311*, 110-116.
- [85] J. O. Jensen, *Spectrochim. Acta Part A* **2004**, *60*, 2537-2540.
- [86] B. W. Tattershall, *Polyhedron* **1990**, *9*, 553-555.
- [87] P. G. Kirk, T. D. Smith, *J. Inorg. Nucl. Chem.* **1968**, *30*, 892-893.
- [88] K. Emerson, D. Britton, *Acta Cryst.* **1964**, *17*, 1134-1139.
- [89] M. A. H. A. Al-Juboori, A. Finch, P. J. Gardner, C. J. Groombridge, *Polyhedron* **1991**, *10*, 1831-1833.
- [90] Reviews: (a) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 133-139; (b) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927-942.
- [91] F. Reiss, A. Schulz, A. Villinger, *Eur. J. Inorg. Chem.* **2012**, *2*, 261-271.
- [92] G. A. Bowmaker, B. J. Kennedy, J. C. Reid, *Inorg. Chem.* **1998**, *37*, 3968-3974.
- [93] A. Veldkamp, G. Frenking, *Organometallics* **1993**, *12*, 4613-4622.
- [94] Q. Wang, G. Guo, T. C. W. Mak, *Polyhedron* **2003**, *22*, 217-223.
- [95] C. Hering, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2012**, *51*, 6241-6245.
- [96] P. G. Kirk and T. D. Smith, *J. Inorg. Nucl. Chem.* **1968**, *30*, 892-893.
- [97] K. Emerson, D. Britton, *Acta Crystallogr.* **1964**, *17*, 1134-1139.
- [98] (a) T. P. Onak, H. Landesman, R. E. Williams, I. Shapiro, *J. Phys. Chem.* **1959**, *63*, 1533-1535; (b) B. M. Graybill, J. K. Ruff, *J. Am. Chem. Soc.* **1962**, *84*, 1062-1063.
- [99] N. A. Barnes, S. M. Godfrey, R. T. A. Halton, L. Suzanna, R. G. Pritchard, *Angew. Chem. Int. Ed.* **2006**, *45*, 1272-1275.
- [100] P. J. Butterfield, J. C. Tebby, T. J. King, *J. Chem. Soc. Perkin Trans.* **1978**, *1*, 1237-1243.
- [101] C. S. Hauser, C. Slugove, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissenteiner *J. Chem. Soc. Dalton Trans* **2001**, 2989-2995.

- [102] (a) A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 1315-1316. (b) B. C. G. Söderberg, *Coord. Chem. Rev.* **2003**, *241*, 147-247.
- [103] B. I. Swanson, *Inorg. Chem.* **1976**, *15*, 253-259.
- [104] D. Kremzow, G. Seidel, C.W. Lehmann, A. Fürstner, *Chem. Eur. J.* **2005**, *11*, 1833-1853.
- [105] R. Das, C. G. Daniliuc, F. E. Hahn, *Angew. Chem. Int. Ed.* **2014**, *53*, 1163-1166.
- [106] R. Rupp, G. Huttner, P. Kircher, R. Soltek, M. Buechner, *Eur. J. Inorg. Chem.* **2000**, 1745-1757.
- [107] S. Trofimenko, J. C. Calabrese, J. S. Thompson, *Inorg. Chem.* **1987**, *26*, 1507-1514.
- [108] C. Fu, H. Zhou, H. Wu, J. Chen, Y. Kuang, *Colloid. Polymer Sci.* **2008**, *286*, 1499-1504.
- [109] M. Galinski, A. Lewandowski, I. Stepniak, *Electrochimica Acta*, **2006**, *51*, 5567-5580.
- [110] E. Amigues, C. Hardacre, G. Keane, M. Migaud, M. O'Neill, *Chem. Commun.* **2006**, 72-74.
- [111] A. Bernsdorf, H. Brand, R. Hellmann, M. Köckerling, A. Schulz, A. Villinger, K. Voss, *J. Am. Chem. Soc.* **2009**, *131*, 8958-8970.
- [112] W. Sacher, A. Schmidpeter, W. Beck, *Z. Anorg. Allg. Chem.* **2015**, *641*, 762-764.
- [113] M. Becker, *Ph.D thesis*, University of Rostock, Germany, **2012**.
- [114] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*. **2010**, *29*, 2176-2179.
- [115] Beyer-Walter, *Lehrbuch der organischen Chemie. 19. Auflage* **1981**, 668.
- [116] X. Ma, Y. He, Y. Hu, M. Lu, *Tetrahedron Lett.* **2012**, *53*, 449-452.
- [117] J. K. Bjernemose, C. J. Mckenzie, P. Raithby, S. J. Teat, *Dalton Trans.* **2003**, 2639-2640.
- [118] N. Kuhn, M. Köckerling, S. Stubenrauch, D. Bläser, R. Boese, *J. Chem. Soc. Chem. Commun.* **1991**, 1368-1370.
- [119] N. Kuhn, G. Henkel, J. Kreutzberg, S. Stubenrauch, C. Janiak, *J. Organomet. Chem.* **1993**, *456*, 97-106.
- [120] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770-12779.
- [121] M. G. B. Drew, P. P. K. Claire, G. R. Willey, *J. Chem. Soc. Dalton Trans.* **1988**, 215-218.

- [122] P. D'Angelo, V. Migliorati, *J. Phys. Chem.* **2015**, *119*, 4061-4067.
- [123] J. A. Bertrand, C. E. Kirkwood, *Inorg. Chim. Acta.* **1972**, *6*, 248-252.
- [124] S. Brooker, B. M. Carter, *Acta Cryst.* **1995**, *C51*, 1522-1524.
- [125] K. Ha, *Acta Cryst.* **2011**, *E67*, m656-m657.
- [126] T. Senapati, C. Pichon, R. Ababei, C. Mathonière, R. Clérac, *Inorg. Chem.* **2012**, *51*, 3796-3812.
- [127] G. Swarnabala, K. R. Reddy, J. Tirunagar, M. V. Rajasekharan, *Transition Met. Chem.* **1994**, *19*, 506-508.
- [128] N. H. Andersen, A. Dossing, A. Molgaard, *Inorg. Chem.* **2003**, *42*, 6050-6055.
- [129] Y. Harada, G. S. Girolami, *Polyhedron*, **2007**, *26*, 1758-1762.
- [130] P. J. Riedel, N. Aruisamy, M. P. Mehn, *Inorg. Chem. Comm.* **2011**, *14*, 734-737.
- [131] S. Suzuki, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui, K. Nakasuji, *Inorg. Chem.* **2005**, *44*, 8197-8199.
- [132] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629-1658.
- [133] K. Schwetlick, H. Becker, G. Domschke, E. Fanghänel, M. Fischer, K. Gewalt, R. Mayer, D. Pavel, H. Schmidt, *Organikum-Organisch-chemisches Grundpraktikum*, Johann Ambrosius Barth Verlag, **1996**.
- [134] C. B. Fischer, S. Xu, H. Zipse, *Chem. Eur. J.* **2006**, *12*, 5779-5784.
- [135] G. Brauer, *Lehrbuch der präparativen anorganischen Chemie* **1978**, 3rd. 548.
- [136] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490-502.
- [137] E. J. Sekabunga, M. L. Smith, T. R. Webb, W. E. Hill, *Inorg. Chem.* **2002**, *41*, 1205-1214.
- [138] A. G. Massey, A. J. Park, *J. Organometal. Chem.*, **1964**, *2*, 245-250.
- [139] E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skolvin, B. C. Smith, *J. Chem. Soc.* **1965**, *541*, 2997-2999.
- [140] M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans.* **1974**, 233-241.
- [141] J. R. Malpass, D. A. Hemmings, A. L. Wallis, S. R. Fletcher, S. Patel, *J. Chem. Soc. Perkin Trans.* **2001**, *1*, 1044-1050.
- [142] C. Mealli, *Acta. Crystal.* **1982**, *B38*, 1040-1043.
- [143] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.
- [144] (a) K.-B. Shiu, L.-Y. Lee, *J. Organomet. Chem.* **1988**, *348*, 357-360., (b) K.-B. Shiu, M. D. Curtis, J. C. Huffman, *Organometallics* **1983**, *2*, 936-938.

- [145] G. J. Kubas, L. S. V. D. Sluys, R. A. Doyle, R. J. Angelici, *Inorganic Syntheses: Reagents for Transition Metal Complex and Organometallic Syntheses*, **1990**, 28, 29-33.
- [146] T. M. G. Carneiro, J. Dupont, M. L. D. Matt, *Quimica Nova*. **1988**, 11, 215-217.
- [147] G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahlenberg, H. Kopacka, T. Röder, H. Sixta, *Lenzinger Berichte*, **2005**, 84, 71-85.
- [148] M. M. Jones, *J. Am. Chem. Soc.* **1959**, 81, 3188-3189.
- [149] R. G. Charles, B. E. Bryant, *Inorg. Synth.* **2007**, 7, 183-184.
- [150] W. C. Fernelius, J. E. Blanch, B. E. Bryant, K. Terada, R. S. Drago, *Inorg. Synth.* **1958**, 5, 130-131.
- [151] M. Gerin, J. Fresco, *Analytica Chimica Acta*. **1978**, 97, 165-176.
- [152] G. M. Sheldrick: SHELXS-97: *Program for the Solution of Crystal Structure*, University of Göttingen, Germany **1997**.
- [153] G. M. Sheldrick: SHELXL-97: *Program for the Refinement of Crystal Structures* University of Göttingen, Germany **1997**.
- [154] G. M. Sheldrick: *SADABS*. Version 2. University of Göttingen, Germany **2004**.

# Curriculum vitae

## **Personal Data:**

*Full name:* Omar Mowafaq Younis AL-Ramadhani

*Gender:* Male

*Date of birth:* 03 August 1976

*Place of birth:* Mosul, Iraq

*Nationality:* Iraqi

*Family status:* Married

*Languages:* Arabic (native)

English (professional proficiency)

German (working proficiency)

*Email:* [omar.younis2@uni-rostock.de](mailto:omar.younis2@uni-rostock.de)

[omar76a@yahoo.com](mailto:omar76a@yahoo.com)

## **Education:**

1991 – 1994: AL-Garbia secondary school, Mosul, Iraq

1994 – 1998: B.Sc., General Chemistry, University of Mosul, College of Science

Department of Chemistry, Iraq

1998 – 2000: M.Sc., Inorganic Chemistry, University of Mosul, College of Science

Department of Chemistry, Iraq

2012 – : Beginning of doctoral studies, University of Rostock , Institute of Chemistry

Department of Inorganic Chemistry, Germany

***Major Research:*** Synthesis and characterization of new CN-based transition metal complexes

### **Scholarships awarded:**

1. Scholarship Awarded by DAAD as doctoral researcher for the year 2011 to 2012 at Friedrich-Schiller-University Jena, Germany.
2. Scholarship Awarded by DAAD as doctoral researcher for the year 2012 to 2015 at University of Rostock, Germany.

### **Employment Record:**

2001 – 2006: Assist. Lecturer of Inorganic Chemistry

2007 – present: Lecturer of Inorganic Chemistry, University of Mosul, College of Science  
Department of Chemistry, Iraq

### **Teaching Tasks:**

- Practical Inorganic Chemistry (*Synthesis of Inorganic Compounds, including techniques and characterization*). Laboratories 2<sup>nd</sup> grade, University of Mosul, College of Science, Department of Chemistry, Iraq
- Practical Inorganic Chemistry (*Coordination Chemistry, Preparation and characterization of Coordination Compounds*). Laboratories 3<sup>rd</sup> grade, University of Mosul, College of Science, Department of Chemistry, Iraq

### **Publications:**

1. Synthesis and Characterization of Dinuclear Metal Complexes Stabilized by Tetradentate Schiff Base Ligands, Eid A. Abdalrazaq, Omar M. AL-Ramadane, Khansa S. AL-Numa, *American Journal of Applied Sciences* **2010**, 7, 628-633.
2. Some new Schiff Base Complexes of Benzion and Amino Pyridine, Tamather H. Mahmood, Khansa S. AL-Numa, Omar M. AL-Ramadane, *Int. J. Chem.* **2010**, 20, 61-65.

3. Synthesis and Characterization of Some Mixed Ligands Complexes from *o*- Phthalic acid as Primary Ligand, Eid A. Abdalrazaq, Omar M. AL-Ramadane, Khansa S. AL-Numa, *Int. J. Chem.* **2008**, *18*, 89-95.
4. Synthesis and Characterization of Organosilicon(IV) Complexes with some Schiff Base Derivatives, Eid A. Abdalrazaq, Omar M. AL-Ramadany, Manal A. AL-Shama'a, Talal A. K. AL-Allaf, *Int. J. Chem. Sci.* **2005**, *3*, 253-262.
5. Synthesis, Characterization and Properties of Heterobimetallic Complexes of Zinc(II) Dithiocarbamate Derivatives with Cobalt, Nickel and Copper Metal Ions, Ihsan A. Mustafa, Omar M. AL-Ramadany, Talal A. K. AL-Allaf, *Asian J. Chem.* **2001**, *13*, 745-751.

### **Research Interests:**

- Organometallic Chemistry
- Bioinorganic Chemistry
- Coordination Chemistry

Rostock, 21 April 2016

**Omar Mowafaq Younis**