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Traditio et Innovatio

Komplexe früher und später Übergangsmetalle mit
kooperativen Liganden:
Synthese, Charakterisierung und Einsatz für die
Dehydrokupplung von Amin-Boran-Addukten

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vorgelegt von Mirko Benjamin Rippke, geboren am 17.02.1997 in Gießen
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1. Gutachter: Prof. Dr. Torsten Beweries, Leibniz-Institut für Katalyse e. V.
2. Gutachter: Prof. Dr. Holger Helten, Julius-Maximilians-Universität Würzburg

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Rostock, 16.07.2025

Mirko Benjamin Rippke

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Zusammenfassung

Die Dehydropolymerisation von Amin-Boran-Addukten wird häufig mit Übergangsmetall-Komplexen durchgeführt. Es wurde gezeigt, dass sowohl Komplexe früher als auch später Übergangsmetalle dazu in der Lage sind diese Reaktion zu katalysieren. In der vorliegenden Arbeit wurden Metall-Komplexe beider Gruppen untersucht. Bei den späten Übergangsmetallen liegt der Fokus vor allem auf Komplexen mit kooperativen PNN-Pincer-Liganden mit einer NH-Funktionalität. Dazu wurden zwei literaturbekannte Liganden ausgewählt und daraus Komplexe des Rhodiums, Iridiums und Rutheniums hergestellt. Diese neuen Komplexe wurden umfassend charakterisiert und ihre katalytische Aktivität in der Dehydrokupplung von Amin-Boranen über volumetrische Messungen bestimmt. Alle hergestellten Präkatalysatoren sind in der Lage $\text{H}_3\text{B}\cdot\text{NMeH}_2$ und $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ umzusetzen, jedoch mit sehr unterschiedlichen Reaktionsgeschwindigkeiten. Des Weiteren konnte gezeigt werden, dass die Verwendung von $\text{KO}t\text{Bu}$ als Additiv zu einer deutlich höheren Aktivität führt. Bei den Komplexen früher Übergangsmetalle wurden dinukleare Alkynyl-verbrückte Zirkonium-Komplexe hergestellt und für die Aktivierung kleiner Moleküle eingesetzt. Dieser formal gemischt-valente Präkatalysator bildet mit dem Substrat sowie mit Wasserstoff hochsensible di- und trinukleare Zirkonocenhydride, welche umfassend charakterisiert wurden.

Summary

The dehydropolymerization of amine borane adducts is often carried out with transition metal complexes. It has been shown that both early and late transition metal complexes can catalyse this reaction. In the present work, metal complexes of both groups were investigated. In the case of late transition metals, the focus is primarily on cooperative PNN pincer ligands with NH functionalities. For this purpose, two ligands known from literature were selected and rhodium, iridium and ruthenium complexes were prepared. These new complexes were characterised, and their catalytic activity was determined by measuring gas evolution curves.

All prepared precatalysts can convert $\text{H}_3\text{B}\cdot\text{NMeH}_2$ and $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$, but with very different reaction rates. Furthermore, it could be shown that the use of KO^tBu as an additive leads to a significantly higher activity. In the case of early transition metal complexes, dinuclear alkynyl-bridged zirconium complexes were prepared and used for the activation of small molecules. This formally mixed valent precatalyst forms highly sensitive di- and trinuclear zirconocene hydrides with the substrate as well as with hydrogen, which were characterised in detail.

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Abkürzungsverzeichnis

Äq.	Äquivalent(e)	<i>i</i> Pr	<i>iso</i> -Propyl
β	beta	κ	kappa
[BAr ^F ₄] [−]	tetrakis[3,5-bis(trifluormethyl)phenyl]borat	<i>m</i>	meta
<i>bite angle</i>	engl. Bisswinkel	MAO	Methylaluminoxan
Bn	benzyl	Me	Methyl
cod	1,5-Cyclooctadien	1,7-Me ₂ -(TACD)H ₂	1,7-Dimethyl-1,4,7,10-tetra-azacyclododecan
COE	Cycloocten	μ	my, verbrückend (in Formeln)
Cp	1,3-Cyclopentadien	nbd	Norbornadien
Cp*	Pentamethylcyclopentadien	NMR	<i>nuclear magnetic resonance</i> (Kernresonanz)
Cy	cyclohexyl	<i>n</i> Bu	<i>n</i> -Butyl
δ	delta	<i>n</i> Pr	<i>n</i> -Propyl
DFT	Dichtefunktionaltheorie	<i>o</i>	ortho
DPEphos	(Oxydi-2,1-phenylen) bis (diphenylphosphin)	<i>p</i>	para
Dppb	1,4-Bis(diphenylamino)butan	Ph	Phenyl
Dppp	1,3-Bis(diphenylphosphino)propan	PNN(H)	2-[5(3)-(tert-Butyl)-1H-pyrazol-3(5)-yl]-6-[(di-tert-butyl-phosphanyl)methyl]pyridine
EA	Elementaranalyse	PN(H)N	2-(di-R-phosphino)-N-((1-methyl-1H-imidazol-2-yl)methyl)ethylamine
EPR	Elektronenspinresonanz	PN(H)P	Bis[(2-diisopropylphosphino)-ethyl]amin
ESI-MS	Elektrosprayionisation-Massenspektroskopie	POCOP	η^3 -1,3-(OP <i>t</i> Bu ₂) ₂ C ₆ H ₃
η	eta	RT	Raumtemperatur
<i>et al.</i>	<i>et alii/aliae</i> (und andere)	σ	sigma
<i>in situ</i>	lateinisch: am Ort		
<i>i</i> Bu	<i>iso</i> -Butyl		
<i>inner</i>	engl. innere Sphäre		
<i>sphere</i>			

<i>single site</i>	engl. einzelne Seite	UV/Vis	ultraviolett und sichtbares Licht
<i>t</i> Bu	<i>tert</i> -Butyl	WAXS	<i>wide-angle X-ray scattering</i>
TMSCl	Trimethylsilylchlorid	Xantphos	4,5-Bis-(diphenylphosphino)-
TOF	turn over frequency (Wechselzahl)		9,9-dimethylxanthen
THF	Tetrahydrofuran		

Maßeinheiten

In dieser Arbeit werden die im Internationalen Einheitensystem (SI) gültigen Maßeinheiten verwendet. Alle davon abweichenden Einheiten und deren Umrechnung in SI-Einheiten sind im Folgenden aufgeführt:

Größe	Einheit	Bezeichnung	Umrechnung in SI-Einheiten
Frequenz	MHz	Megahertz	$1 \text{ MHz} = 1 \times 10^6 \text{ s}^{-1}$
	Hz	Hertz	$1 \text{ Hz} = 1 \text{ s}^{-1}$
Länge	Å	Ångström	$1 \text{ Å} = 1 \times 10^{-10} \text{ m}$
Temperatur	°C	Grad Celsius	$\vartheta/^{\circ}\text{C} = T/\text{K} - 273.15$
Volumen	mL	Milliliter	$1 \text{ mL} = 1 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$
Wärmemenge	kJ	Kilojoule	$1 \text{ kJ} = 1 \times 10^3 \text{ m}^2 \text{ kg s}^{-2}$
Wellenzahl	cm^{-1}	reziproke Zentimeter	$1 \text{ cm}^{-1} = 100 \text{ m}^{-1}$
Zeit	h	Stunde	$1 \text{ h} = 3.6 \times 10^3 \text{ s}$
	min	Minute	$1 \text{ min} = 60 \text{ s}$

1 Zielsetzung und Motivation

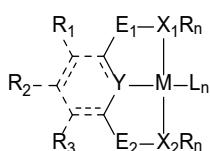
Die Dehydropolymerisation von Amin-Boran-Addukten ist seit dem Beginn des Jahrhunderts bekannt. Bei dieser Reaktion können Polymere gebildet werden, welche isovalenzelektronisch zum vielseitig einsetzbaren und unverzichtbaren Polyethylen sind. Der Mechanismus der katalytischen Dehydropolymerisation von Amin-Boranen ist in Abhängigkeit vom Katalysator sehr unterschiedlich. Nicht nur Komplexe früher und später Übergangsmetalle unterscheiden sich stark, auch strukturell verwandte Rhodium- und Iridium-Pincer-Komplexe zeigen teilweise diametral verschiedene Reaktivitäten gegenüber Amin-Boran-Addukten. In den letzten Jahren wurde eine sehr hohe Aktivität unter Verwendung eines kooperativen PN(H)P-Pincer-Liganden mit Rhodium als Metallzentrum gefunden. Im Rahmen dieser Arbeit sollte untersucht werden, ob eine ähnlich hohe Aktivität mit strukturverwandten PNN-Liganden erreichen werden kann. Dazu sollten geeignete Liganden aus der Literatur ausgewählt werden und zusammen mit späten Übergangsmetallen zu möglichen Präkatalysatoren umgesetzt werden. Nach ersten Untersuchungen von PNN(H)-Rhodium-Komplexen wurde in Anlehnung an Vorarbeiten aus der Literatur ein PNN-Ligand gesucht, welcher *facial* koordiniert und die NH-Funktionalität am zentralen Stickstoffatom trägt. Außerdem sollte ein Diolefin an das Metall-Zentrum gebunden sein, welches unter katalytischen Bedingungen leicht dissoziieren kann. Es sollten Norbornadien- (nbd) und 1,5-Cyclooctadien-Derivate (cod) synthetisiert und das Gegenanion der kationischen Komplexe variiert werden, um diese neuen Komplexe systematisch zu untersuchen. Im Anschluss sollten all diese Komplexe hinsichtlich ihrer Eigenschaften, die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ und Dehydropolymerisation von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ zu katalysieren untersucht werden.

Dinukleare Komplexe früher Übergangsmetalle zeigen eine Reihe an interessanten Reaktivitäten. Es konnte unter anderem gezeigt werden, dass sich dinukleare Alkinyl-verbrückte Zirconocene während der katalytischen Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ mit einem dinuklearen allenverbrückten Zirconocen bilden. Daher sollten strukturell ähnliche dinukleare Alkinyl-verbrückte Zirconocene synthetisiert und die Reaktivität mit Amin-Boranen und weiteren kleinen Molekülen untersucht werden.

2 Pincer-Komplexe

2.1 Allgemeine Aspekte

Pincer-Komplexe sind mittlerweile seit fast 50 Jahren bekannt.^[1] Dennoch sind aufgrund einer Vielzahl an möglichen Variationen am Grundgerüst längst nicht alle möglichen Kombinationen erforscht. Bei Pincer-Liganden handelt es sich um einen Chelatliganden mit drei Donoratomen. Das zentral σ -bindende Atom (**Y**) kann Teil eines aromatischen Ringes sein (z.B. Benzol, Pyridin, usw.). Die beiden anderen Donoratome (**X**) sind über zwei Linker (**E**) mit dem σ -bindende Atom (**Y**) verbunden. Es sind auch Pincer-Komplexe mit einer längeren Linkereinheit aus mehreren Atomen bekannt. Dadurch wird der, bei der Koordination entstehende Metall-Ligand-Cyclus größer und somit direkt der Bindungswinkel beeinflusst.^[2] Neben CH_2 -Einheiten als Linker sind auch Heteroatome, wie Sauerstoff^[3] und Schwefel^[4] bekannt. Auch die Donoratome (**X**) können Teil eines Ringsystems sein. Es werden beispielsweise Pincer-Liganden mit Oxazol-,^[5] Imidazol-^[6] und Pyrazol-Ringen,^[7] aber auch N-heterocyclischen Carbenen^[8] an dieser Position verwendet. Die drei Donoratome koordinieren ein Metall-Zentrum (**M**), welches zusätzliche Liganden (**L**) tragen kann. Als Metall-Zentrum eignen sich Hauptgruppenelemente,^[9] Selten-Erd-Metalle^[10] und Übergangsmetalle,^[11] auf welche in dieser Arbeit der Fokus gelegt werden soll. Der Pincerligand kann symmetrisch aufgebaut sein, was die Synthese häufig vereinfacht. Es sind aber auch viele unsymmetrische Pincer-Liganden bekannt.^[12] Durch die vielen Variationsmöglichkeiten können Pincer-Komplexe ideal an die Anforderungen einer Reaktion angepasst werden.



E: Linkeratome (CR_2 , NR , O , S)

X: Donoratome (P , N , O , S , Se , Carbene)

Y: σ -bindendes Atom (C , B , N , P , Si)

M: Metall-Zentrum

L_n: weitere Liganden

Abbildung 1: Genereller Aufbau eines Pincer-Komplexes.

Pincer-Komplexe weisen in der Regel eine hohe thermische Stabilität und starke Metall-Ligand-Bindungen auf.^[11d, 13] Dadurch können sie auch mit anderen Liganden und

Reduktionsmitteln reagieren, während der Pincerligand koordiniert bleibt. Es sind sowohl *meridional* als auch *facial* koordinierende Pincer-Liganden bekannt.^[11d] Für *facial* koordinierende Pincer-Liganden mit sp^2 C oder N als σ -bindendes Atom gibt es jedoch wenige Beispiele. Der Ligand kann auch an der Reaktivität des Komplexes beteiligt sein. In diesem Fall spricht man von einem kooperativen Liganden.^[14] Ein Beispiel hierfür sind PCP-Pincer-Liganden mit einer Ethylgruppe an der Position Y des σ -Donors, welche mit $[\text{Rh}(\text{H})(\text{PPh}_3)_4]$ oder $[\text{Rh}(\text{PPh}_3)_4]$ einen Rhodium-Komplex bilden, in dem die CH_2 -Gruppe neben den beiden Phosphor-Donoren an das Rhodium koordiniert (1, Abbildung 2).^[15] Diese Komplexe sind nur bis 120 °C stabil. Bei höheren Temperaturen wird Ethen eliminiert und es bildet sich eine Aryl-Rhodium-Bindung aus (2). Die Zugabe von Wasserstoff führt zur Freisetzung von Ethan und der gleiche Komplex (2) entsteht. Mit $[\text{Rh}(\text{Cl})(\text{PPh}_3)_3]$ als Präkursor wird dieser Komplex direkt gebildet. Unter Verwendung eines Methyl-substituierten Liganden insertiert das Rhodium teilweise in die C-H-Bindung der Methylgruppe und bildet einen Hydridkomplex (3). Zusätzlich erfolgt die oxidative Addition der C-C-Bindung und es kommt zur Bildung eines Methylkomplexes (4), welcher auch langsam aus dem Hydridokomplex gebildet wird. Die Kombination des gut untersuchten Bis(diphosphinoethyl)amin-Liganden $i\text{Pr-PN}(\text{H})\text{P}$ ^[6, 16] mit $[\text{IrCl}(\text{COE})_2]_2$ (COE, Cycloocten) führt in protischen Lösungsmittel zur Bildung des Komplexes $[(\text{PN}(\text{H})\text{P})\text{IrH}_2\text{Cl}]$ (5).^[17] In aprotischen Lösungsmittel oder unter Zugabe von Base wird jedoch der deprotonierte Komplex $[(\text{PNP})\text{Ir}(\text{COE})]$ (6) gebildet.

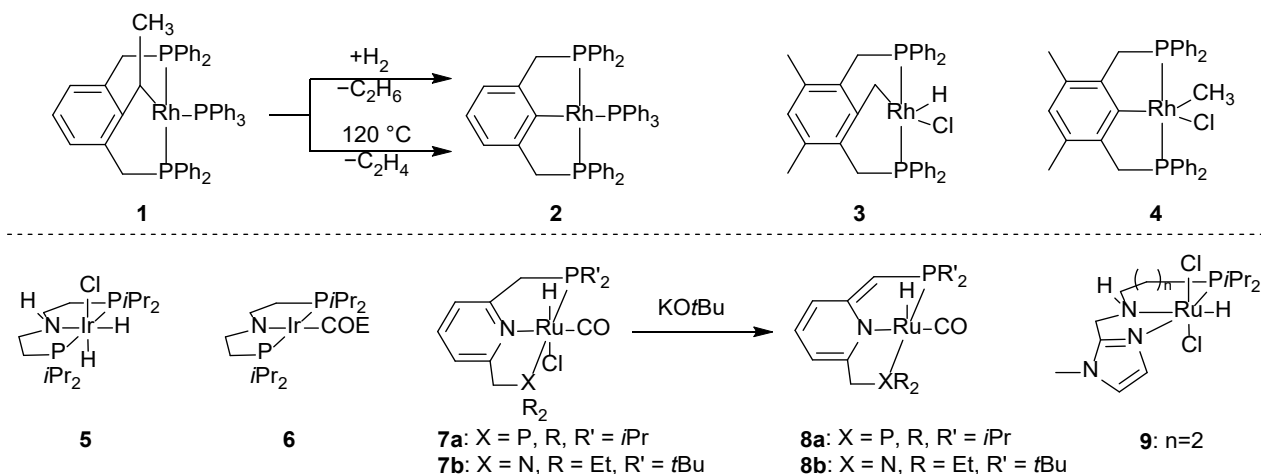


Abbildung 2: Einige der in diesem Kapitel besprochenen kooperativen Komplexe.

Ein weiteres Beispiel sind die vielfach von MILSTEIN und Mitarbeitern untersuchten Ruthenium-Komplexe mit einem PNN- oder PNP-Liganden mit zentralem Pyridinring, welche durch Zugabe von KO^tBu am CH_2 -Linker deprotoniert werden können (7).^[18] Dadurch wird

die Aromatizität des Pyridinringes aufgehoben und eine Doppelbindung zu dem deprotonierten Linker ausgebildet (**8**). Die so gebildeten Komplexe erwiesen sich als sehr reaktive Katalysatoren für die Hydrierung von Estern zu Alkoholen. Dabei trägt das zentrale Stickstoffatom eine negative Ladung und bildet eine dative Bindung zum Metallzentrum aus. *Ein weiteres Beispiel (siehe Anlage 4) für einen für einen solchen PNP-Liganden mit Amid als zentrales Donoratom, jedoch mit Phosphaalkenen als X-Donoren wurde von uns untersucht. Mit dem Liganden konnten ausschließlich Rh-Komplexe hergestellt werden, in denen zwei Rhodium-Zentren pro Ligand koordiniert werden. In einem Fall wird der Ligand dabei aktiviert und ein Phosphaindan-Fragment wird gebildet.*

Strukturell ähnliche PN(H)N-Komplexe wurden von BELLER *et al.* für die Hydrierung von Benzonitril verwendet.^[6a] Bei den Liganden wurden die Substituenten am Phosphor und die Länge der Linkerarme zum Phosphor variiert. Bei den *iso*-Propylderivaten [(PN(H)N)RuCl₂(PPh₃)] (**9**) ist der ethyl-verbrückte Komplex aktiver als das Propylen-verbrückte Analogon. Bei Verwendung eines anderen Ru-Präkursors unterscheiden sich die nicht-Pincer-Liganden am Metall-Zentrum in Abhängigkeit von der Linkerlänge. Bei den Propylen-verbrückten Derivaten koordiniert der Chloridoligand direkt am Metall-Zentrum und Triphenylphosphin ist nicht Teil des Komplexes. Bei dem Ethylderivat koordiniert ein PPh₃-Ligand und das Chlorid befindet sich in der sekundären Koordinationssphäre als Gegenion mit Wasserstoffbrückenbindung zum NH-Proton. Sowohl mit *iso*-Propyl- als auch Phenyl-Gruppen am Phosphor sind hier die Propylen-verbrückten Komplexe aktiver. Diese Komplexe können auch die Hydrierung von Amiden zu den entsprechenden Alkoholen und Aminen ohne Base katalysieren.^[6b] Am effektivsten für diese Reaktion ist der *t*Bu-substituierte Propylen-verbrückte Komplex [(PN(H)N)RuH(CO)(BH₄)].

2.2 Pincer-Komplexe mit frühen Übergangsmetallen in der homogenen Katalyse

Pincer-Komplexe früher Übergangsmetalle sind in der Lage eine ganze Reihe an chemischen Reaktionen zu katalysieren. So kann die Polymerisation von Ethen mit Titan-Pincer-Komplexen realisiert werden.^[19] GIBSON *et al.* verwendeten beispielsweise einen Bis(carben)pyridin-Liganden um TiCl₃ zu koordinieren. Mit Methylaluminoxan (MAO) als Co-Katalysator wird eine TOF von 28.000 h⁻¹ für 1 bar Ethen bei Raumtemperatur in Toluol

beobachtet. Der Komplex 2,6-Bis[(dimethylamino)methyl]phenyltitan(IV)trichlorid (**10**, Abbildung 3) wurde in späteren Untersuchungen für die selbe Reaktion eingesetzt.^[20] Versuche aus diesem Ti(III)-NCN-Pincer-Komplex mit Natrium einen Ti(II)-Komplex zu bilden scheiterten. Bei Raumtemperatur findet keine Reaktion statt und refluxieren in Toluol unter Stickstoff führt zur Zersetzung. Bei der Reaktion mit Ethen zeigt der Komplex nur eine geringe Aktivität, jedoch wird diese deutlich höher, wenn der Präkatalysator auf MgCl₂ fixiert wird. Auch Zirconium-Pincer-Komplexe können die Polymerisation von Ethen katalysieren. Ein NON-Pincerligand mit Xanthen-Rückgrat wurde mit [Zr(NMe₃)₄] bei 110 °C umgesetzt um den entsprechenden Komplex zu bilden (**11**).^[21] Durch Zugabe eines Überschuss an AlMe₃ oder TMSCl gefolgt von MeLi, kann ein Zirconium-Dimethylkomplex hergestellt werden. Dieser kann durch Zugabe von Tris(pentafluorophenyl)boran zu einem kationischen Komplex (**12**) umgesetzt werden. Auch die Reaktion mit [Ph₃C][B(C₆F₅)₃] führt zur Abstraktion einer Methylgruppe und der Bildung eines kationischen Komplexes, welcher Benzol (**13**) oder Toluol am Metall-Zentrum η^6 -koordiniert. Diese kationischen Komplexe wurden für die Polymerisation von Ethen verwendet und bildeten Polymere mit hohen Massenmitteln der Molmasse (52.000 – 88.000 g/mol). Hafnium-Komplexe wurden ebenfalls für die Reaktion untersucht.^[22] Sowohl NNC- als auch NNN-Pincer-Liganden (**14**, **15**), welche HfMe₂ koordinieren bilden nur kurze Polymerketten, verglichen mit einem ebenfalls untersuchten HfMe₃-NN-Chelatkomplex.

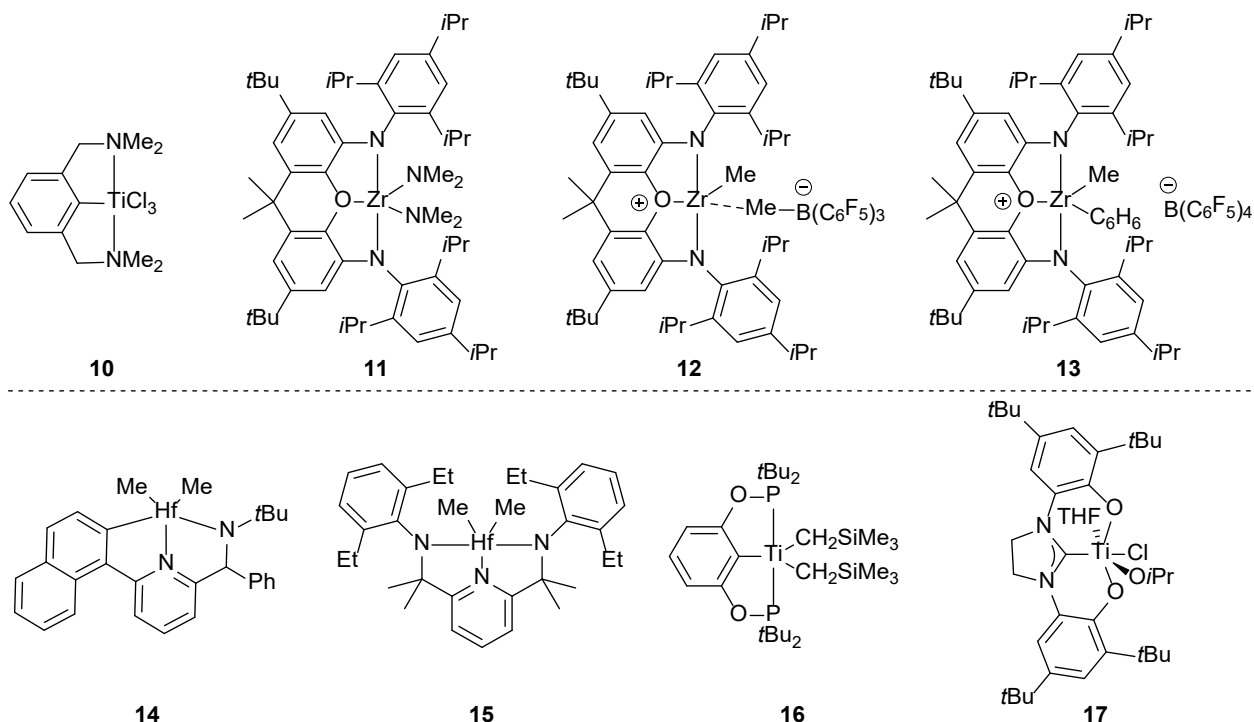


Abbildung 3: Einige der in diesem Kapitel behandelten Komplexe mit frühen Übergangsmetallen.

Pincer-Liganden mit Phosphanen können ebenfalls mit einem Titanzentrum kombiniert werden.^[3a] Ein solcher POCOP-Titan-Pincer-Komplex (**16**) eignet sich für die katalytische Polymerisation von Styrol. Mit dem Präkatalysator $[(\text{POCOP})\text{Ti}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_2]$ werden 42% Polymer gebildet. Eine weitere vielfach untersuchte Polymerisationsreaktion ist die von *D,L*-Lactid. Zum Beispiel wurden ein OCO-Pincerligand mit einem zentralen N-heterocyclischen Carben als Ligand für Titan(IV) verwendet.^[23] Der Präkatalysator mit zwei zusätzlichen Isopropoxy-Liganden am Titan-Zentrum zeigt eine geringe Aktivität, verglichen mit dem $[(\text{OCO})\text{TiCl}(\text{O}i\text{Pr})\text{THF}]$ -Derivat (**17**). Ähnliche, chirale Liganden wurden am Titan, Zirkonium und Hafnium koordiniert um Präkatalysatoren für die gleiche Reaktion zu erhalten.^[24] Bei diesen Komplexen weist das Titan-Derivat die geringste katalytische Aktivität auf.

Die intermolekulare Hydroaminierung ist ein weiteres Beispiel für eine Reaktion die mit Titan-,^[25] Zirkonium-^[26] und Hafnium-Pincer-Komplexen^[8] katalysiert werden kann. Dazu werden Biscarben-Liganden mit einem verbrückenden Phenylring mit den jeweiligen Tetrakis(dimethylamino)-Metall-Komplexen kombiniert. Die gebildeten Komplexe können direkt für die Katalyse eingesetzt werden oder erst, die nicht-Pincerliganden ausgetauscht werden.

Zirkonium- und Titan-Komplexe mit verbrückenden Stickstoff-Liganden können für die katalytische Reduktion von Stickstoff zu Ammoniak verwendet werden.^[27] An jedes Metall-Zentrum koordiniert in diesen Komplexen ein PNP-Pincerligand und ein Cp-Ring. Bei dem Titan-Derivat ist im dinuklearen Komplex eines der Phosphane pro Metall-Zentrum nicht koordinierend. Der mononukleare Komplex mit zusätzlichen Chloridoliganden ist deutlich inaktiver in der Katalyse.

2.3 Pincer-Komplexe mit späten Übergangsmetallen in der homogenen Katalyse

Ein frühes Beispiel für die Nutzung von Pincerkomplexen später Übergangsmetalle in der homogenen Katalyse wurde von MILSTEIN *et al.* vorgestellt, in welchem die katalytische Heck-Reaktion mit einem Palladium-Pincer-Komplex untersucht wird.^[28] Es werden PCP-Liganden mit *i*Pr- und *t*Bu-Gruppen am Phosphor verwendet (**19**, Abbildung 4). Diese Präkatalysatoren zeigen eine sehr hohe Aktivität bei der Arylierung von Olefinen. Außerdem sind die Komplexe alle luftstabil und thermisch bis 140 °C stabil (300 h), was erneut den stabilisierenden Effekt

von Pincer-Liganden unterstreicht.^[13] Weitere Untersuchungen der Substituenten am Phosphor führten zur Entdeckung des aktivsten Präkatalysators zu dieser Zeit. Die Verwendung eines Palladium-Komplexes mit *para*-Methoxyphenyl-substituierten Phosphit-Donoren (**20**) ermöglichten eine TOF von 400.000 h⁻¹ für die Reaktion von Iodobenzol mit *n*-Butylacrylat.^[29] Ähnliche PCP-Palladium-Komplexe (**18Ph**) können auch in der Stille-Kupplung verwendet werden um C-C-Bindungen zu knüpfen.^[30] Bei den von FRECH *et al.* verwendeten PCP-Liganden wurden die Linkeratome E₁ durch Sauerstoff und Stickstoff ausgetauscht.^[31] Diese so erhaltenen Palladium-Komplexe mit der allgemeinen Formel [Pd(Cl)(C₆H₃(XP(piperidinyl)₂)₂)](X=NH, O) sind ausgezeichnete Präkatalysatoren für die Suzuki-Kupplung.

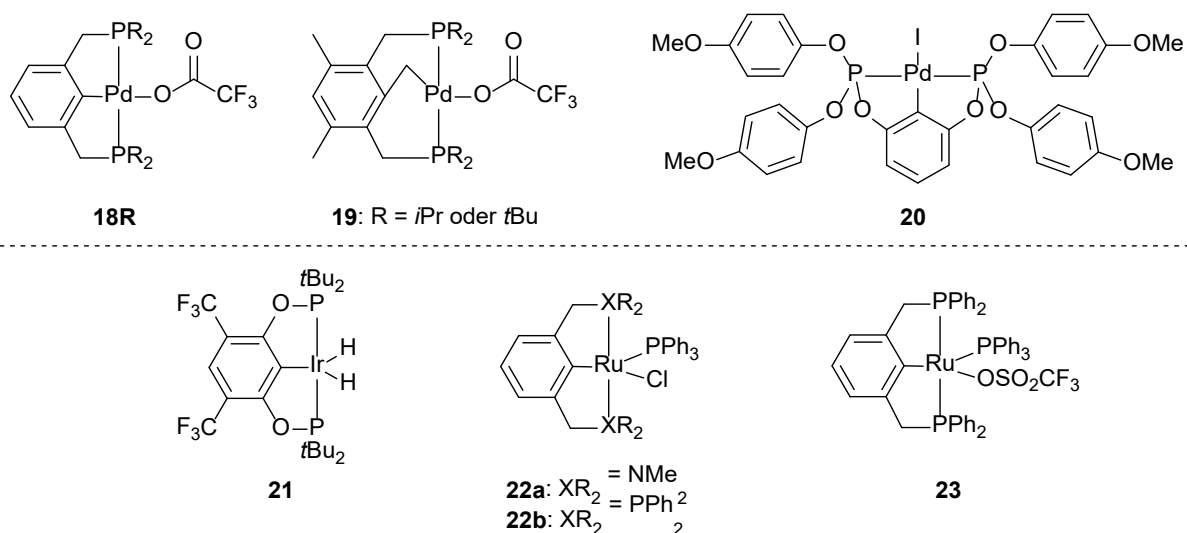


Abbildung 4: Einige der in diesem Kapitel behandelten Komplexe mit späten Übergangsmetallen.

Die Transferdehydrierung von Alkanen wurde vielfach mit PCP-Iridium-Komplexen untersucht. Dabei wurde unter anderem von BROOKHART *et al.* der Einfluss von unterschiedlichen Substituenten, die Größe des aromatischen Rückgrats und der Einfluss von Heteroatomen als Linker untersucht.^[32] Es wurde gezeigt, dass ein Komplex mit 3,5-Bis(trifluoromethyl)phenyl-Ring im Rückgrat (**21**) die höchste Aktivität aufweist. Alkane und Alkohole können mit Iridium-PCP-Komplexen dehydriert werden.^[33] Auch die Metathese von Alkanen ist mit PCP- oder POCOP-Liganden am Iridium möglich.^[33-34] Mit Hilfe eines [(PN(H)P)Ir(H)₂Cl] (**5**) Komplexes können in *iso*-Propanol diverse Ketone transferhydriert werden.^[35] Dieser und ähnliche Komplexe können auch Ester zu den entsprechenden Alkoholen reduzieren.^[36] Der Umfang der Reaktion umfasst mehr als 20 Ester, die erfolgreich gespalten

werden können. Der Chloridodihydrido-iridium-Komplex (**5**) ist dabei aktiver als der entsprechende Ir-Trihydrido-Komplex.

Auch die Bildung von Estern ist mit einem Ruthenium-Pincer-Komplex möglich.^[37] Bei den verwendeten Pincer-Liganden handelt es sich um PNP- (**7a**, **8a**) und PNN-Liganden (**7b**, **8b**) mit einem Pyridinring, welcher über den Stickstoff als σ -Donor koordiniert. Die Reduktion von Ketonen ist mit einem NCN- (**22a**) oder PCP-Ruthenium-Komplex (**22b**, **23**) ebenfalls möglich.^[38] Neben dieser Reaktivität sind Ruthenium-Pincer-Komplexe in der Lage eine ganze Reihe von Verbindungen zu hydrieren und zu dehydrieren.^[39] Außerdem können viele E-H-Bindungen (E = H, C, N, O, B, Si) mit Hilfe von Ruthenium-Pincer-Komplexen aktiviert werden.^[39]

3 Dehydrokupplung von Amin-Boran-Addukten

3.1 Allgemeine Aspekte

Bei Amin-Boran-Addukten handelt es sich um ein Lewis-Säure-Base-Paar, in dem das freie Elektronenpaar desamins mit dem unbesetzten $2p$ -Orbital des Borans interagiert.^[40] Durch diese koordinative Bindung werden die Addukte stabilisiert und sind im Vergleich zu anderen Boran-Addukten thermisch stabil.^[41] Am Stickstoff können sich neben Wasserstoffatomen auch organische Reste befinden. Es sind z.B. Polymere der Struktur $[H_2BNRH]_n$, ($R = H, Me, Et, nPr, nBu, CH_2Ph, (CH_2)_4Ph, CH_2(C_4H_3S)$ und $CH_2CH=CH_2$) bekannt.^[42] Diese Substituenten haben einen großen Einfluss auf die thermische Stabilität und Löslichkeit. So zersetzt sich Methylamin-Boran ($H_3B \cdot NMeH_2$), die Verbindung mit einer Methylgruppe am Stickstoff, bei $70\text{ }^\circ\text{C}$, wohingegen Dimethylamin-Boran ($H_3B \cdot NMe_2H$) Wasserstoff erst ab einer Temperatur von $150\text{ }^\circ\text{C}$ freisetzt.^[43] Substrate mit von Wasserstoff verschiedenen Substituenten am Bor-Zentrum sind kaum bekannt. Die Substituenten erhöhen die Elektronendichte am Bor wodurch die B-N-Interaktion geschwächt wird.^[42] Zu den wenigen Beispielen zählen die Polymere $[HRBNH_2]_n$ ($R = Ph, p\text{-}C_6H_4CF_3$).^[44] Neben der erhöhten thermischen Stabilität haben Methyl-Gruppen auch zur Folge, dass die Löslichkeit von gebildeten Polymeren erhöht ist und diese so über NMR-Spektroskopie untersucht werden können.^[45]

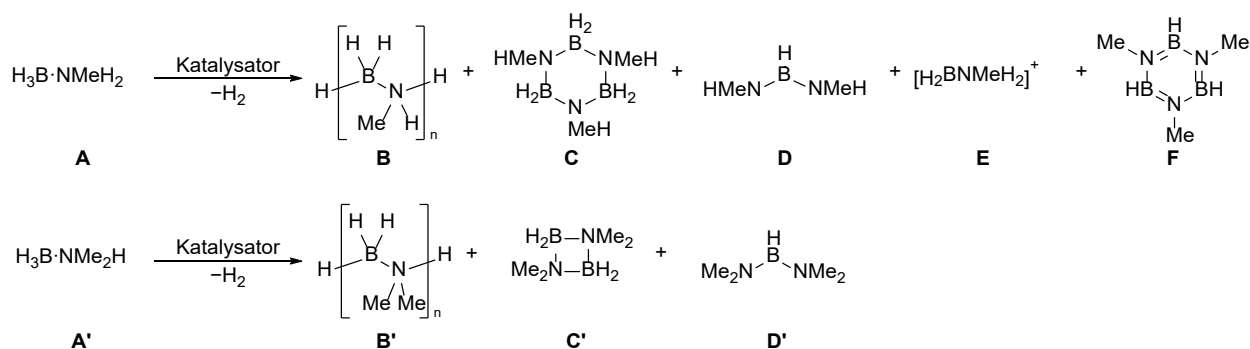


Abbildung 5: Die bei der Dehydropolymerisation von Amin-Boran-Addukten am häufigsten gebildete Produkte.

Bei der thermischen Zersetzungsreaktion entstehen cyclische Produkte, wie Cyclodiborazan, $[\text{H}_2\text{BNMe}_2]_2$ (**C'**), und im Fall von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ Cyclotriborazan, $[\text{H}_2\text{BNMeH}]_3$ (**C**, Abbildung 5). Unter katalytischen Bedingungen ist auch die selektive Bildung von Poly(aminoboranen), $[\text{H}_2\text{BNMeH}]_n$ (**B**), bekannt. Diese sind anorganische Analoga zu Polyolefinen und ebenfalls isovalenzelektronisch.^[46]

Amin-Boran-Addukte haben einen hohen Anteil an Wasserstoff. Bei Ammoniak-Boran macht Wasserstoff bei einer molaren Masse von 30,7 g/mol 19,6 Gewichtsprozent aus.^[41] Aus diesem Grund wurden Amin-Boran-Addukte vor allem zu Beginn des Jahrhunderts als mögliche Wasserstoffspeicher diskutiert. Die Dehydrierung der Addukte ist stark exotherm und exergon, da ein Äquivalent an Wasserstoff freigesetzt wird.^[47] Entsprechend ist die Rückreaktion, also die Hydrierung der dehydrierten B-N-Verbindungen durch einen Überdruck an Wasserstoff nicht möglich.^[47] In der Transferhydrierung wird die Eigenschaft der Amin-Boran-Addukte Wasserstoff freizusetzen genutzt um diverse Substrate zu reduzieren.^[48] Für diese Anwendung ist die geringe molare Masse auch ein Vorteil, da vergleichsweise wenig Abfall anfällt.

Bei der kinetischen und mechanistischen Untersuchung der Dehydrokupplung von Amin-Boran-Addukten wird die Wasserstoffentwicklung genutzt, da diese proportional zum Umsatz an Amin-Boran-Addukt ist. So kann durch Messung der Gasvolumenzunahme der Fortschritt der Reaktion verfolgt werden. Um diese Apparativ umzusetzen wird eine Gasbürette verwendet. Es werden sowohl automatische als auch manuelle Büretten benutzt, wobei die Funktionsweise grundsätzlich identisch ist. Die Reaktionslösung befindet sich in einem geschlossenen isothermen und isobaren System und die Volumenzunahme wird während der Reaktion pro Zeit gemessen.^[49]

Seit einigen Jahren hat sich der Fokus der Amin-Boran-Chemie vom Gebiet der Wasserstoffspeicherung hin zur Entwicklung neuer Hauptgruppenelement-basierter Verbindungen mit interessanten Materialeigenschaften verschoben. Poly(aminoborane) werden als mögliche Vorstufe für B-N-Keramiken diskutiert.^[50] Es gab bereits einige Untersuchungen zu den eng verwandten Boracylenen, welche sich hervorragend als Vorstufen für B-N-Keramikfasern eignen.^[51] Auch Ammoniak-Boran kann direkt verwendet werden, um solche Keramikfasern herzustellen.^[52] Erste Untersuchungen von Poly(aminoboranen) zeigten, dass diese zu dünnen Filmen verarbeitet oder zu B-N-Keramiken pyrolysiert werden können.^[50b, 53] Bisher gibt es jedoch keine Anwendung für diese Materialien.

3.2 Komplexe früher Übergangsmetalle für die Dehydrokupplung von Amin-Boran-Addukten

3.2.1 Katalysatoren der Gruppe 3

Die ersten Beispiele für die Dehydrokupplung mit Gruppe 3 Katalysatoren stammen aus dem Jahr 2010. In diesen Arbeiten wurden 3 mol% $[Y(N(SiMe_3)_2)_3]$ (**24**, Abbildung 6) in C_6D_6 verwendet um innerhalb von 12 h bei 60 °C $H_3B \cdot NMe_2H$ zu einer Mischung bestehend aus 90% Cyclodiborazan $[H_2BNMe_2]_2$ und weniger als 10% Diaminoboran $HB(NMe_2)_2$ umzusetzen.^[54] Nach 15 Minuten Reaktionszeit wird ein NMR-Signal detektiert, welches einem $[H_3BMe_2NH_2BMe_2N]^-$ -Anion zugeordnet werden kann. Der strukturverwandte Scandium-Komplex $[Sc(N(SiHMe_2)_2)_3(THF)_2]$ ist reaktiver, was durch die höhere Ladungsdichte am Metall-Zentrum begründet wird. Aus der Reaktionslösung kann eine Scandium-Spezies mit einem $N(SiHMe_2)_2$ - und zwei $(H_3BMe_2NH_2BMe_2N)^-$ -Liganden kristallisiert werden. Diese Struktur wurde, zusammen mit DFT-Berechnungen verwendet, um einen Katalyseccyclus zu postulieren. Darin reagiert $H_3B \cdot NMe_2H$ mit dem Metall-Zentrum unter β -Eliminierung. Es entsteht Aminoboran, welches mit einem an das Metall gebundenen Amin-Boran zu einem Intermediat reagiert und unter δ -Eliminierung das Produkt $[H_2BNH_2]_2$ freisetzt.

Eine Reihe von weiteren Yttrium-Komplexen des Typs $[(C_5H_5BR)_2MCH(SiMe_3)_2]$ ($M = Y$ oder Lu ; $R = Me$ oder NEt_2) wurden synthetisiert, wobei der Yttrium-Komplex mit Methyl-Substituenten ($M = Y$, $R = Me$ **25a**, $M = Lu$, $R = Me$ **25b**) die größte Aktivität zeigt (**25a**: 0,5 mol%, >99% Umsatz nach 11,7 min, **25b**: 1,0 mol%, >99% Umsatz nach 28,5 min).^[55] Zusätzlich wurden die bereits bekannten Komplexe $[M(CH_2SiMe_3)_3(THF)_2]$ ($M = Sc, Y, Lu$) und $[(C_5H_4Me)_2YCH(SiMe_3)_2]$ (**26**) für die Dehydrokupplung von Amin-Boran-Addukten eingesetzt. Die Komplexe mit 4d- und 5d-Metallen zeigen dabei eine geringere Aktivität. Während der Reaktion wird das lineare Diborazan ($H_3B \cdot NMe_2BH_2 \cdot NMe_2H$) als Zwischenprodukt beobachtet.

Die Komplexe $[Cp^*_2ScCH(SiMe_3)_2]$ ($Cp^* = Cp^*$ **27a**, Cp **27b**) katalysieren die Umsetzung von $H_3B \cdot NMe_2H$ in C_6D_6 bei Raumtemperatur in wenigen Minuten.^[56] Das Cp^* -Derivat ist reaktiver und benötigt mit einer Katalysatorkonzentration von 0,5 mol% nur zwei Minuten um vollständigen Umsatz zu erreichen. Bei geringeren Katalysatorkonzentration (0,2 mol%) wird primär $H_3B \cdot NMe_2BH_2 \cdot NMe_2H$ gebildet. Dieses wird auch mit dem Cp -Derivat selektiv

gebildet. Der Komplex $[\text{Cp}^*_2\text{ScCH}_2\text{SiMe}_3]$ (**28**) ist weniger selektiv und bildet nur zu 81% $[\text{H}_2\text{BNH}_2]_2$. Die stöchiometrische Reaktion von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ mit diesem Komplex bei $-30\text{ }^\circ\text{C}$ bildet ein Intermediat indem Amin-Boran β -agostisch mit dem Metall interagiert. Dieses ist vergleichbar mit den 2013 von MANNERS *et al.* beobachteten Titan- und Zirkonium-Intermediaten (**33**, **34**, siehe Kapitel 3.2.2).^[57] Die gleiche Reaktion mit Diisopropylamin-Boran, ($\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$), als Substrat führt zu einem Hydrido-Scandium-Komplex. In diesem bindet der $\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$ -Ligand über zwei Wasserstoffatome am Scandium-Zentrum.

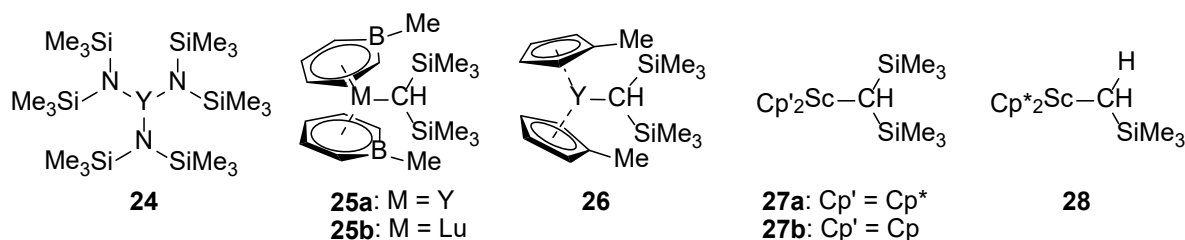


Abbildung 6: Einige der für die Dehydrokupplung von Amin-Boran-Addukten eingesetzten Präkatalysatoren mit Metallen der Gruppe 3.

3.2.2 Katalysatoren der Gruppe 4

Die Verwendung von Komplexen früher Übergangsmetalle für die katalytische Dehydrokupplung von Amin-Boran-Addukten wurde 2003 zum ersten Mal berichtet.^[58] Der Komplex $[\text{Cp}_2\text{TiMe}_2]$ katalysiert den Umsatz von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ jedoch nicht. Der $[\text{Cp}_2\text{Ti}]$ -Komplex (**29a**), welcher *in situ* aus $[\text{Cp}_2\text{TiCl}_2]$ und $n\text{BuLi}$ hergestellt wird ist hingegen ein aktiver Katalysator für die Reaktion von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ und $\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$.^[59] Aus $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ wird primär $[\text{H}_2\text{BNMe}_2]_2$ gebildet, wogegen unter Verwendung von $\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$ das freie Aminoboran, $\text{H}_2\text{B}=\text{NiPr}_2$, entsteht. Die Zugabe von Quecksilber zu dem Reaktionsgemisch hat, anders als bei Verwendung von Präkursoren auf Basis später Übergangsmetalle wie $[\text{Rh}(\text{cod})\text{Cl}]_2$ keinen inhibierenden Einfluss. Das Filtrieren der beiden Reaktionsgemische führt zu dem gleichen Ergebnis. Daher nahmen MANNERS *et al.* an, dass der Titan-Katalysator die Reaktion in einem homogen-katalytischen, molekular definierten Reaktionsmechanismus katalysiert. Es wurden eine Reihe an unterschiedlichen Titan- und Zirkonium-Komplexe hinsichtlich ihrer Fähigkeit, die Dehydrokupplung von Amin-Boran-Addukten zu katalysieren untersucht.^[60] Die Reaktionen von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ in THF sind grundsätzlich langsamer als in Benzol. Größere Substituenten an den Cp-Ringen senken ebenfalls die Aktivität. Außerdem sind die Titan-Komplexe tendenziell reaktiver als die Zirkonium-Derivate, wobei ein dinuklearer Titan(III)-Komplex (**30**, Abbildung 7) mit Abstand die größte Reaktivität aufweist.

Die unterschiedlichen Produkte und Intermediate der Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ wurden durch *in situ* Bildung von $[\text{Cp}_2\text{Ti}]$ (**29a**) aus dem Dichlorid Cp_2TiCl_2 und *n*BuLi in Toluol und anschließender Zugabe von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ untersucht.^[61] Während den ersten 15 Minuten bildet sich $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ als Intermediat, welches anschließend zu $[\text{H}_2\text{BNMe}_2]_2$ cyclisiert. In vier Stunden entstehen 98% $[\text{H}_2\text{BNMe}_2]_2$ und jeweils 1% $\text{HB}(\text{Me}_2\text{N})_2$ sowie $\text{H}_2\text{B}=\text{NMe}_2$. Um die Grenzen der Substratspezifität zu testen, wurde die Dehydrokupplung mit unterschiedlich substituierten Amin-Boran-Addukten durchgeführt. Das Substrat $\text{H}_3\text{B}\cdot\text{NMeBnH}$ ($\text{Bn} = \text{CH}_2\text{Ph}$) wird ebenfalls zu $[\text{H}_2\text{BNMeBn}]_2$ umgesetzt, $\text{H}_3\text{B}\cdot\text{NMeH}_2$ reagiert nur zu 1% zu $[\text{H}_2\text{BNMeH}]_3$ (nach 16 h bei 20 °C) und $\text{H}_3\text{B}\cdot\text{NH}_3$ reagiert gar nicht.

Zusätzlich wurden Komplexe anderer Metalle der Gruppe 4 hinsichtlich ihrer katalytischen Eigenschaften untersucht. Die Spezies $[\text{Cp}_2\text{M}]$ ($\text{M} = \text{Zr}$ (**29b**), Hf) werden analog *in situ* durch Zugabe von *n*BuLi zu den Dichlorid-Komplexen gebildet. In Toluol setzen diese Komplexe keine Amin-Boran-Addukte um. In THF findet bei Verwendung des Zirkonium-Katalysators eine Reaktion von $\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$ zu $\text{H}_2\text{B}=\text{NiPr}_2$ statt. $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ reagiert hingegen nicht. Der Titan-Komplex $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\text{Ti}]$ setzt $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ zu 50% und $\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$ vollständig um. Die Verwendung des Zirkonium-Derivates führt zu keiner Reaktion. Der Komplex $[\eta^5\text{-(C}_5\text{Me}_4(\text{SiMe}_2\text{tBu}))_2\text{Ti}]$ gehört zu den wenigen bekannten durch Liganden stabilisierten Titan(II)-Komplexen. Daher wurde dieser als Katalysator für die Dehydrokupplung von Amin-Boran-Addukten getestet, jedoch wurden nur 5% $\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$ nach 92 h umgesetzt.

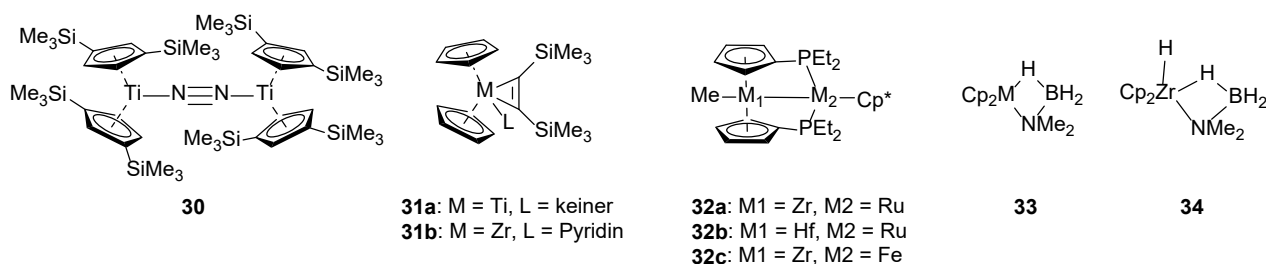


Abbildung 7: Katalysatoren auf Basis von Metallocenen der Gruppe 4, die für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ eingesetzt wurden.

Der weniger sterisch anspruchsvolle Titan(II)-Komplex $[\text{Cp}_2\text{Ti}(\text{PMe}_3)_2]$ setzt beide Substrate vollständig um. Die Titan(III)-Komplexe $[\text{Cp}_2\text{TiCl}]$ und TiCl_3 führen mit beiden Substraten zu keinem Umsatz. Der Komplex $[\text{Cp}_2\text{Ti}(\text{PMe}_3)_2]$ zeigt, im Vergleich zum $[\text{Cp}_2\text{Ti}]$ -Komplex^[59] eine längere Induktionsperiode, die der Dissoziation des PMe_3 -Liganden zugeschrieben wird. Auch bei dieser Reaktion wird $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ als Intermediat beobachtet. Aus diesem

Grund wurde diese Verbindung synthetisiert und als Substrat für die Reaktion eingesetzt. Dabei bildet sich fast ausschließlich $[\text{H}_2\text{BNMe}_2]_2$. Die Metall(II)-Komplexe des Typs $[\text{Cp}_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ (**31**) sind in der Lage $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ umzusetzen.^[62] Der Titan-Komplex ($\text{M} = \text{Ti}$, kein L, **31a**) erreicht nach 16 h 86% Umsatz, wobei der Zirkonium-Komplex ($\text{M} = \text{Zr}$, L = Pyridin, **31b**) in dieser Zeit nur 42% Umsatz erreicht. Diese unterschiedliche Reaktivität wird durch die stärkere Bindung zwischen Zirkonium und dem Alkin-Liganden begründet. Die Cp^* -Derivate dieser Komplexe sind nicht aktiv. Die beiden Metall(IV)-Komplexe $[\text{M}(\text{NMe}_2)_4]$ ($\text{M} = \text{Ti}$, Zr) weisen die gleiche Aktivität auf (22 h, für etwa 86% Umsatz). Die Verbindungen $[\text{Ti}(\text{OiPr})_4]$ und $[\text{TiCl}_4]$ zeigen hingegen keine Aktivität in der Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$. Der Komplex $[(\eta^5\text{-iPrC}_5\text{H}_4)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ ist aktiver (8 h, 96% Umsatz) als das Cp -Derivat, wobei bei dieser Reaktion $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ als Nebenprodukt gebildet wird und ein Titanocenhydrid während der Reaktion entsteht.^[63] Optimale Bedingungen für diese Reaktion sind 40 °C in Toluol mit 2 mol% Katalysator. Bei diesen Bedingungen nimmt die Aktivität erst nach der dritten Zugabe von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ ab. Kinetische Untersuchungen zeigen eine Kinetik nullter Ordnung für Präkatalysatorkonzentrationen von mehr als 2 mol%, für eine Konzentration von 0,2 mol% jedoch eine Kinetik erster Ordnung. Dies passte nicht zu einer angenommenen Michaelis-Menten-Kinetik. Die Teilordnung des Katalysators liegt bei 0,46, was einen Reaktionsmechanismus unter Beteiligung von Monomer-Dimer-Umwandlungen impliziert.

Die dinuklearen, heterobimetallischen Komplexe $[\text{M}^1\text{Me}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{PEt}_2)_2\text{M}^2\text{Cp}^*]$ ($\text{M}^1 = \text{Zr}$, $\text{M}^2 = \text{Ru}$ **32a**; $\text{M}^1 = \text{Hf}$, $\text{M}^2 = \text{Ru}$ **32b**; $\text{M}^1 = \text{Zr}$, $\text{M}^2 = \text{Fe}$ **32c**) kombinieren ein Gruppe 4-Element mit einem Gruppe 8-Element.^[64] Alle drei Komplexe sind effektive Präkatalysatoren für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ und $\text{H}_3\text{B}\cdot\text{NiPr}_2\text{H}$, wobei der Zirkonium-Ruthenium-Komplex (**32a**) am aktivsten ist (6 h, 93% Umsatz). Bemerkenswert ist außerdem, dass der 2011 erstmals beschriebene Hafnium-Ruthenium-Komplex der erste Hafnium-Komplex ist, der die Dehydrokupplung von Amin-Boran-Addukten katalysiert.

Durch die Reaktion von $[\text{Cp}_2\text{TiCl}_2]$ mit $\text{Li}[\text{NMe}_2\text{BH}_3]$ kann der Amin-Boran-Komplex (**33**) hergestellt werden.^[57] Der entsprechende Zirkonium-Komplex bindet einen zusätzlichen Hydrido-Liganden. Daher handelt es sich bei diesem um einen diamagnetischen Zirkonium(IV)-Komplex (**34**). Der Zirkonium-Komplex setzt innerhalb von zwei Stunden kein $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ um. Der Titan-Komplex ist andererseits sehr aktiv (2 h, 97% Umsatz). Die UV/Vis- und EPR-Reaktionsspektren des Titan(III)-Komplexes und des Reaktionssystems unter Verwendung von *in situ* generierten $[\text{Cp}_2\text{Ti}]$ zeigen große Übereinstimmungen, was ein

weiteres Indiz dafür ist, dass es sich bei dem synthetisierten Komplex tatsächlich um ein Intermediat der katalytischen Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ mit $\text{Cp}_2\text{TiCl}_2/n\text{BuLi}$ handelt.

Der Amid-Komplex $[(\text{DippNSi}(i\text{Pr})_2\text{NDipp})\text{Zr}(\text{NMe}_2)_2(\mu\text{-Cl})\text{Li}(\text{THF})_3]$ (**35**, Abbildung 8) ist ein weiterer geeigneter Präkatalysator für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ und $\text{H}_3\text{B}\cdot\text{N}i\text{Pr}_2\text{H}$.^[65] Bei Konzentrationen von 0,1 mol% ist der Komplex aktiver und bildet $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$, wogegen bei 1 mol% $[\text{H}_2\text{BNMe}_2]_2$ gebildet wird. Diese Reaktionen werden in Benzol durchgeführt. In Chloroform findet keine Reaktion statt. Auch $\text{H}_3\text{B}\cdot\text{N}n\text{BuH}_2$ kann als Substrat verwendet werden, bildet aber zu 60% das Cyclotriborazan $[\text{H}_2\text{BN}n\text{BuH}]_3$.

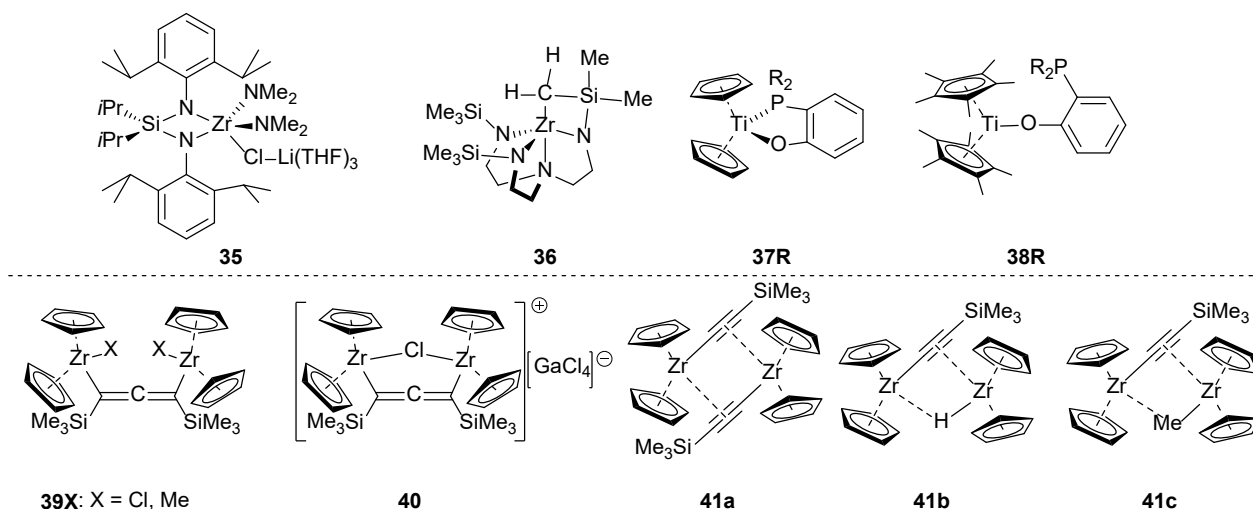


Abbildung 8: Weitere Katalysatoren auf Basis von Metallen der Gruppe 4, die für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ eingesetzt wurden.

Der Triamidoamin-Komplex $[\kappa^5\text{-(Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{N-(CH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2\text{)Zr}]$ (**36**) katalysiert die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$, $\text{H}_3\text{B}\cdot\text{NH}_2t\text{Bu}$ und $\text{H}_3\text{B}\cdot\text{NH}_3$.^[66] Die Reaktionen zeigen bei 65 °C den größten Umsatz und werden in C_6D_6 durchgeführt, ausgenommen der Reaktionen mit $\text{H}_3\text{B}\cdot\text{NH}_3$, welche aufgrund der Löslichkeit in $\text{THF-}d_8$ durchgeführt wird.

Die Reaktion von $\text{H}_3\text{B}\cdot\text{NH}_3$ mit dem Schwartz-Reagenz $[\text{Cp}_2\text{ZrHCl}]$ liefert nach 48 Stunden bei 50 °C *B*-(cyclotriborazanyl)amin-Boran mit 40% Ausbeute.^[67] BAKER *et al.* verwendeten die Komplexe $[\text{Cp}_2\text{Zr}(\text{BH}_4)_2]$ und $[\text{Cp}_2\text{ZrCl}(\text{BH}_4)]$ für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NH}_3$.^[18] Der erste Komplex wurde mit 20 Äq. $\text{H}_3\text{B}\cdot\text{NH}_3$ zur Reaktion gebracht, konnte das Substrat jedoch nur unselektiv und in geringen Mengen zu *B*-(cyclotriborazanyl)amin-Boran umsetzen. Dennoch lieferten diese Arbeiten wichtige Erkenntnisse für die Abfolge der Bildung von

Intermediaten der sonst wenig mechanistisch untersuchten Dehydrokupplung des schwer löslichen Ammoniak-Boran.

Bei den Komplexen $[\text{Cp}_2\text{Ti}(\kappa^2\text{-O, } P\text{-O-C}_6\text{H}_4\text{-PR}_2)]$ ($R = i\text{-Pr}$ oder Ph , **37R**) und $[\text{Cp}^*_2\text{Ti}(\kappa^1\text{-O-O-C}_6\text{H}_4\text{-PR}_2)]$ ($R = i\text{-Pr}$ oder Ph , **38R**) sind die Phenyl-Derivate durch ihren sterischen Anspruch weniger reaktiv.^[68] Die Reaktionen wurden bei 50 °C ohne Lösungsmittel durchgeführt, wo sie eine besonders hohe Aktivität zeigen. Auch die Zugabe von neuem Substrat führt zu keiner verringerten Reaktivität. Mit Konzentrationen von 1 und 2 mol% zeigt der Komplex eine Induktionsperiode.

Die dinuklearen Komplexe $[\text{Cp}_2\text{Zr}(\text{Cl})(\mu\text{-Me}_3\text{SiC}_3\text{SiMe}_3)\text{Zr}(\text{Cl})\text{Cp}_2]$ (**39Cl**) und $[\text{Cp}_2\text{Zr}(\mu\text{-Cl})(\mu\text{-Me}_3\text{SiC}_3\text{SiMe}_3)\text{ZrCp}_2][\text{GaCl}_4]$ (**40**) erfordern die Aktivierung mit MeLi um die Dehydrokupplung von Amin-Boran-Addukten katalysieren zu können.^[69] Die Wasserstoffentwicklung verläuft nach einer Kinetik nullter Ordnung ohne eine Induktionsperiode, aber nur zu ca. 85% ab (2,5 mol%, Toluol, 25 °C). Für die Aktivierung der Reaktion mit MeLi wurden zwei Reaktionswege in Betracht gezogen. Zum einen die Aktivierung des Komplexes mit anschließender Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ und zum anderen die Aktivierung des Substrates durch Deprotonierung und anschließende Dehydrokupplung. Beide Reaktionswege wurden untersucht, indem einmal das Substrat und einmal der Katalysator mit MeLi aktiviert wird, führten jedoch zu den gleichen Produkten und Reaktivitäten. Die Reaktion verläuft homogen-katalytisch, denn die Zugabe von Quecksilber hemmte die Dehydrokupplung nicht. Weitere mechanistische Untersuchungen zeigten, dass es sich bei dem Komplex $[\text{Cp}_2\text{Zr}(\text{Me})(\mu\text{-Me}_3\text{SiC}_3\text{SiMe}_3)\text{Zr}(\text{Me})\text{Cp}_2]$ (**39Me**) nicht um die katalytisch aktive Spezies handelt.^[70] Die NMR- und UV/Vis-spektroskopische Verfolgung der Reaktion belegt, dass eine Reihe ineinander umwandelbarer Zirkonium-Verbindungen in der Reaktionsmischung vorliegen. Zwei diamagnetische Komplexe $[\text{Cp}_2\text{Zr}(\text{C}_2\text{SiMe}_3)(\mu\text{-R})\text{ZrCp}_2]$ ($R = \text{CH}_2\text{SiMe}_3$ **41a** und $R = \text{H}$ **41b**) wurden in stöchiometrischen Reaktionen nachgebildet. Darüber hinaus konnte ein methyl-verbrückter Komplex $[\text{Cp}_2\text{Zr}(\text{C}_2\text{SiMe}_3)(\mu\text{-Me})\text{ZrCp}_2]$ (**41c**) synthetisiert werden. Diese Komplexe **41a-c** reagiert deutlich langsamer als **39Cl** mit Aktivierung durch MeLi. Der Komplex **41c** zeigt eine Induktionsperiode führt aber auch zu fast vollständigem Umsatz des Substrats. Diese Komplexe sind ein weiteres Beispiel für Komplexe früher Übergangsmetalle in der Oxidationsstufe +III, die in der Dehydrokupplung von Amin-Boranen eingesetzt werden (vgl. *CHIRIK et al.*^[60] und *MANNERS et al.*^[71]). *An diesem Punkt knüpfen aktuelle Untersuchungen zu dinuklearen Alkynyl-verbrückten Zirkonocenen an (siehe Anlage 2).*^[72] Diese formal gemischtvalenten Komplexe wurden synthetisiert und die Struktur

der entsprechenden verbrückten Hydride zum ersten Mal mit Hilfe der Röntgenkristallstrukturanalyse nachgewiesen. Neben einer umfangreichen Charakterisierung, inklusive einer genauen Betrachtung der Bindungssituation mit Hilfe von DFT-Rechnungen wurde die Aktivierung kleiner Moleküle mit diesen Komplexen untersucht.

Der Titan(III)-Komplex $[\text{Cp}^*_2\text{TiH}]$ katalysiert die Reaktion von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ zu $[\text{H}_2\text{BNMe}_2]_2$ und Wasserstoff.^[71] Bei derselben Reaktion mit dem Komplex $[\text{Cp}^*_2\text{TiMe}]$ wird zusätzlich Methan freigesetzt, wobei die gleichen Produkte entstehen. Mit $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ als Substrat findet keine Reaktion statt. Die beiden Komplexe zeigen die gleiche Reaktionskinetik, nur bei dem Methyl-Komplex wird eine Induktionsperiode von weniger als zwei Sekunden beobachtet. Für den Mechanismus wird eine σ -Bindungsmetathese mit β -Hydrid-Eliminierung in einem redoxneutralen Mechanismus mit einem Ti(III)-Hydrid als Zwischenprodukt postuliert.

3.3 Rhodium-Komplexe für die Dehydrokupplung von Amin-Boran-Addukten

3.3.1 Präkursoren

Bereits 2001 wurde gezeigt, dass die Rhodium-Präkursoren $[\text{Rh}(\text{cod})\text{Cl}]_2$ und $\text{RhCl}_3\cdot\text{H}_2\text{O}$ in der Lage sind $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ zu $[\text{H}_2\text{BNMe}_2]_2$ und $\text{H}_3\text{B}\cdot\text{NH}_3$ sowie $\text{H}_3\text{B}\cdot\text{NMeH}_2$ zu den jeweiligen Borazinen umzusetzen.^[73] Ein vollständiger Umsatz von $\text{H}_3\text{B}\cdot\text{NH}_3$ wurde erst nach 72 h bei 25 °C in Diglyme und Tetraglyme erreicht und $[\text{HB}=\text{NH}]_3$ mit 10% Ausbeute isoliert. Wird hingegen THF als Lösungsmittel verwendet, kann dieser Komplex auch Polyaminoboran ($M_w = 42.000 \text{ g/mol}$) bei 20 °C aus $\text{H}_3\text{B}\cdot\text{NMeH}_2$ erzeugen.^[45] Nach 20 h wurde das Polymer in einer Ausbeute von 75% isoliert. In einer darauf aufbauenden Studie wurde die Reaktion optimiert. Die Reaktion von 0,5 mol% $[\text{Rh}(\text{cod})\text{Cl}]_2$ in Toluol bei 25 °C führt schon nach 8 h zu vollständigem Umsatz von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$.^[74] Erhöhte Temperaturen oder Katalysatorkonzentrationen beschleunigen die Reaktion. Ein Vergleich mit dem strukturgleichen Iridium-Präkursor $[\text{Ir}(\text{cod})\text{Cl}]_2$ zeigte, dass dieser deutlich weniger aktiv ist (vgl. Kapitel 3.4). Die Zugabe eines Überschusses an Quecksilber während der Reaktion führt zur Vergiftung des Katalysators. Dies spricht dafür, dass es sich bei der katalytisch aktiven

Spezies um heterogene Rhodium-Kolloide handelt. Auch $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ ist ein geeignetes Substrat für die Reaktion und kann katalytisch zu cyclischen Produkten umgesetzt werden. Somit stellt die Cyclisierung eine kompetitive Nebenreaktion zur Bildung von Polymeren dar. Auch bei dem Umsatz von $\text{H}_2\text{PhB}\cdot\text{NH}_3$ war die Reaktion des Präkatalysators $[\text{Rh}(\text{cod})\text{Cl}]_2$ langsamer als die des Komplexes $[(\text{POCOP})\text{IrH}_2]$, auf den in Kapitel 4.3 eingegangen werden soll, und es wurden trotz vollständigem Umsatz nur 25% $[\text{HPhBNH}_2]_n$ gebildet.^[44]

3.3.2 Komplexe mit Phosphan-Liganden

Um den Katalysator während der Reaktion homogen in Lösung zu halten, eignen sich vor allem σ -Donor-Liganden. Als solche werden Phosphan-Liganden häufig eingesetzt. Ein Komplex mit zwei *i*Bu₃P-Liganden neben einem Amin-Boran, welches über zwei Wasserstoffatome am Rhodium-Zentrum koordiniert wurde für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ eingesetzt.^[75] Dabei wird $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ als Intermediat während der Reaktion gebildet, welches weiter zu $[\text{H}_2\text{BNMe}_2]_2$ reagiert. Der Rhodium-Komplex **42*i*Bu** (Abbildung 9) bleibt während des gesamten Reaktionsverlaufs homogen in Lösung, denn eine Zugabe von Quecksilber hat keine vermindernde Wirkung auf die Reaktionsgeschwindigkeit. In 1,2-Difluorbenzol sind nach 35 min 100% Umsatz erreicht (5 mol% **42*i*Bu**, 25 °C), was einer TOF von 34 h⁻¹ entspricht. Der Komplex **43*i*Bu** wurde nach der Reaktion isoliert, ist aber kein Teil des Katalysezyklus. Die Bildung des Aminoborans $\text{H}_2\text{B}=\text{NMe}_2$ erfolgt dabei entweder durch N-H Aktivierung gefolgt von B-H Aktivierung oder andersherum. Der Wechsel vom *i*Bu₃P-Liganden zu *i*Pr₃P-Liganden führt zu einer langsameren Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$.^[76] Der Präkatalysator **44*i*Bu** erreicht nach 80 min 100% Umsatz (TOF 15 h⁻¹), wobei das *i*Pr-Analogon **44*i*Pr** ganze 300 min benötigt (TOF 4 h⁻¹). Aber auch mit diesen Katalysatoren wird $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ als Intermediat gebildet. Dies wird durch eine stärkere Interaktion mit den σ -Liganden und einer höheren Stabilität gegenüber der Eliminierung von Wasserstoff begründet. Die Abwinkelung des ML₂ Fragmentes ist durch elektronische Interaktionen unterschiedlich. Dennoch werden die σ -Liganden bei einem Überschuss an Acetonitril dagegen ausgetauscht.

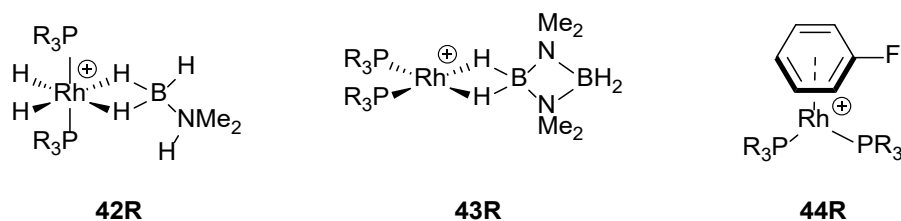


Abbildung 9: Einige der von WELLER *et al.* untersuchten kationischen Rhodium-Komplexe ([BAr^F₄][−] wurde zur besseren Übersicht nicht dargestellt).

3.3.3 Komplexe mit Diphosphan-Liganden

Diphosphane, welche über CH₂-Gruppen verbrückt sind, haben in Abhängigkeit von der Kettenlänge unterschiedliche P-M-P Bindungswinkel (auch: Bisswinkel, engl. *bite angle*). Die höchste Aktivität für die Dehydrokupplung von H₃B·NMe₂H zu [H₂BNMe₂]₂ wurde für Komplexe mit den propylen-verbrückten Liganden (1,3-Bis(diphenylphosphino)propan, dppp) gefunden (TOF 1.250 h^{−1}).^[77] Dieser Ligand hat einen P-M-P Bindungswinkel von etwa 93°. Jedoch wird das höchste Massenmittel der Molmasse für Polymere aus H₃B·NMeH₂ erreicht, wenn der Komplex mit dem butan-verbrückten Liganden dppb (1,4-Bis(diphenylamino)butan) eingesetzt wird (*M_w* = 180.000 g/mol). Während der katalytischen Reaktion bildet sich ein dinuklearer Komplex (**45**, Abbildung 10).^[78] Das *in situ* gebildete Dimer und der mononukleare Komplex zeigen die gleiche Aktivität (TOF 200 h^{−1} THF, TOF 1.000 h^{−1} 1,2-Difluorbenzol), wenn die gleiche Konzentration an Rhodium verwendet wird ([Rh] = 0.5 mol%). Bei dieser Reaktion mit H₃B·NMeH₂ werden lösliche Polymere (*M_w* = 30.600 g/mol, *D* = 2.6) gebildet. In Abhängigkeit von der Katalysatorkonzentration wird ein unterschiedlicher Mechanismus postuliert.^[79] Bei niedrigen Konzentrationen folgt dieser einem Stufenwachstum, bei höheren Konzentrationen hingegen handelt es sich um einen Kettenwachstums-Mechanismus.

Der Xantphos-Ligand bietet einen größeren P-M-P Bindungswinkel von etwa 108 ° und ein starrereres Rückgrat.^[80] In Kombination mit einem Rhodium(I)-Zentrum ist auch dieser Komplex in der Lage die Dehydrokupplung von H₃B·NMeH₂ und H₃B·NMe₂H zu katalysieren.^[81] Mit nur 0,2 mol% Katalysator (**46**) werden Polymere (*M_n* = 22.700 g/mol, *D* = 2.1) aus H₃B·NMeH₂ gebildet, wogegen H₃B·NMe₂H zu [H₂BNMe₂]₂ gekuppelt wird. Stöchiometrische Reaktionen und kinetische Untersuchungen weisen darauf hin, dass beiden Reaktionen ein ähnlicher Mechanismus zugrunde liegt. Dabei handelt es sich vermutlich um ein Kettenwachstum, welches, wie bei der *single site* Olefinpolymerisation durch Insertion vom H₂B=NMeH in die Rhodium-Amido-Bindung abläuft. Höhere Katalysatorkonzentrationen führen daher auch zur Bildung kürzerer Polymerketten. Der Präkatalysator zeigt zu Beginn der

Reaktion eine Induktionsperiode in der die katalytisch aktive Spezies, möglicherweise ein Rhodium-Amido-Boran-Komplex, gebildet wird.

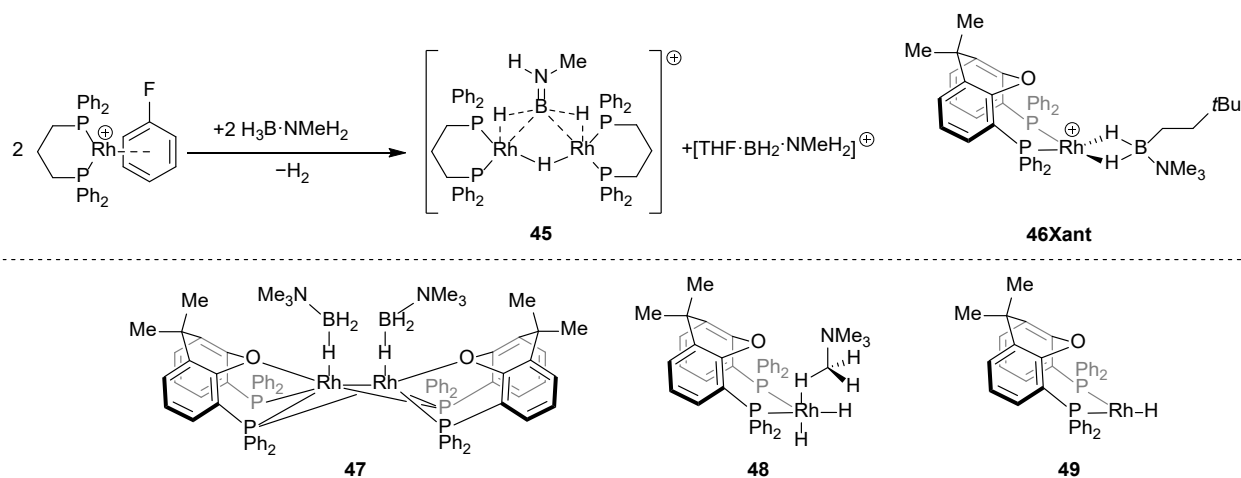


Abbildung 10: Einige der für die Dehydrokupplung von Amin-Boran-Addukten eingesetzten Rhodium-Chelat-Komplexe.

Am Ende der katalytischen Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ wurde eine dimere Rhodium-Spezies isoliert.^[82] Aus diesem Grund wurde ein dinuklearer Rhodium-Komplex (**47**, Abbildung 10) synthetisiert und für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ eingesetzt. Bei der Reaktion wird $\text{H}_2\text{B}=\text{NMe}_2$ als Intermediat beobachtet bevor $[\text{H}_2\text{BNMe}_2]_2$ entsteht ($[\text{Rh}] = 0.2 \text{ mol\%}$, 1.150 h^{-1}). Ein Vergiftungsexperiment mit Quecksilber zeigt, dass der Katalysator während der Reaktion homogen in Lösung bleibt. Außerdem ist der Präkatalysator in der Lage $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ zu Polymeren ($M_n = 28.700 \text{ g/mol}$) umzusetzen. In einer darauf aufbauenden Studie wurden die Substituenten am Phosphor systematisch untersucht. Neben den zuvor verwendeten Phenyl-Derivaten wurden Komplexe mit Ethyl-, *iso*-Propyl- und *tert*-Butyl-Gruppen am Phosphan untersucht.^[83] Die höchste Aktivität wurde mit Rhodium-Komplexen, die *iso*-Propyl-Gruppen am Phosphan haben erreicht ($0.2 \text{ mol\%}$, $\text{TOF } 1.500 \text{ h}^{-1}$). Diese ist für die beiden Präkatalysatoren vom Typ **48** und **49** gleich, jedoch bildet der neutrale Komplex **49** längere Polymerketten aus ($M_n = 28.000 \text{ g/mol}$, $D = 1,9$ vs. $M_n = 9.000 \text{ g/mol}$, $D = 2,9$). Auch für diese Komplexe wird angenommen, dass die Bildung der Polymere einem klassischen Kettenwachstums-Mechanismus folgt. In Abhängigkeit von den Substituenten am Phosphor koordiniert der Liganden auf unterschiedliche Weise. Der Xantphos-Ph-Ligand bevorzugt im Festkörper eine *cis*- κ^2 -P,P Koordinationsgeometrie wogegen der Xantphos-*i*Pr-Ligand über drei Donoren *mer*- κ^3 -P,O,P-koordiniert. Im Vergleich mit den Propylen-verbrückten Diphosphan-Liganden hat der Xantphos-Ligand einen großen P-M-P

Bindungswinkel. Der DPEphos-Ligand ist dagegen weniger rigide in seinem Rückgrat und bietet außerdem einen kleineren Bindungswinkel von 104° .^[80]

Analoge DPEphos-Komplexe zu den Xantphos-Komplexen (**46Xant**) sind ebenfalls in der Lage Polymere aus $\text{H}_3\text{B}\cdot\text{NMeH}_2$ zu bilden ($M_n = 5.500\text{--}34.900$ g/mol, $\bar{D} = 1,5\text{--}1,8$).^[84] Auch hier ist der Zusammenhang von Katalysatorkonzentration (0,1–1 mol%) und Polymermasse antiproportional. Die Zugabe von $\text{NMeH}_2\cdot\text{THF}$ entfernt die Induktionsperiode und führt zu Bildung von Polymeren mit höheren Molmassen ($M_n = 40.000$ g/mol). Im Gegensatz dazu inhibiert das Amin einige Iridium-Komplexe (vgl. Kapitel 3.4). Möglicherweise spielen die Komplexe $[\text{Rh}(\kappa^2\text{-DPEphos})(\text{NMeH}_2)_2][\text{BAR}^{\text{F}}_4]$ und $[\text{Rh}(\kappa^2\text{-DPEphos})(\text{H})_2(\text{NMeH}_2)_2][\text{BAR}^{\text{F}}_4]$ bei dieser Reaktion eine Rolle, denn diese zeigen eine ähnliche Reaktivität und bilden gleiche Produkte, wie bei Zugabe von Amin zum Präkatalysator (**46DPE**). Bei der Reaktion mit 10 mol% **46DPE** werden Hinweise auf eine dimere Aminoboran-verbrückte Spezies $[\text{Rh}_2(\kappa^2\text{-P,P-DPEphos})_2(\mu\text{-H})(\mu\text{-H}_2\text{BN}=\text{HMe})][\text{BAR}^{\text{F}}_4]$ gefunden. Insgesamt unterscheidet sich die Reaktivität der DPEphos- und Xantphos-Komplexe hinsichtlich des Einflusses von Katalysatorkonzentration, Auswirkung von Amin- und Wasserstoff-Zugabe. Weitere Untersuchungen des Präkatalysators **46DPE** zeigten, dass $[\text{Rh}(\text{DPEphos})\text{H}_2]_2$ der Ruhezustand des Katalysezyklus ist.^[85] Das Boronium-Kation $[\text{H}_2\text{B}(\text{NMeH}_2)_2]^+$ fungiert während der Bildung des Polymers als Kettenkontrollreagenz indem das terminale nukleophile Amin protoniert wird und so das Kettenwachstum gestoppt wird. Der $[\text{Rh}(\text{DPEphos})\text{H}_2]_2$ Komplex kann direkt aus $[\text{Rh}(\text{DPEphos})(\text{benzyl})]$ synthetisiert werden. Der dafür verwendete Komplex ist ebenfalls ein geeigneter Präkatalysator und bildet Poly(methylaminoboran) (0,25 mol% Katalysator, $M_n = 15.000$ g/mol, $\bar{D} = 2,5$). Das Xantphos-Derivat bildet Polymere mit höheren Zahlenmitteln der Molmasse (0,1 mol% Katalysator, $M_n = 85.000$ g/mol, $\bar{D} = 1,5$).

3.3.4 Komplexe mit Pincer-Liganden

Neben dem über drei Atome koordinierenden *i*Pr-Xantphos-Liganden wurden noch weitere Pincer-Liganden mit Rhodium-Zentren kombiniert, um aktive Katalysatoren zu bilden. Ausgehend vom Komplex $[(\text{PONOP})\text{Rh}(\text{H}_2)][\text{BAR}^{\text{F}}_4]$ (**50**, Abbildung 11) wurde ein Amin-Boran σ -koordiniert (**51**).^[3b] Wird für diese Reaktion Trimethylamin-Boran verwendet entsteht ein stabiler Komplex (**51**, $n = 3$). Mit Dimethylamin-Boran (**51**, $n = 2$) hingegen erfolgt die Dehydrokupplung zu $[\text{H}_2\text{BNMe}_2]_2$ und es bildet sich der Wasserstoff-Komplex (**50**) zurück. Dieser ist dementsprechend auch gut als Katalysator für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ geeignet (2 mol%, 30 min). Während der Katalyse wurde ein neutraler Hydrido-Komplex als

Intermediat beobachtet. Das Methylamin erfüllt bei der Katalyse zwei Aufgaben. Erstens dient es zur Deprotonierung des σ -Amin-Boran-Komplexes um den neutralen Hydrido-Komplex zu bilden und zweitens die erfolgt die Reprotonierung des Hydrido-Komplexes.

Der Komplex $[(\text{PN}(\text{H})\text{P})\text{Rh}(\text{nbd})]\text{Cl}$ (**52**) bildet selektiv Poly(methylaminoboran) aus $\text{H}_3\text{B}\cdot\text{NMeH}_2$.^[53] Diese Reaktion ist in bemerkenswerter Weise in der Lage bis zu 10 g $\text{H}_3\text{B}\cdot\text{NMeH}_2$ mit nur 0,01 mol% des Katalysators an Luft innerhalb von zwei Stunden umzusetzen. Die Polymere mit dem höchsten Zahlenmittel der Molmasse ($M_n = 78.100 \text{ g/mol}$) werden für niedrige Katalysatorkonzentrationen (0,01 mol%) erhalten. Diese Reaktion zeigt eine Induktionsperiode in welcher der aktive Katalysator, ein Trihydrid-Komplex $[(\text{PN}(\text{H})\text{P})\text{RhH}_3]$, gebildet wird (Abbildung 12). Nach der Katalyse wird der inaktive Komplex $[(\text{PN}(\text{H})\text{P})\text{RhH}_2\text{Cl}]$ gefunden, welcher durch Zugabe von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ wieder zum aktiven Katalysator $[(\text{PN}(\text{H})\text{P})\text{RhH}_3]$ umgesetzt werden kann. Die Molekülstruktur des Präkatalysators zeigt, dass der $\text{PN}(\text{H})\text{P}$ -Ligand *facial* koordiniert.

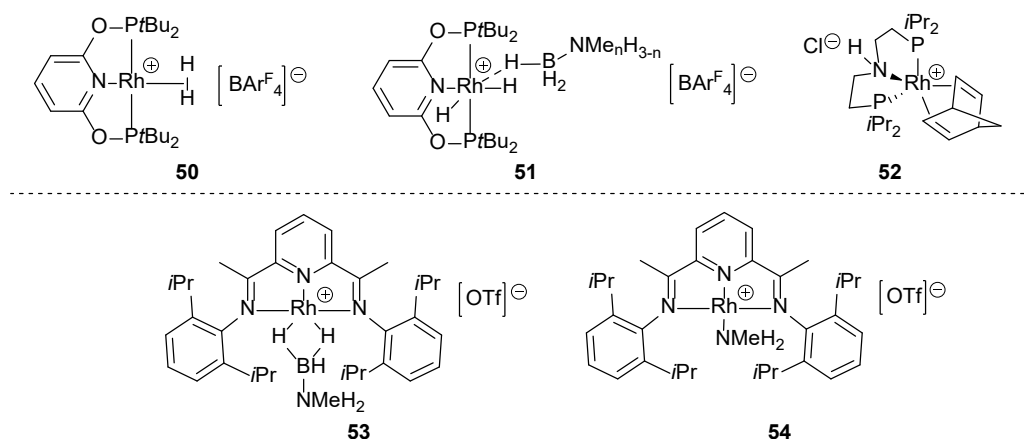


Abbildung 11: Einige der für die Dehydrokupplung von Amin-Boran-Addukten eingesetzten Rhodium-Pincer-Komplexe.

Der PSCSP-Ligand ($\text{C}_6\text{H}_4\text{-2,6-S}(\text{PR}_2)$, $\text{R} = i\text{Pr, Ph}$) kann mit $[\text{Rh}(\text{cod})\text{Cl}]_2$ in Gegenwart von Pyridin zu Rhodium(III)-Komplexen $[(\text{PSCSP})\text{Rh}(\text{py})(\text{H})(\text{Cl})]$ umgesetzt werden.^[4] Diese Komplexe katalysieren die Bildung von Polymeren aus $\text{H}_3\text{B-NMeH}_2$. Dabei wurde gezeigt, dass die B-N-Bindungsspaltung dabei ein wichtiger Prozess ist. Das dabei gebildete BH_3 -Addukt inhibiert die Reaktion. Die Zugabe von Amin entfernt die Induktionsperiode, indem das Boran entfernt wird.

Auch Pincer-Komplexe mit ausschließlich Stickstoff-Donoratomen können Rhodium koordinieren.^[86] Der Bis(imino)pyridin-Komplex (**53**) bildet bei einer Konzentration von 1 mol% aus H₃B·NMeH₂ selektiv Poly(methylaminoboran). Die Zugabe von Methylamin oder

die direkte Verwendung des entsprechenden Amin-Komplexes **54** ist jedoch notwendig, um die Reaktion zu starten. Auch diese Reaktion verläuft vermutlich über einen neutralen Hydrido-Komplex. Unter Verwendung von 0,025 mol% (**54**) können 2 g $\text{H}_3\text{B}\cdot\text{NMeH}_2$ zu Polyaminoboran ($M_n = 30.900 \text{ g/mol}$, $D = 1,8$) umgesetzt werden. Am Ende der Katalyse werden Rhodium-Nanopartikel (1-5 nm) beobachtet, welche zu einem großen Teil vom Polymer getrennt werden können.

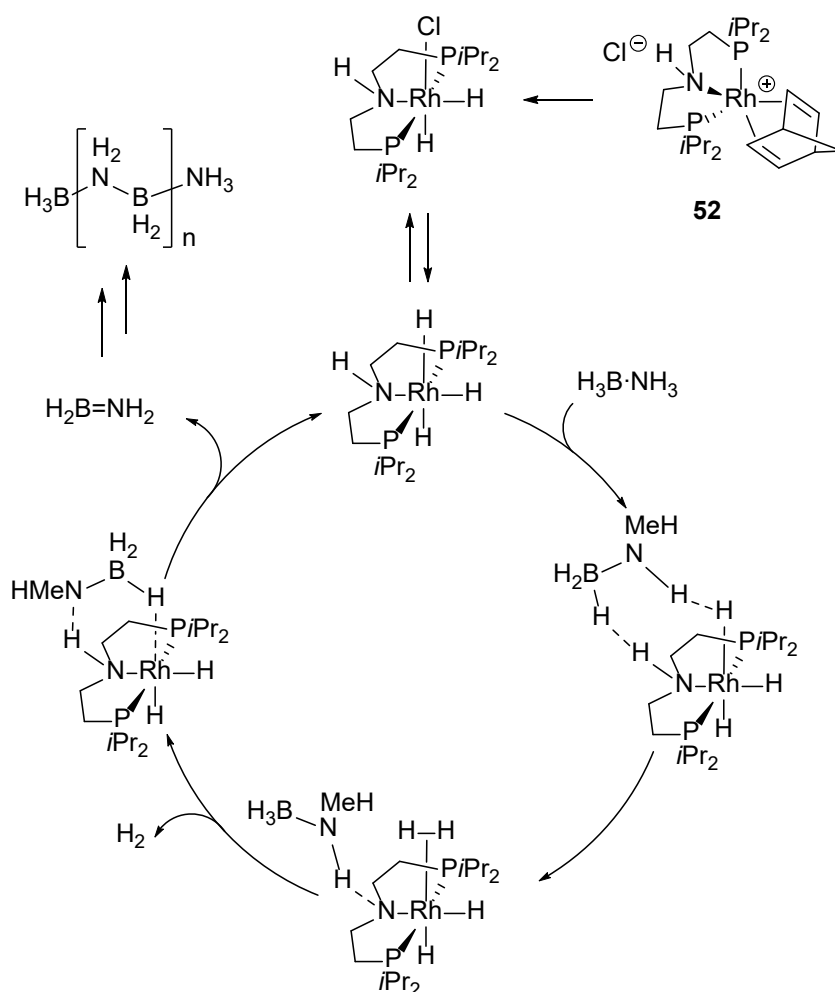


Abbildung 12: Der von WELLER *et al.* vorgeschlagene Katalysezyklus für die Dehydropolymerisation von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ mit dem Komplex $[(\text{PN}(\text{H})\text{P})\text{Rh}(\text{nbd})]\text{Cl}$ (**52**).^[53]

In eigenen Untersuchungen wurden Pyrazol-basierte PNN-Liganden mit einer NH-Funktionalität ausgewählt und zusammen mit Rhodium-Präkursoren zu Komplexen umgesetzt (siehe Anlage 1). Unter Verwendung des PNN(H)-Liganden, in dem diese Funktionalität an dem nicht koordinierenden Stickstoffatom im Pyrazol-Ring sitzt, werden verzerrt quadratisch planare Komplexe mit einem Chloridoliganden am Rhodium-Zentrum gebildet.^[87] Die Komplexe wurden für die katalytische Dehydropolymerisation von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ eingesetzt.

Jedoch benötigt die Reaktion 40 h um vollständigen Umsatz zu erreichen. Dabei wird Borazan als Hauptprodukt gebildet. Die Zugabe von KOtBu beschleunigt die Reaktion, wohingegen Boran und Boronium-Ionen die Aktivität herabsetzen.

In einer weiteren Studie wurden Rh(I) -Komplexe mit verwandten Imidazol-basierten PN(H)N -Pincer-Liganden untersucht. Der PN(H)N -Ligand trägt diese Funktionalität am zentralen Stickstoff-Donor und koordiniert facial in einer pseudo-oktaedrischen Koordinationsgeometrie (siehe Anlage 5). In diesen Komplexen vom Typ $[(\text{PN(H)N})\text{Rh}(\text{diolefin})]^+$ ist das Diolefin der einzige weitere Ligand. Das Gegenanion, Chlorid oder BF_4 , interagiert über Wasserstoffbrücken mit der NH -Funktionalität, befindet sich aber in der sekundären Koordinationssphäre. Diese Komplexe wurden für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ und $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ eingesetzt. Dabei zeigen sie keine hohe Aktivität. Diese kann, anders als bei den PNN(H) -Komplexen jedoch nicht durch Zugabe von KOtBu erhöht werden. Wird $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ als Substrat verwendet, beschleunigt die Zugabe von KOtBu die Reaktion. Borazan wird wieder als Hauptprodukt beobachtet.

3.4 Iridium-Komplexe für die Dehydrokupplung von Amin-Boran-Addukten

Zusammen mit dem in Kapitel 3.3.1 erwähnten Rhodium-Dimer wurde auch $[\text{Ir}(\text{cod})\text{Cl}]_2$ für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ getestet.^[74] Der Rhodium-Komplex erreicht nach 8 h unter diesen Bedingungen 100% Ausbeute, wogegen der Iridium-Komplex auch nach 136 h erst 95% umgesetzt hat. Der vielfach in der Transfer-Dehydrierung von Alkanen eingesetzte Pincer-Komplex $[(\text{POCOP})\text{IrH}_2]$ (**55**) ist deutlich reaktiver und setzt innerhalb von 14 min ein Äquivalent Wasserstoff aus $\text{H}_3\text{B}\cdot\text{NH}_3$ frei.^[88] Als die Ergebnisse in 2006 von MANNERS *et al.* veröffentlicht wurden war dies der aktivste bekannte Katalysator für diese Reaktion. Ein Vergiftungsexperiment mit Quecksilber ergab, dass der Katalysator während der Reaktion homogen in Lösung bleibt. Bei der Reaktion wird ein weißer Feststoff gebildet, der analysiert wurde.^[50b] Dabei handelt es sich um unlösliche Polymere, die über IR-Spektroskopie und Weitwinkel-Röntgenstreuung (WAXS, *wide-angle X-ray scattering*) charakterisiert wurden. In weiteren Untersuchungen konnte gezeigt werden, dass Komplex **55** auch in der Lage ist $\text{H}_3\text{B}\cdot\text{NMeH}_2$ und ein Gemisch aus $\text{H}_3\text{B}\cdot\text{NH}_3$ und $\text{H}_3\text{B}\cdot\text{NMeH}_2$ zu dehydrokuppeln.^[89] Bei dem Produkt aus $\text{H}_3\text{B}\cdot\text{NMeH}_2$ handelt es sich trotz der guten Löslichkeit um ein Polymer.^[50b] Auch

die Produkte der Copolymerisation sind löslich und können als weitere Hinweise für die polymere Struktur des aus $\text{H}_3\text{B}\cdot\text{NH}_3$ gebildeten Produktes betrachtet werden. In einer darauf aufbauenden Untersuchung wurden die Polymere zusätzlich über Elektrosprayionisation-Massenspektroskopie (ESI-MS) analysiert.^[45] Diese Analysen bestätigten, dass es sich um lineare Polymere handelt, wobei das unlösliche Produkt aus $\text{H}_3\text{B}\cdot\text{NH}_3$ nur aus ungefähr 20 Monomer-Einheiten besteht. Höhere Katalysatorkonzentrationen führen zu Polymeren mit höheren Molmassen. Aus diesem Grund war es besonders überraschend, dass die Polymerisation nach einem Kettenwachstumsmechanismus abläuft und schon nach 40% Umsatz Polymere mit hohen Molmassen gebildet werden. Es wird angenommen, dass die Katalyse über einen zweistufigen Prozess abläuft. In der ersten Stufe wird $\text{H}_3\text{B}\cdot\text{NMeH}_2$ dehydriert und es entsteht $\text{H}_2\text{B}=\text{NMeH}$, welches im nächsten Schritt mit demselben Katalysator polymerisiert. Neben den vielfach untersuchten, am Stickstoff substituierten Amin-Boran-Addukten kann Komplex **55** auch Polymere mit hohen Molmassen aus $\text{H}_2\text{PhB}\cdot\text{NH}_3$ und $\text{H}_2(p\text{-CF}_3\text{C}_6\text{H}_4)\text{B}\cdot\text{NH}_3$ bilden.^[44] In einer detaillierten Folgeuntersuchung wurden von MANNERS und Mitarbeitern eine Reihe unterschiedlicher Präkatalysatoren für die Reaktion getestet und herausgefunden, dass Pincer-Liganden nicht notwendig für die Polymerisation sind, aber die höchste Reaktivität aufweisen.^[45]

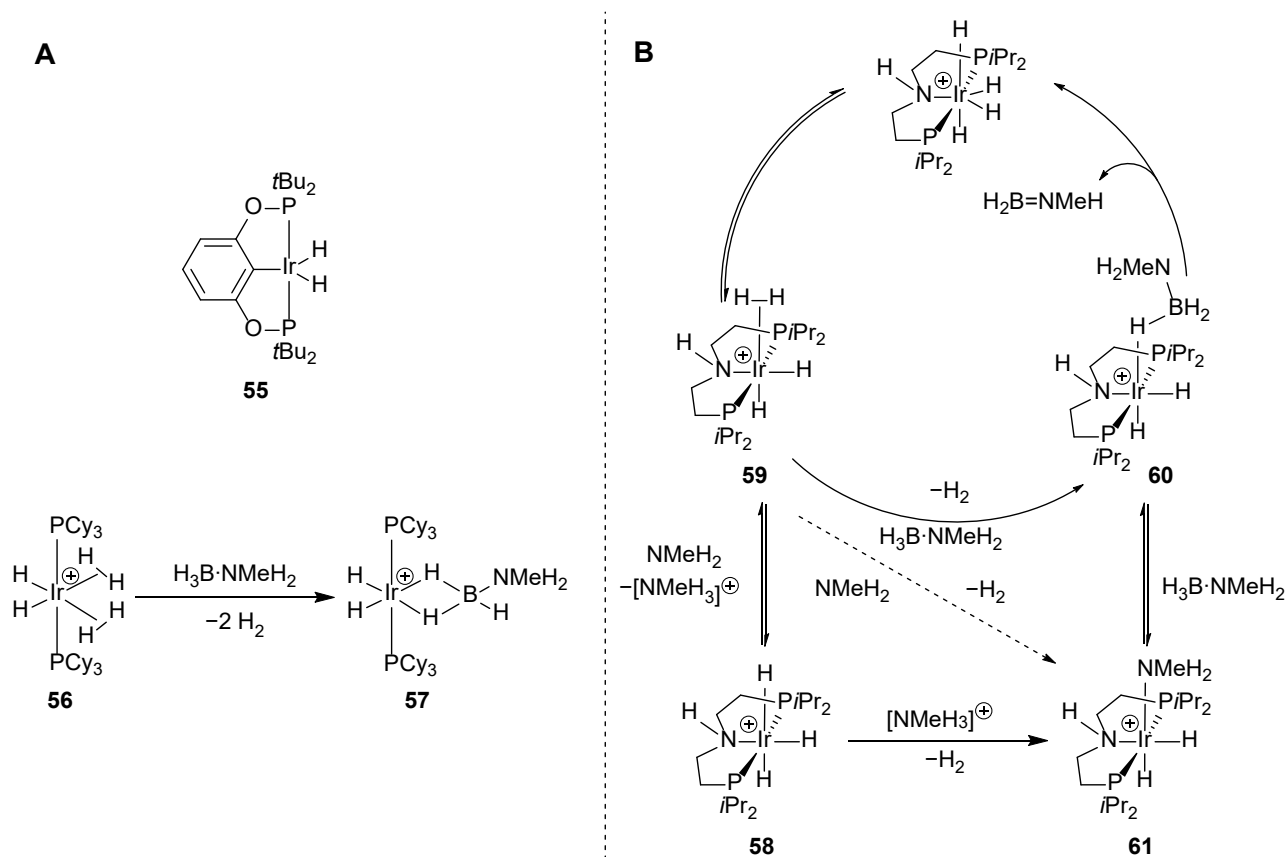


Abbildung 13: Einige Iridium-Komplexe (**A**)^[90] und der von WELLER *et al.* vorgeschlagene Katalysezyklus für die Dehydropolymerisation von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ mit dem Komplex $[(\text{PN}(\text{H})\text{P})\text{Ir}(\text{H}_2)(\text{H})_2]$ (**B**).^[91]

Ein Beispiel für einen Iridium-Komplex ohne Pincer-Liganden, der die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ langsam katalysiert ist der Dihydrido-Diwasserstoff-Komplex $[(\text{PCy}_3)_2\text{Ir}(\text{H})_2(\text{H}_2)_2]$ (**56**).^[90] Ein vollständiger Umsatz des Substrats wird erst nach etwa fünf Tagen mit 10 mol% Katalysatorkonzentration erreicht. Durch die lange Reaktionszeit kann die Reaktion mit spektroskopischen Methoden verfolgt werden und die Insertion des Substrates zum ersten Mal beobachtet werden. Die Zugabe eines Äquivalents $\text{H}_3\text{B}\cdot\text{NMeH}_2$ zu dem Komplex führt zur Bildung eines Hydrid-verbrückten Iridium-Boran-Komplexes (**57**) unter Bildung von zwei Äquivalenten Wasserstoff. Die Zugabe eines weiteren Äquivalentes $\text{H}_3\text{B}\cdot\text{NMeH}_2$ ermöglicht eine erste Insertion und somit die Bildung von $\text{H}_3\text{B}\cdot\text{NMeHBH}_2\cdot\text{NMeH}_2$ am Metall-Zentrum, welches außerdem das Hauptprodukt der katalytischen Reaktion ist.

Analog zu den in den Kapiteln 3.3.4 und 3.5 beschriebenen $[(\text{PN}(\text{H})\text{P})\text{Ru}/\text{Rh}]$ -Komplexen wurden von WELLER und Mitarbeitern Iridium-Komplexe mit dem gleichen Liganden synthetisiert.^[91] Erstaunlicherweise zeigen die beiden neutralen Komplexe $[(\text{PN}(\text{H})\text{P})\text{IrH}_3]$ (**58**) und $[(\text{PN}(\text{H})\text{P})\text{IrH}_2\text{Cl}]$ (**5**) keine Aktivität für die Dehydropolymerisation von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ bei 25 °C in 1,2-Difluorbenzol. Die kationischen Komplexe $[(\text{PN}(\text{H})\text{P})\text{Ir}(\text{H}_2)(\text{H})_2][\text{BArF}_4]$ (**59**), $[(\text{PN}(\text{H})\text{P})\text{Ir}(\text{H})_2(\text{H}_3\text{BNMe}_3)][\text{BArF}_4]$ (**60**) und $[(\text{PN}(\text{H})\text{P})\text{Ir}(\text{H})_2\text{NMeH}_2][\text{BArF}_4]$ (**61**) sind hingegen aktiv und erzeugen Poly(methylaminoborane) ($M_n = 40.000 \text{ g/mol}$). DFT-Rechnungen liefern einen Erklärungsansatz für diese Beobachtung, da die Energiebarriere für einen Mechanismus unter Einbeziehung kationischer Intermediate etwas niedriger ist (22,5 kcal/mol vs. 24,3 kcal/mol). Es handelt sich um einen sogenannten *inner-sphere* Mechanismus ohne die für Eisen-,^[92] Rhodium-^[53] und Ruthenium-Komplexe^[93] gefundene Metall-Ligand-Kooperativität. Zusätzlich zu den Berechnungen wurde dies durch die Verwendung eines am zentralen N-Donor methylierten Präkatalysators belegt. Dieser ist nicht in der Lage das Substrat kooperativ zu binden, zeigt aber trotzdem katalytische Aktivität. Die Zugabe von NMeH_2 hat im Gegensatz zu den Reaktionen mit den analogen Rhodium-Präkatalysatoren (vgl. Kapitel 3.3.4) eine inhibierende Rolle, da es die Bildung von inaktiven neutralen $[(\text{PN}(\text{H})\text{N})\text{IrH}_3]$ Komplexen begünstigt (Abbildung 13B). Ausgehend von diesem neutralen Komplex kann die Dehydropolymerisation durch Zugabe von Ammoniumsalzen wie $(\text{NMeH}_3)(\text{BArF}_4)$ gestartet werden. Diese Untersuchungen zeigen eindeutig, dass die Katalyse in Abhängigkeit von der Metall/Ligand-Kombination unterschiedlichen Mechanismen folgt

(vgl. Kapitel 3.3.4 Abbildung 12). Für Rhodium wurde gezeigt, dass neutrale Katalysatoren wie $[(\text{PN}(\text{H})\text{N})\text{Rh}(\text{H})_3]$, die über einen Mechanismus mit Metall-Ligand- Kooperativität reagieren, begünstigt sind.

Im Rahmen dieser Arbeit wurden Iridium-PN(H)N-Komplexe mit Imidazol-basierten Liganden untersucht (siehe Anlage 5), da die Reaktivität von Rhodium- und Iridium-Komplexen bei der Dehydrokupplung von Amin-Boran-Addukten gegenläufig ist. So waren ionische Rhodium-Komplexe bisher nicht sehr reaktiv, wogegen ionische Iridium-Komplexe eine hohe Aktivität zeigten. Auch im hier untersuchten Fall koordiniert der PN(H)N-Ligand facial in einer pseudo-oktaedrischen Koordinationsgeometrie an das Iridium-Zentrum. Diese ionischen Komplexe sind isostrukturell zu den Rhodium-Komplexen. Dennoch zeigen sie in der Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMeH}_2$ und $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ eine geringere Aktivität als die Rhodium-Komplexe.

3.5 Ruthenium-Komplexe für die Dehydrokupplung von Amin-Boran-Addukten

Eines der ersten Beispiele dafür, dass auch Ruthenium-Komplexe in der Lage sind Amin-Boran-Addukte umzusetzen wurde von MANNERS *et al.* beschrieben.^[74] Der Komplex *trans*- $[\text{RuMe}_2(\text{PMe}_3)_4]$ setzt $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ bei 25 °C bei einer Katalysatorkonzentration von 0,5 mol% innerhalb von 16 Stunden vollständig zu $[\text{H}_2\text{BNMe}_2]_2$ um. Einige Jahre später konnte von FAGNOU und Mitarbeitern gezeigt werden, dass die aus der Oxidation und Reduktion von Alkoholen bekannten Ruthenium-Amido-Komplexe (**62-64**, Abbildung 14) nach Aktivierung mit 30 Äquivalenten KO^{*t*}Bu Poly(aminoborane) erzeugen können.^[94] Bei einer Konzentration von 5 M $\text{H}_3\text{B}\cdot\text{NH}_3$ in THF wird ein weißes unlösliches Polymer gebildet. Der Phenyl-substituierte Komplex (**64**) ist am wenigsten reaktiv und benötigt daher höhere Katalysatorkonzentrationen. Der *iso*-Propyl-Präkatalysator (**62**) setzt bei einer Konzentration von 0,5 mol% ein Äquivalent Wasserstoff in nur 10 s aus $\text{H}_3\text{B}\cdot\text{NMeH}_2$ frei. Ein weiteres Äquivalent Wasserstoff wird nach 10 Minuten gebildet.

Die Bildung von Poly(methylaminoboran) mit diesem Katalysator bei 20 °C in THF konnte in Folgeuntersuchungen nicht reproduziert werden.^[45] Der Komplex reagiert auch mit Poly(methylaminoboran) unter Bildung von Wasserstoff und Borazin. Daher wird angenommen, dass der Präkatalysator (**62**) bei diesen Bedingungen zu reaktiv ist und die Bildung von Polymeren wurde bei -20 °C durchgeführt, wodurch Polymere

($M_w = 89.000 \text{ g/mol}$) isoliert werden konnten. Folgeuntersuchungen von WELLER und Mitarbeitern zeigten, dass der Komplex $[\text{RuCl}_2(\text{iPr}_2\text{PCH}_2\text{CH}_2\text{NH}_2)_2]$ (**62**) nicht katalytisch aktiv ist. Dieser kann jedoch mit zwei Äquivalenten KO^tBu oder NMeH_2 aktiviert werden und bildet dabei den Katalysator $[\text{Ru}(\text{iPr}_2\text{PCH}_2\text{CH}_2\text{NH})_2]$.^[95] Nach einer Induktionsperiode, in der Reste an Wasser unter der Bildung von $[\text{RuH}(\text{OH})(\text{iPr}_2\text{PCH}_2\text{CH}_2\text{NH}_2)_2]$ abreagieren, werden aus $\text{H}_3\text{B}\cdot\text{NMeH}_2$ Polymere gebildet ($M_n = 138.700 \text{ g/mol}$). Diese Reaktion zeigt eine der höchsten TOFs (270 s^{-1}) bei Verwendung von nur $0,03 \text{ mol\%}$ Präkatalysator. Wird getrocknetes THF als Lösungsmittel verwendet, wird keine Induktionsperiode bei der Katalyse beobachtet. Auch der durch Reaktion mit Wasser entstehende Komplex $[\text{RuH}(\text{OH})(\text{iPr}_2\text{PCH}_2\text{CH}_2\text{NH}_2)_2]$ ist ein geeigneter Präkatalysator, welcher jedoch eine sehr lange Induktionsperiode aufweist.

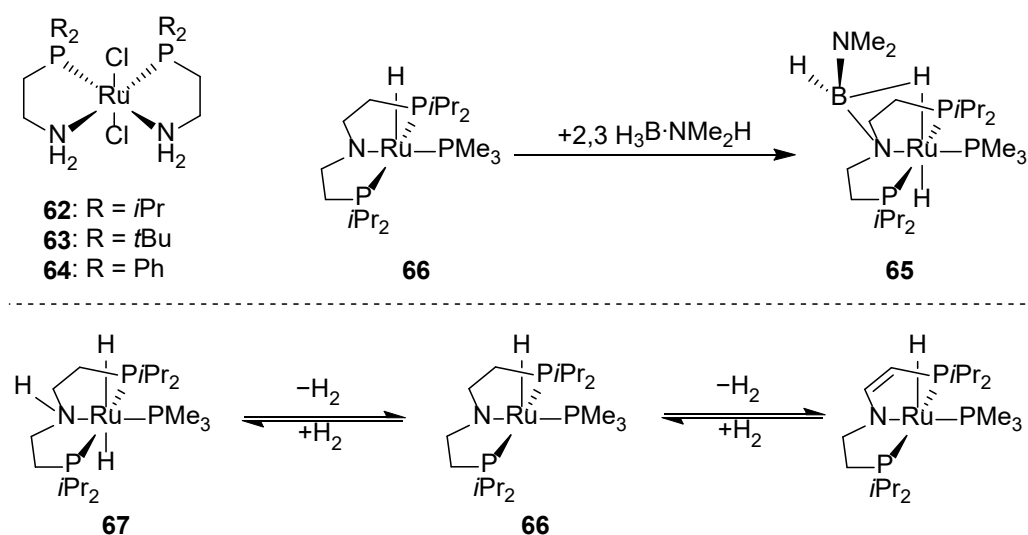


Abbildung 14: Einige der für die Dehydrokupplung von Amin-Boran-Addukten eingesetzten Ruthenium-Komplexe.

Der bereits in den voran gegangenen Kapiteln beschriebene kooperative Pincer-Ligand $(\text{iPr}_2\text{PCH}_2\text{CH}_2)_2\text{NH}$ wird verwendet, um einen Hydrido-Ruthenium-Komplex zu bilden, welcher in wenigen Sekunden ein Äquivalent Wasserstoff aus $\text{H}_3\text{B}\cdot\text{NH}_3$ freisetzt.^[96] Die Zugabe von Quecksilber führt zu keiner verminderten Reaktivität, weshalb davon ausgegangen wird, dass der Katalyse ein homogener Mechanismus zugrunde liegt. Auch die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ ist möglich.^[97] Bei dieser Reaktion wird eine TOF von bis zu 3.600 h^{-1} erreicht, das System wird aber schon nach einigen Sekunden langsamer bevor ein Äquivalent Wasserstoff entstanden ist. Ein vollständiger Umsatz des Substrates wird erst nach 28 h erreicht. Die Reaktivität an diesem Punkt ($\text{TOF } 1,5 \text{ h}^{-1}$) der Katalyse entspricht der Reaktivität des Ruthenium-Aminoboran-Komplexes (**65**), welcher durch Zugabe von 2,3

Äquivalenten zum Präkatalysator (**66**) synthetisiert werden kann. Während der Reaktion wird $[\text{H}_2\text{BNMe}_2]_2$ als Hauptprodukt neben $(\text{Me}_2\text{N})_2\text{BH}$ gebildet. Zusätzlich können während der Katalyse $\text{H}_2\text{B}=\text{NMe}_2$ und $\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H}$ als Intermediate beobachtet werden. Mit $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ als Substrat werden Polymere gebildet, welche mit einer Ausbeute von 90% isoliert werden können ($M_w = 460.000 \text{ g/mol}$).^[14] Der Ru-Amin-Hydrid-Komplex (**67**) wurde *in situ* generiert und für die Katalyse eingesetzt, da sich der Komplex nicht isolieren lässt.^[93] Über DFT-Rechnungen wurde gezeigt, dass der Amin-Wasserstoff eine wichtige Rolle bei der Koordination des Substrates und somit der Kooperativität des Liganden spielt. Wird diese Position methyliert liegen die Übergangszustände und Intermediate energetisch ca. 10 kcal/mol höher. Für den Mechanismus der Reaktion wird postuliert, dass es sich um zwei verbundene Katalysezyklen handelt (Abbildung 15), wobei zum einen die Bildung des $\text{H}_2\text{B}=\text{NMeH}$ und andererseits die Polymerisation dieses Intermediates ablaufen. Die Bildung linearer Produkte hat eine solch geringe Aktivierungsenergie, dass fast ausschließlich lineare Polymere gebildet werden. Dennoch ist der methylierte Präkatalysator in der Lage $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ zu Polymeren umzusetzen (71% isolierte Ausbeute, $M_w = 344.000 \text{ g/mol}$), wenngleich Ausbeute und Polymerlänge etwas geringer ausfallen.^[45] Um Poly(aminoborane) mit Ruthenium-Komplexen zu bilden ist es nicht notwendig dass es sich um einen Pincer-Komplex handelt, wenngleich diese höhere Aktivitäten aufweisen.^[45]

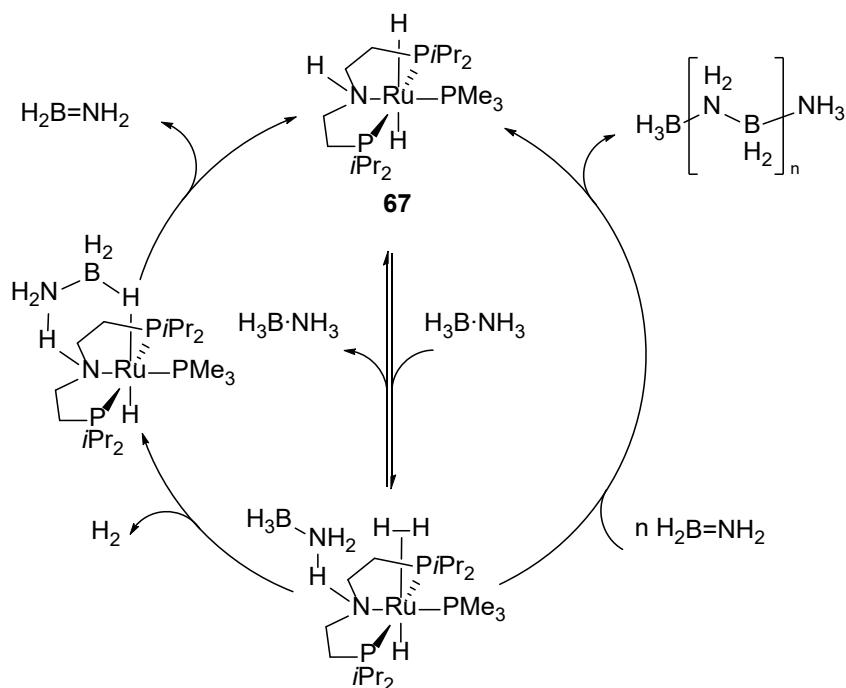


Abbildung 15: Der von SCHNEIDER *et al.* vorgeschlagene Katalysezyklus für die Dehydrokupplung von $\text{H}_3\text{B}\cdot\text{NH}_3$ mit dem $[(\text{PN}(\text{H})\text{P})\text{RuH}_2(\text{PMe}_3)]$ Komplex (**67**).^[93]

Mit dem Imidazol-basierten PN(H)N-Liganden wurden auch Ruthenium-Komplexe gebildet (siehe Anlage 5). Bei diesen koordiniert der Ligand ebenfalls facial an das Metallzentrum. Diese Komplexe zeigen eine verzerrt-oktaedrische Koordinationsgeometrie, in der darüber hinaus ebenfalls ein Carbonyl-, Hydrido- und Triphenylphosphanligand am Metall-Zentrum koordinieren. Auch hier liegt das Chlorid in der sekundären Koordinationssphäre vor. Diese Komplexe katalysieren die Dehydrokupplung von Amin-Boran-Addukten langsam. Die Zugabe von KOtBu führt zu einer deutlichen Erhöhung der katalytischen Aktivität. Dadurch werden außerdem Poly(aminoborane) mit einer Ausbeute von ca. 50% ($M_n = 7.800 \text{ g/mol}$) gebildet. Ohne Verwendung von Base beträgt die Ausbeute nur etwa 10% mit deutlich geringerer Molmasse ($M_n = 4.200 \text{ g/mol}$).

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5 Liste der Publikationen

Die Originalpublikationen, welchem im Rahmen dieser kumulativen Dissertation veröffentlicht wurden, sind im folgenden Kapitel beigelegt. Der eigene Anteil an den Publikationen ist gesondert gekennzeichnet.

Anlage 1: Mirko Rippke, Hans-Joachim Drexler, Torsten Beweries, *Eur. J. Inorg. Chem.* **2023**, 26, e202300463.

“Rhodium(I) PNN Pincer Complexes with Proton-responsive Ligands: Synthesis, Characterisation, and Catalytic Dehydrocoupling of Amine Boranes”

Die experimentellen Arbeiten und die Auswertung der analytischen Daten, mit Ausnahme der Röntgenkristallstrukturanalytik wurden von mir durchgeführt. Der eigene Anteil liegt bei 70%.

Anlage 2: Hanan Al Hamwi, Mirko Rippke, Kevin Lindenau, Anke Spannenberg, Martin Lamac, Fabian Reiß, Torsten Beweries, *Chem. Eur. J.* **2025**, e202500857.

„The Dinuclear Zirconocene Complex [(Cp₂Zr)₂(μ-Me)(μ-C₂Ph)] as a Platform for Small Molecule Activation”

Die Synthese des dinuklearen Zirconocenkomplexes wurde von mir entwickelt und erste Reaktivitäten wurden untersucht. Mein Anteil an der Arbeit beträgt 20%.

Anlage 3: Mirko Rippke, Ximei Tian, Fabian Reiß, Lipeng Wu, Torsten Beweries, *Chem. Eur. J.* **2025**, 31, e202403982.

“Dehydrocoupling of Ammonia/Amine Boranes and Related Transformations Catalysed by Group 4 Metal Complexes”

Die Kapitel über die Dehydrokupplung von Amin-Boran-Addukten wurden von mir recherchiert und das Manuskript entwickelt. Mein Anteil beträgt 30%.

Anlage 4: Kushik, Mirko Rippke, Hans-Joachim Drexler, Fabian Dankert, Christian Hering-Junghans, Torsten Beweries, *Chem. Eur. J.* **2025**, e202500857.

„Coordination and C-H Activation of a Amidobis(phosphaalkene) Ligand at Rhodium (I)“

Die Rhodium-Komplexe wurden von mir erstmals synthetisiert und kristallisiert. Mein Anteil liegt bei 30%.

Anlage 5: PNN-Type Pincer Imidazolylphosphine Complexes of Late Transition Metals for the Catalytic Dehydrocoupling of Amine Boranes: Mirko Rippke, Marie-Sophie Lenz, Annika Queißer, Marcus Klahn, Hans-Joachim Drexler, Torsten Beweries *Eur. J. Inorg. Chem.* **2025**, 28, e202500364.

„PNN-Type Pincer Imidazolylphosphine Complexes of Late Transition Metals for the Catalytic Dehydrocoupling of Amine Boranes“

Die experimentellen Arbeiten und die Auswertung der analytischen Daten, mit Ausnahme der Röntgenkristallstrukturanalytik wurden von mir durchgeführt. Der eigene Anteil liegt bei 70%.



Rhodium(I) PNN Pincer Complexes with Proton-responsive Ligands: Synthesis, Characterisation, and Catalytic Dehydrocoupling of Amine Boranes

Mirko Rippke,^[a] Hans-Joachim Drexler,^[a] and Torsten Beweries^{*,[a]}

Coordination of a pyridine-pyrazole-based PNN(H) ligand to Rh^I produces a family of neutral (1) and cationic (2Cl) Rh^I complexes. Deprotonation of the parent Rh chloride complex with LiNtPr₂ results in formation of a dinuclear LiCl bridged species 3 bearing a pyrazolate fragment. Complexes 1, 2Cl and 3 were tested as precatalyst for the dehydrocoupling of amine boranes. All complexes studied show activity for the formation

of cyclic oligomers with *N*-methylcyclotriborazane as the main product. Base activation of the neutral Rh chloride complex 1 produces catalyst systems that are significantly more active than the parent system, suggesting that dehydrohalogenation of the Rh chloride precatalyst 1 is one of the key steps for catalyst formation.

Introduction

Over the past 20 years tridentate pincer ligands have been applied for a wide range of stoichiometric and catalytic bond activation reactions.^[1] While pioneering work on PCP based systems^[2] mainly focused on the advantageous rigidity of the ligand and the associated high thermal stability, in recent years so-called cooperative ligands have been developed, which activate the substrate in concert with the transition metal.^[3] This so-called outer-sphere substrate activation has been demonstrated for a wide variety of substrates, including amine boranes H₃B-NMe_nH_{3-n} (*n*=0–2), commonly referred to as isoelectronic main group analogues of alkanes with great potential for the construction of oligomeric, polymeric and heterogeneous B–N materials.^[4,5]

The iron complex [Fe(N(CH₂CH₂PiPr₂)₂)(H)(CO)], often studied for organic transformations, is an excellent precatalyst for the dehydropolymerisation of ammonia borane, H₃B-NH₃,^[6] its singly methylated analogue H₃B-NMeH₂, silyl functionalised derivatives, and hydrazine borane (Figure 1a).^[7] Recently, Weller and co-workers showed that the same aliphatic PN(H)P pincer ligand NH(CH₂CH₂PiPr₂)₂ forms a highly active and air-tolerant cationic Rh^I precatalyst that can be used for the production of processable poly(aminoborane)s from H₃B-NMeH₂ on scale (Fig-

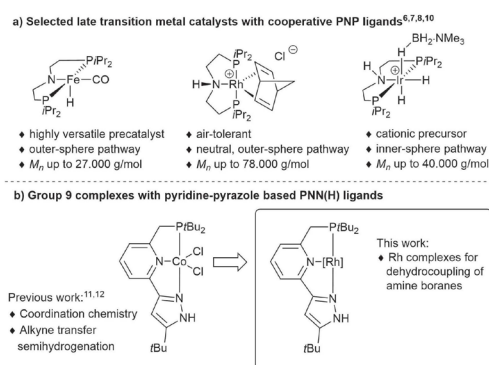


Figure 1. Contextualisation of the present work.

ure 1a).^[8] Mechanistic analysis supports a scenario in which the cooperative pincer ligand is key to outer-sphere dehydrogenation at neutral Rh^{III} trihydride, releasing the dehydrogenated product aminoborane H₂B-NMeH, followed by chain propagation via nucleophilic head-to-tail attack of metal-bound oligomer to H₂B-NMeH.^[9] Of note, the structurally related neutral PN(H)P Iridium(III) trihydride complex is a poor catalyst that can be activated by transformation into a cationic species that dehydrogenates the amine borane via an inner-sphere mechanism (Figure 1a).^[10]

This observation of significant differences when changing the metal using the identical pincer ligand prompted us to investigate the influence of other potentially cooperative phosphine-based ligands in combination with group 9 metals. Based on previous work on a Co system bearing a pyridine-pyrazole PNN(H) ligand, that was initially reported by Caulton and co-workers,^[11] for catalytic transfer semihydrogenation of alkynes using H₃B-NH₃ as the hydride source,^[12] we now present the coordination chemistry of this ligand at Rh^I along with a

[a] M. Rippke, Dr. H.-J. Drexler, Prof. Dr. T. Beweries
Leibniz-Institut für Katalyse e.V.
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
E-mail: torsten.beweries@catalysis.de
Homepage: <http://www.catalysis.de/en/research/coordination-chemistry-and-catalysis>

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study of selected complexes for the dehydrocoupling of amine boranes (Figure 1b). The pyrazole moiety was chosen as a highly versatile functional group that can not only act as a proton shuttle during dehydrogenation of the amine borane or as a directing group for controlling the B–N bond formation event during oligomerisation via hydrogen bonding, but also undergo ligand-to-metal tautomerisation (i.e., from a square planar L(H)–M to an octahedral L–M(H) complex) to produce a potentially active Rh^{III} hydride species.^[13]

Results and Discussion

Synthesis and characterisation of Rh PNN(H) complexes

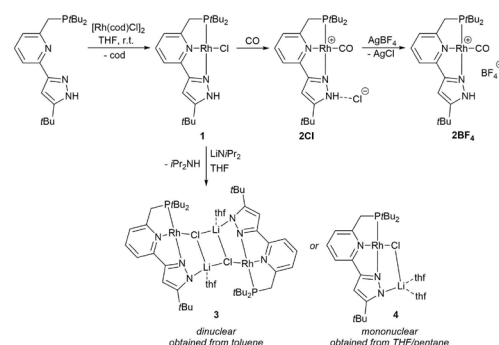
Reaction of the PNN(H) ligand with [Rh(cod)Cl]₂ (cod = 1,5-cyclooctadiene) in THF results in the immediate formation of complex **1** (Scheme 1), indicated by a colour change from yellow to dark red. Complex **1** can be isolated and recrystallised in excellent yields from diethyl ether/THF.^[14] The molecular structure of the benzene solvate (Figure 2, left) shows the Rh centre in distorted square planar coordination environment (Rh1–Cl1 2.3475(9) Å, $\tau_4 = 0.17^{[15]}$) with the phosphorus atom being located above the plane defined by the metal, the pyridine and the pyrazole nitrogen atoms by 0.205(4) Å. In solution, both *t*Bu groups on phosphorus are equivalent, which

is also reflected in the ¹H NMR spectrum where a doublet is found at δ 1.41 ppm. The pyrazole proton resonates as a broad singlet at 12.48 ppm, suggesting acidic behaviour. In the ³¹P{¹H} NMR spectrum a doublet is found at δ 87.3 ppm ($J_{\text{Rh,P}} = 197.8$ Hz). Metal-ligand tautomerism, producing a Rh^{III} hydride species, as it was observed for Ir complexes bearing a related bis(pyrazole) based NNN pincer ligand^[13] was not observed in this complex.

Admission of CO to a benzene solution of **1** furnishes the cationic carbonyl complex **2Cl** (Scheme 1) which is characterised by an intense CO vibration at 1988 cm^{−1}, indicating significant back-donation from the Rh^I pincer scaffold, and a downfield shift of the ³¹P{¹H} resonance to δ 97.7 ppm ($J_{\text{Rh,P}} = 153.8$ Hz). Hydrogen bonding of the pyrazole N–H to the chloride anion is evident from the absence of this signal in the ¹H NMR spectrum and the molecular structure (Figure 2, centre; N3–H3...N1 3.046(3) Å). An additional weak intermolecular hydrogen bonding interaction to a second PNN(H)Rh cation is found via H8 in the backbone of the pyrazole group and a second chloride ion (C8–H8...Cl2 3.631(3) Å). Salt metathesis of **2Cl** with AgBF₄ produces the related cationic species **2BF₄** (Scheme 1), showing similar spectroscopic data as its chloride analogue (ν_{CO} 1994 cm^{−1}; δ (³¹P) 97.8 ppm, $J_{\text{Rh,P}} = 152.4$ Hz), including a prominent ¹H NMR signal at δ 13.16 ppm for the N–H proton due to the absence of hydrogen bonding.

The acidity of the NH proton of complex **1** was probed by reaction with LiNIPr₂, which results in deprotonation of the pyrazole unit and formation of a dinuclear LiCl bridged Rh^I complex **3**, which could be obtained from toluene solution (Scheme 1). The metal coordination sphere in **3** is similar to that of the parent complex **1** ($\tau_4 = 0.15$) with the [(PNN)Rh] chloride species as part of a Li–Cl–Li–Cl square, located above and below the plane defined by Li and Cl (Figure 3).

The phosphorus atom is now located in plane with the metal centre and the nitrogen donor atoms. As a consequence of Li coordination, the Rh1–Cl1 bond (2.3812(5) Å) is slightly elongated compared to complex **1**. One molecule of THF coordinates to both Li centres bound to the pyrazole unit of the pincer ligand. Of note, the crystallisation of the mononuclear Li(thf)₂ complex **4** that resembles a Co complex previously reported by Caulton and co-workers^[11] could be observed from THF solutions, layered with pentane. Its molecular structure is depicted in Figure S2. Simple dehydrohalogenation and coordi-



Scheme 1. Synthesis of Rh(I) complexes **1**, **2Cl**, **2BF₄**, **3**, and **4**.

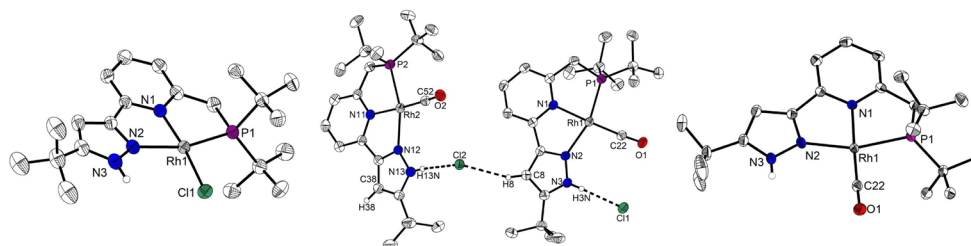


Figure 2. Molecular structures of complexes **1** (left), **2Cl** (centre), and **2BF₄** (right). Thermal ellipsoids correspond to 30% probability. Hydrogen atoms (except NH atoms of the pyrazole unit), co-crystallised benzene in **1**, and the BF₄ anion in **2BF₄** are omitted for clarity.

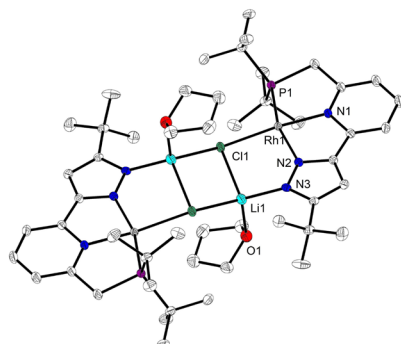


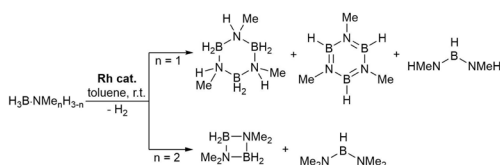
Figure 3. Molecular structure of complex **3**. Thermal ellipsoids correspond to 30 % probability. Hydrogen atoms are omitted for clarity.

nation of THF to the Rh centre coordinated with the anionic PNN ligand is not observed.

Catalytic dehydrocoupling of amine boranes

Rhodium bis(phosphine) complexes^[16] as well as complexes with neutral and anionic pincer ligands^[17] are well-suited for the catalytic dehydrocoupling of amine boranes. In the past, several systems have been reported to selectively produce cyclic oligomers or poly(aminoborane)s with the opportunity to modify the catalyst performance and polymer properties by addition of amine, ammonium, or boronium salts.^[18] Most importantly, amine doping was reported to promote formation of catalytically active metal hydride species.^[16a,18] We have therefore tested complex **1**, its cationic derivative **2Cl**, as well as base-activated **3** for dehydrocoupling of $\text{H}_3\text{B-NMeH}_2$ and $\text{H}_3\text{B-NMe}_2\text{H}$ (Scheme 2, Figure 4, top and Supporting Information).

In the reaction of $\text{H}_3\text{B-NMeH}_2$ using 1 mol% of complex **1** in toluene results in release of one equivalent of H_2 and the formation of isomer mixtures of *N*-methylcyclotriborazane (H_2BNMeH)₃ ($\delta^{11\text{B}} = -4.8$ ppm, $J_{\text{B,H}} = 108$ Hz^[19]) as the main product along with diaminoborane (MeNH_2BH) ($\delta^{11\text{B}} = 28.0$ ppm, $J_{\text{B,H}} = 120$ Hz^[20]) and *N*-trimethylborazine (HBNMe_3) ($\delta^{11\text{B}}$



Scheme 2. PNN(H) Rh complex catalysed dehydrocoupling of amine boranes. Only the main products are shown. Further details, including NMR spectra of catalytic reactions and peak assignments can be found in the Supporting Information.

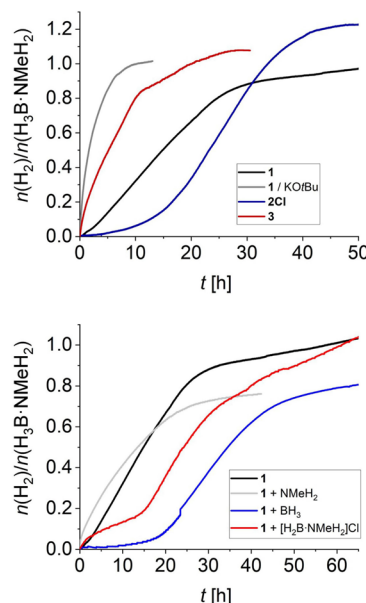


Figure 4. Top: Volumetric curves of the dehydrocoupling of $\text{H}_3\text{B-NMeH}_2$ using 1 mol% of Rh PNN complexes. Bottom: Volumetric curves of the dehydrocoupling of $\text{H}_3\text{B-NMeH}_2$ using complex **1**, with addition of 3 mol% NMeH_2 , 3 mol% BH_3 , THF, and 4 mol% $[\text{H}_2\text{B-NMeH}_2]\text{Cl}$. Conditions: $T = 25^\circ\text{C}$, toluene, 1 mol% **1**.

33.2 ppm, $J_{\text{B,H}} = 134$ Hz^[19]) within a reaction time of approximately 40 h, including a short period of lower activity. Formation of poly(aminoborane) was not observed. While addition of NMeH_2 to the reaction mixture removes this time of induction, it has only a minor effect on overall activity and selectivity. In contrast, BH_3 and boronium $[\text{BH}_2\text{NMeH}_2]\text{Cl}$ inhibit catalysis, resulting in pronounced induction periods and reaction times of up to 80 h (Figure 4, bottom). Borane poisoning of a heterogeneous Rh catalyst species was reported before by Manners and co-workers.^[21] We have therefore performed a Hg test^[22] to identify whether a heterogeneous catalyst species is responsible for catalytic turnover. Addition of an excess of Hg at approximately 50 % conversion did not inhibit catalysis (Figure S26). Also, reactions in the presence of substoichiometric amounts (0.5 equivalents) of PMe_3 as a fractional catalyst poison^[17a,23] did not reduce the catalytic activity, excluding a mechanistic scenario based on a heterogeneous catalyst.

With 1 mol% of the cationic complex **2Cl** similar activity and selectivity for $(\text{H}_2\text{BNMeH})_3$ was observed, however in this case turnover and maximum activity are preceded by an induction period that is typical for formation of a heterogeneous catalytically active species. Addition of amine results in a significantly increased activity and removal of this induction period with one equivalent of H_2 released after 20 h. Again, boronium and borane doping slow down catalysis (Figure S36). Hg and PMe_3

poisoning experiments show a reduction of activity upon addition of the catalyst poison. However, in both cases catalytic activity is almost fully restored after a short delay (Figure S41). These ambiguous results suggest the involvement of a heterogeneous catalyst derived from **2Cl**, in concert with a molecular species that is not affected by these catalyst poisons.

Comparative studies on the dehydrocoupling of dimethylated and thus sterically more hindered H_3B-NMe_2H show that complexes **1** and **2Cl** show different activities with the parent neutral complex quantitatively converting the substrate into the cyclic dimer $(H_2BNMe_2)_2$ (δ ^{11}B 5.4 ppm, $J_{B,H} = 113$ Hz^[24]) after only 20 h (Figure S29) compared to almost 80 h for the cationic precatalyst. Again, an induction period is found for **2Cl**, pointing to contributions of a heterogeneous active species (Figure S44).

Attempts to obtain mechanistic insights into the reactions that are catalysed by the molecular components of the system by multinuclear NMR spectroscopy were not successful. $^{31}P\{^1H\}$ NMR spectra of catalytic reactions of both complexes with H_3B-NMe_2 only showed the decay of the precatalyst and formation of a single main species (**1**: δ ^{31}P 96.9 ppm, $J_{RhP} = 172$ Hz, Figure S65; **2Cl**: δ ^{31}P 93.6 ppm, $J_{RhP} = 140$ Hz, Figure S67) that cannot be further characterised by control experiments such as addition of $NMeH_2$, BH_3 , $[BH_2(NMeH_2)Cl]$, or the substrate $H_3B-NMeH_2$ (Figures S52–S57).

We have furthermore studied the effect of cyclohexene as trapping agent for free aminoborane $H_2B-NMeH$, which could be responsible for the formation of cyclic oligomers instead of polymer. Unfortunately, this also affected the selectivity of reactions using **1** as the precatalyst. However, the presence of free $H_2B-NMeH$, likely the reason for oligomer formation, was confirmed by the singlet ^{11}B resonance of the hydroboration product $Cy_2B-NMeH$ at δ 45 ppm (Figures S68 and S74).^[25] Furthermore, a slightly higher activity was found in the presence of cyclohexene, suggesting that release of the aminoborane from the catalyst after dehydrogenation is beneficial for higher turnover.

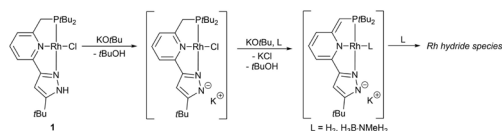
Next, we have evaluated the potential of base activation of parent complex **1** for the catalytic dehydrocoupling reaction. We have therefore tested the isolable complex **3**, formed by reaction of **1** with $LiNPr_2$, as well as complex **1**, activated with $KOtBu$ (Scheme 3). The reaction of late transition metal complexes possessing a combination of cooperative pincer ligand and monoanionic ligands with base typically leads to deprotonation of the pincer scaffold, removal of the X-type ligand and dearomatisation. Caulton and co-workers have shown that this sequence can be observed in a stepwise fashion.^[26] Thus formed activated systems are typically discussed as key-species for stoichiometric and catalytic bond

activation.^[27] In case of complex **1**, twofold reaction with base should lead to deprotonation of the pyrazole unit and deprotonation of the benzylic position, giving a dianionic PNN pincer ligand coordinated to Rh^I .

Complex **3** is active for dehydrocoupling of $H_3B-NMeH_2$, releasing approximately one equivalent of hydrogen within 30 hours. Interestingly, much less $(H_2BNMeH)_3$ could be detected in ^{11}B NMR spectra. Instead, $(H_2BNMeH)_3$ and $(MeNH)_2BH$ are the main boron species (Figure S35). The same product distribution was observed when activating complex **1** with $KOtBu$. Of note, ^{11}B NMR spectra of both reactions show a prominent broad singlet resonance at δ 24.5 ppm, which has not been reported for dehydrocoupling of $H_3B-NMeH_2$ to date. Both reactions are significantly faster than those of **1** or **2Cl** and do not show induction periods (Figure 4, top), suggesting that initial removal of the chloride ligand is one of the key steps of catalysis. Based on the doping experiments discussed above (Figure 4, bottom), it can be concluded that $NMeH_2$ is insufficiently Brønsted basic to effect this dehydrohalogenation step. The 1H NMR spectrum recorded after reaction of complex **1** with $KOtBu$ shows full conversion of the starting material, the absence of NH and benzylic CH_2 protons, and CH signals of the former pyridine ring shifted to higher field, suggesting the formation of a doubly deprotonated species with dearomatised pyridine unit.^[28] In the ^{31}P NMR spectrum two new doublets can be detected (Figures S58 and S59), suggesting the presence of both activated species shown in Scheme 3. In the presence of $H_3B-NMeH_2$, the 1H NMR spectrum shows weak upfield resonances at δ –24.66 and –12.93 ppm that do not sharpen upon ^{11}B decoupling, suggesting the presence of terminal Rh hydride species. Of note, the latter signal could also be observed in the reaction of **1**/ $KOtBu$ in the presence of H_2 . Unfortunately, none of these species could be further characterised or isolated (Figures S60–S63). Attempts to prepare a Rh alkyl complex that could serve as a masked Rh hydride^[18] that would readily react with amine borane were not successful to date and only led to decomposition of complex **1**, likely due to the presence of the acidic pyrazole NH proton.

Conclusions

In summary, we have presented the coordination chemistry of a potentially cooperative pyridine-pyrazole-based PNN(H) ligand at Rh^I along with a study of three of the complexes for catalytic dehydrocoupling of amine boranes. Coordination of the ligand to Rh^I produces the square planar complex **1** that displays an acidic pyrazole NH proton. This position undergoes deprotonation in a reaction with $LiNPr_2$, producing a dinuclear $LiCl$ bridged species **3**. The parent PNN(H) Rh chloride complex **1**, its cationic derivative **2Cl**, as well as complex **3** are competent catalysts for the dehydrogenation of amine boranes, producing mainly cyclic oligomers with *N*-methylcyclotriborazane $(H_2BNMeH)_3$ as the main species. Activation of the parent complex **1** with $KOtBu$ yields a much more active catalyst system that likely operates via Rh hydride species as catalytically relevant intermediates. Based on these findings we



Scheme 3. Activation of complex **1** with $KOtBu$.

conclude that dehydrohalogenation of the Rh chloride precatalyst is key to formation of the catalytically active species. Future studies will aim at the extension of the coordination chemistry of this ligand and the application of related complexes for amine borane chemistry, harnessing the cooperative ligand motif and aiming at the identification of relationships between ligand structure, catalyst activity and product selectivity.

Experimental Section

Synthesis of complex 1: *Method A:* In a Schlenk flask the PNN(H) ligand (146 mg, 0.406 mmol) was dissolved in 2 mL of THF. To this pale brown solution a solution of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (100 mg, 0.203 mmol) in 2 mL of THF was added. The solution immediately turns deep red. After 30 minutes the solution was layered with 20 mL of diethyl ether and cooled to -78°C over night. During that time dark red solid material precipitated. The red solution was filtered off and the remaining dark red solid (198 mg, 0.398 mmol, 98%) was dried in vacuum. *Method B:* The precursor $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (28 mg, 0.061 mmol) was dissolved in 2 mL of THF. The orange solution turns dark red when the PNN(H) ligand (44 mg, 0.122 mmol) was added. The solution was stirred for 30 minutes and then layered with 10 mL of *n*-pentane. During cooling to -78°C a dark red solid precipitated. The solution was filtered off and the remaining dark red solid (11 mg, 0.022 mmol, 18%) was dried in vacuum. Single crystals suitable for X-ray analysis were obtained from saturated benzene or diethyl ether solutions (layered with *n*-hexane). ^1H NMR (300.2 Hz, THF- d_6 , 25°C): δ 12.48 (s, 1 H, NH), 7.71 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, C4H), 7.21 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, C5H), 7.11 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, C3H), 6.65 (s, 1 H, pyrazole CH), 3.02 (d, $J = 8.9$ Hz, 2 H, CH₂), 1.45 (s, 9 H, pyrazole tBu), 1.41 ppm (d, $^3J_{\text{H,H}} = 12.8$ Hz, 18 H, PtBu). ^{13}C NMR (100.63 MHz, THF- d_6 , 25°C): δ 162.7 (C2), 154.6 (HNCC(CH₃)₃), 152.5 (C6), 151.7 (NCCH), 128.6 (C4), 121.5 (C3), 119.4 (C5), 99.1 (pyrazole-CH), 37.6 (CH₂), 35.4 (PC(CH₃)₃), 35.2 (PC(CH₃)₃), 32.3 (CC(CH₃)₃), 30.4 (CC(CH₃)₃), 29.8 (PC(CH₃)₃), 29.8 ppm (PC(CH₃)₃). ^{31}P NMR (121.53 MHz, THF- d_6 , 25°C): δ 87.3 ppm ($J_{\text{Rh,P}} = 197.8$ Hz). MS (Cl^-): m/z [PNN(H)RhCl] $^+$ 497 (44), [PNN(H) + H] $^+$ 360 (24), [NN(H)] $^+$ 216 (100). EA: calc(%) for $\text{M}(\text{C}_{21}\text{H}_{34}\text{ClN}_3\text{OPRh})$ C 50.66, H 6.88, N 8.44; Found: C 51.96, H 7.05, N 7.13. IR: 801 (vs), 818 (vs), 830 (s), 885 (s), 920 (w), 1017 (m), 1052 (s), 1164 (m), 1181 (m), 1207 (w), 1234 (m), 1260 (m), 1301 (m), 1366 (s), 1395 (m), 1458 (s), 1560 (w), 2867 (w), 2934 (m), 2961 cm^{-1} (m). Melting point: 162°C .

Synthesis of complex 2Cl: In a Schlenk flask complex 1 (190 mg, 0.382 mmol) was dissolved in 5 mL of benzene, 1 atm of dry CO, produced from formic acid/sulfuric acid was bubbled through the dark red solution. The colour of the solution slowly changed to yellow and a yellow solid precipitated. The liquid was filtered off and the residue was dried in vacuum (47 mg, 0.089 mmol, 23%). ^1H NMR (300.2 Hz, acetone- d_6 , 25°C): δ 8.09 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, C4H), 7.88 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, C5H), 7.69 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, C3H), 6.86 (s, 1 H, pyrazole CH), 4.07 (d, $^3J_{\text{H,H}} = 9.5$ Hz, 2 H, CH₂), 1.48 (s, 9 H, pyrazole tBu), 1.44 ppm (d, $^3J_{\text{H,H}} = 14.5$ Hz, 18 H, PtBu). ^{13}C NMR (100.63 MHz, MeOH- d_4 , 25°C): δ 193.4 (CO), 165.0 (C2), 159.2 (pyrazole HNCC(CH₃)₃), 155.0 (pyrazole NCCH), 152.5 (C6), 142.4 (C4), 124.0 (C3), 120.1 (C5), 102.2 (pyrazole CH), 37.1 (PC(CH₃)₃), 36.9 (PC(CH₃)₃), 32.6 (CC(CH₃)₃), 30.2 (CC(CH₃)₃), 29.5 ppm (PC(CH₃)₃), 29.5 ppm (PC(CH₃)₃). ^{31}P NMR (121.53 MHz, MeOH- d_4 , 25°C): δ 97.7 ppm ($J_{\text{Rh,P}} = 153.8$ Hz). MS (Cl^-): m/z [PNN(H)RhCO + H] $^+$ 491 (100). EA: calc(%) for $\text{M}(\text{C}_{21}\text{H}_{34}\text{ClN}_3\text{OPRh})$ C 50.25, H 6.52, N 7.99; Found: C 48.42, H 8.21, N 6.38. IR: 807 (w), 832 (m), 879 (w), 1160 (w), 1272 (w), 1368 (m), 1470 (m), 1560 (w), 1609 (w), 1988 (vs), 2867 (w), 2961 cm^{-1} (w). Melting point: $266.6\text{--}277.5^\circ\text{C}$.

Synthesis of complex 2BF₄: *Method A:* The complex $[\text{Rh}(\text{acac})(\text{CO})_2]$ (26 mg, 0.100 mmol), the PNN(H) ligand (36 mg, 0.100 mmol) and AgBF₄ (20 mg, 0.100 mmol) were placed in a Schlenk flask. Upon addition of 4 mL of THF a yellow solution formed, and CO gas evolved. Over night a brown solid formed. The solution was filtered off and the filtrate was layered with 20 mL of diethyl ether. Cooling to -78°C produces yellow crystals of 2BF₄, which were isolated by filtration and dried in vacuum (65 mg, 0.055 mmol, 55%). *Method B:* Complex 2Cl (28 mg, 0.053 mmol) was dissolved in 4 mL of THF. To this yellow solution AgBF₄ (10 mg, 0.053 mmol) was added, resulting in the precipitation of a dark solid. The solution was filtered and the filtrate was concentrated to a volume of 2 mL in vacuum. A fivefold excess of pentane was added and the mixture was cooled to -78°C , resulting in the formation of a voluminous yellow solid. After removing the liquid, the residue was dried in vacuum (20 mg, 0.035 mmol, 66% yield). ^1H NMR (300.2 Hz, THF- d_6 , 25°C): δ 13.16 (s, 1 H, NH), 8.07 (m, 1 H, C4H), 7.97 (m, 2 H, meta-CH), 7.03 (s, 1 H, pyrazole CH), 4.16 (d, $^3J_{\text{H,H}} = 9.8$ Hz, 2 H, CH₂), 1.43 (s, 9 H, pyrazole tBu), 1.42 ppm (d, $^3J_{\text{H,H}} = 14.7$ Hz, 18 H, PtBu). ^{13}C NMR (75.5 MHz, THF- d_6 , 25°C): δ 193.4 (CO), 165.3 (C2), 158.5 (HNCC(CH₃)₃), 155.3 (NCCH), 151.5 (C6), 142.5 (C4), 124.9 (C3), 120.1 (C5), 102.4 (pyrazole CH), 37.0 (PC(CH₃)₃), 36.7 (CH₂), 32.4 (CC(CH₃)₃), 30.1 (CC(CH₃)₃), 29.5 ppm (PC(CH₃)₃), 29.5 ppm (PC(CH₃)₃). ^{31}P NMR (121.53 MHz, THF- d_6 , 25°C): δ 97.8 ppm ($J_{\text{Rh,P}} = 152.4$ Hz). ^{11}B NMR (128.38 MHz, THF- d_6 , 25°C): δ -0.9 ppm. MS (Cl^-): m/z [PNN(H)RhCO + H] $^+$ 491 (100), [PNN(H) + H] $^+$ 360 (66). EA: calc(%) for $\text{M}(\text{C}_{21}\text{H}_{34}\text{F}_4\text{N}_3\text{OPRh})$ C 45.78, H 5.94, N 7.28; Found: C 46.35, H 6.19, N 5.91. IR: 812 (m), 832 (m), 883 (w), 981 (s), 1005 (s), 1056 (vs), 1160 (m), 1207 (w), 1240 (w), 1272 (m), 1372 (w), 1472 (m), 1562 (w), 1611 (w), 1994 (s), 2871 (w), 2963 (w), 3240 cm^{-1} (w). Melting point: $185.2\text{--}194.9^\circ\text{C}$.

Synthesis of complex 3: Complex 1 (50 mg, 0.100 mmol) and $\text{LiN}(\text{Pr})_2$ (11 mg, 0.100 mmol) were weighed in a Schlenk flask and dissolved in 5 mL of THF. The red-brown solution was stirred for 30 min, followed by concentration of the solution to 2 mL in vacuum. The solution was layered with 8 mL of *n*-pentane and cooled to -78°C . The product precipitates over night as of red-brown crystals (26 mg, 0.045 mmol, 45%). Single crystals suitable for X-ray analysis were obtained from a saturated toluene solution. ^1H NMR (300.2 Hz, THF- d_6 , 25°C): δ 7.46 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, C4H), 6.96 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, C5H), 6.84 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, C3H), 6.34 (d, $^3J_{\text{H,H}} = 0.9$ Hz, 2 H, pyrazole CH), 3.62 (m, 8 H, THF), 2.93 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4 H, CH₂), 1.78 (m, 8 H, THF), 1.40 (d, $^3J_{\text{H,H}} = 12.3$ Hz, 36 H, PtBu), 1.35 ppm (s, 18 H, pyrazole tBu). ^{13}C NMR (100.63 MHz, THF- d_6 , 25°C): δ 162.5 (C2), 160.7 (HNCC(CH₃)₃), 155.6 (C6), 151.9 (NCCH), 129.3 (C4), 118.0 (C3), 116.3 (C5), 97.2 (pyrazole-CH), 68.3 (thf), 37.5 (CH₂), 35.1 (PC(CH₃)₃), 35.0 (PC(CH₃)₃), 32.8 (CC(CH₃)₃), 31.9 (CC(CH₃)₃), 29.9 (PC(CH₃)₃), 29.8 (PC(CH₃)₃), 26.4 ppm (thf). ^{31}P NMR (121.53 MHz, THF- d_6 , 25°C): δ 85.2 ppm ($J_{\text{Rh,P}} = 184.7$ Hz). MS (ESI^+): m/z [PNN(H)RhCl] $^+$ 497 (100). EA: calc(%) for $\text{M}(\text{C}_{21}\text{H}_{34}\text{ClN}_3\text{OPRh})$ C 52.12, H 7.18, N 7.30; Found: C 48.23, H 8.66, N 6.72. IR: 816 (s), 828 (w), 916 (m), 1003 (w), 1020 (m), 1040 (m), 1154 (m), 1181 (w), 1205 (w), 1256 (m), 1360 (s), 1387 (m), 1458 (vs), 1601 (m), 2863 (s), 2893 (s), 2950 cm^{-1} (s). Melting point: 227°C .

General procedure for dehydrocoupling of amine boranes: Amine boranes $\text{H}_3\text{B-NMe}_2$ or $\text{H}_3\text{B-NMe}_2\text{H}$ (1.33 mmol) and the precatalyst (1 mol%) were weighed into a double-walled, three-necked reaction vessel in the glove box. The reaction vessel was connected to an automatic gas buret²⁴ under Ar atmosphere. The system was initialised, the solvent and additional reagents (NMe_2 , BH_3 , THF or $[\text{H}_3\text{BNMe}_2]\text{Cl}$) were added and the measurement was started immediately. At maximum gas evolution a gas sample was taken and analysed using TCD-GC to confirm the presence of H_2 . An aliquot was taken from the reaction solution and analysed by ^1H , $^{31}\text{P}\{^1\text{H}\}$, ^{11}B , and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy.

Deposition Number(s) 2262584 and 2256443 (for 1), 2256441 (for 2Cl), 2256440 (for 2BF₄), 2256442 (for 3), 2262583 (for 4) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Supporting Information

The authors have cited additional references within the Supporting Information.^[29–34]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Boranes · Dehydrocoupling · Main group compounds · Pincer ligands · Rhodium

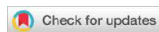
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The Dinuclear Zirconocene Complex [(Cp₂Zr)₂(μ-Me)(μ-C₂Ph)] as a Platform for Small Molecule Activation

Hanan Al Hamwi,^[a] Mirko Rippke,^[a] Kevin Lindenau,^[a] Anke Spannenberg,^[a] Martin Lamac,^[b] Fabian Reiß,^{*,[a]} and Torsten Beweries^{*,[a]}

Dedicated to Prof. Uwe Rosenthal on the occasion of his 75th birthday

The dinuclear title compound [(Cp₂Zr)₂(μ-Me)(μ-C₂Ph)] **5** was prepared from a zirconocene alkynyl methyl complex and Rosenthal's zirconocene source [Cp₂Zr(py)(η²-Me₃SiC₂SiMe₃)] in a formal comproportionation reaction. This complex shows catalytic activity for the dehydrocoupling of amine boranes, with a dinuclear hydride-bridged alkynyl complex **6** being formed as a catalytically relevant species. The structure of this complex was confirmed for the first time by single-crystal X-ray analysis. The reaction of complex **5** with hydrogen results in hydrogenation of the alkynyl ligand, yielding a highly labile trinuclear hydride-

bridged complex as a possible intermediate of zirconocene dihydride/ethylbenzene formation. This complex shows an unusual distorted planar tetracoordinate environment at the central carbon atom positioned between the three Zr centers. The reaction of complex **5** with 2-cyanopyridine and acetonitrile is characterized by a reduction of the substrates. The herein reported reactivity of complex **5** demonstrates the remarkable potential of well-established dinuclear zirconocenes to stabilize unusual bond situations, which were analyzed comprehensively using spectroscopic, structural, and computational methods.

1. Introduction

The concept of multinuclear complexes is a well-established but still intriguing field in organometallic chemistry and homogeneous catalysis. The idea of multinuclear complexes has gained renewed interest due to their potential to enhance orthogonal catalytic activity and selectivity in various reactions.^[1] For example, the development of polynuclear catalysts has greatly facilitated the production of high-performance polyolefin materials.^[2] The cooperative effects of polynuclear catalysts composed of early transition metals compared to mononuclear catalysts affect catalytic performance and polymer structure through multiple factors, such as steric hindrance, electronic effects, heteroatom effects, hydrogen bonding, and the distance between metal centers in polynuclear metal catalysts.^[3] The fine-tuning of these parameters allows for a wide range of variations in the future design of di- and polynuclear transition metal complexes, which will have customized properties that can be applied in catalysis and/or stoichiometric bond activation. The development of group 4 non-metallocene multinuclear complexes is, in this con-

text, an increasingly important area of current research.^[4] However, the metallocene-based group 4 complexes still hold many interesting transformations of both catalytic and stoichiometric nature.

The chemistry of alkynyl bridged group 4 metallocenes dates back to seminal work of Teuben and de Liefde Meijer from 1969 in which the alkynyl bridged titanocene complex (**A**, Figure 1a) was synthesized starting from the Ti(III) precursor [Cp₂Ti(μ-Cl)]₂ (Cp = η⁵-cyclopentadienyl) and two equivalents of NaC₂Ph.^[5] Mass spectrometric and IR spectroscopic analysis suggested the presence of a dinuclear complex with bridging alkynyl units. Later, unexpected C–C coupling of the alkynyl groups in **A'** was confirmed by single crystal X-ray diffraction (SC-XRD) analysis of the corresponding singly methylated Cp analogue.^[6] The first zirconocene analogue **B** was synthesized and characterized by Erker and co-workers using a comproportionation reaction between a bis-alkynyl zirconocene(IV) and the in situ generated zirconocene(II) (Figure 1b).^[7] Interestingly, this complex **B** shows no C–C coupling, but σ-Cα–Zr binding and π-coordination to the second zirconocene. Theoretical investigations were carried out to better understand the electronic situations in these and related systems.^[8] Later, the related dinuclear zirconocene trimethylsilylalkynyl complex [Cp₂Zr(μ-C₃SiMe₃)]₂, was characterized and investigated by several research groups.^[9] Rosenthal and co-workers extended the scope of these alkynyl complexes to di- and polynuclear Ti and Zr complexes bearing C–C activated and non-activated butadiynes and octatetraynes and demonstrated that compounds of this type are of relevance for the single bond metathesis of 1,3-diyne.^[10]

Erker et al. further explored the concept of comproportionation reactions between bis-alkynyl Zr(IV)/Hf(IV) and masked Zr(II)/Hf(II) butadiene metallocene complexes to prepare differently substituted complexes of the type [Cp₂M(μ-C₂R)]₂; M = Zr,

[a] H. A. Hamwi, M. Rippke, K. Lindenau, A. Spannenberg, F. Reiß, T. Beweries
Leibniz Institute for Catalysis, Albert-Einstein-Strasse 29a, Rostock, Germany
E-mail: Fabian.Reiss@catalysis.de
Torsten.Beweries@catalysis.de

[b] M. Lamac
J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of
Sciences, Dolejškova 2155/3, Prague, Czech Republic

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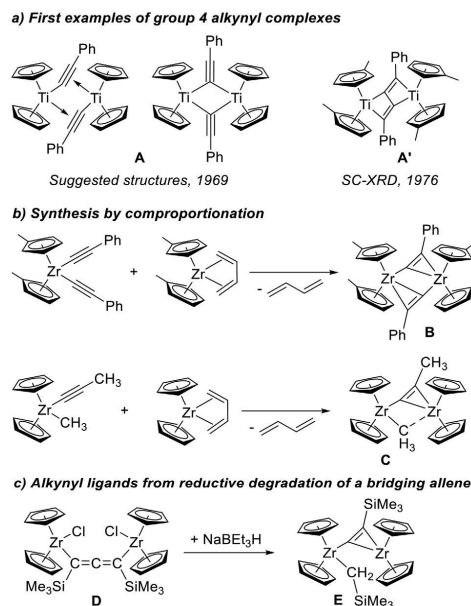
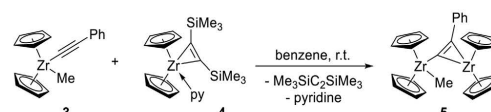


Figure 1. a). The alkynyl bridged titanocene complex A as two different suggested forms and the determined connectivity of a related complex A'; b) First example of a fully characterized alkynyl bridged zirconocene B and schematic representation of the comproportionation approach to homo- and heterobimetallic alkynyl methyl bridged complexes, C; c) Reductive transformation of an allenediide ligand in D, yielding Zr alkynyl complex E.

Hf; R = H, CH₃, Ph, C₂H₅, CH₂Ph) (similar to B).^[11] This transformation can also be performed starting from metallocene alkynyl halide and alkynyl methyl complexes, yielding halide or methyl bridged dinuclear complexes (example C, Figure 1b), in which the alkynyl unit can oscillate between both metal centers. Recently, some of us have reported the formation of a related dinuclear alkynyl bridged zirconocene complex during catalytic dehydrocoupling of dimethylamine borane, H₃B-NMe₂H, using a dinuclear allenediide Zr chloride complex D, activated with MeLi,^[12] formally by cleavage of one of the C=C bonds of the C=C=C unit under reductive conditions. Targeted synthesis of this complex [(Cp₂Zr)₂(μ-CH₂SiMe₃)(μ-C₂SiMe₃)] (E) is possible from the Zr chloride precatalyst with NaBEt₃H as a hydride source (Figure 1c).^[13] Complex E and related [(Cp₂Zr)₂(μ-CH₃)(μ-C₂SiMe₃)] (F) can act as a precatalyst for the dehydrocoupling of amine boranes.

Inspired by the modular comproportionation approach for the synthesis of these dinuclear complexes that allows facile variations at both metal centers as well as at the alkynyl unit, we herein present the synthesis and characterization of the dinuclear phenylalkynyl bridged zirconocene complex [(Cp₂Zr)₂(μ-CH₃)(μ-C₂Ph)] along with an investigation of its reactivity toward small molecules. These studies reveal a variety of unexpected and hitherto unknown bond activation motifs. The chemically robust metallocene platform thus once again provides insights



Scheme 1. Synthesis of 5 using complex 3 and Rosenthal's reagent (4).

into the potential diversity of possible transformations with electropositive early transition metals and small molecules.

2. Results and Discussion

2.1. Synthesis of [(Cp₂Zr)₂(μ-Me)(μ-C₂Ph)] (5)

In previous studies, for example, in the synthesis of the allene bridged complex (D),^[14] trimethylsilyl-substituted alkynyl bridged complex F,^[13] and highly strained metallacyclobutadiene complexes,^[15] it turned out to be crucial to isolate the organolithium precursor in pure form instead of using the commonly applied in situ lithiation protocol. Therefore, LiC₂Ph (1) was prepared by slow addition of one equivalent of *n*-BuLi to a cooled (−78°C) diethyl ether solution of freshly distilled phenylacetylene, followed by stirring overnight at ambient conditions and washing with *n*-hexane. Reaction of 1 with [Cp₂Zr(Me)Cl] (2) in toluene at −78°C produces the mononuclear complex 3 as a red oil in high yields of up to 93%. Of note, the resulting oily material contains minor amounts of unidentified Cp-containing species (Figure S1), however, the described procedure is the best method out of the different approaches that were tested. Reaction of 3 with an equimolar amount of Rosenthal's zirconocene(II) source [Cp₂Zr(py)(η²-Me₃SiC₂SiMe₃)] (4, py = pyridine) in benzene solution at ambient temperature produces the dinuclear Zr alkynyl methyl complex 5, which can be isolated as an orange solid material in yields of up to 77% (Scheme 1).

¹H NMR spectrum of 5 in benzene-*d*₆ shows two resonances for cyclopentadienyl ligands at 5.28 and 5.27 ppm. The resonance of the methyl group is found at −2.60 ppm, thus exhibiting a remarkable shift to a higher field compared to the value of δ 0.26 ppm in 3, highlighting the different electronic situation imposed by the second Zr center in 5. These data suggest a slightly more deshielded situation due to the phenyl substituent compared to the trimethylsilyl substituted complex F (cf. ¹H NMR in benzene-*d*₆: δ 5.19, 5.17 (Cp), −2.92 ppm (Me)). Crystals of 5 suitable for SC-XRD analysis were obtained by slow cooling of a toluene/pentane solution from room temperature to −70°C (Figure 2, discussion of structural data).

2.2. Reactivity of Complex 5

2.2.1. Reactivity Toward Amine Boranes and Hydrogen

Trimethylsilyl alkynyl complexes E and F react with an excess of H₃B-NMe₂H by protonation of the CH₂R (R = SiMe₃ (E), H (F)) moiety and formation of SiMe₄ or CH₄, respectively, and

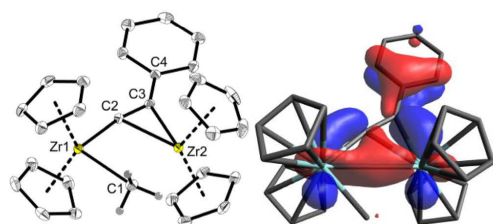
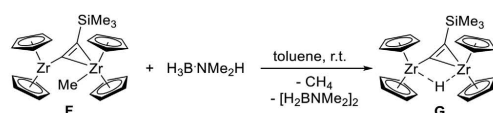


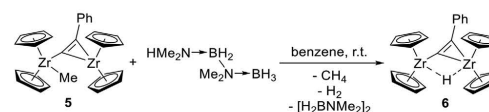
Figure 2. Left: Molecular structure of complex 5. Thermal ellipsoids correspond to 30% probability at 170 K. Hydrogen atoms except at C1 are omitted for clarity. Selected bond lengths are given in Table 1. Right: NLM038 of 5. Analysis of the formal lone pair at C4 reveals a strong delocalization with only 14.6% of the original NBO lone pair. It shows bonding contributions between both Zr centers and anti-bonding features of the alkynyl unit. It can be interpreted as an alkynyl-assisted Zr–Zr binding orbital.



Scheme 2. Exemplary reaction of compound F (showing Zr(III)/Zr(III) connectivity found by SC-XRD analysis) with $\text{H}_3\text{B-NMe}_2\text{H}$, producing the dinuclear Zr hydride G.^[13]

cyclodiborazane $[\text{H}_2\text{BNMe}_2]_2$ (Scheme 2). Hydride transfer leads to the labile hydride-bridged analogue $[(\text{Cp}_2\text{Zr})_2(\mu\text{-H})(\mu\text{-C}_2\text{SiMe}_3)]$ (G), a catalytically relevant species for the dehydrocoupling of amine boranes.^[16] Experiments with partially B- and N-deuterated amine boranes demonstrated that the formation of the Zr hydride predominantly occurs via a B–H hydride transfer.^[13] To compare the influence of the alkynyl moiety on the reactivity, the same reaction was performed with complex 5.

Initial experiments were carried out in Young NMR tubes under strict exclusion of air and moisture. When adding a ten-fold excess of $\text{H}_3\text{B-NMe}_2\text{H}$ to an orange benzene solution of 5 an intensification of color to red was observed, along with gas evolution, likely hydrogen. Gas release was allowed for 12 h and ^1H and ^{11}B NMR spectra showed, as expected, the formation of cyclodiborazane $[\text{H}_2\text{B-NMe}_2]_2$, a new metallocene species (^1H NMR in benzene- d_6 : δ 5.84, 5.78 ppm (Cp) and the presence of the starting compound 5. The addition of further three equivalents of $\text{H}_3\text{B-NMe}_2\text{H}$ reduced the amount of 5 and produced a hydride signal at δ –5.81 ppm, which is associated with the aforementioned new Cp resonances. These three resonances are in line with those of the trimethylsilyl substituted derivative G and reveal a greater deshielding of the hydride in the new complex 6 (cf. species G: ^1H NMR in benzene- d_6 : δ 5.77, 5.76 (Cp), –7.22 ppm ($\mu\text{-H}$)). The color of the reaction solution changed to turquoise, but all further handling of this reaction mixture, such as drying in vacuo, filtration, or even storage, led to decomposition, indicated by a color change to yellow-brownish. In all further attempts to repeat this reaction on a larger scale, it was not possible to isolate the turquoise/blue species. Nevertheless, these experiments



Scheme 3. Synthesis of 6 using complex 5 and diborazane $\text{H}_3\text{B-NMe}_2\text{-BH}_2\text{-NMe}_2\text{H}$.

suggest that complex 5 acts as a precatalyst in the dehydrocoupling of $\text{H}_3\text{B-NMe}_2\text{H}$, undergoing the same conversion as its trimethylsilyl-substituted analogue.^[13]

This motivated us to further evaluate methods for isolating this catalytically relevant zirconocene hydride species. In particular, the true nature of these complexes has not yet been determined, although various Lewis structures of related group 4 metallocene were postulated as early as 1997 by Shur and co-workers.^[17] The high sensitivity of the postulated zirconocene hydride species 6 requires all experiments to be conducted in sealed NMR tubes. To replace $\text{H}_3\text{B-NMe}_2\text{H}$ as the hydrogen source, hydrogen gas was employed directly, with experiments conducted at different reaction times and temperatures to form the desired hydride species in the highest possible concentration. Using a reaction time of 48 h at 80°C, blue crystals were obtained, which were unfortunately unsuitable for SC-XRD analysis. However, CI-MS analysis shows a signal at m/z 542, clearly identifying this blue species as the hydride $[(\text{Cp}_2\text{Zr})_2(\mu\text{-H})(\mu\text{-C}_2\text{Ph})]$ (6). Finally, we used linear diborazane $\text{H}_3\text{B-NMe}_2\text{-BH}_2\text{-NMe}_2\text{H}$ as the hydrogen source and observed a color change from reddish-brown to dark blue within 24 h (Scheme 3). SC-XRD analysis of blue crystals formed from this solution clearly confirmed the structure of dinuclear complex 6 with the assumed bridging hydride ligand (Figure 3, discussion of structural data, see below).

In all previous experiments, poorly selective reactions were observed, indicated by the presence of several Cp-containing species in reaction solutions. In particular, reactions with molecular hydrogen showed a set of ^1H NMR signals that could be assigned to a polynuclear zirconocene hydride species: four low-field signals with an integral ratio of 5:5:10:10 at δ 6.20, 6.02, 5.82 and 5.40 ppm, in line with Cp ligands, as well as a signal at higher field (δ –1.45 ppm) with an integral of 2, corresponding to a bridging Zr dihydride. Formation of ethylbenzene, likely by hydrogenation of the bridging phenylalkynyl unit in 5 is corroborated by characteristic ^1H NMR signals at δ 2.44 (q , 2H, $^3J = 7.6$ Hz) and 1.08 ppm (t , 3H, $^3J = 7.6$ Hz). An additional set of ^1H NMR signals indicates formation of the known zirconocene hydride dimer $[(\text{Cp}_2\text{Zr}(\text{H})(\mu\text{-H}))_2]$ (δ 5.60 (Cp), 3.70 (m , Cp_2ZrH), –3.60 ppm (m , $\mu\text{-H}$)).^[18] Optimization of the reaction conditions, reducing the reaction temperature to 60°C and extending the reaction time to two weeks allowed for the enrichment of the postulated Zr dihydride species (Scheme 4).

Single crystals suitable for SC-XRD analysis could be obtained from deep purple reaction solutions after slow cooling to ambient temperature (Figure 3, discussion of structural data, see below). The molecular structure confirms the new species 7 as a trinuclear complex in which a formal PhC(H)C unit is

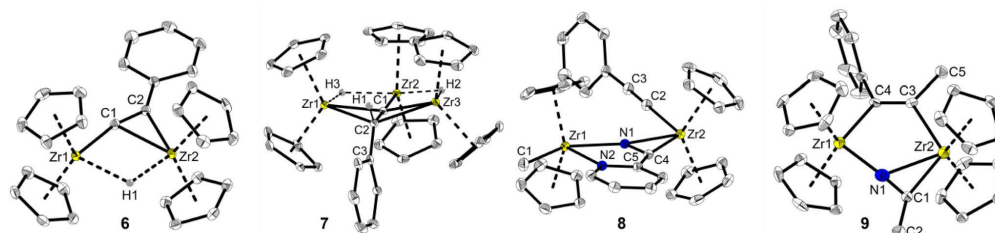
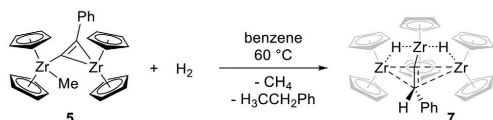
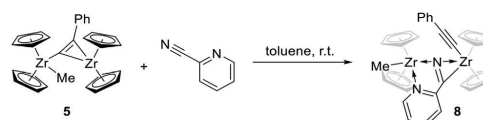


Figure 3. Molecular structures of complexes 6–9. Thermal ellipsoids correspond to 30% probability at 150 K. Hydrogen atoms, except H1 in 6 and H1–H3 in 7, as well as the minor occupied disordered Cp orientation in 6 and the solvent molecules (C_6H_6) in 7 were omitted for clarity. Selected structural data are depicted in Table 1.



Scheme 4. Hydrogenation of complex 5 and formation of 7.



Scheme 5. Reaction of complex 5 with 2-cyanopyridine, producing 8.

positioned between three zirconocene centers that are additionally connected by two Zr–H bridges. This unexpected structural motif is in excellent agreement with the above described unusual 1H NMR pattern and can be understood as an intermediate of complete hydrogenation of the phenylalkynyl group to ethylbenzene. Selective zirconocene hydride-catalyzed semi-hydrogenation of terminal alkynes has recently been investigated by the Bayeh–Romero group, using *i*-PrOH and silanes as proton and hydride source, respectively, instead of molecular hydrogen.^[19] In this context it might be worth investigating hydrogenation reactions using a broader set of zirconocene hydride species and hydrogen in the future. Furthermore, activation of other poorly-reactive small molecules like N_2 ^[20] or CO_2 ^[21] will be studied using these and related oligonuclear Zr hydride complexes.

Hydride complexes 6 and 7 are intensely colored, however, due to their high sensitivity it was not possible to record UV–vis spectra of these complexes. Thus, time-dependent DFT (TD-DFT) analysis on the PBE0^[22]-D3^[23]/def2-TZVP^[24] level of theory, based on optimized geometries derived from experimental data, was performed to identify the key charge distributions and transfers that are responsible for the intense color of 6 (Tables S16 and S17) and 7 (Tables S18 and S19). For the title compound 5, an intense absorption is computed at 433 nm which can be interpreted as ligand-to-metal charge transfer (LMCT). This mainly involves the donation of electron density from the alkynyl unit to a d orbital at Zr2. The analogous LMCT bands in the hydride complexes show a substantial bathochromic shift to 519 and 514 nm in 6 and 498 nm in 7, respectively. It can thus be assumed that the presence of small μ -hydride ligands indirectly influences the color of the complexes, without contributing significantly to the HOMO/LUMO responsible for the color. More specifically, a decrease of the Zr–Zr distance from complex 5 to 6 results in more efficient orbital overlap, leading to a reduction of the

HOMO–LUMO gap from 3.68 eV in 5 to 3.35 and 3.23 eV in 6 and 7, respectively.

2.2.2. Reactivity Toward 2-Cyanopyridine and Acetonitrile

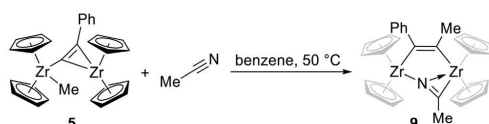
Zirconocene complexes are known to activate small unsaturated molecules such as nitriles and isocyanides in diverse and mostly unpredictable ways.^[25] Reductive nitrile–nitrile^[26] C–C coupling or Zr–C insertion and nitrile-substrate C–C coupling^[27] reactions are well studied, mostly for group 4 metallocene alkyne complexes. In complex 5, both the alkyne moiety and the bridging methyl unit could react with nitriles. This species was thus reacted with 2-cyanopyridine and acetonitrile, two nitriles that showed C–C coupling in previous studies, at the NMR scale in benzene- d_6 . The reaction of 5 with 2-cyanopyridine at room temperature produced a new zirconocene species, showing two 1H NMR signals at δ 5.78 and 5.80 ppm, whereas a similar reaction with acetonitrile gave a complex reaction mixture. In both experiments, a considerable amount of precipitate was formed. Although the NMR scale reaction showed promising conversion of 5 and 2-cyanopyridine, only low yields of 14% of the newly formed compound 8 (Scheme 5) could be isolated on a small preparative scale. Recrystallization of the brown solid from hexane/pentane mixture at low temperatures produced crystals of 8 suitable for SC-XRD analysis (Figure 3, discussion of structural data, see below). The molecular structure shows a dinuclear zirconocene complex in which the 2-cyanopyridine connects both Zr centers. The methyl ligand of the starting complex is found on Zr1 and the alkynyl ligand on Zr2, without insertion or coupling to the nitrile substrate. The formation of this complex supports the assumption of a flexible methyl bridging unit in 5, which can shift between both Zr centers.

A slightly better yield could be achieved by reacting two equivalents of acetonitrile and 5 in benzene solution at 50 °C for

Table 1. Selected experimental and DFT-optimized (italics) bond lengths, angles, dihedral angles and Zr...Zr distances of complexes 5–9.

Complex	C _α –C _β [Å] ^[a]	C _α –C _β –C _{Ph} [°]	Zr–C _α –C _β –Zr [°] ^[d]	Zr...Zr [Å] ^[b]
5	1.298(6)	135.4(4)	2.3(15)	3.380
	1.292	137.3	12.7	3.390
6	1.297(3)	136.7(2)	2.8(6)	3.323
	1.297	137.0	2.0	3.288
7	1.468(2)	130.37(15)	158.16(7)	3.332
	1.457	129.7	159.4	3.303
8	1.214(2)	177.7(2)	–43.1	4.499
	1.221	174.3	2.6	4.474
9	1.334(5) ^[d]	124.2(3)	25.5(3)	3.583
	1.344	123.0	6.0	3.647

^[a] C–C distance of the alkynyl/former alkynyl unit.
^[b] Distances were measured with the programme Diamond. For complex 7 the shortest distance Zr1–Zr2 is given.
^[c] For complex 7 Zr3–C1–C2–Zr1 is depicted.
^[d] In complex 9 C_α represents C3 and C_β represents C4 (Figure 3).



Scheme 6. Reaction of complex 5 and acetonitrile, producing 9.

12 h (Scheme 6). The resulting yellow solid was washed with fresh benzene and isolated, resulting in a yield of 39%. SC-XRD analysis of yellow single crystals that were isolated from the yellow wash solution reveals complex 9 as a dinuclear complex with bridging acetonitrile. However, in this case, C–C coupling between the alkynyl and methyl ligands produced a dianionic alkenyldide as a second bridging unit (Figure 3, discussion of structural data, see below). Complex 9 is poorly soluble in most non-polar solvents, decomposed in acetonitrile and DMSO, and showed moderate solubility in THF that led to slow decomposition (Figure S10).

2.3. Discussion of Structure and Bonding Features

2.3.1. General Discussion

Based on the experimental SC-XRD data of complexes 5–9, characteristic structural changes can be identified. In particular, the C_α–C_β bond and the C_α–C_β–C_{Ph} angle of the (transformed) alkynyl unit (Figure 3; Table 1, columns 1 and 2), which are present in all complexes, undergo the most significant changes as a result of the described reactions.

The C_α–C_β distance of this unit in 8 is shortest at 1.214(2) Å and can be described as a triple bond (cf. d(C≡C) = 1.20 Å^[28]). The nearly linear C_α–C_β–C_{Ph} unit (C_α–C_β–C_{Ph} 177.7(2)°) also indicates that there is almost no π interaction between the alkyne unit and the second zirconocene center in 8. As soon as this unit bridges two Zr centers as found in 5 and 6, the C_α–C_β distance increases and the C_α–C_β–C_{Ph} angle decreases signifi-

cantly (Table 1). In 5 and 6 this bond is best described as a shortened double bond (cf. d(C=C) = 1.34 Å),^[28] whereas in complex 7 the long C_α–C_β distance of 1.468(2) Å is close to a single bond (cf. d(C–C) = 1.50 Å),^[28] reflecting the partial hydrogenation of the former alkynyl unit and pointing to a highly unusual coordination environment of C_α.

In this unit of complex 9, the two carbon atoms C_α and C_β (Figure 3, C3–C4) bridge the two zirconocene centres via Zr–C, σ bonds, which is consistent with the double bond-like C3–C4 distance. In complexes 8 and 9 an uncommon bridging motif is found in which the N of the nitrile connects both Zr centers. The C atom of the nitrile fragments is connected to one Zr as well; this formal (μ - π -N≡CR) coordination leads to a bending of the nitrile unit (8: N1–C4–C5 119.5(2)°; 9: N1–C1–C2 126.5(2)°) and elongation of the N–C distance (8: N1–C4 1.263(2); 9: N1–C1 1.242(5) Å; cf. d(N≡C) = 1.14, d(N=C) = 1.27 Å).^[28] These values are well in line with related aryl and alkyl nitrile bridged dizirconium complexes, for example, d(N–C) = 1.255(9) Å and N–C–C = 127.4(7)° in [Zr₂Cl₆py₂(μ -NC-*t*-Bu)]^[29] or d(N–C) = 1.23(2) Å and N–C–C = 130(2)° in [(Cp₂Zr)₂(μ -C₂Me)(μ -NC-Tol)].^[30]

In 5 and 6 the Zr centers and the alkynyl unit are found in almost the same plane, reflected by the small Zr–C_α–C_β–Zr dihedral angles. The distance between the Zr atoms in all discussed complexes ranges between 3.323 and 4.499 Å, with the largest distance found in complex 8 and the second largest in 7 for the two opposing Zr atoms (d(Zr1...Zr3) = 4.329 Å). In all other cases, this distance is shorter than 3.6 Å, in the range of values found in other Zr(III)–Zr(III) complexes such as Zr₂Cl₆(dppe)₂ (3.099 Å^[31]) or (Cp₂Zr)₂ (3.699 Å^[32]). Of note, this is in the range of so called “superlong” Zr–Zr bonds.^[33] The diamagnetism of these dinuclear compounds was explained using ab initio computations.^[33] From a synthetic point of view, complex 5 was synthesized by reacting the Zr(IV) complex 3 with a Zr(II) source, which could lead to a similar electronic situation if comproportionation to a Zr(III)–Zr(III) system takes place. In fact, this was observed for complex F.^[13] However, a closer examination of the Zr–C1 distances in 5 reveals two significantly

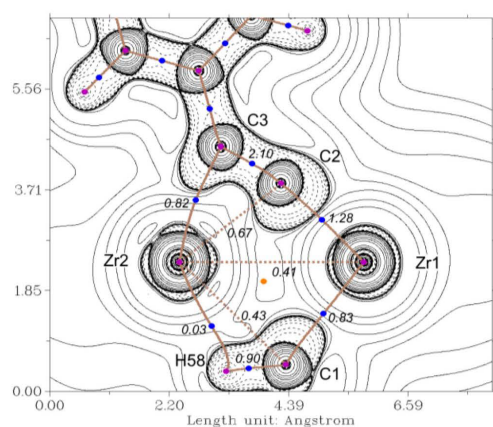


Figure 4. Contour plot of the Laplacian of the electron density $\nabla^2\rho$ of complex 5 in the Zr1-Zr2-C3 plane. Dashed lines indicate negative (local charge depletion), solid lines indicate positive values (local charge concentration). The Laplacian plot is overlaid with the molecular graph from QT-AIM analysis and Wiberg bond indices (small italic numbers). Brown lines indicate bond paths, brown dashed lines are hypothetical bonds, blue dots correspond to bond critical points, and light brown dots indicate ring critical points. Density from B3LYP-D3/def2-TZVP calculation.

different bond lengths (Zr1–C1 2.453(5), Zr2–C1 2.580(5) Å), both of which are longer than the reference Zr–C single bond value (c.f. $d(\text{Zr}–\text{C}) = 2.29$ Å)^[28] and the Zr1–C2 distance of the σ -bonded alkynyl unit (5: Zr1–C2 2.110(4) Å). These data suggest the same mixed-valent Zr(IV)–Zr(II) electronic situation in the solid state as observed before for E (Figure 1c).^[13]

2.3.2. Structural Analysis of Complexes 5 and 6

To further analyze the electronic situations in complexes 5–9, a set of bond analyses, based on gas phase structures on the B3LYP^[34]-D3^[23]/def2-TZVP^[24] level of theory (with Gaussian16^[35]) was performed. A comparison of experimental and calculated structural parameters (Table 1) shows good agreement and reliable structures for further bond analyses. Next, a quantum theory of atoms in molecules (QT-AIM)^[36] and natural bond orbital (NBO)^[37] analysis, as well as inspection of the Wiberg bond indices (WBI) was done. For complex 5, a combination of the contour plot of the Laplacian of the electron density $\nabla^2\rho$ with the QT-AIM and WBI analysis (Figure 4) provides insight into the bond situation along the Zr1–C1–Zr2 unit in this complex and shows two distinct bonds between the Zr centers and the C atom of the methyl unit.

While a bond path with a bond critical point and a WBI of 0.83 to Zr1 can be identified, both criteria are missing between Zr2 and C1. The WBI of 0.43 supports the weak interaction in this case. The η^2 -coordination of the alkynyl unit is represented by the electron density pointing from C2/C3 in the direction of Zr2 even though no bond critical point and path was found between Zr2 and C2 in QT-AIM. The longer C2–C3 distance compared to PhC₂H (Figure S25, C–C 1.202 Å, WBI 2.90) or to 8

(WBI 2.74) is well reflected by the smaller WBI of 2.1 in this unit of complex 5. A comparison of the shape of the Laplacians of electron density at Zr1 and Zr2 reveals no significant differences, in agreement with its identical calculated natural charges ($q_{\text{nat.NBO}}(\text{Zr1/Zr2}) = 1.52$). The sum of the natural charges of the zirconocene units ($q_{\text{nat.NBO}}(\text{Cp}_2\text{Zr1/Cp}_2\text{Zr2}) = 0.74/0.73$) shows only minor differences and the charges of the negatively charged bridging substituents are summed up to $q_{\text{nat.NBO}}(\text{alkynyl}) = -1.01$ and $q_{\text{nat.NBO}}(\text{CH}_3) = -0.46$. These data suggest a well-balanced Zr(III)–Zr(III) electronic situation instead of a mixed-valent Zr(IV)–Zr(II) complex.

As the compound 5 could be unambiguously identified by NMR spectroscopy, the presence of a “superlong” Zr–Zr bond would explain the diamagnetism in this case. An inspection of the natural localized molecular orbitals (NLMOs) shows that NLMO38 can be interpreted as an alkynyl assisted Zr–Zr bond orbital (Figure 2, right) with major contributions from in-plane d orbitals at Zr1 (14%) and Zr2 (21%) and almost pure p orbitals along the C2–C3–C4_{ph} unit (13%/15%/15%) with a node in the plane between C2 and C3 (Table S4). The Zr–C1 interaction is best described by NLMO44 (Table S4) as a strongly polarized orbital in which the sp^2 hybrid orbital at C1 has a major contribution (77%) to the Zr1–methyl σ bond, along with minor portions of the Zr2–methyl interaction ($\text{sd}^4\text{-Zr1: 16, sd}^6\text{-Zr2: 6\%}$). Weak interactions between the two Zr atoms as well as between C1 and Zr2 are also reflected by lower WBI of 0.41/0.43 (Figure 4) and the absence of bond critical points and paths in QT-AIM. Alternatively, the connectivity determined by SC-XRD analysis suggests a Zr(IV)–Zr(II) electronic situation, which seems to be different in solution. For the analogous trimethylsilyl-alkynyl complex F a low-lying barrier was found for the methyl group shift between the Zr centers ($\Delta G^\ddagger = 5.4$ kJ/mol). In this case, the Zr(III)–Zr(III) geometry is slightly preferred ($\Delta_R G^\circ = -0.6$ kJ/mol) and found by SC-XRD analysis as well. In the phenyl derivative 5 also the thermodynamically preferred Zr(IV)–Zr(II) isomer ($\Delta_R G^\circ = 1.6$ kJ/mol) is obtained in the solid-state structure. A barrier of $\Delta G^\ddagger = 5.2$ kJ/mol suggests facile conversion into the Zr(III)/Zr(III) isomer in solution. These calculated values are significantly lower than the experimentally determined barriers of the alkynyl group shift, referred to as automerization, in B and related complexes, which range between 52.7 and 61.9 kJ/mol.^[11a] The low barriers for the methyl group shift reflect its reactivity, explaining the facile transformation of this unit in the reactions shown here. We suggest that—supported by DFT computations—the thermodynamically favored electronic situation can be tuned by the choice of the substituent at the bridging alkynyl unit.

Based on these considerations, it can be assumed that similar dynamics play a role in complexes 6–9, which were synthesized from 5. Indeed, ¹H and ¹³C NMR signals of the phenyl groups indicate free rotation of these groups in complexes 6–9. For simplicity, the following bond analyses were conducted only on the isomers that were determined experimentally by SC-XRD. In complex 6, the QT-AIM parameters are mostly in line with those of 5 (Figure S15). The hydride ligand shows a natural charge of -0.3 and is computed to be positioned almost equidistantly to the Zr centers (Zr1–H1 2.017, Zr2–H1 2.043 Å), supported by the WBIs of the Zr–H bonds of 0.45 and 0.47, respectively. NLMO96 reveals

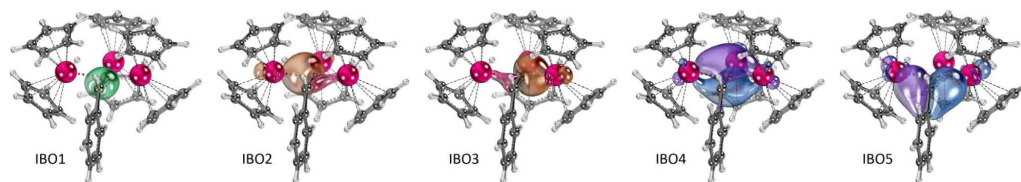


Figure 5. Plot of selected IBOs, describing the bond situation in the trinuclear complex **7**. Atoms/charges: IBO1: C1/0.946, C2/0.993, Zr1/0.027, Zr3/0.028; IBO2: C1/1.764, Zr1/0.090, Zr2/0.090; IBO3: C1/1.763, Zr3/0.090, Zr2/0.089; IBO4: C1/1.746, Zr2/0.057, C2/0.037, Zr1/0.036, Zr3/0.035, H1/0.021; IBO5: C2/1.599, C3/0.133, Zr3/0.077, Zr1/0.075.

almost equal contributions of both Zr atom orbitals (Table S6, NLM096: 19% Zr1 sd^5 hybrid; Zr2 17% sd^6 hybrid; 63% H1 s orbital), allowing for a description as a classical three centre-two electron [Zr–H–Zr] bridging unit (Figures S15 and S28). It is also noteworthy that the WBI of the Zr–Zr interaction is 0.63, corresponding to the shortened Zr–Zr distance observed in this compound.

2.3.3. Structural Analysis of the Hydrogenation Product **7**

The bond analysis of the two bridging hydrides in the trinuclear complex **7** is very similar to that in **6**, showing natural charges of -0.3 . Bridging [Zr–H–Zr] units are, in this case, slightly polarized with the zirconocenes coordinated side-on to the C_2 fragment contributing slightly more (Table S8, NLM0150, 151). The charge distributions of the intrinsic bond orbitals (IBOs)^[38] for these two bonds show a similar picture (Table S8, comparison of NLMOs and IBOs). Of note, the central carbon atom C1 is only located 0.352 Å (computed: 0.328 Å) out of the plane defined by the three Zr atoms, close to planar coordinated with an angle between the planes C1–Zr1–Zr2 and C1–Zr3–Zr2 of 21.8° (computed: 20.2°). This C atom is significantly closer to the end-on coordinated Zr2 atom than to the two side-on coordinated metals Zr1 and Zr3 (C1–Zr2 2.144(2)/2.134; C1–Zr1 2.235(2)/2.219; C1–Zr3 2.232(2)/2.220 Å). C2 is found at a significantly greater distance from the side-on Zr atoms but remains within the range of metal–carbon bonds (C2–Zr1 2.464(2)/2.466; C2–Zr3 2.471(2)/2.471 Å) that is also found in complex **5** (Figure 2, Zr1–C1 2.453(5), Zr2–C1 2.580(5) Å). However, for C2–Zr1 and C2–Zr3 no bond paths or bond critical points could be found in QT-AIM analysis, although the WBI is 0.5 for both contacts, similar to Zr–H hydride bonds (Figure S17). When evaluating this unusual structural feature using an interaction region indicator^[39] (IRI) analysis (Table S9) a clear binding interaction is found between C2, Zr1, and Zr3. Furthermore, this analysis shows large areas of attractive van der Waals interactions between the Cp ligands and additionally between Cp and the phenyl groups, thus stabilizing this structural feature inside the pocket formed by the three zirconocenes. Planar tetra-coordinate carbon environments have fascinated molecular chemists for decades.^[40] While this structural feature is rather unusual, its stabilization in the coordination sphere of transition metals has been reported on several occasions.^[41]

Although it does not provide a formal hybridization composition, the IBO analysis gives a more balanced description for this fragment than the NBO/NLMO analysis (Table S8 and Figure 5). IBO1 represents a classical C–C σ bond orbital, likely a sp^2 hybrid.

IBO2 and IBO3 can be interpreted as three center-two electron bond orbitals in the plane connecting sp^2 hybrid orbitals at C1 with all three Zr centers with strong polarization to C1, reflected by the high charges at C1 (Figure 5) that agree with the corresponding NLMOs (Table S8). IBO4 is orthogonal to IBOs 2 and 3, mainly consisting of a p orbital at C1, which connects all three metal centers and C2 in π geometry, only showing minor contributions/charges. This IBO4 can formally be interpreted as a five center-two electron bond interaction and, due to its π type C_α – C_β bond contributions, provides an explanation for the slightly shortened single bond, supported by a WBI of 1.36 for this bond. IBO5 is mainly composed of a p orbital at C2 that lies in the plane defined by the three Zr atoms and connects both side-on coordinated Zr centers. In contrast to IBO analysis, the NBO analysis found a triply bonded C1 atom to Zr2 with occupancies below 1.6 electrons in two of these NBOs. This again points to a delocalized electronic system, which is well reflected in the IBO analysis. The large natural charge $q_{\text{nat.NBO}}(C_\alpha-C_\beta)$ of -1.57 allows for an interpretation of this fragment as a tetraanionic ligand, which is in line with the five IBOs and NLMOs describing the C1–C2 unit and its binding contributions to the Zr centers (Figure 5 and Table S8). Assuming that **7** is composed of three Zr(IV) centers with six monoanionic Cp and two hydride ligands, formally, four negative charges should be located on the hydrocarbon bridging unit. In line with this the side-on coordinated zirconocene fragments show higher natural charges $q_{\text{nat.NBO}}(\text{Cp}_2\text{Zr1 } 0.77; \text{Cp}_2\text{Zr3 } 0.76)$ compared to the metallocene σ coordinated to the terminal C atom (Cp₂Zr2 0.64), compensated by the negative charges of its hydride ligands.

2.3.4. Structural Analysis of Nitrile Insertion Products **8** and **9**

The 2-cyanopyridine complex **8** shows the former methyl and alkynyl units of the starting complex **5**, now coordinated to a different Zr center. The 2-cyanopyridine substrate is positioned between both metal centers and forms three- (Zr1–N1–C4) and five-membered ring systems (Zr1–N1–C4–C5–N2) that show an angle of about 6° between the two planes (Figure 6). A QT-AIM analysis reveals the presence of ring critical points at the centers of these metallacycles (Figure 6). Coordination of 2-cyanopyridine is associated with a formal reduction, as evidenced by the significant bending of the nitrile unit and a computed natural charge of -0.81 . The N atom of the nitrile unit formally acts as a bridging element between the two Zr centers. Both the contour plot of the Laplacian of the electron density

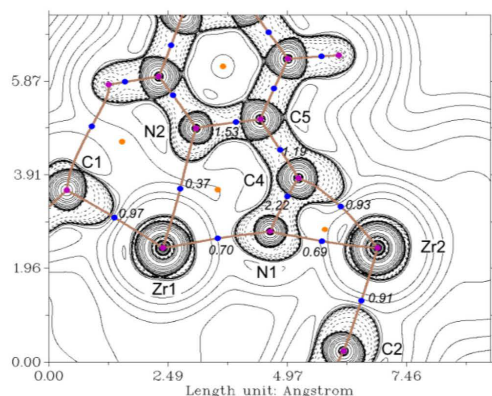


Figure 6. Contour plot of the Laplacian of the electron density $\nabla^2 r$ of complex **8** in the Zr1-Zr2-N2 plane. Dashed lines indicate negative (local charge concentration) and solid lines indicate positive values (local charge depletion). The Laplacian plot is overlaid with the molecular graph from QT-AIM analysis and Wiberg bond indices (small italic numbers). Brown lines indicate bond paths, blue dots correspond to bond critical points, and light brown dots indicate ring critical points. Density from B3LYP-D3/def2-TZVP calculation.

(Figure 6) and the NBO analysis indicate two lone pairs on the central N1 atom (Table S11, NLM052 and NLM053). Elongation of the former nitrile group is evidenced by its experimental bond length (C4-N1 1.263(2) Å), which is in line with a C=N double bond and supported by the WBI of 2.2. NLMO analysis shows that this bond can be described as a classical C–N π bond which shows only minor contributions of Zr2 and C5 orbitals (NLM065). The interaction of the former nitrile carbon C4 and Zr2 can be understood as a polarized σ bond with major contributions from the C atom (Table S11, NLM062 73% C4 sp^2 hybrid; 22% Zr1 sd^{14} hybrid).

Finally, in the acetonitrile complex **9** formation of a new C–C bond between the alkynyl and methyl ligands present in the precursor **5** yields the formally dianionic bridging alkenyldiide unit. This description is well in line with the experimentally observed C3–C4 double bond, its WBI of 1.92 and the Laplacians of the electron density pointing from both C to the Zr center (Figure S24). NLMO analysis shows contributions of classical σ and π C–C bond orbitals as well as two polarized Zr–C σ bonds (Table S13, NLM055, NLM056; NLM060; and NLM062). Similarly as in **8**, the bridging acetonitrile is reduced, evidenced by its bending, a $q_{\text{nat.NBO}}$ value of -0.8 , and the five NLMOs that describe the bond situation in the CN unit and its connectivity to both Zr centers (Table S13).

3. Conclusion

This study highlights the potential of a formally mixed-valent dinuclear zirconocene complex that can be generated from a Zr(IV) alkynyl complex and a Zr(II) source for a variety of bond activation reactions. Detailed experimental and computational studies reveal unique structural and bonding features in the

title compound $[(\text{Cp}_2\text{Zr})_2(\mu\text{-Me})(\mu\text{-C}_2\text{Ph})]$ with a highly fluxional bridging methyl group that allows for a wide range of unusual reactivity. Hydrogenation of this species using amine boranes or molecular hydrogen furnishes rare examples of highly sensitive di- and trinuclear zirconocene hydride complexes that are relevant in stoichiometric and catalytic (de)hydrogenation reactions. The complex formed in the latter case possesses the unusual structural feature of a planar tetracoordinate carbon atom, surrounded by three Zr centers that are connected through three-center two-electron-bonded hydrides and a side-on interaction with the formally tetraanionic former alkynyl unit. In reactions with nitriles, the formation of rare examples of nitrile coordination to the Zr center and reduction of the substrate without further coupling can be observed.

The modular protocol used for the preparation of the title compound suggests the facile extension of this structural motif to other, related complexes that allows for a more detailed study of structure-activity relationships. Thus, the experimental and theoretical results presented herein form the basis for further systematic applications of such mixed-valent homo- and hetero-bimetallic early transition metal complexes for stoichiometric and catalytic bond activation reactions.

Supporting Information

The authors have cited additional references within the Supporting Information.^[42]

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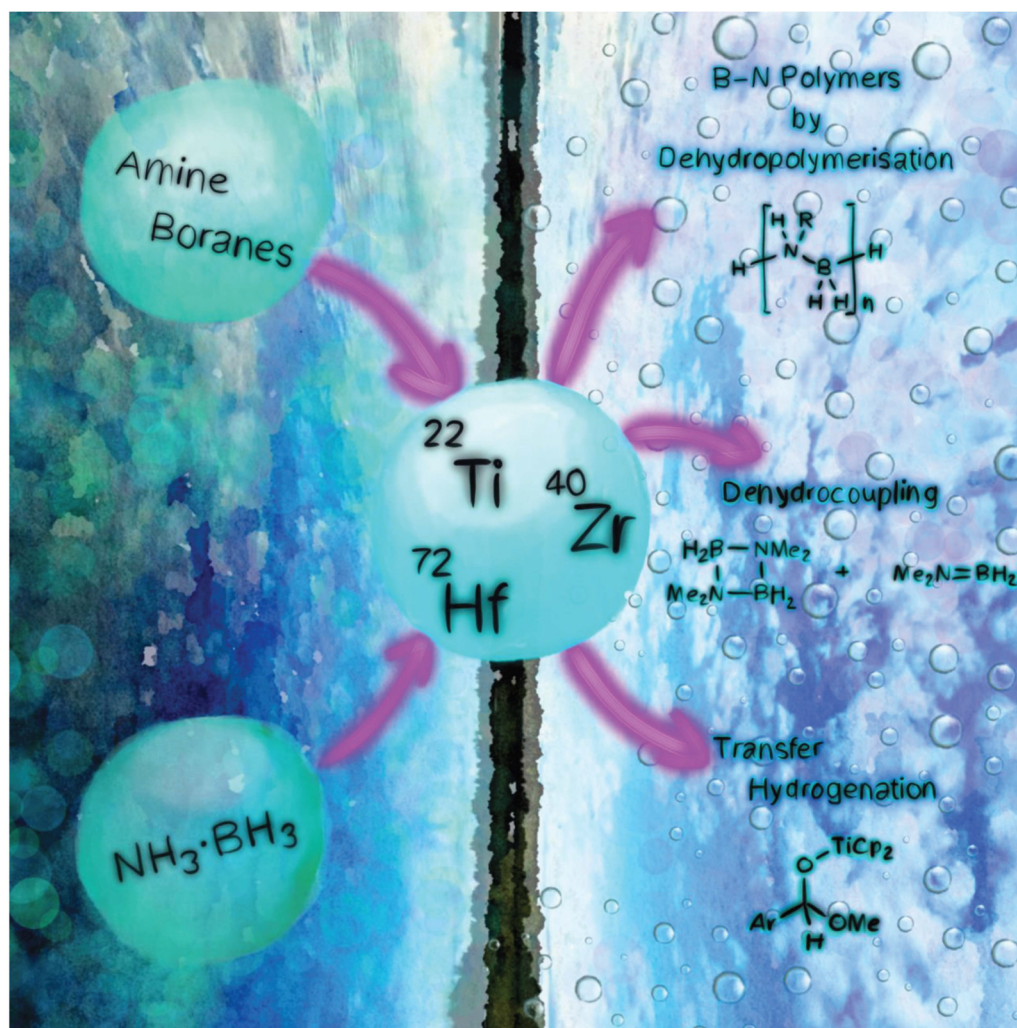
5.3 Anlage 3



Dehydrocoupling of Ammonia/Amine Boranes and Related Transformations Catalysed by Group 4 Metal Complexes

Mirko Rippke,^[a] Ximei Tian,^[b, c] Fabian Reiß,^[a] Lipeng Wu,^{*,[b, d]} and Torsten Beweries^{*,[a]}

In memory of Ian Manners.



Ammonia borane and amine boranes are main group analogues of alkanes, which are characterised by their large gravimetric hydrogen content. This hydrogen can be released in dehydrocoupling and dehydropolymerisation reactions to obtain B–N oligomers and polymers that are of importance as precursors for functional B–N materials. Furthermore, amine boranes are potent reagents for application in transfer hydrogenation reactions, representing a versatile, easy-to-handle alternative to the use of gaseous hydrogen for the reduction of organic

compounds. Compared to late transition metals, complexes of readily available and comparatively inexpensive electropositive group 4 metals have been used to a much lesser extent. This review summarises the developments in the field of dehydrocoupling of amine boranes and transfer hydrogenation with these reagents, catalysed by complexes of group 4 metals. We analyse the background for these developments using examples and reaction mechanisms and provide an outlook for future developments in this field of research.

1. Introduction

Ammonia and amine boranes are formally isoelectronic with alkanes.^[1] Due to their high weight percentage of H₂ (e.g., 19.6% for NH₃BH₃) and relatively stable physical and chemical properties, they were historically considered as potential hydrogen storage materials.^[2] Re-hydrogenation of the dehydrogenated materials “spent fuels” however proved difficult due to the thermodynamic preference for the corresponding B–N compounds in its dehydrogenated form.^[3] Nonetheless, amine boranes showed great potential as bench-stable hydrogen sources that can be readily used for well-defined addition of hydrogen to organic substrates.^[4] The products obtained after dehydrogenation have found application as precursors for ceramic thin films and advanced polymeric main-group materials.^[5] Therefore, dehydrocoupling reactions of ammonia and amine boranes have attracted great attention in the past two decades.^[6] Indeed, the N–H and B–H bonds in ammonia/amine boranes are oppositely polarised, thus thermally induced release of H₂ at elevated temperatures is known and readily possible.^[7] For example, NH₃BH₃ decomposes with release of hydrogen at temperatures higher than 120 °C. The use of catalysts allows to perform the dehydrogenation reactions at milder reaction conditions, improving the efficiency, and controlling the selectivity towards various dehydrocoupling products.^[8] Hence, a great deal of effort has been devoted to the development of catalysts for dehydrogenation and dehy-

drocoupling reactions. Since the first report of catalytic dehydrocoupling of ammonia/amine boranes using rhodium catalysts by Manners and co-workers, a wide variety of transition metal and main group catalysts have been developed.^[9,10] Among them, the majority of the catalysts are based on precious metals, such as Rh, Ir, and Ru,^[7,10] as well as non-noble late transition metals such as Fe or Co.^[11]

Early transition metal complexes often bind to different ligands, show divergent coordination geometries and thus possess orthogonal reactivities compared with its late transition metal counterparts.^[12] Moreover, several are earth-abundant, e.g., titanium is the second most abundant transition-metal and the 9th most abundant of all elements in the earth's crust. Zirconium is also one of the more available elements, with an abundance similar to that of carbon. Traditionally, Ti and Zr compounds have been used as stoichiometric organometallic reagents in organic synthesis with the Schwartz and Tebbe reagents, Cp₂Zr(H)Cl and Cp₂Ti(μ-Cl)(μ-CH₃)AlMe₂, respectively, as prominent examples.^[13] Catalytic applications for Ti and Zr complexes can mainly be found in the field of polymerisation and oxidation of olefins.^[14] Although recent developments have expanded their utilisation as catalysts in many types of stoichiometric and catalytic organic transformations,^[15] their use still lags behind that of late transition metals.^[16] Nevertheless, the use of group 4 complexes as a catalyst for the dehydrocoupling of ammonia/amine boranes has been established in the past two decades. This review summarises the history and recent developments of using the group 4 metals Ti, Zr, and Hf for the dehydrocoupling of NH₃BH₃ and related amine boranes. Catalyst developments, catalytically active species, and reaction pathways are discussed. Apart from dehydrogenation and dehydrocoupling reactions, closely related reactions of using ammonia/amine boranes as hydrogen transfer reagents^[17] with focus on hydrogenation reactions are also included in this review.

2. Dehydrocoupling Reactions

2.1. Titanium Catalysts

Group 4 metal complexes were first mentioned for the dehydrocoupling of dimethylamine borane, Me₂NH-BH₃, by Manners *et al.* in 2003 as part of a study of late transition-metal catalysed dehydrocoupling of primary or secondary amine boranes to aminoboranes and borazine derivatives.^[18] However,

[a] M. Rippke, F. Reiß, T. Beweries
Leibniz Institute for Catalysis Rostock (LIKAT), Albert-Einstein-Str. 29a, 18059
Rostock, Germany
E-mail: torsten.beweries@catalysis.de

[b] X. Tian, L. Wu
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou
Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou
730000, P. R. China
E-mail: lipengwu@licp.cas.cn

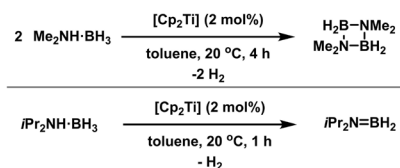
[c] X. Tian
University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[d] L. Wu
College of Material Chemistry and Chemical Engineering, Key Laboratory of
Organosilicon Chemistry and Material Technology, Ministry of Education,
Hangzhou Normal University, Hangzhou 311121, P. R. China

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Petasis' reagent Cp_2TiMe_2 ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$) shows no conversion even after reaction times of 160 h at 25 °C. Later, the same authors reported the successful dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ and the isopropyl substituted analogue $i\text{Pr}_2\text{NH-BH}_3$ using a more reactive 14-electron $[\text{Cp}_2\text{Ti}]$ complex.^[19] The active catalyst is generated *in situ* by addition of $n\text{BuLi}$ to Cp_2TiCl_2 (**6**). The reaction of $\text{Me}_2\text{NH-BH}_3$ leads to the formation of cycloborazane ($\text{Me}_2\text{N-BH}_2$), whereas the reaction of $i\text{Pr}_2\text{NH-BH}_3$ forms the monomeric aminoborane species $i\text{Pr}_2\text{N-BH}_2$, formally an isoelectronic B–N analogue of an olefin (Scheme 1). Furthermore, the key question of whether the reaction was homogeneous or heterogeneous was investigated by Hg poisoning and filtration experiments, both leading to the conclusion that the catalytic reaction is homogeneous in nature.

In 2007, Chirik *et al.* investigated a series of structurally related Ti (Figure 1) and Zr dinitrogen complexes for the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ and $\text{NH}_3\text{-BH}_3$.^[20] All experiments were conducted in benzene- d_6 using 2 mol % of the respective catalyst. Reactions in THF show lower conversion, likely due to coordination to the electropositive metal centre. Lower activity is observed for complexes with sterically demanding Cp ligands. In general, Ti complexes show higher activity compared to the



Scheme 1. Homogeneous titanocene-catalysed dehydrocoupling of amine boranes.

investigated Zr complexes. The highest reactivity is observed for a dinuclear Ti(II) dinitrogen complex **3** bearing sterically demanding SiMe_3 substituents at the Cp ligand. A comparison of turnover frequencies (TOF) is given below. However, we would like to point out that a comparative analysis of these values for different catalyst systems tested in different laboratories should be carried out with caution due to the variable experimental conditions (e.g., open vs. closed systems with or without H_2 venting, NMR scale vs. reactions in Schlenk tubes).

Later, in 2010 Manners *et al.* presented a detailed study on the use of a series of group 4 metallocene-based complexes as pre-catalysts for the dehydrocoupling of amine boranes



Mirko Rippke joined the Beweries group at the Leibniz Institute for Catalysis (LIKAT) in 2020 and received the B.S. degree the same year from the University of Rostock. In 2022 he obtained his M.S. degree from the same university and continued his research in the Beweries group as a Ph.D. student thereafter. His current research focuses on dehydrocoupling reactions of amine boranes with late transition metal complexes.



Ximei Tian received her B.S. degree in the School of Materials Science and Engineering from Tianjin University of Technology in 2021. She is a graduate student in Lipeng Wu's lab at the Lanzhou Institute of Chemical Physics, University of Chinese Academy of Sciences. Her research interests focus on early transition metal-catalyzed functionalization of alkenes and alkynes.



Dr. Fabian Reiß obtained his diploma in chemistry at the University of Rostock in the group of Axel Schulz. His Ph.D. thesis in the same group dealt with the activation of small nitrogen-containing molecules with super Lewis acids. After graduating in 2014, he joined Uwe Rosenthal's research group at LIKAT. He investigated the activation of small molecules with group 4 alkyne complexes. Since 2020, he has been a topic leader in the subgroup "Catalysis of Early Transition Metals" of Torsten Beweries' research group, studying the coordination chemistry of group 4 metallocene complexes and their activity in catalysis.



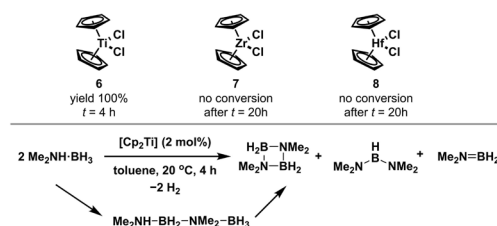
Dr. Lipeng Wu received his BSc in Biology at the Agricultural University of Hebei and MSc in Biochemistry at Lanzhou University. Then, he joined Matthias Beller's group at LIKAT as a Ph.D. student working on alkene carbonylation. After graduating in 2014, he moved to the US and worked with F. Dean Toste in Berkeley, studying biomass conversion. In 2016, he was awarded a European Marie Curie Fellowship with Ian Manners and worked on main group chemistry. He started his independent research career in 2018 in LICP with focus on the catalytic application of early transition metals.



Prof. Torsten Beweries is a research group leader at LIKAT. After undergraduate studies at the University of Rostock he studied for his Ph.D. at LIKAT, supervised by Uwe Rosenthal. After postdoctoral work at the University of York with Robin N. Perutz he returned to LIKAT as a group leader, working on his habilitation. He was appointed as professor at the University of Rostock in 2022. With his group he investigates the organometallic chemistry and mechanisms of amine borane dehydrocoupling, as well as the coordination chemistry of group 4 metallocene and group 8–10 metal pincer complexes.

(Scheme 2).^[21] The reactive metallocenes $[\text{Cp}_2\text{M}]$ ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$) are generated *in situ* by treatment of the corresponding Cp_2MCl_2 precursor with 2 equiv. of $n\text{BuLi}$. In addition, $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ can also be used as a synthon for the generation of the $[\text{Cp}_2\text{Ti}]$ pre-catalyst. Comparison of the catalytic activities of different metal catalysts in the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ and $i\text{Pr}_2\text{NH-BH}_3$ shows that the Hf complexes give no conversion. The Zr species show 65% conversion of $i\text{Pr}_2\text{NH-BH}_3$ in THF solvent, whereas the Ti pre-catalysts show the highest activity. The phenomenon of decreasing catalytic activity associated with descending the group is similar to Chirik's findings. Similarly, it could be shown that substitution of the cyclopentadienyl ligands has a significant effect on the catalytic performance, with sterically demanding or electron-donating substituents resulting in a decrease of activity. Mechanistic studies suggest a homogeneous catalytically active Ti(II) species. The linear dimer diborazane $\text{Me}_2\text{NH-BH}_2\text{-NMe}_2\text{-BH}_3$ was identified as the key intermediate for the formation of the cyclic dehydrogenation product cyclodiborazane ($\text{Me}_2\text{N-BH}_2$)₂ (Figure 2).

A computational reconsideration of this mechanism using dispersion-corrected density functional theory (DFT-D) by Alikhani and co-workers supported an energetically favoured reaction mechanism that is in line with Manners' experimental findings (Figure 2).^[22] Van der Waals interactions that stabilise the interaction of a second $\text{Me}_2\text{NH-BH}_3$ molecule with a metal-coordinated amidoborane subunit via dihydrogen bonds are proposed to play a central role in the formation of the linear dimer intermediate. This model furthermore explains the lack of aminoborane dimerisation in the case of more sterically demanding $i\text{Pr}_2\text{NH-BH}_3$, where formation of a van der Waals complex is not possible, thus resulting in the formation of a stable aminoborane $i\text{Pr}_2\text{N-BH}_2$ as the only product. Further computational studies were carried out by Luo and Ohno,^[23] who found that the formation of $\text{Me}_2\text{N-BH}_2$ is kinetically and energetically favoured. Furthermore, Tao and Qi proposed that the above-mentioned intermolecular and intramolecular pathways should be competitive for the reaction mechanism.^[24] Of note, the results of both computational studies contradict experimental data, which suggest on-metal steps for both,



Scheme 2. Homogeneous group 4 metallocene type pre-catalysts for the dehydrocoupling of amine boranes.

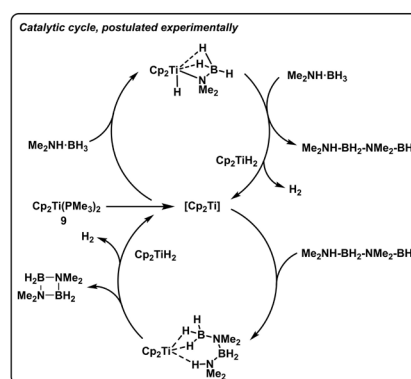


Figure 2. Proposed pathway of $[\text{Cp}_2\text{Ti}]$ -catalysed dehydrocoupling of amine boranes.

formation of the intermediate $\text{Me}_2\text{NH-BH}_2\text{-NMe}_2\text{-BH}_3$ and the major product ($\text{Me}_2\text{N-BH}_2$)₂.

In all the work described thus far, the catalytic cycle was postulated to involve the interplay of Ti(II) and Ti(IV) species. In 2013 Manners *et al.* found that also Ti(III) species might play a key role in the dehydrocoupling of ammonia/amine boranes with titanocene complexes (Figure 3).^[25] However, attempts to isolate Ti(III) species from the stoichiometric reaction of the

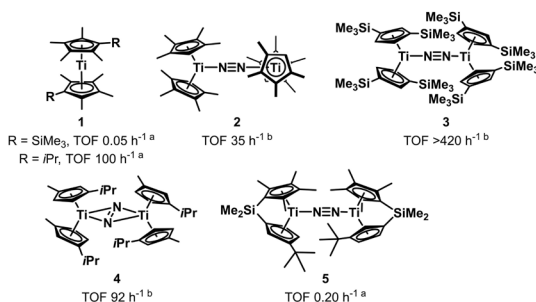


Figure 1. Isolable titanocene complexes as pre-catalysts for the dehydrocoupling of amine boranes. Reaction conditions: benzene- d_6 , 2 mol % precatalyst, $[\text{Me}_2\text{NH-BH}_3] = 0.61 \text{ M}$, ^a $T = 65^\circ\text{C}$, ^b $T = 23^\circ\text{C}$.

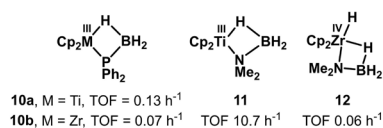
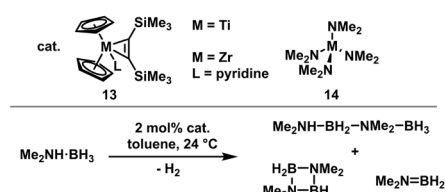


Figure 3. Isolated Ti(III), Zr(III) and Zr(IV) species for the catalytic dehydrocoupling of amine boranes. Reaction conditions: toluene, 2 mol% precatalyst, [Me₂NH-BH₃] = 1.3 M, T = 20 °C.

Cp₂TiCl₂/nBuLi system were not successful. Note that using this system phosphine boranes, valence isoelectronic to amine boranes, do not undergo dehydrocoupling under standard catalytic conditions. With diphenylphosphine borane, Ph₂PHBH₃, as the substrate, isolation of a titanocene(III) phosphidoborane compound **10a** as the prospective reaction intermediate was possible. The amidoborane Ti(III) complex **11** can be obtained by reaction of Cp₂TiCl₂ (**6**) with Li[NMe₂BH₃]. Both isolated Ti(III) species were investigated as pre-catalysts for the dehydrocoupling of Me₂NH-BH₃ and show high activity. Compound **11** shows comparable activity to that of the Cp₂TiCl₂/nBuLi system. Furthermore, reaction monitoring by UV-vis and EPR analysis revealed that spectroscopic signatures characteristic of the isolated Ti(III) species could also be detected in the Cp₂TiCl₂/nBuLi system. Thus, Ti(III) species might be formed in the Cp₂TiCl₂/nBuLi system and play a key role for this and related systems that require activation by organolithium reagents. In addition, the Zr analogues of **10a** and **11** were also synthesised (**10b** and **12**) and tested for the catalytic dehydrocoupling reactions. In line with related studies (vide infra), these Zr species show much lower catalytic activities.

Rosenthal *et al.* demonstrated the homogeneous catalytic dehydrocoupling of Me₂NH-BH₃ using group 4 metal(III) complexes of the type Cp₂Ti(η²-Me₃SiC₂SiMe₃) (**13**) (Scheme 3).^[26] Catalytically active [Cp₂M] species can be generated *in situ* by release of the alkyne ligands. Again, the [Cp₂Zr] species is significantly less active than the corresponding titanocene, which is similar to Manners' Cp₂MCl₂/nBuLi system. The Cp* (Cp* = η⁵-pentamethylcyclopentadienyl) derivatives of this type show no activity at all. Moreover, homoleptic metal(IV) amide complexes (**14**) are suitable for dehydrogenation of Me₂NH-BH₃ as well (Scheme 3). In contrast to the [Cp₂M] catalysed reactions, in this case no influence of the metal is observed. Other homoleptic Ti(IV) precursors Ti(OiPr)₄ and TiCl₄ show no



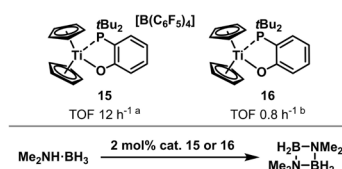
Scheme 3. Dehydrocoupling of Me₂NH-BH₃ catalysed by group 4 metal-alkyne complexes and homoleptic amido compounds.

reactivity for this reaction, highlighting the necessity of either a low-valent metal centre or an amide functionality.

In a follow-up study the same authors also investigated the related species [(η⁵-iPrC₅H₄)₂Ti(η²-Me₃SiC₂SiMe₃)], which shows higher activity for the dehydrocoupling of Me₂NH-BH₃ than the analogous non-substituted Cp-derivatives, a phenomenon that is different from the previous findings.^[27] The reaction conditions were optimised and found to be optimal at T = 40 °C in toluene with 2 mol% catalyst. At these conditions the durability of the catalyst was tested by adding additional Me₂NH-BH₃ after full conversion, showing a decrease in activity after the third addition. Kinetic data show divergent behaviour with variation of the catalyst concentration, i.e. zero-order kinetics at high catalyst loading and a first-order scenario at low concentrations. Half-order in catalyst suggests a catalytically relevant increase in molecular weight of the systems due to rapid, off-cycle dimer-monomer transformation or a ligand dissociation step. Furthermore, ¹B NMR data of reaction monitoring suggest that the linear aminoborane dimer is not an intermediate of the dehydrocoupling reaction with this system.

Wass *et al.* extended the concept of Frustrated Lewis Pairs (FLPs) to group 4 metallocenes, reporting a convenient way to prepare the Ti(IV) and Ti(III) phosphinoaryloxide species [Cp₂TiOC₆H₄P(tBu)₂][B(C₆F₅)₄] (**15**) and [Cp₂TiOC₆H₄P(tBu)₂] (**16**) (Scheme 4).^[28] However these are less active (TOF = 12 and 0.8 h⁻¹) in the dehydrocoupling of Me₂NH-BH₃ than the analogous Zr complexes [Cp₂ZrOC₆H₄P(tBu)₂] (**35**) studied previously (*vide infra*).^[29] This contrasts with the trend found for other reported group 4 systems.

Structurally related Ti(III) phosphinoaryloxide complexes Cp₂Ti(κ²-O,P-O-C₆H₄-PR₂) (**17**, R = iPr or Ph) and Cp₂Ti(κ¹-O-O-C₆H₄-PR₂) (**18**, R = iPr or Ph) also show activity in the dehydrocoupling of Me₂NH-BH₃ when used in toluene at room temperature and at 50 °C with and without solvent (Figure 4).^[30]



Scheme 4. Titanocene phosphinoaryloxide catalysed dehydrocoupling of Me₂NH-BH₃. Reaction conditions: ^a PhCl, 2 mol% precatalyst, T = 23 °C. ^b C₆D₆, 10 mol% precatalyst, T = 23 °C.

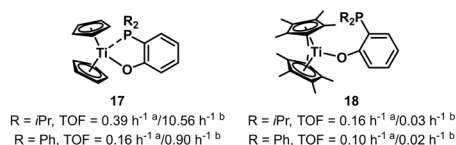


Figure 4. 2-Phosphinoaryloxide ligated Ti(III) complexes for the catalytic dehydrocoupling of Me₂NH-BH₃. Reaction conditions: ^a toluene, 2 mol% precatalyst, [Me₂NH-BH₃] = 2.05 M, T = 25 °C. ^b no solvent, 2 mol% precatalyst, 4.1 mmol Me₂NH-BH₃, T = 25 °C.

Under neat reaction conditions the complex $\text{Cp}_2\text{Ti}(k^2\text{-O},P\text{-O-C}_6\text{H}_4\text{-P}i\text{Pr}_2)$ (**17iPr**) shows the highest activity followed by the more sterically demanding Ph derivative. The most active complex shows no diminished reactivity after further additions of substrate to the finished reaction. EPR data show that Ti(III) species are present throughout the dehydrogenation process.

The synthesis of poly(aminoboranes), formally B–N analogues of polyolefins, is possible using primary amine boranes such as methylamine borane, $\text{MeNH}_2\text{-BH}_3$. The first Ti systems that selectively produce these types of polymers were reported by Manners *et al.* in 2018, using a set of structurally related titanocene dichlorides, activated with $n\text{BuLi}$ (Figure 5).^[31] In these studies, increased electron-donating character of the Cp ligands leads to a higher catalytic activity. Thus, the best catalyst system was identified as Cp^*TiCl_2 (**21**)/ $n\text{BuLi}$, the first early transition metal complex that produces high molecular weight B–N polymers from $\text{MeNH}_2\text{-BH}_3$. This complex also catalyses the dehydropolymerisation of benzylamine borane, *N*-4-phenylbutylamine borane and *N*-thiophenylmethylamine borane. Analysis of conversion/degree of polymerisation plots suggest a step-growth rather than a chain-growth mechanistic scenario with high molecular weight polymers only produced at later stages of the dehydropolymerisation reaction.

The isolable Ti(III) complexes Cp^*TiH (**22c**) and Cp^*TiMe (**22**) show activity for the dehydrocoupling of a series of primary and secondary amine boranes.^[32] These complexes produce the cyclodiborazane and hydrogen from the secondary amine borane $\text{Me}_2\text{NH-BH}_3$. Activation of the methyl complex Cp^*TiMe (**22**) proceeds via release of methane, yielding a catalyst that shows exceptionally high activity of 8800 h^{-1} , corresponding to a > 50-fold increase in rate compared to the parent $\text{Cp}_2\text{TiCl}_2/n\text{BuLi}$ system. Of note, this corresponds to one of the fastest systems reported for this transformation to date. Mechanistic investigations suggest a scenario that involves σ -bond metathesis with β -hydride elimination in a redox neutral reaction mechanism with a Ti(III) hydride **22c** as intermediate (Scheme 5A).

The dehydrogenation reactivity of the methyl species **22** could be extended towards primary amine boranes. This system represents the first isolable early transition metal pre-catalyst for the dehydropolymerisation of primary amine boranes $\text{RNH}_2\text{-BH}_3$, producing high molecular weight poly(aminoboranes) (Scheme 5B). Of note, a variety of primary amine boranes, including examples possessing olefin- and aryl halide-containing functional groups can be polymerised.

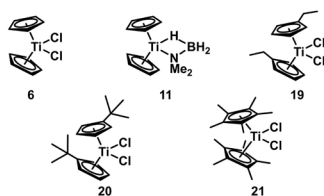
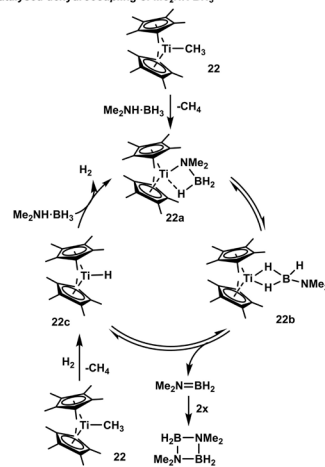
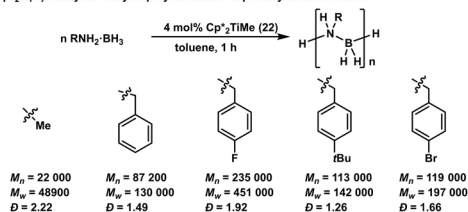


Figure 5. Titanocene precatalysts for the dehydropolymerisation of primary amine boranes.

A. $\text{Cp}^*\text{Ti(III)}$ catalysed dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$



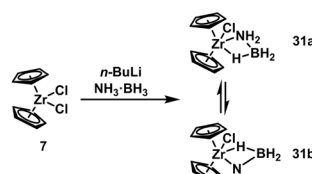
B. $\text{Cp}^*\text{Ti(III)}$ catalysed dehydropolymerisation of primary amine boranes



Scheme 5. Titanocene(III) complex-catalysed dehydrocoupling and dehydropolymerisation of amine boranes.

2.2. Zirconium Catalysts

In addition to the previously discussed Ti complexes Manners *et al.* also investigated the catalytic behaviour of Zr complexes.^[21] The $[\text{Cp}_2\text{Zr}]$ fragment can be generated from Cp_2ZrCl_2 (**7**) by addition of two equivalents of $n\text{BuLi}$, but does not show activity for the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ or $i\text{Pr}_2\text{NH-BH}_3$ in toluene. This might be explained by the formation of amidoborane ligated complexes such as $\text{Cp}_2\text{Zr(Cl)NH}_2\text{-BH}_3$ (**31a/b**) and $\text{Cp}^*\text{Zr(H)NH}_2\text{-BH}_3$, possessing strong covalent Zr–N bonds that were reported by Roesler and co-workers (Scheme 6).^[33] However, in THF $i\text{Pr}_2\text{NH-BH}_3$ is converted to



Scheme 6. Isolated zirconocene amidoborane complexes.

$i\text{Pr}_2\text{N}=\text{BH}_2$. The *ansa*-zirconocene(II) fragment $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\text{Zr}]$ shows no reaction.

As detailed above, Chirik *et al.* investigated different Ti and Zr complexes for the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ using benzene- d_6 and THF as solvents.^[20] In general, reactions in THF show lower conversion and Zr complexes **23–27** are less active than Ti complexes. This trend can be explained by the formation of catalytically inactive borohydride species (**28–30**) which only occurs in the case of Zr complexes (Figure 6).

The zirconocene alkyne complex $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**13**, py = pyridine) catalyses the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ giving a H_2 yield of 42% while the corresponding titanocene species gives a much higher yield of 86% (*vide supra*).^[26] The lower reactivity of the Zr complex can be rationalised by a stronger metal-alkyne interaction that was reported for this type of complexes on numerous occasions.^[34] However, this species shows higher activity compared to the *in situ* system $\text{Cp}_2\text{ZrCl}_2/n\text{BuLi}$, likely due to the higher stability of the zirconocene source under reaction conditions, preventing ill-defined reactivity of the $[\text{Cp}_2\text{Zr}]$ fragment.^[35]

In 2011, Nishibayashi *et al.* reported the synthesis of a series of novel heterobimetallic complexes of the type $[\text{M}^1\text{Me}(\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{PEt}_2)_2\text{M}^2\text{Cp}^*]$ (**32**, $\text{M}^1=\text{Zr}$ or Hf , $\text{M}^2=\text{Ru}$ or Fe) which combine group 4 and group 8 metals.^[36] These complexes are bridged by a phosphine-appended cyclopentadienyl ligand and catalyse the dehydrocoupling of secondary and primary amine boranes, as well as $\text{NH}_3\text{-BH}_3$. Among them, the Zr–Ru-complex shows the best catalytic performance. Although the catalytic activities are only moderate compared to other systems, this allowed for detailed studies of the metal-metal cooperative reaction mechanism (Figure 7). Initial cooperative activation of N–H and B–H bonds of the amine borane leads to the formation of a heterobimetallic hydride complex **34a**, followed by oxidative addition of the N–H bond of a second amine borane to Zr(II). The thus formed amidoborane dihydride complex **34b** undergoes reductive elimination of H_2 , affording the amidoborane complex **34c**. Finally, the B–H bond of the amidoborane ligand in **34d** is activated by the Ru centre to regenerate **34a** and release the aminoborane that further couples to produce $(\text{Me}_2\text{N-BH}_2)_2$.

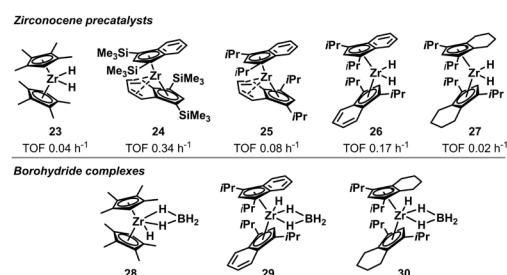


Figure 6. Isolable zirconocene species for dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$. Reaction conditions: benzene- d_6 , 2 mol % precatalyst, $[\text{Me}_2\text{NH-BH}_3] = 0.61 \text{ M}$, $T = 65^\circ\text{C}$.

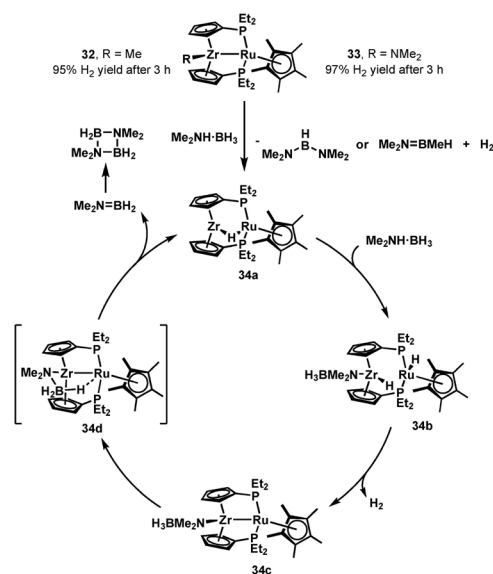


Figure 7. Proposed reaction pathway for the dehydrocoupling of amine boranes catalysed by heterobimetallic complexes. Reaction conditions: toluene, 5 mol % precatalyst, $[\text{Me}_2\text{NH-BH}_3] = 0.1 \text{ M}$, $T = 50^\circ\text{C}$.

As detailed above, Wass *et al.* investigated metallocene-based FLPs for the catalytic dehydrocoupling of amine borane.^[29] Both cationic Zr phosphinoaryloxy complexes $[\text{Cp}_2\text{ZrO}(\text{C}_6\text{H}_4\text{PtBu}_2)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**35**) and $[\text{Cp}^*\text{Zr}(\text{OC}_6\text{H}_4\text{PtBu}_2)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**36**) are stable against thermal decomposition but unstable in polar solvents THF and CH_2Cl_2 . Both complexes catalyse the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ with **35** showing full conversion after only ten minutes with 1 mol % catalyst loading, corresponding to an exceptionally high TOF of 600 h^{-1} (Figure 8). Notably, the linear diborazane is not observed during this reaction. Dehydrogenation of $i\text{Pr}_2\text{NH-BH}_3$ is possible, but requires 19 h under the same conditions, or 3 h with 5 mol % catalyst concentration. For the reaction with $\text{NH}_3\text{-BH}_3$, 5% borazane and poly(aminoborane), $(\text{H}_2\text{N-BH}_2)_n$, is obtained. The related cationic alkoxide complex $[\text{Cp}_2\text{ZrO}^t\text{Bu}][\text{B}(\text{C}_6\text{F}_5)_4]$ shows no activity for these reactions which is explained by the absence of the Lewis basic phosphinoaryloxy unit. The activity of permethylated complex **36** for dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ and $\text{NH}_3\text{-BH}_3$ is much lower (full conversion after 8.5 h) and reactions are reported to be less defined.

Later, the same authors used related cationic zirconocene phosphinoaryloxy complexes with η^5 -indenyl instead of η^5 -cyclopentadienyl ligands for the synthesis of a series of intramolecular IV/P frustrated Lewis pairs.^[37] In the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$, $[(\text{indenyl})_2\text{Zr}(\text{OC}_6\text{H}_4\text{PtBu}_2)][\text{B}(\text{C}_6\text{F}_5)_4]$ is the most active catalyst, showing a very high TOF of 600 h^{-1} . A comparative study of related intermolecular FLPs $[\text{Cp}_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{PR}_3$ ($\text{R} = t\text{Bu}$, Cy, Et, Ph, Mes and C_6F_5)

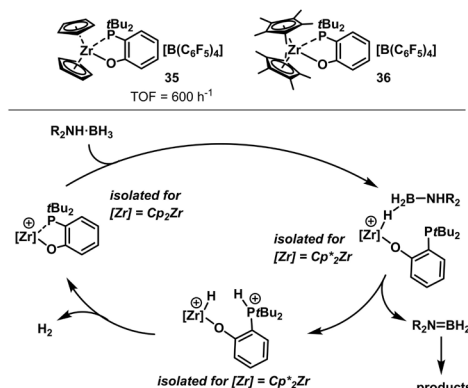


Figure 8. Cationic zirconocene phosphinoaryloxy complexes for the catalytic dehydrocoupling of amine boranes. Reaction conditions: fluorobenzene, 1 mol% precatalyst, $T = 25^\circ\text{C}$.

shows that, in line with other studies, the sterically demanding Cp^* derivatives are less active. Highest activity is observed with the PtBu_2 containing intermolecular system, giving 97% conversion with 10 mol% catalyst loading after 7.5 h. However, activity of this species is inferior compared to most intramolecular FLPs. NMR spectroscopic monitoring of the reaction shows that linear and cyclic diborazane are generated simultaneously. Mechanistic studies of this reaction using the Lewis acidic component of the intermolecular FLP, $[\text{Cp}^*_2\text{ZrOMes}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**37**), revealed initial formation of an aminoborohydride complex in the absence of the phosphine Lewis base. Reaction of this complex with the Lewis base results in release of $\text{H}_2\text{N}=\text{BH}_2$ and formation of a Zr hydride complex. Also the phosphonium salt $[\text{HPR}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ is formed, which only slowly protonates the Zr hydride complex for H_2 release. Based on these findings a cooperative two-cycle catalytic process can be proposed in which the first cycle involves a two-step process with coordination of amine borane, followed by phosphine-mediated release of H_2 (Figure 9). In a second cycle redistribution of the linear diborazane intermediate proceeds mediated by the Lewis acid component.

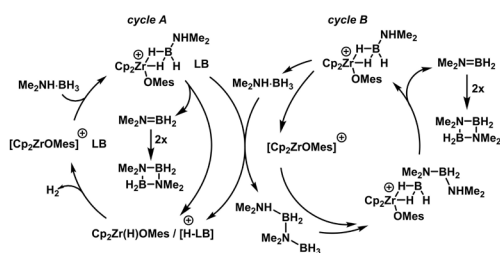


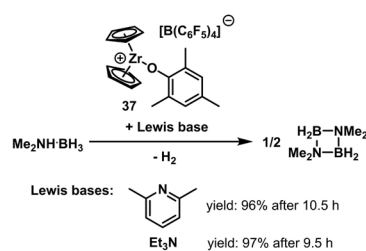
Figure 9. Catalytic cycle of the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ using Zr(IV)/P FLPs (LB=Lewis base, phosphine, amine, or pyridine derivative).

The study of further intermolecular zirconium/nitrogen FLP complexes $[\text{Cp}'_2\text{Zr(OMes)}]^+$ ($\text{Cp}' = \text{Cp}$ **37**, Cp^*) bearing amines or pyridine as the Lewis base component showed that systems with 2,6-dimethylpyridine or triethylamine are most active, giving full conversion of $\text{Me}_2\text{NH-BH}_3$ and H_2 yields higher than 95% (Scheme 7).^[38] Again, catalytic systems composed of Cp^* complexes are much less active than Cp analogs. This demonstrates that the reactivity of these systems is mostly affected by steric bulk and the basicity of the Lewis base.

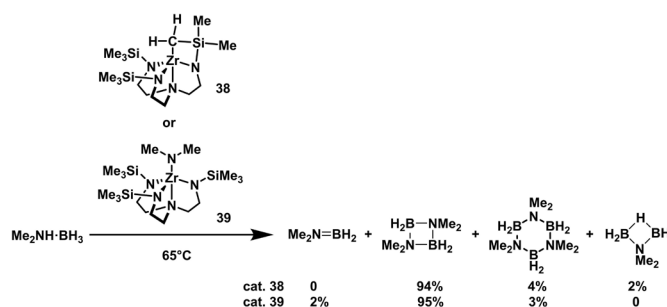
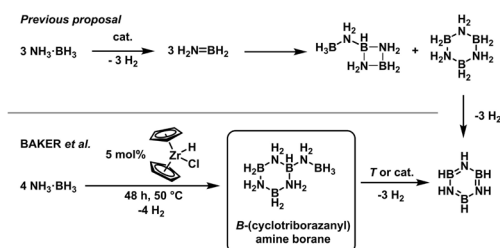
In 2015, Waterman and co-workers reported the synthesis of a series of triamido-amine supported zirconium complexes of the type $(\text{N}_3\text{N})\text{ZrX}$ [$(\text{N}_3\text{N}) = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2)_3$, $\text{X} = \text{NMe}_2$ (**39**), Cl and OtBu], and studied their catalytic performance in the dehydrocoupling of amine boranes and $\text{NH}_3\text{-BH}_3$.^[39] The cyclo-metallated complex $\kappa^5\text{-(Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2)_2\text{Zr}$ (**38**) is not only especially active in the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$, but also converts the sterically demanding substrate $\text{tBuNH}_2\text{-BH}_3$ as well as parent $\text{NH}_3\text{-BH}_3$ with borazines and borazanes being the main reaction products (Scheme 8). With the exception of $\text{NH}_3\text{-BH}_3$, which can only be reacted in THF due to its poor solubility, the reactions in benzene show the highest conversions at 65°C in benzene.

Using the well-known Schwartz reagent $\text{Cp}_2\text{Zr(H)Cl}$ as a catalyst in the dehydrogenation of $\text{NH}_3\text{-BH}_3$, Baker and co-workers successfully isolated and characterised the key boron-based intermediate in the second step of metal-catalysed dehydrogenation of $\text{NH}_3\text{-BH}_3$ (Scheme 9).^[40] In previous reports, the branched cyclic aminoborane trimer *B*-(cycloborazanyl)amineborane was assigned as the key intermediate for formation of borazine. Using $\text{Cp}_2\text{Zr(H)Cl}$ tetrameric *B*-(cycloborazanyl)amineborane can be observed as the key intermediate in 40% yield after 48 h at 50°C . During the reaction the complexes $[\text{Cp}_2\text{Zr(BH}_4)_2]$ and $[\text{Cp}_2\text{ZrCl(BH}_4)]$ are formed. Thermal or catalytic transformation of the *B*-(cycloborazanyl)amineborane intermediate results in dehydrogenation and formation of cyclic trimers and borazine.

Considering the fact that bis(amido)silyl ligands are structurally similar to tethered *ansa*-metallocene ligands, the Rivard group synthesised a series of zirconium complexes bearing hindered bis(amido)silyl ligands of the type $(\text{DippNSi}^i\text{Pr}_2\text{NDipp})$ ($[\text{NSiN}]^{\text{Dipp}}$, $\text{Dipp} = 2,6\text{-iPr-C}_6\text{H}_3$).^[41] The complex $[\text{NSiN}]^{\text{Dipp}}\text{Zr-(NMe}_2)_2(\mu\text{-Cl})\text{Li(THF)}_3$ (**40**) shows highest activity for the dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$, catalysing the dehydrocoupling

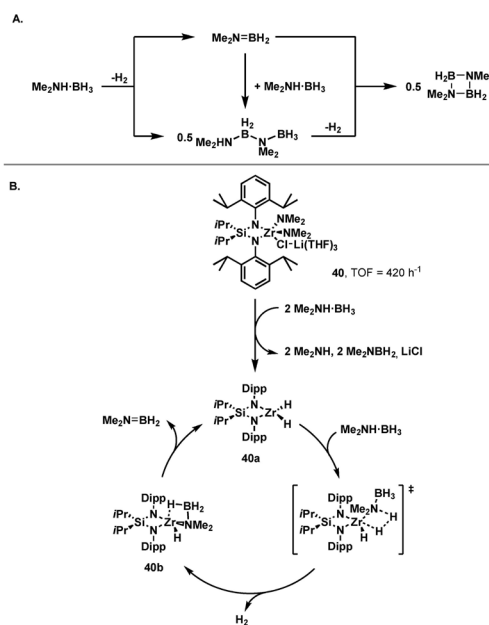


Scheme 7. Dehydrocoupling of $\text{Me}_2\text{NH-BH}_3$ catalysed by intermolecular Zr(IV)/N FLPs. Reaction conditions: PhBr-d_6 , 10 mol% precatalyst, $T = 25^\circ\text{C}$.

Scheme 8. Dehydrogenation of NH₃-BH₃ catalysed by triamido-amine supported zirconium complexes.Scheme 9. Characterisation and reactivity of the key intermediate B-(cyclotriborazanyl)amineborane using Cp₂Zr(H)Cl.

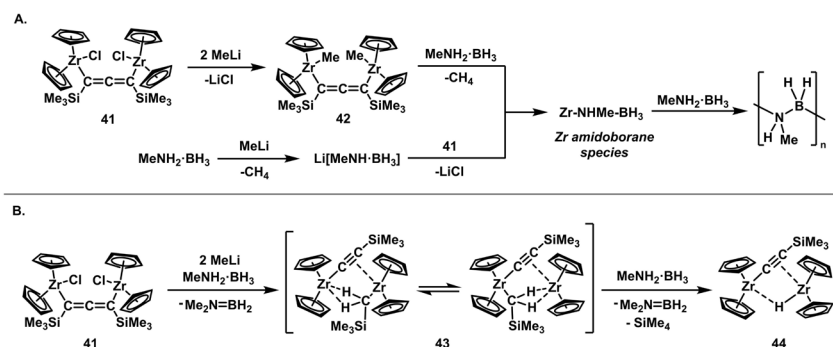
reaction at room temperature in aromatic solvents. This complex shows concentration and solvent dependent product selectivity: using Me₂NH-BH₃ as the substrate, both cyclic (Me₂N-BH₂)₂ and linear dimer Me₂NH-BH₂-NMe₂-BH₃ are formed as the products. At low catalyst loading the linear product Me₂NH-BH₂-NMe₂-BH₃ is mainly formed (Scheme 10A). Changing the solvent from benzene to CH₂Cl₂ results in full loss of catalytic activity, although the complex remains stable in this solvent. The Zr dihydride species [NSiN]^{Dipp}ZrH₂ (**40a**) is proposed to be the active species forming [NSiN]^{Dipp}Zr(H)-NMe₂BH₂(μ-H) (**40b**) as the key intermediate after reaction with Me₂NH-BH₃ and release of H₂ (Scheme 10B).

Inspired by studies of Rh complexes that show the potential of dinuclear complexes for stabilisation of reactive aminoborane intermediates during catalysis,^[42] some of us have tested dinuclear Zr complexes as pre-catalysts for the dehydropolymerisation of MeNH₂-BH₃ (Scheme 11A).^[43] After activation with MeLi the dinuclear allenediide bridged monochloride complex Cp₂Zr(μ-Cl)(μ-Me₃SiC₃SiMe₃)Zr(μ-Cl)Cp₂ (**41**) shows higher activity than the related cationic species [Cp₂Zr(μ-Cl)(μ-Me₃SiC₃SiMe₃)ZrCp₂][GaCl₄] and the mononuclear analogue Cp₂ZrCl₂ (**7**). Hydrogen evolution follows zero-order kinetics without an induction period, giving a hydrogen yield of approximately 85%. A preliminary mechanistic proposal included two different reaction pathways: either MeLi activation of the complex, or the substrate. Both pathways were demonstrated to be feasible by initial addition of either MeLi to

Scheme 10. Sterically demanding bis(amido)silyl ligated zirconium complexes for dehydrocoupling of amine boranes. Reaction conditions: C₆D₆, 1 mol % precatalyst, [Me₂NH-BH₃] = 3.53 M, T = 25 °C.

the precatalyst, or the substrate, giving identical activity and product distribution.

A more detailed study of the reaction mechanism of the dehydrocoupling of Me₂NH-BH₃ using Cp₂Zr(μ-Cl)(μ-Me₃SiC₃SiMe₃)Zr(μ-Cl)Cp₂ (**41**) revealed that the methyl complex Cp₂Zr(Me)(μ-Me₃SiC₃SiMe₃)Zr(μ-Cl)Cp₂ (**42**) is a suitable pre-catalyst (Scheme 11B).^[44] Combination of NMR and UV-vis studies suggest the presence of several interconvertible Zr complexes in the reaction mixture out of which two diamagnetic dinuclear Zr(III) complexes Cp₂Zr(C₂SiMe₃)(μ-R)ZrCp₂ (R=CH₂SiMe₃, **43** and R=H, **44**) bearing a cleaved allenediide



Scheme 11. Proposed activation of dinuclear Zr complexes in the dehydropolymerisation of $\text{MeNH}_2\cdot\text{BH}_3$ and degradation reactions of the dinuclear zirconocene pre-catalyst **41** to give dinuclear complexes **43** and **44**, relevant for dehydrocoupling of amine boranes.

ligand can be identified using stoichiometric control reactions. Both species can be separately prepared but show much lower catalytic activity than the parent pre-catalyst, activated with methylolithium. Computational analysis of catalytic cycles based on Zr complexes with intact and cleaved allenediide ligands demonstrate the feasibility of both pathways and once more highlight the complexity of catalytic systems formed by activation with organolithium reagents.

2.3. Hafnium Catalysts

Due to the often-discussed analogy with its Zr congeners, Hafnium complexes are generally much less used as catalysts. Stronger metal-ligand bonds when going from 4d–5d metals typically result in lower catalytic activities. For example in Manners' study of titanocene and zirconocene complexes,^[21] the $[\text{Cp}_2\text{Hf}]$ fragment, generated using $\text{Cp}_2\text{HfCl}_2/n\text{BuLi}$, shows no conversion of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ or $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$. The first active Hf catalyst for the dehydrocoupling of amine boranes was presented by Nishibayashi *et al.*^[36] The phosphine-substituted metallocene complex $[\text{Hf}(\text{Me})(\mu-\eta^5-\eta^1-\text{C}_5\text{H}_4\text{PEt}_2)_2\text{RuCp}^*]$ (**45**) is however significantly less active than the zirconium derivative, producing cyclodiborazane. Furthermore, the cationic FLP Hf complex $[\text{Cp}_2\text{HfOC}_6\text{H}_4\text{P}(\text{tBu})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**46**) fully converts $\text{Me}_2\text{NH}\cdot\text{BH}_3$ but the reaction requires one hour for full conversion, much longer than for the Zr analogue (Figure 10).^[29]

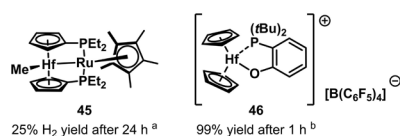


Figure 10. Hf complexes as precatalysts for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$. Reaction conditions: ^a toluene, 10 mol % precatalyst, $[\text{Me}_2\text{NH}\cdot\text{BH}_3] = 0.1 \text{ M}$, $T = 50^\circ\text{C}$; ^b fluorobenzene, 1 mol % precatalyst, $T = 25^\circ\text{C}$.

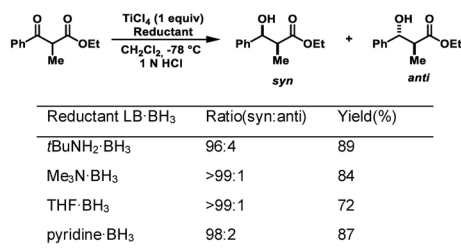
3. Transfer Hydrogenation and Related Reductions

The use of molecular hydrogen is probably the most frequently employed method for hydrogenation reactions.^[45] On the other hand, owing to its safety and operational simplicity, the catalytic transfer hydrogenation (TH) using replacements to molecular hydrogen has emerged as an alternative and effective way for reduction reactions.^[46] In this respect, $\text{NH}_3\cdot\text{BH}_3$ has received considerable attention as TH reagent owing to its high hydrogen storage density and relatively stable properties. There are three different mechanistic scenarios of TH, namely classical TH processes, in which both hydrogen atoms originate from both the amine and the borane unit, non-classical TH, in which hydroboration of the substrate by the amine-borane is followed by solvolysis, and hydrogenation by molecular hydrogen, formed by dehydrogenation of the amine borane.^[47] The nature of the B–N by-products is different for all three of these pathways. Despite the great advances of using $\text{NH}_3\cdot\text{BH}_3$ as TH reagent, the use of group 4 metals as the catalysts has gained much less attentions, which is summarised in the following section.

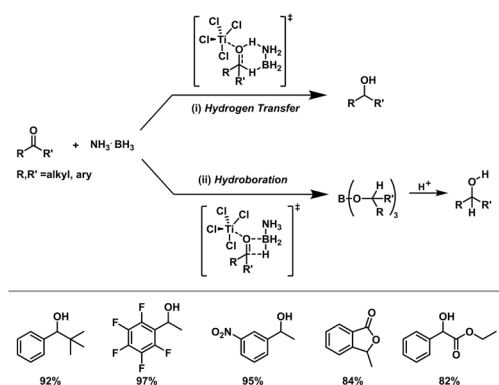
3.1. Titanium Catalysts

The diastereoselective reduction of chiral acyclic ketones using stoichiometric amounts of titanium tetrachloride (TiCl_4) was reported as early as 1994 by DiMare *et al.*^[48] In the system, a number of borohydride and $\text{LB}\cdot\text{BH}_3$ adducts such as $t\text{BuNH}_2\cdot\text{BH}_3$, $\text{Me}_2\text{N}\cdot\text{BH}_3$, and $\text{THF}\cdot\text{BH}_3$ are used as the reductant (Scheme 12).

In 2022, Ramachandran *et al.* revealed that catalytic amounts of TiCl_4 in diethyl ether can accelerate the hydroboration-hydrolysis (reduction) of ketones with $\text{NH}_3\cdot\text{BH}_3$ as the hydroboration reagent (Scheme 13).^[49] In this system, various ketones can be reduced and then hydrolysed to obtain their corresponding alcohol products. For the reaction mechanism, the authors initially proposed two different reaction pathways:



Scheme 12. Diastereoselective reduction of chiral acyclic ketones using LB-BH₃, mediated by stoichiometric amounts of TiCl₄.

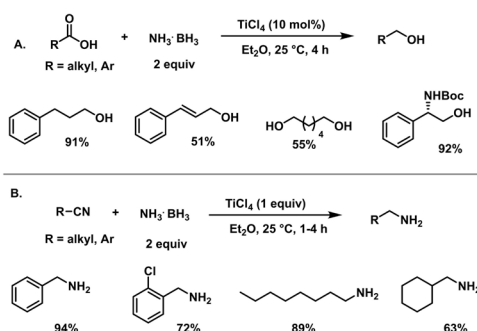


Scheme 13. TiCl₄-catalysed hydroboration-hydrolysis of ketones with NH₃-BH₃.

a **TH** pathway wherein hydrogen is simultaneously transferred from NH₃ and BH₃ across the carbonyl unit (Scheme 13, path i), as well as a hydroboration-hydrolysis pathway. Deuterium labelling experiments and ¹¹B NMR analysis support a catalytic cycle that is based on hydroboration of a TiCl₄-activated carbonyl unit (Scheme 13, path ii). Starting from NH₃-BH₃, a TiCl₄-activated ketone is hydroborated three times to yield the trialkylborate, which is subsequently hydrolysed to give the alcohol product.

Later, the same group extended the use of this TiCl₄ system for the reduction of carboxylic acids to their corresponding alcohols at room temperature. The system is suitable for conversion of both aromatic and aliphatic substrates, producing alcohols in good yield (Scheme 14A).^[50] Application to the reduction of dicarboxylic acids and amino acids was also achieved. In addition, selective reduction of the carboxylic acid functional group in the presence of amides, nitriles, and esters have also been demonstrated. Furthermore, the reduction of nitriles to their corresponding amines is also possible, albeit with stoichiometric amounts of TiCl₄ (Scheme 14B).^[51]

In 2023, Zhu *et al.* reported a convenient and effective method for direct deoxygenative reduction of amides to corresponding amines catalysed by TiCl₄ using NH₃-BH₃ as

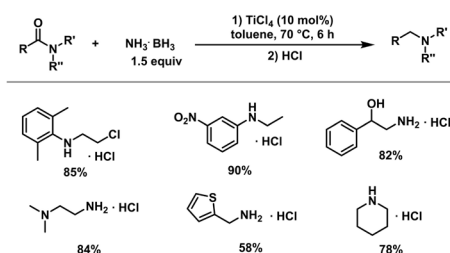


Scheme 14. TiCl₄-catalysed and mediated reduction of carboxylic acids and nitriles.

reducing agent (Scheme 15).^[52] A variety of substrates possessing electron-withdrawing and electron-donating substituents on the aromatic ring, as well as various functional groups such as halide, nitro, and hydroxy groups are well tolerated. Formation of dehalogenated products is not observed for the halogen-substituted amides, indicating good chemoselectivity.

Almost at the same time, Ramachandran *et al.* extended their TiCl₄-catalysed reduction of aldehydes, ketones, carboxylic acids, and nitriles with NH₃-BH₃ to the deoxygenation reduction of a variety of aromatic and aliphatic amides.^[53] In this system, various aromatic, heteroaromatic, benzyl and aliphatic amides are effectively reduced. The reaction is described to take place by activating the carbon-based part of the amide with TiCl₄, followed by above-described reduction with borane.

In 2022, some of us have reported the use of Cp₂TiCl₂ (**6**) as a catalyst for the exhaustive reduction of carboxylic acids and esters to the corresponding methyl-containing products using NH₃-BH₃ as the **TH** reagent.^[54] Addition of MeOLi as an additive largely improves the yields. The reaction has broad functional group tolerance and works for various other types of oxochemicals such as alcohols, aldehydes, ketones, lactones, and carboxylates. Mechanistic studies including deuterium labeling experiments and EPR studies revealed that the *in situ* generated Ti(III) hydride species is vital for this transformation. In the proposed catalytic cycle the Ti(III)-H species **48a** is formed by



Scheme 15. TiCl₄-catalysed reduction of amides using NH₃-BH₃.

the consecutive reaction of Cp_2TiCl_2 (**6**) with MeOLi and then NH_3BH_3 , with the generation of $\text{B}(\text{OMe})_3$ (Scheme 16). Then, insertion of the carbonyl fragment $\text{C}=\text{O}$ into the Ti–H bond generates intermediate **48b**, which after β -O elimination gives a Ti–OMe species **48c** and aldehyde as intermediate. Following this, consecutive reduction of aldehyde by Ti–H species delivers the final product. Finally, the Ti–H active catalytic species is regenerated by the reaction of the Ti–O species with NH_3BH_3 .

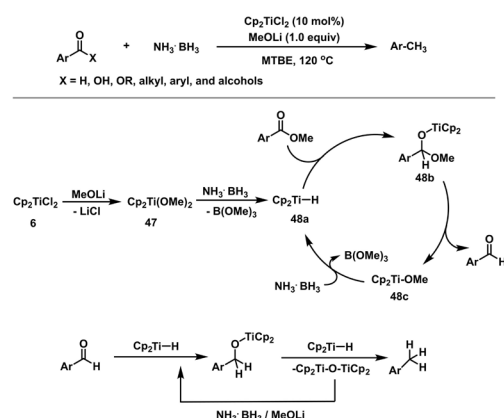
Under similar reaction conditions, Cp_2TiCl_2 was used as the pre-catalyst for the dehalogenation of a series of benzyl halides as well as unactivated alkyl halides (including alkyl chlorides) using NH_3BH_3 as the reductant (Scheme 17).^[55] Compared to the exhaustive reduction of oxo-chemicals, the catalyst loading can be reduced to 2.5 mol%. For the dehalogenation of benzyl halides, only Cp_2TiCl_2 (**6**) catalyses the reaction at 35 °C, while for the unactivated alkyl halides, the addition of MeOLi is crucial to promote the transformation, and slightly higher temperatures of 60 °C facilitate high conversion. Deuterium labelling experiments indicate BH_3 as the main H source. Radical trapping experiments suggest that a radical process might also be involved. Similarly, a catalytic reaction pathway initiated by *in situ* generated Ti(III) hydride species from the Ti(IV) chloride

precursor is proposed. During the catalysis Ti(III)–H species **48a** is formed by the reaction of Cp_2TiCl_2 (**6**) with NH_3BH_3 . The formation of the hydride complex **48a** can be accelerated by MeOLi. Then, Ti–H species **48a** interacts with alkyl halides to produce the hydrodehalogenation product and a Ti–X species **48d** which reacts with NH_3BH_3 to regenerate the Ti–H species. Alternatively, the alkyl halides could also be reduced by the Ti(III) species to the corresponding alkyl radical, which is protonated by N–H or by residual water present in the solvent.

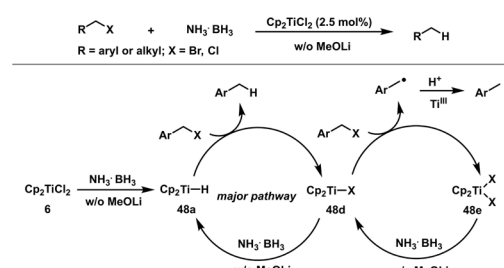
3.2. Zirconium Catalysts

As part of the above-mentioned study on the use of $[\kappa^5\text{-(Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{N(CH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2)_2\text{Zr}]$ (**38**) and $[\kappa^4\text{-(N(CH}_2\text{CH}_2\text{NSiMe}_2)_3\text{)ZrNMe}_2]$ (**39**) for the dehydrocoupling of amine boranes, Waterman *et al.* also presented the application of these two catalysts for TH of various alkenes (Scheme 18).^[39] Use of $\text{Me}_2\text{NH-BH}_3$ and 10 mol% of **39** only gives limited conversion of styrene to ethylbenzene. According to the authors rapid amine borane dehydrogenation is probably the reason for low conversion of the alkene. Using less reactive $t\text{BuNH}_2\text{-BH}_3$ as the TH reagent, ethylbenzene is formed along with hydroboration products. With NH_3BH_3 , using a reduced catalyst loading of 2 mol%, full conversion of the alkene substrate and formation of the alkane product is observed after 6 h at 65 °C. These conditions are also compatible with substituted styrene derivatives, alpha olefins, 2,3-dimethylbutadiene and 2-vinylpyridine, all furnishing the alkane as the major product. Control experiments using 1 atm of dihydrogen instead of amine borane gave no conversion, indicating that the amine borane serves as a TH reagent that sequentially hydrogenates the substrate without the presence of free H_2 .

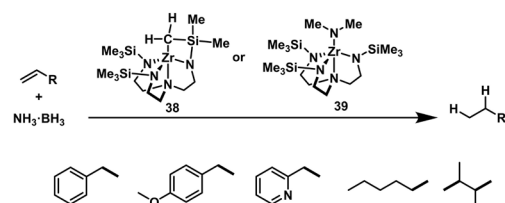
Synergistic catalysis of zirconium and magnesium, using $i\text{Pr}_2\text{NH-BH}_3$ as boration reagent for the synthesis of alkenyl amine boranes from terminal alkynes was reported by Pucheault *et al.* (Scheme 19).^[56] This $\text{Cp}_2\text{Zr(H)Cl}$ catalysed reaction tolerates a wide range of functional groups, including alcohols and halides. The reaction is proposed to go through two catalytic cycles. In a dehydrogenation cycle $i\text{Pr}_2\text{NH-BH}_3$ is first dehydrogenated catalysed by the ion pair $[i\text{Pr}_2\text{NBH}_3][\text{MgBr}]$, (generated from PhMgBr and $i\text{Pr}_2\text{NH-BH}_3$) to produce diisopropylaminoborane $i\text{Pr}_2\text{N-BH}_2$. Hydroboration of the alkene occurs in a second cycle that is catalysed by Zr. $\text{Cp}_2\text{Zr(H)Cl}$ is first 1,2-



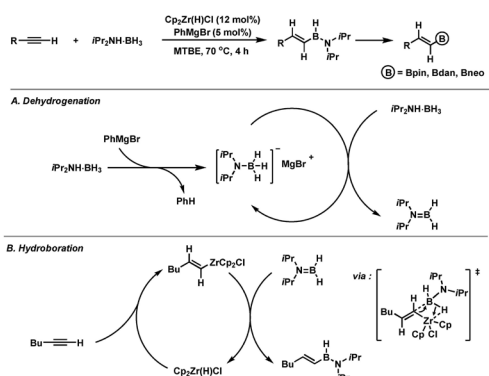
Scheme 16. Titanium-catalysed exhaustive reduction of various oxo-chemicals using NH_3BH_3 .



Scheme 17. Titanium-catalysed dehalogenation of halides using NH_3BH_3 .



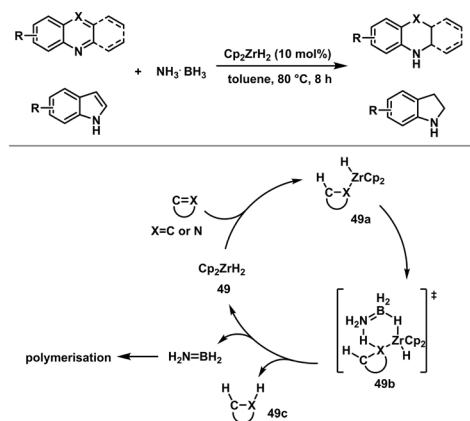
Scheme 18. TH of alkenes using triamidoamine supported zirconium complexes.



Scheme 19. Zirconium/magnesium-catalysed synthesis of alkenyl boronates.

added to the alkyne to form a well-known zirconocene alkenyl intermediate. This is followed by σ -bond metathesis with $i\text{Pr}_2\text{N}=\text{BH}_2$, forming the alkenylborane product and $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ to complete the catalytic cycle.

In 2021, Wu lab reported the **TH** of quinoline and indole derivatives using a zirconocene dihydride complex Cp_2ZrH_2 (**7**) as catalyst and NH_3BH_3 as proton and hydride source (Scheme 20).^[57] Substrates with electron-donating and electron-withdrawing groups at different positions of the quinoline ring are well-tolerated and show good conversion. Unsubstituted, mono-substituted, and polysubstituted indole compounds give the **TH** products in good yields. Mechanistic studies suggest a reaction pathway that involves concerted N–H and B–H activation. In a first step, insertion of the unsaturated double bonds ($\text{C}=\text{C}$ and $\text{C}=\text{N}$) of quinoline or indole into the $\text{Zr}–\text{H}$ bond produces intermediate **49a**. Then, intermediate **49a** interacts with NH_3BH_3 in a concerted way via a six-membered

Scheme 20. Zirconium-catalysed TH of quinoline and indole using NH_3BH_3 .

cyclic transition state **49b** and transfers both the proton and hydride to intermediate **49a**, regenerating Cp_2ZrH_2 and producing the hydrogenated product **49c** as well as intermediate $\text{H}_2\text{N}=\text{BH}_2$, which subsequently undergoes polymerisation.

4. Summary and Outlook

The past two decades have witnessed remarkable achievements in the use of group 4 metal complexes (Ti, Zr, and Hf) for the dehydrocoupling, dehydrogenation and transfer hydrogenation or related reduction using ammonia/amine boranes. The catalytic activities are mostly lower than those obtained with late transition metal systems. This is however compensated by the relatively high abundance of group 4 metals in the earth's crust, lower toxicities, and the possibility to use readily available and cost-efficient ligand platforms such as those based on cyclopentadienyl or amide moieties. This review summarises the accomplishments in this area in the past 20 years, highlighting mechanistic foundations and drawing insights from related reactions.

Despite the achievements in group 4 metal catalysed dehydrocoupling and transfer hydrogenation reactions, there is still a lot of room that could be further developed in the future. First, the nature of catalyst species involved in the catalytic systems is debatable in many cases, especially along the M(II)/(III)/(IV) series that is commonly present in reductive transformations with group 4 complexes. The use of group 4 metal complexes for the synthesis of main group polymers from amine boranes is still relatively rare. This could be due to the high and comparatively undefined reactivity of the electro-positive catalysts and intermediates towards N–H and B–H bonds of the polymer as well as towards the by-product hydrogen. Furthermore, the comparatively high stability of potentially formed metal–nitrogen bonds can be an obstacle to efficient catalyst turnover and high activity. A detailed understanding of these aspects and approaches to mitigate them, e.g. by adding suitable H_2 acceptors (as already shown in the transfer hydrogenation of organic substrates), which influence the activity and selectivity of dehydrocoupling reactions, are still pending. As a practical limitation, catalyst loadings for dehydrocoupling and especially for transfer hydrogenation reactions are still relatively high, which limits the widespread, potentially industrial application of these systems. Group 4 metal catalysed asymmetric transfer hydrogenation with ammonia/amine boranes is still underdeveloped but should be possible using well-established ligand platforms and protocols known from asymmetric catalysis. Finally, the majority of the used pre-catalysts are based on non-modified cyclopentadienyl scaffolds with notable exceptions that employ amide, triamido-amine, or bis(amido)silyl ligands. The development of new and implementation of established ligand systems should hold great potential to further improve the catalytic activities.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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Coordination and C–H activation of an amidobis(phosphaalkene) ligand at rhodium(i)†

Kushik,^a Mirko Rippke,^a Hans-Joachim Drexler,^{id}^a Fabian Dankert,^{id}^b
Christian Hering-Junghans^{id}^{*a} and Torsten Beweries^{id}^{*a}

Phosphaalkenes are an underrepresented class of phosphorus-based ligands that hold great potential for the stabilisation of low-valent transition metal and main group fragments. We present the synthesis of a monoanionic PNP-type bis-phosphaalkene ligand and its reactions with [Rh(cod)(Cl)]₂, which furnish two unique dinuclear Rh(I) complexes. These complexes show C–H activation of the Mes* groups of the PNP ligand and the presence of three different phosphaalkene coordination modes, respectively. Computational analyses suggest the presence of a unique Rh–Rh donor–acceptor interaction in the C–H-activated complex. Stabilisation of the desired tricoordinate PNP-supported Rh(I) species is possible in the presence of the strongly donating CO ligand, yielding a mononuclear square-planar complex of the type [(PNP)Rh(CO)].

Introduction

Phosphaalkenes (PAs), RP=CR₂, are organophosphorus compounds characterised by a P=C double bond and are related to alkenes and imines as their lighter group 15 homologues,¹ showing great potential for various applications in modern organophosphorus chemistry.² The coordination chemistry of PAs to transition metals is characterised by their unique ligand properties (HOMO P=C π-bond, high s character of the lone pair at P, and inverse polarity of the P^(δ+)–C^(δ−) bond), making these compounds weaker σ-donors than imines, but considerable π-acceptors due to the low-lying P–C π* orbital (LUMO). Coordination of neutral PA ligands to late transition metals has been reported on several occasions,³ and some of such complexes have found applications in stoichiometric and catalytic transformations such as N–H activation,⁴ aza-Claisen rearrangements,⁵ or upgrading of alcohols.⁶

Although tri-⁷ and tetradentate⁸ PNP- (Fig. 1, top left) and PPPP-type PAs have been reported, to the best of our knowledge, mono-anionic PNP pincer-type PA architectures have not been designed to date. The coordination chemistry of tridentate ligands is well-studied for related amido-bis(phosphines),

and their structural variety and versatility for synthesis and catalysis has been highlighted on several occasions.⁹ Recent examples include work by Ozerov and co-workers on phosphine-based group 9 PNP systems bearing diphenylamine based amido-bis(phosphine) ligands (Fig. 1, top right) for alkyne dimerisation and C–H activation,¹⁰ as well as studies by Gade and co-workers on the stabilisation of unusual T-shaped 14-electron Rh(I) using amido-bis(phosphine) PNP ligands based on a carbazole backbone.¹¹ In the latter case, Rh(I) is κ³-coordinated by the PNP ligand with additional stabilisation

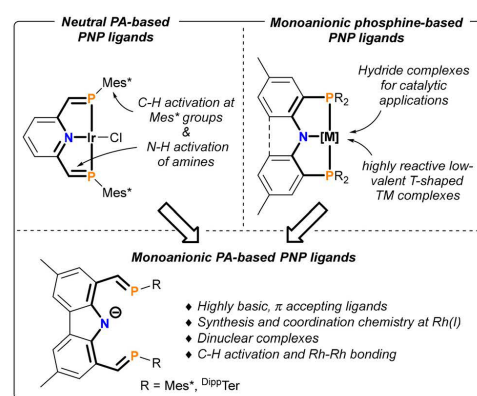


Fig. 1 Contextualisation of this work. Mes* = 2,4,6-tBu₃-C₆H₂, DippTer = 2,6-(2,6-iPr₂C₆H₃)-C₆H₃.

^aLeibniz-Institut für Katalyse e.V. (LIKAT Rostock), Albert-Einstein-Str. 29a, 18059 Rostock, Germany. E-mail: Christian.hering-junghans@catalysis.de, Torsten.beweries@catalysis.de

^bUniversity of Kassel, Heinrich-Plett Str. 40, 34132 Kassel, Germany

† Electronic supplementary information (ESI) available: Synthesis and characterization of compounds, NMR spectra, and crystallographic and computational details. CCDC 2451040–2451044 and 2474838. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5dt01734c>

enabled through non-covalent interactions with flanking PtBu_2 groups.

An extension of the concept of electronically unique PA ligands to tridentate, monoanionic representatives is desirable, since the resulting pincer ligands would create a well-defined reactive site due to their meridional coordination to the metal in combination with the sterically demanding flanking substituents that are typically required for the stabilisation of PAs (Fig. 1, bottom). The resulting monoanionic system should possess the typical electronic properties of PAs and at the same time be able to stabilise highly reactive low-valent transition metals, such as $\text{Fe}(\text{I})$ complexes,¹² potentially without the need for additional stabilising L-type ligands at the metal centre. In this contribution, we present the synthesis and characterisation of the first monoanionic bis-PA ligands along with their coordination chemistry to $\text{Rh}(\text{I})$, resulting in the formation of two dinuclear Rh complexes that possess intact as well as C-H-activated PA donor sites, as well as a rare $\text{Rh}(\text{I})$ – $\text{Rh}(\text{I})$ donor-acceptor interaction in one case.

Results and discussion

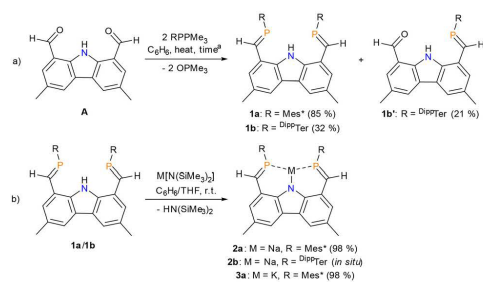
Novel PNP-based bis-PA pincer ligands were synthesised by treating 3,6-dimethyl-9H-carbazole-1,8-dicarbaldehyde (**A**) with two equivalents of the phospho-Wittig reagent $\text{Mes}^*\text{PPMe}_3$ ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2$)¹³ in benzene at 50 °C for 24 hours in the absence of light, giving the desired bis-PA $\text{Mes}^{*2}\text{PNP}$ (**1a**, Scheme 1) in good yield.

$^{31}\text{P}\{^1\text{H}\}$ NMR analysis shows the PA units at 249.9 ppm, at the lower end of literature reported Mes^* -substituted PA ligands ($\delta(^{31}\text{P})$ 250 to 291 ppm),³ presumably due to delocalisation of electron density from the carbazole unit to the P–C π^* orbitals. When heating a mixture of DippTerPPMe_3 and **A** in benzene in a 2 : 1 ratio at 80 °C for 14 days, the analogous PNP ligand $\text{DippTer}_2\text{PNP}$ with DippTer groups on the P atoms (**1b**) was prepared (Scheme 1, see the ESI† for details). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture showed the characteristic resonance for the bis-PA PNP ligand **1b** at 239.5 ppm. In

addition, the mono-PA PNO species **1b'**, with only one PA arm and an intact aldehyde group,¹⁴ is formed as indicated by a resonance at 244.6 ppm. In the ^1H NMR spectrum of **1b'**, three deshielded resonances for the NH (10.80 ppm), $\text{C}(\text{O})\text{H}$ (9.73 ppm) and $\text{P}=\text{CH}$ (9.23 ppm) protons, with the NH only showing a doublet signature, underline the presence of a single PA arm. In contrast, the bis-PA PNP ligands **1a** and **1b** show a triplet resonance (11.29 ppm, C_6D_6 , $J_{\text{PH}} = 11.6$ Hz) for the NH proton due to coupling with two P atoms. The formation of **1b'** can be suppressed, though, when using a slight molar excess of DippTerPPMe_3 . This facilitates selective access of **1b**.

Crystals of **1a** suitable for single-crystal X-ray diffraction (SC-XRD) analysis were obtained from a saturated *n*-hexane solution at –30 °C overnight. SC-XRD analysis of **1a** (Fig. 2) revealed the expected structure of the $\text{Mes}^{*2}\text{PNP}$ ligand with moderate hydrogen-bonding interactions between the N–H proton and both phosphorus atoms of the PA units, resulting in *E*-configured PA units ($\text{P1}–\text{C15}$ 1.679(2) Å, $\text{P2}–\text{C34}$ 1.686(2) Å), with both Mes^* substituents pointing away from the binding pocket. In **1b**, both PA units are likewise *E*-configured (Fig. S2†), while one of the P atoms points away from the carbazole N atom to account for the increased steric strain from the DippTer substituents. In both **1a** and **1b**, the $\text{P}=\text{C}$ bonds are nearly co-planar with the carbazole backbone.

To facilitate transmetalation, ligand **1a** was deprotonated using the non-nucleophilic bases $\text{M}[\text{N}(\text{SiMe}_3)_2]$ ($\text{M} = \text{Na}, \text{K}$), in either benzene or THF at room temperature, yielding the alkali metal complexes $[\text{Na}(\text{Mes}^{*2}\text{PNP})]$ (**2a**) and $[\text{K}(\text{Mes}^{*2}\text{PNP})]$ (**3a**) in quantitative yields as red or violet solids, respectively. According to TD-DFT calculations, the red colour of **2a** is associated with a $\pi\text{--}\pi^*$ transition, with the Na^+ resulting in a smaller HOMO–LUMO gap compared to **1a** and thus a red shift in the longest wavelength absorption ($\lambda_{\text{max,calc}}(\text{2a}) = 546.3$ nm). Both salts are highly moisture sensitive, necessitating careful handling under strictly anhydrous conditions. The deprotonation of **1a** was confirmed by ^1H NMR spectroscopy, revealing the absence of the deshielded N–H signal. Moreover, IR spectroscopy showed the absence of the N–H stretching mode in the spectra of **2a** and **3a** (1a : $\tilde{\nu}(\text{N–H}) = 3300$ cm^{-1}). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the salts show considerably shielded signals for the Na salt **2a** ($\delta(^{31}\text{P}) = 228.4$ ppm) and the K salt **3a** ($\delta(^{31}\text{P}) = 236.8$ ppm) compared to the free ligand **1a**,



Scheme 1 (a) Synthesis of novel R_2PNP PA ligands **1a** and **1b**. ^a Conditions for **1a**: C_6H_6 , 50 °C, 24 h; for **1b**: C_6H_6 , 80 °C, 14 d. (b) Synthesis of $\text{M}[\text{Mes}^{*2}\text{PNP}]$ ($\text{M} = \text{Na}$ (**2a**) and K (**3a**)).

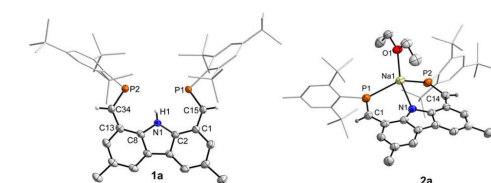


Fig. 2 Molecular structures of **1a** (left) and **2a** (right). ORTEP diagrams are drawn at 50% probability. H atoms (except NH and RP = CHR) are omitted, and Mes^* groups are rendered as wireframes for clarity.





reflecting the subtle electronic differences induced by the counterions. SC-XRD-quality red crystals of **2a** were afforded by slow diffusion of Et₂O into a saturated *n*-hexane solution of **2a** at room temperature. The molecular structure of **2a** shows the sodium ion in a distorted seesaw coordination environment ($\tau_4 = 0.32$)¹⁵ with the fourth coordination site occupied by Et₂O (note that Et₂O is only present in the solid state), resulting in Na located above the PNP mean plane. The sodium contacts to the PNP ligand are in the expected range for elongated Na–N (Na1–N1 2.324(3) Å; $\Sigma r_{\text{cov}}(\text{Na–N}) = 2.26$ Å)¹⁶ and Na–P single bonds (Na1–P1 2.735(2) Å, Na1–P2 2.732(2) Å; $\Sigma r_{\text{cov}}(\text{Na–P}) = 2.66$ Å).¹⁶ The PA units coordinate to Na in κ^2 -fashion through the s-type lone pair on P, as indicated by short P–C distances (P1–C1 1.674(4) Å, P2–C14 1.673(4) Å).

Next, **2a** was reacted with [Rh(cod)(Cl)]₂ in THF in a 2 : 1 molar ratio (Scheme 2), accompanied by a colour change from red to dark brown. The ³¹P{¹H} NMR spectrum of the reaction mixture revealed two species, free ligand **1a** ($\delta(^{31}\text{P}) = 249.9$ ppm) and a second species giving a doublet at 46.7 ppm ($^1J_{\text{P–Rh}} = 132$ Hz), indicative of a Rh(i) complex (Scheme 2). The significant shielding of the ³¹P NMR signal compared to ligand **1a** and two sets of doublets with a large $^2J_{\text{H–H}}$ coupling of 14 Hz for four diastereotopic benzylic protons in the ¹H NMR spectrum indicated that the Mes*P = CH unit underwent intramolecular C–H addition/cyclisation to form a phospholanyl-methyl (phosphaindane) moiety.¹⁷ Such cyclisation reactions have been reported for PN-type PAs (e.g., [Rh(quin-P,N)]₂ OTf, $\delta(^{31}\text{P}) = 55.1$ ppm)^{3a,b} and BPEP-based systems [RhCl (Mes*₂-BPEP), $\delta(^{31}\text{P}) = 28.9$ ppm].¹⁸

Surprisingly, SC-XRD analysis of green crystals obtained from a concentrated THF solution layered with *n*-pentane and stored at ambient temperature revealed the formation of the dinuclear Rh(i) phosphaindane complex **4** (Fig. 3, left). The formation of such dinuclear species can be rationalised by the intermediate formation of a T-shaped 14 electron complex, which then undergoes C–H bond activation of the *o*-tBu groups and eventually adds a second equivalent of [Rh(cod)Cl]. When not considering the Rh–Rh interaction (Rh1–Rh2 2.6334(9) Å, cf. $\Sigma r_{\text{cov}}(\text{Rh–Rh}) = 2.50$ Å), Rh2 resides in a trigonal pyramidal coordination sphere, coordinated by cod and the carbazole N atom. This rather unusual coordination sphere for a 16-valence electron complex makes the metal centre Lewis-acidic.^{19,20} In contrast, Rh1 is best described as a 16-valence

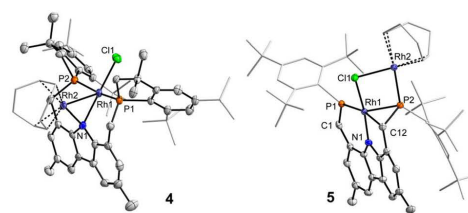
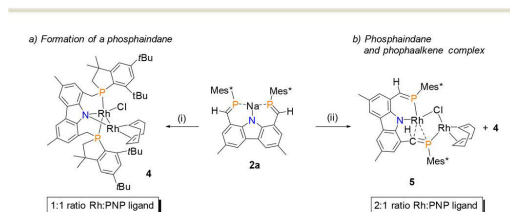


Fig. 3 Molecular structures of complexes **4** and **5**. ORTEP diagrams are drawn at 50% probability. For clarity, hydrogen atoms are omitted, and Mes* groups and cod ligands are rendered as wireframes for clarity.

electron square-planar Rh(i) centre (not considering the Rh–Rh interaction), making the metal centre Lewis-basic. Rh1 is coordinated by both phosphaindane arms in a *trans*-arrangement (Rh1–P1 2.311(2) Å, Rh1–P2 2.317(2) Å), in addition to Cl[−] and the carbazole N atom. Both metal centres are bridged by the carbazole N atom, with inequivalent Rh2–N1 (2.094(6) Å) and Rh1–N1 (2.149(7) Å) distances.

To elucidate the Rh–Rh bonding in complex **4**, DFT studies at the PBE0-D3/def2-SVP level of theory were carried out (see the ESI† for details). The HOMO is best described as non-bonding with significant d-orbital contributions at both Rh centres with a higher coefficient at the square-planar Rh1 centre. The Rh1–Rh2 interaction is represented in HOMO−1 (Fig. 4, top left) and shows donation from a d_{z^2} on Rh1 to a d-orbital at Rh2, while the Rh–N bonding is represented in HOMO−2 and HOMO−5. The LUMO is metal centred, and thus the longest wavelength absorption ($\lambda_{\text{max,exp.}} = 652$ nm, $\lambda_{\text{max,calc.}} = 609$ nm) can be best described as a metal-to-metal charge transfer (HOMO–LUMO transition). An NBO analysis also shows a d_{z^2} orbital on Rh1 (Fig. 4, top right), which is delocalised into a d-type lone valence at Rh2. In the NBO



Scheme 2 Reactions of **2a** with varying amounts of [Rh(cod)(Cl)]₂. Conditions: (i) 0.5 [Rh(cod)(Cl)]₂, THF, 1 h, r.t.; (ii) [Rh(cod)(Cl)]₂, THF, 1 h, r.t.

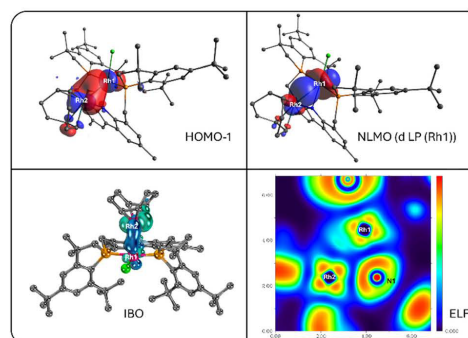


Fig. 4 Illustration of the Rh–Rh interaction in complex **4**. HOMO−1 (PBE0-D3/def2-SVP), NLMO of a d_{z^2} type lone pair (LP) on Rh1, IBO of the Rh–Rh interaction (r2SCAN-3c//PBE0-D3/def2-SVP), and electron localisation function (ELF, PBE0-D3/def2-SVP).

picture, the sp^2 -type lone pair on the carbazole N atom is delocalised into d-type lone valencies at each Rh centre. Complementary IBOs also illustrate the donor-acceptor character of the Rh–Rh bond (Fig. 4, bottom left, Fig. S86), while the electron localisation function (ELF) shows considerable localised electron density between the Rh atoms (Fig. 4, bottom right). In line with this, AIM analyses show a bond critical point.

Next, the reaction of **2a** and $[Rh(cod)(Cl)]_2$ in a 1:1 molar ratio was studied to explore whether full ligand consumption could be achieved. The reaction mixture in THF at room temperature revealed the formation of **4** according to $^{31}P\{^1H\}$ NMR spectroscopy, along with a new set of signals: a doublet at 169.2 ppm ($^1J_{P-Rh} = 152$ Hz) and a doublet of doublets at 125 ppm ($^1J_{P-Rh} = 157$ Hz, $^1J_{P-Rh} = 70$ Hz). These lower field signals suggest the presence of intact P=C units and of another dinuclear Rh(i) species. SC-XRD analysis of dark red crystals revealed the first example of a dinuclear Rh(i) complex featuring three different coordination modes of its PA units (Fig. 3, right). Both Rh atoms are μ -bridged by a chloride, and one of the PA units (P2–C12 1.765(3) Å) shows both a side-on η^2 -coordination to Rh1 and end-on η^1 - κ^P coordination to Rh2. The P2–C12 distance is in line with a previously reported η^2 -PA Ni complex (e.g., 1.773(8) Å).²¹ Even though such a coordination mode has been theoretically considered,¹ this is the first synthetic realisation of PA η^1, η^2 -coordination. Interestingly, the P2–C12 PA is *Z*-configured, resulting in π - π interactions of the Mes* group at P2 with the phenyl ring of the carbazole moiety (distance between centroids of both rings = 3.686 Å). The other PA unit shows a considerably shorter P1–C1 bond (1.694(2) Å), in line with P1 coordinating to Rh1 in η^1 -fashion. The coordination sphere at Rh1 is saturated by the carbazole N atom (Rh1–N1 1.975(2) Å) in the *trans*-position to the μ -bridging Cl^- . According to TD-DFT studies, the longest wavelength absorption ($\lambda_{max,exp.} = 796$ nm, $\lambda_{max,calc.} = 735$ nm) in the UV-Vis spectrum is associated with a HOMO–LUMO transition that can be best described as charge redistribution within the PNP framework with little contribution from the Rh centres. The second absorption at 564 nm is associated with an MLCT process (HOMO–1 to LUMO). The side-on coordination of the P2–C12 arm is best visualised in HOMO–1 and HOMO–5, while in the NBO picture, this interaction is reflected in a Rh–P bonding orbital which is best described as an interaction of a Rh-centred d-orbital with the P–C π^* orbital. The discovery of complex **5** adds a novel dimension to the coordination chemistry of PAs, expanding the known modes of interaction with transition metals.

Mechanistically, the formation of complexes **4** and **5** is assumed to be facilitated by a putative, tricoordinate Rh(i) $14e^-$ species. Such complexes have only recently been structurally authenticated and are shown to be highly reactive.¹¹ This prompted us to test whether starting from $[Rh(Cl)(CO)_2]_2$ the mononuclear $16e^-$ complex of the type $LRh(CO)$ could be isolated, postulating that the small CO ligand could effectively stabilise such a complex. Gratifyingly, when **2a** was combined with $[Rh(Cl)(CO)_2]_2$, irrespective of whether a 1:1 or

2:1 metal-to-ligand ratio was used, in THF at room temperature, the colour of the reaction mixture turned brown. According to ^{31}P NMR spectroscopy, a new species with a doublet at 181.7 ppm ($^1J_{Rh-P} = 163.6$ Hz), significantly shielded compared to **2a** and the neutral bis-PA **1**, was detected. The 1H NMR spectrum indicated a C_{2v} symmetric species in solution, and the complex could be crystallised from the reaction mixture by adding *n*-pentane. SC-XRD experiments confirmed the formation of $[Rh(CO)(^{Mes*}PNP)]$ (**6**) as a C_{2v} symmetric complex, crystallising in the monoclinic space group $C2/c$ with eight molecules in the unit cell (Fig. 5). In line with the ^{31}P NMR shift, the P=CH distances (P1–C15 1.666(2) Å; P2–C16 1.663(2) Å) indicate intact PA units, and the sum of angles at Rh ($\Sigma(\angle Rh) = 360^\circ$) is in line with a minimally distorted square-planar geometry. The Rh–CO distance (C53–O1 1.139(3) Å) is in the range of those of related PNP–Rh(i) complexes (cf. $[Rh(CO)\{N(CH_2CH_2PCy_2)_2\}]$ 1.1575(14) Å).²² IR spectroscopy revealed a CO stretching vibration at 1996 cm^{-1} , which is considerably blue-shifted compared to related amido-PNP Rh carbonyl complexes (cf. $[Rh(CO)\{N(CH_2CH_2PCy_2)_2\}]$, $\nu(C\equiv O) = 1905\text{ cm}^{-1}$).²² The UV-vis spectrum shows a longest wavelength absorption at 505 nm, which, according to TD-DFT calculations, corresponds to a π - π^* transition ($\lambda_{max,calc}(\mathbf{2a}) = 459$ nm), in line with orange-coloured crystals. The formation of **6** clearly shows the potential of ligand **1a** to form mononuclear Rh(i) complexes.

To determine whether the observed formation of dinuclear rhodium complexes is exclusive to $[Rh(cod)(Cl)]_2$, further investigations were carried out using related group 9 metal precursors. $^{31}P\{^1H\}$ NMR monitoring of the reactions of **2a** and 1 or 0.5 equivalents of $[Ir(cod)(Cl)]_2$ in THF indicated the formation of the protonated ligand **1a** (250.0 ppm) as the major species along with several unidentified products that show resonances between 20–25 ppm and 150–250 ppm (see the ESI† for details), suggesting unselective formation of PA and phosphaindane complexes. The formation of the protonated form of the ligand, likely through proton abstraction from the solvent, supports the strong basicity of **2a**. While the $^{31}P\{^1H\}$ NMR spectra of the reaction of **2a** with 1 equiv. of $[Rh(coe)_2Cl]_2$ (coe = cyclooctene) show mainly phosphaindane-type signals at ca. 50 ppm, when using 0.5 equiv. of $[Rh(coe)_2Cl]_2$ mainly ligand **1a** was obtained. Similarly, reactions

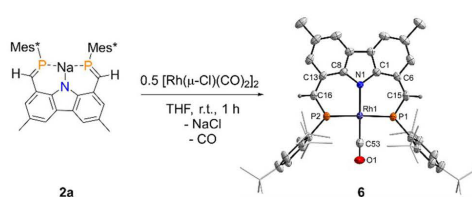


Fig. 5 Reaction of **2a** with $[Rh(Cl)(CO)_2]_2$ giving complex **6**. Molecular structure of complex **6**. ORTEP diagrams are drawn at 50% probability. For clarity, hydrogen atoms (except H15 and H16) are omitted, and tBu-groups are rendered as wireframes for clarity.



of **2a** with $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (nbd = 2,5-norbornadiene) produce mixtures of several species. However, in this case, the reaction with 1 equiv. of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ shows minor signals at 172.8 and 137.3 ppm that could correspond to a species similar to **5**. These results suggest that the reactivity leading to **4** and **5** is unique for $[\text{Rh}(\text{cod})\text{Cl}]_2$ and warrants further exploration to fully understand the underlying mechanisms.

Conclusions

A new class of anionic PNP-type bis-PA ligands **1a** and **1b** based on a carbazole backbone have been prepared, and their facile deprotonation yields the corresponding Na and K salts. With $[\text{Rh}(\text{cod})\text{Cl}]_2$, a unique dinuclear Rh complex with a Rh–Rh donor–acceptor interaction is obtained, while with an excess of the Rh precursor, a bis-PA complex with three different PA-coordination modes was accessed. The formation of such dinuclear complexes suggests the intermediate formation of a T-shaped $14e^-$ electron complex. Such species can be trapped in the presence of the small, strongly donating CO ligand, yielding the square-planar $16e^-$ electron complex **6**. The formation of this species clearly shows the potential of ligand **1a** in organometallic chemistry. Future studies will focus on expanding these concepts to main group elements and to utilise the Rh complexes in catalysis.

Author contributions

K. K.: investigation, data curation, formal analysis, funding acquisition, and writing – original draft. M. R.: investigation and formal analysis. H.-J. D.: investigation and formal analysis. F. D.: DFT calculations. C. H.-J.: conceptualisation, resources, DFT calculations, supervision, and writing – review and editing. T. B.: conceptualisation, funding acquisition, resources, supervision, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI†. Crystallographic data have been deposited at the CCDC under the identification numbers 2451040 (**1a**), 2451041 (**1b**), 2451042 (**2a**), 2451043 (**4**), and 2451044 (**5**), respectively. Further details can be obtained from the authors.

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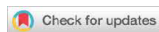
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PNN-Type Pincer Imidazolylphosphine Complexes of Late Transition Metals for the Catalytic Dehydrocoupling of Amine Boranes

Mirko Rippke, Marie-Sophie Lenz, Annika Queißer, Marcus Klahn, Hans-Joachim Drexler, and Torsten Beweries*

The catalytic dehydrocoupling of amine boranes produces well-defined B–N compounds and polymers that are isovalent electronic to hydrocarbon analogs. In this study, the synthesis and characterization of a set of Rh, Ir, and Ru complexes with tridentate imidazolylphosphine PN(H)N ligands of the type (imidazolyl)CH₂N(H)CH₂CH₂PR₂ (R = *i*Pr, *t*Bu) are presented. These complexes potentially engage in metal–ligand cooperative dehydrogenation of amine boranes, followed by B–N coupling. All complexes show facial coordination of the PN(H)N ligands to the metal centers

with pronounced hydrogen bonding to an outer-sphere chloride ligand. All Rh and Ir complexes are active catalysts for the dehydrogenation of H₃B–NMeH₂ and H₃B–NMe₂H, producing mainly linear and cyclic B–N oligomers. Only the Ru complex [Ru(PN(H)N)(PPh₃)(CO)(H)]Cl (**8**) produces low-molecular-weight poly(aminoboranes) from H₃B–NMeH₂ with high activity after activation with KO^tBu, supporting metal–ligand cooperativity during activation of the amine borane substrates.

1. Introduction

The dehydrocoupling and dehydropolymerisation of amine borane adducts H₃B–NR_nH_{3–n} (*n* = 1, 2; R = alkyl or aryl group) has attracted significant attention in the past two decades as it allows for the construction of molecularly defined B–N compounds and polymers that are isovalent electronic to ubiquitous hydrocarbon analogs.^[1,2] These main group compounds are of significant fundamental interest and show potential for a wide range of applications, e.g., as precursors for piezoelectric materials^[3] or as oligo- and polymeric precursors to functional B–N materials.^[4,5] In addition to noncatalytic methods for B–N bond linkage,^[6–8] transition metal complex-catalyzed dehydrocoupling and dehydropolymerisation in particular offer selective and atom economic access to these compounds.^[9,10] While several examples of promising catalyst systems based on electropositive transition metals have been reported,^[11] most of the highly active and selective representatives are still found in the field of electron-rich late transition metals. Among these, the use of systems with cooperative bis(phosphinoethyl) amine pincer ligands such as K³–(iPr)₂PCH₂CH₂)₂NH has proven to be particularly promising in the past.^[12–16] Using this

approach, the dehydrogenation of amine boranes via metal–ligand cooperative outer-sphere activation is possible, followed by B–N coupling of the transient aminoborane, either metal-free, via coupling on the metal fragment, or assisted by the ligand through nucleophilic head-to-tail chain growth at the amine donor site.^[17] For primary amine boranes such as methylamine borane, H₃B–NMeH₂, these processes can either result in the desired formation of linear poly(aminoboranes), or produce thermodynamically preferred oligomeric cyclic noncyclic products (Figure 1).

Systematic studies on the use of group 9 complexes possessing the PNP ligand K³–(iPr)₂PCH₂CH₂)₂NH for the catalytic dehydropolymerisation of H₃B–NMeH₂ have been presented in recent years by Weller and coworkers. While the organometallic details of the Co-based system remained ambiguous, with redox-neutral, outer-sphere activation of the amine borane at Co(II) and a Co(I)/Co(II)-based catalytic cycle as the most likely options,^[18] detailed mechanistic scenarios were proposed for the Rh- and Ir-based catalyst systems. In case of Rh selective dehydropolymerisation using the precatalyst [Rh(^{IP}PN(H)P(^{IP}))(cod)]⁺ (cod = 1,5-cyclooctadiene) occurs via initial formation of Rh(III) hydride species, which activate the substrate through outer-sphere interaction and formation of a Rh(III) dihydrogen species.^[19] Of note, this system is air-tolerant and allows for the formation of poly(methylaminoborane) on a multigram scale. Studies of the related Ir PNP complexes showed divergent behavior of neutral and cationic Ir(III) hydride precatalysts with the cationic system giving polymers via initial dehydrogenation through an inner-sphere mechanism.^[20]

To extend the scope of potentially cooperative group 9 pincer catalysts for the dehydrocoupling of amine boranes and shine light on the role of the ligand motif, we have recently studied Co^[21] and Rh^[22] complexes possessing Caulton's pyridine-pyrazole-based PNN(H) ligand.^[23,24] While the Co complex [(^{IP}PNN(H))CoCl₂] is

M. Rippke, M.-S. Lenz, A. Queißer, M. Klahn, H.-J. Drexler, T. Beweries
Modern Concepts in Molecular Catalysis
Leibniz-Institut für Katalyse e.V. (LIKAT Rostock)
Albert-Einstein-Str. 29a, 18059 Rostock, Germany
E-mail: torsten.beweries@catalysis.de

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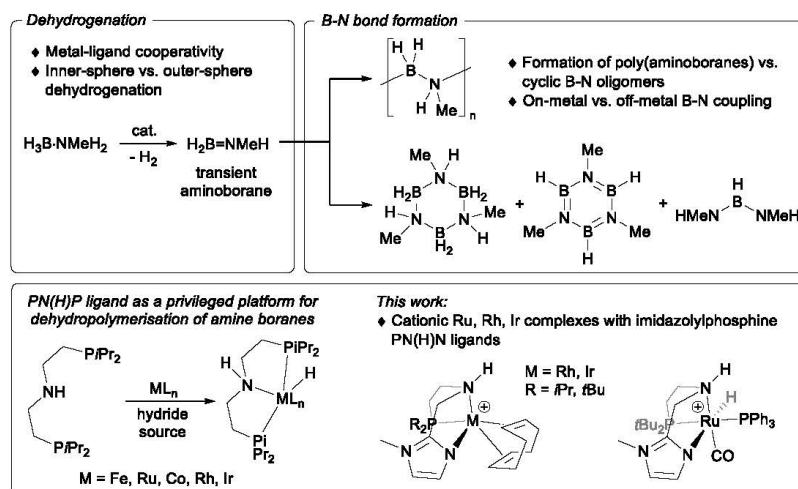


Figure 1. Contextualization of the present work

not suited for the dehydrocoupling of amine boranes, but can be used for the transfer semihydrogenation of alkynes with ammonia borane, H_3B-NH_3 , a series of Rh complexes shows moderate activity for the dehydrocoupling of amine boranes H_3B-NMe_n , H_{3-n} ($n = 1, 2$). Polymer formation could not be observed in case of $H_3B-NMeH_2$. We were thus interested in further variations of the pincer ligand, moving to a ligand motif with a potentially cooperative N-H functionality in the central position of the ligand framework. Imidazolylphosphine-based $^P\text{PN}(\text{H})\text{N}$ pincer ligands were developed by the groups of Zhou, Liu, and Beller and showed excellent activity for the Co-catalyzed transfer hydrogenation of nitriles and the Ru-catalyzed hydrogenation of aromatic and aliphatic nitriles and amides.^[25–27] More recently, these ligands were applied as part of Mn systems for the hydrogenation of *N*-heterocycles.^[28] In the present contribution, we report the coordination chemistry of these imidazolylphosphine-based $^P\text{PN}(\text{H})\text{N}$ ligands at Rh, Ir, and Ru and present the application of these systems for the catalytic dehydrocoupling of amine boranes.

2. Results and Discussion

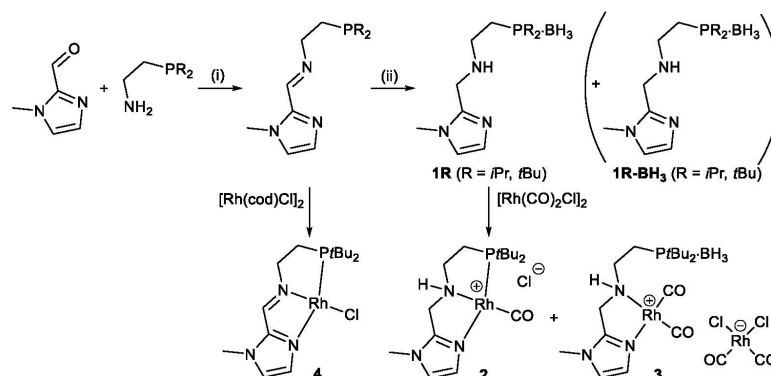
2.1. Synthesis and Characterization of Rh, Ir, and Ru Complexes

Ligand synthesis was performed according to procedures reported before by Zhu, Liu, Beller, and coworkers.^[25-27] In previous work, the imidazole-based ³¹P(N)H ligands were prepared in a two-step one-pot procedure by the combination of 1-methyl-2-imidazole carboxaldehyde with the aminophosphine, followed by reduction of the imine functionality with NaBH₄ and formation of borane-free ligands was suggested.^[25-27] In our hands, along with formation of

the desired ligand **1R**, formation of significant amounts of phosphine-borane adduct **1R-BH₃** was observed, as evidenced by ¹B NMR (**1P**R-BH₃: δ -43.8 ppm, **1tBu**-BH₃: δ -43.6 ppm) and ³¹P{¹H} NMR data (**1P**R-BH₃: δ 43.8 ppm, **1tBu**-BH₃: δ 41.2 ppm, **Scheme 1**). A single crystal X-ray diffraction (SC-XRD) analysis of **1P**R-BH₃ supports this finding (P1-B1 1.916(3) Å, **Figure 2**). As demonstrated below, the presence of borane does not affect coordination to [Rh(cod)Cl]₂ (vide infra, **Scheme 2**). Use of a Rh precursor with strongly π accepting ligands such as [Rh(CO)₂Cl]₂ produces the cationic complex [Rh(^{RBu}-PN(H)P)CO]Cl (**2**) with δ (³¹P) 103.9 ppm (d, ¹J_{P, Rh} = 152 Hz) along with small amounts of a second cationic species **3** in which the phosphine-borane moiety is intact with the phosphine unit noncoordinating to Rh. The broad singlet resonance at δ (³¹P) 43.7 ppm (Figure S12, Supporting Information) is well in line with the value found for the free BH₃-adduct **1tBu**-BH₃ (vide supra^[27]), related tBu₂P(H)-BH₃ (δ 48.3 ppm)^[29] and other alkyl phosphine-borane adducts.^[30]

The molecular structure of complex **3** could be determined by SC-XRD analysis using material that was obtained from saturated MeOH solutions. It shows a Rh dicarbonyl cation (Rh1–C16 1.887(5), Rh1–C17 1.860(5) Å) that is coordinated by the ^{tr}PN(H)N-borane adduct through the N atoms (Rh1–N1 2.151(3), Rh1–N2 2.049(3) Å), as detailed above with a noncoordinating phosphine unit (Figure 2). The anionic fragment consists of a Rh dichloride dicarbonyl unit with shorter Rh–C(carbonyl) distances due to the presence of chloride ligands (Rh2–C18/19 1.838(6) Å).

As mentioned above, synthesis of the imidazole-based PN(H) P ligands requires a reduction step that transforms the imine, formed by condensation of aminophosphine and imidazole carboxaldehyde, into the amine ligand. The imine intermediate can be isolated as a colorless oily compound (δ (^3P) 22.8 ppm) that can be used for a brief study of its coordination chemistry.



Scheme 1. Synthesis of imidazole-based $^3\text{PN}(\text{H})\text{N}$ ligands, formation of the ligand- BH_3 adducts and formation of complexes **2**, **3** and **4**. Reaction conditions: (i) THF, 1 h, room temperature. (ii) NaBH_4 , THF, 16 h, 0°C to room temperature.

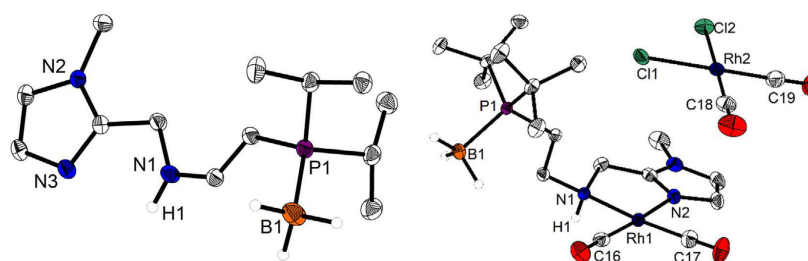
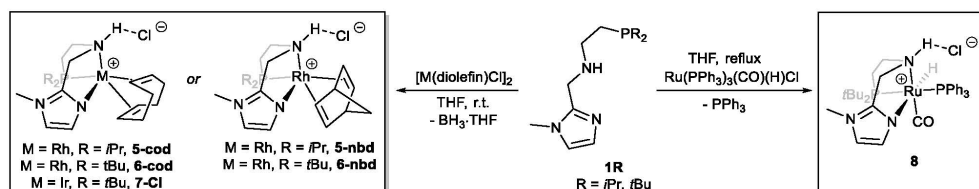


Figure 2. Molecular structures of the $\text{PN}(\text{H})\text{N}$ -borane adduct **1Pr-BH₃** (left) and the Rh carbonyl complex **3** (right). Thermal ellipsoids correspond to 30% probability at $T = 150(2)\text{ K}$. Hydrogen atoms (except N-H and B-H), as well as the second molecule of the asymmetric unit (for **1Pr-BH₃**) are omitted for clarity.



Scheme 2. Formation of imidazole-based $\text{PN}(\text{H})\text{P}$ Rh and Ir complexes.

Reaction with $[\text{Rh}(\text{cod})\text{Cl}]_2$ results in the formation of the neutral complex $[\text{Rh}(\text{tBu}^{\text{imine}}\text{N})\text{Cl}]$ (**4**, Scheme 1), which shows a characteristic doublet resonance in $^3\text{P}\{\text{H}\}$ NMR at δ 98.7 ppm ($^1J_{\text{P,Rh}} = 190.5\text{ Hz}$). The molecular structure (Figure 3) shows the Rh center in distorted square-planar coordination geometry ($\tau_4 = 0.07$)^[31] with a Rh1–N1 distance of 1.965(2) Å and the slightly elongated imine fragment (N1–C3 1.306(3) Å, $\Sigma_{\text{C=O}, \text{C=N}} = 1.27\text{ Å}^{[31]}$).

Next, the coordination of the phosphine-borane adducts **1R-BH₃** to Rh and Ir diolefin precursors was studied (Scheme 2). Addition of the *i*Pr and *t*Bu ligand precursors to $[\text{Rh}(\text{cod})\text{Cl}]_2$ in

THF produces complexes $[\text{Rh}(\text{PN}(\text{H})\text{N})(\text{cod})\text{Cl}]$ **5-cod** (*R* = *i*Pr) and **6-cod** (*R* = *t*Bu) as yellow and orange-colored, sparingly soluble solids, respectively. $^3\text{P}\{\text{H}\}$ NMR analysis shows doublets at δ 47.9 (**5-cod**, $^1J_{\text{P,Rh}} = 132.3\text{ Hz}$) and 58.9 ppm (**6-cod**, $^1J_{\text{P,Rh}} = 127.3\text{ Hz}$), shifted to lower field compared to the ligand precursor. Whereas for the *t*Bu substituted complex, a broad NH resonance could be found in ^1H NMR spectra at δ 7.43 ppm, this signal is absent for the *i*Pr analog, likely due to hydrogen bonding to the chloride anion. Similar hydrogen bonding was observed before, e.g., by Weller and coworkers for the above-mentioned related

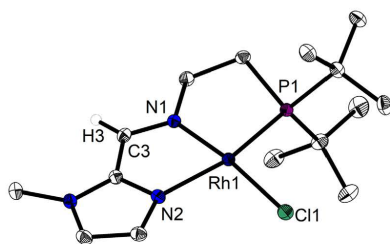


Figure 3. Molecular structure of the Rh chloride complex **4**. Thermal ellipsoids correspond to 30% probability at $T = 150(2)$ K. Hydrogen atoms (except H3) are omitted for clarity.

complex $[\text{Rh}(\text{P}^{\text{tBu}}\text{PN}(\text{H})\text{P}^{\text{tBu}})(\text{cod})]\text{Cl}$.^[19] The presence of broad ^1H NMR signals at room temperature (most pronounced for **6-cod** in CD_2Cl_2) indicates fluxionality of the diolefin ligand.

In general, moving from cod to nbd complexes can result in significant differences in catalysis, with nbd complexes typically showing significantly shorter prehydrogenation times due to the presence of the more strained diolefin,^[32,33] thus resulting in shorter induction periods in (de)hydrogenation reactions. Following the same protocol as for the cod complexes, reaction of **1*i*Pr-BH₃** and **1*t*Bu-BH₃** with the nbd precursor $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (nbd = 2,5-norbornadiene, bicyclo[2.2.1]hepta-2,5-diene) furnishes the structurally related species and $[\text{Rh}(\text{P}^{\text{tBu}}\text{PN}(\text{H})\text{N})(\text{cod})]\text{Cl}$ ($R = i\text{Pr}$, **5-nbd** and $R = t\text{Bu}$, **6-nbd**, Scheme 2) which are characterized by its doublet resonances at δ 55.7 ($J_{\text{P,Rh}} = 155.4$ Hz, **5-nbd**) and 66.1 ppm ($J_{\text{P,Rh}} = 138.8$ Hz, **6-nbd**) in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. ^1H NMR signals corresponding to the CH and CH₂ groups of the nbd ligand are well-resolved at room temperature, suggesting the absence of rapid rotation of the nbd ligand at room temperature.

The molecular structures of complexes **5-cod** and **5-nbd** show the cationic 18-electron Rh center in distorted pseudo-trigonal bipyramidal coordination geometry with the $\text{P}^{\text{tBu}}\text{PN}(\text{H})\text{N}$ ligand coordinated facially (Figure 4). In both complexes, the chloride anion is hydrogen bonded to the N–H proton (**5-cod**: 2.451, **5-nbd**: 2.421 Å; $\Sigma r_{\text{vdW}} = 3.02$ Å^[34]). A comparison with complex

4 and the previously reported pyridine-pyrazole-based Rh complex $[\text{Rh}(\text{P}^{\text{tBu}}\text{PN}(\text{H})\text{N})(\text{H})\text{RhCl}]$ shows that in **5-cod** and **5-nbd** the chloride ligand is positioned in the secondary coordination sphere instead of directly at the Rh center, likely due to the presence of the weaker amine donors instead of the imine in **4**.^[35,36] Of note, these structural motifs resemble those of Weller's highly active $\text{Rh}(\text{I})$ $\text{PN}(\text{H})\text{P}$ complex that can be used for large-scale dehydro-polymerisation of $\text{H}_3\text{B-NMeH}_2$ in air.

An analogous Ir complex $[\text{Ir}(\text{P}^{\text{tBu}}\text{PN}(\text{H})\text{N})(\text{cod})]\text{Cl}$ (**7-Cl**) as well as a tetrafluoroborate analog $[\text{Ir}(\text{P}^{\text{tBu}}\text{PN}(\text{H})\text{N})(\text{cod})]\text{BF}_4$ (**7-BF₄**) can be prepared as yellow solids using a similar protocol starting from **1*t*Bu-BH₃** and $[\text{Ir}(\text{cod})\text{Cl}]_2$ or $[\text{Ir}(\text{cod})_2]\text{BF}_4$, respectively (Scheme 2). Its solution NMR data in $\text{THF-}d_6$ show ^{31}P signals at δ 49.7 ppm (**7-Cl**) and 48.9 ppm (**7-BF₄**) as well as N–H resonances at δ 9.37 (**7-Cl**) and 5.85 ppm (**7-BF₄**). The latter values suggest differences due to the presence of hydrogen-bonded versus noncoordinating BF_4 anions. The molecular structure of complex **7-BF₄** is depicted in the Supporting Information. Similarly as for the Rh congeners, the metal center in **7-Cl** is found in distorted pseudo-trigonal bipyramidal coordination mode with facial coordination of the $\text{P}^{\text{tBu}}\text{PN}(\text{H})\text{N}$ ligand and the chloride anion hydrogen bonded to the N–H unit (N–H...Cl 2.369 Å, Figure 4). These similarities allow for a direct comparison of this set of structurally related group 9 complexes in catalytic dehydrocoupling reactions.

In the past, several catalyst systems based on Ru complexes with cooperative pincer or cyclopentadienyl ligands were reported for the dehydrocoupling/dehydropolymerisation of amine boranes.^[12,13,35–38] As mentioned above, related PNN-type pincer imidazolylphosphine Ru complexes with PPh_2 and $\text{P}^{\text{tBu}}\text{Pr}_2$ donor groups and variation of the alkyl bridging unit between amine and phosphine were used for catalytic hydrogenation. Reaction of $[\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})\text{Cl}]$ with the ligand precursor **1*t*Bu-BH₃** in refluxing THF results in the formation of complex $[\text{Ru}(\text{PN}(\text{H})\text{N})(\text{PPh}_3)(\text{CO})(\text{H})]\text{Cl}$ (**8**) as a white solid (Scheme 2). Its ^1H NMR spectrum shows a characteristic doublet of doublets at δ –13.20 ppm ($J_{\text{P,H}} = 22.3$ Hz), corresponding to a Ru hydride coupling to two *cis*-phosphine ligands. In line with this, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** shows doublet resonances at δ 90.9 and 44.5 ppm ($J_{\text{P,P}} = 265.6$ Hz) for the imidazolylphosphine ligand and coordinated PPh_3 , respectively, positioned *trans* to each

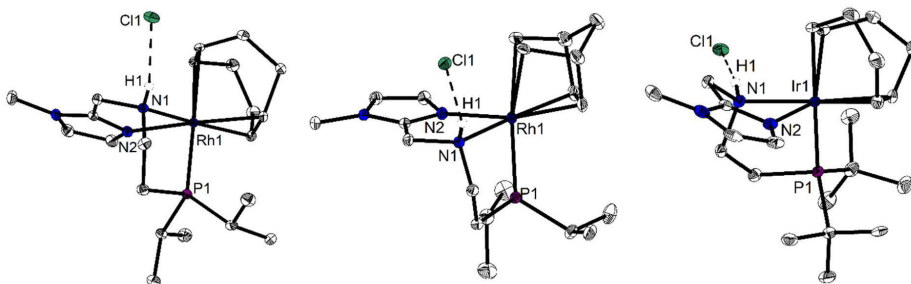


Figure 4. Molecular structures of the diolefin complexes **5-cod** (left), **5-nbd** (center) and **7-Cl** (right). Thermal ellipsoids correspond to 30% probability at $T = 110(2)$ (**5-cod**) and $150(2)$ K (**5-nbd** and **7-Cl**), respectively. Hydrogen atoms (except N–H), as well as cocrystallised MeCN (for **5-cod**) are omitted for clarity.

other. The presence of a CO ligand is corroborated by a low-field ^{13}C resonance at δ 206.9 ppm and an IR band at 1919 cm^{-1} . The latter value is in the same range as found in other Ru amine pinners such as $[\text{Ru}(\text{tBu}_2\text{PCH}_2\text{CH}_2\text{NH})(\text{CO})(\text{H})\text{Cl}]$ [39,40] (1897 cm^{-1}) and Beller's structurally related Ru imidazolylphosphine complex with PtBu_2 donors and a C3 bridge between NH group and phosphine unit (1890 cm^{-1}), [25] but suggests weaker back-bonding, potentially caused by the chloride hydrogen bonded to the amine *trans* to the CO ligand. The molecular structure (Figure S2, Supporting Information) confirms the structural motif found in solution; however, a detailed discussion of bond parameters is not possible due to the poor quality of the data.

2.2. Catalytic Dehydrocoupling of Amine Boranes

Inspired by previous studies of dehydropolymerisation of $\text{H}_3\text{B-NMe}_2$ using late transition metal pincer complexes, we have

first tested the Rh and Ir complexes **4**, **5-cod**, **5-nbd**, **6-cod**, and **7-Cl** for dehydrocoupling of $\text{H}_3\text{B-NMe}_2$ and $\text{H}_3\text{B-NMe}_2\text{H}$ using 2 mol% of precatalyst in toluene at room temperature. Conversion was followed by volumetric monitoring the amount of hydrogen gas (Figure 5). Details of all catalytic runs can be found in the Supporting Information. In general, all Rh complexes show catalytic activity for dehydrogenation of amine boranes with reactions of $\text{H}_3\text{B-NMe}_2\text{H}$ typically proceeding significantly slower (Figure 5A,B). Comparison of the structurally related *cod* and *nbd* complexes **5-cod** and **5-nbd** possessing the $^{18}\text{P}(\text{H})\text{N}(\text{H})$ ligand shows that the nature of the diolefin does not affect catalytic activity (**5-cod**: TOF 20.4 h^{-1} , **5-nbd**: TOF 20.5 h^{-1} ; determined after $t = 1\text{ h}$, see Supporting Information for details). Of note, the Rh chloride complex **4**, containing the unsaturated $^{18}\text{P}(\text{H})\text{N}(\text{H})$ ligand, shows the highest activity for dehydrocoupling of $\text{H}_3\text{B-NMe}_2$ (TOF 40.3 h^{-1}), which could be caused by substrate activation at the unsaturated ligand backbone.

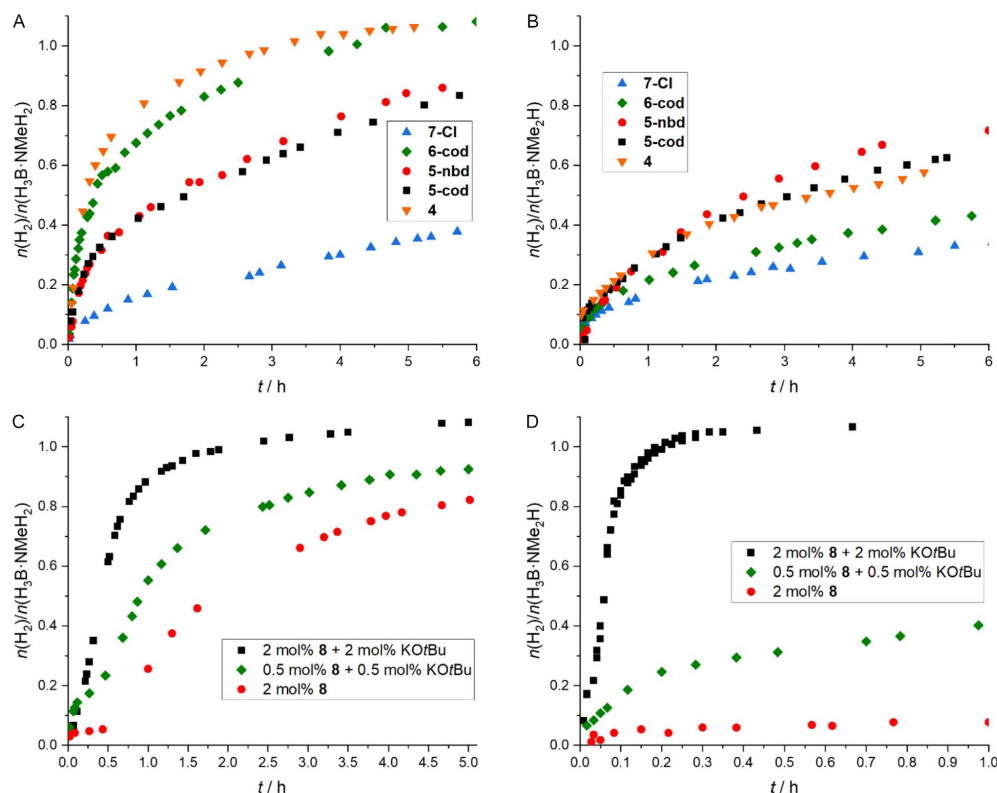


Figure 5. (Top left): A) Comparison of volumetric traces of catalytic dehydrocoupling of $\text{H}_3\text{B-NMe}_2$ using complexes **4**, **5-cod**, **5-nbd**, **6-cod**, and **7-Cl**. ($[\text{H}_3\text{B-NMe}_2] = 1.33\text{ mmol}$, 2 mol% precatalysts in 10 mL toluene, $T = 25^\circ\text{C}$). (Top right): B) Comparison of volumetric traces of catalytic dehydrocoupling of $\text{H}_3\text{B-NMe}_2\text{H}$ using complexes **4**, **5-cod**, **5-nbd**, **6-cod**, and **7-Cl**. ($[\text{H}_3\text{B-NMe}_2\text{H}] = 1.33\text{ mmol}$, 2 mol% precatalysts in 10 mL toluene, $T = 25^\circ\text{C}$). (Bottom left): C) Effect of addition of KOtBu when using complex **8** as the precatalyst ($[\text{H}_3\text{B-NMe}_2] = 1.33\text{ mmol}$ in 10 mL toluene, $T = 25^\circ\text{C}$). (Bottom right): D) Effect of addition of KOtBu when using complex **8** as the precatalyst ($[\text{H}_3\text{B-NMe}_2\text{H}] = 1.33\text{ mmol}$ in 10 mL toluene, $T = 25^\circ\text{C}$).

However, further mechanistic investigations were not carried out due to the absence of the structural motif of a cationic PN(H)N complex with diolefin ligands, which would have been desirable for comparison purposes. The Ir complex **7-Cl** shows inferior catalytic activity compared to all Rh complexes ($\text{TOF } 8.5 \text{ h}^{-1}$).

^{11}B NMR analysis of aliquots taken from reaction mixtures at maximum conversion showed that with $\text{H}_3\text{B-NMeH}_2$, all reactions produce mixtures of cyclotriborazane $[\text{H}_2\text{BNMeH}]_3$ as the main product ($\delta -4.8 \text{ ppm}^{[41]}$), diaminoborane HB(NMeH)_2 ($\delta 28.6 \text{ ppm}^{[29]}$), and traces of borazine $[\text{HBNMe}]_3$ ($\delta 33.5 \text{ ppm}^{[41]}$) and boronium chloride $[\text{H}_2\text{B(NMeH)}_2]\text{Cl}$ ($\delta 2.0 \text{ ppm}^{[6]}$) (Figure S50, Supporting Information). Formation of poly(*N*-methylaminoborane) $[\text{H}_2\text{BNMeH}]_n$, indicated by broad ^{11}B NMR signals centered at $\approx \delta -5 \text{ ppm}$ was observed in no case. However, selective formation of cyclotriborazane $[\text{H}_2\text{BNMeH}]_3$ is rather unusual and could serve as a molecular precursor for functional B–N materials. In this context, Gianetti, Trincado, Grützmacher, and coworkers have recently reported the selective Rh catalyzed dehydrocoupling of ammonia borane, $\text{H}_3\text{B-NH}_3$, to borazine, $[\text{HBNH}]_3$.^[42] Dehydrocoupling of the related $\text{H}_3\text{B-NMe}_2\text{H}$ results in highly selective formation of cyclodiborazane $[\text{H}_2\text{BNMe}_2]_2$ (^{11}B NMR: $\delta 5.4 \text{ ppm}$) in all cases. In previous studies, the addition of bases such as KOtBu or the amine NMeH_2 was found to accelerate the catalytic reaction, removing induction periods through formal deprotonation^[22] or chloride abstraction as boronium chloride.^[19] Addition of amine was furthermore found to modify the nature of the formed B–N products.^[43,44] We have thus studied **6-cod** ($\text{TOF } 33.8 \text{ h}^{-1}$), the most active cationic PN^+N precatalyst with a diolefin ligand, in more detail and found that neither addition of KOtBu nor NMeH_2 accelerates the reaction or changes the spectrum of B–N products when using $\text{H}_3\text{B-NMeH}_2$ (see Supporting Information for details). While these results suggest that removal of the outer-sphere chloride ligand is not involved in the activation of the precatalyst or in a rate-determining step of catalysis, addition of KOtBu to **6-cod** in the dehydrocoupling reaction of $\text{H}_3\text{B-NMe}_2\text{H}$ was found to significantly accelerate the reaction, giving quantitative conversion of $\text{H}_3\text{B-NMe}_2\text{H}$ in $\approx 15 \text{ min}$ (Figure S58, Supporting Information). Although speculative, deprotonation of the amine borane N–H with the strong base KOtBu could play a role in this case, followed by a sequence of anion exchange steps with a Rh chloride species.

Evaluation of the Ru complex **8** for the catalytic dehydrocoupling of $\text{H}_3\text{B-NMeH}_2$ in toluene using a precatalyst concentration of 2 mol% shows that this species shows a pronounced induction period of $\approx 45 \text{ min}$, with post-induction activity being similar to that of Rh complexes mentioned above (Figure 5C, $\text{TOF } 16.4 \text{ h}^{-1}$). Dehydrocoupling reactions using alternative solvents THF or 1,2-difluorobenzene gave poorly reproducible results and showed formation of significant amounts of borazine. With $\text{H}_3\text{B-NMe}_2\text{H}$, almost no catalytic activity was observed for several hours (Figure 5D). Similarly as for the Rh complexes addition of NMeH_2 to catalytic dehydrocoupling reactions of $\text{H}_3\text{B-NMeH}_2$ has no effect. Consistent with this, complex **8** is stable in the presence of amine and shows no conversion to a new Ru species. In contrast, addition of KOtBu removes the induction period and significantly accelerates the reaction (Figure 5C,

$\text{TOF } 45.6 \text{ h}^{-1}$). Interestingly, similarly as for **6-cod** base activation of complex **8** in the reaction of $\text{H}_3\text{B-NMe}_2\text{H}$ produces a highly active system which converts the substrate in $\approx 15 \text{ min}$ (Figure 5D, $\text{TOF } 53.3 \text{ h}^{-1}$). A control experiment in which KOtBu was added at the maximum rate instead of at the beginning of the reaction does not affect the kinetic profile (Figure S56, Supporting Information). Thus, we conclude that the base is only relevant for the activation of the precatalyst and does not play a role in catalytic turnover. NMR spectroscopic monitoring of a catalytic dehydrocoupling reaction using 2 mol% **8** and KOtBu shows resonances of the precatalyst as well as characteristic signals at $\delta(^1\text{H}) -8.35, -6.50 \text{ ppm}$ and $\delta(^{31}\text{P}) 45.3, 57.4 \text{ ppm}$, indicating the formation of the previously reported Ru dihydride complex $[\text{Ru}(\text{PPh}_3)_3(\text{H})_2(\text{CO})]$ (Figure S64 and S65, Supporting Information).^[45] A control experiment using this species as a precatalyst shows inferior catalytic activity. We thus assume that slow deactivation of **8** occurs through dissociation of the $^{\text{tr}}\text{PNN}$ ligand under catalytic conditions and formation of the Ru dihydride. Catalytic reactions of $\text{H}_3\text{B-NMeH}_2$ in the presence of complex **8** in toluene show the formation of different amounts of a colorless precipitate. This was isolated by filtration, dissolution in THF and re-precipitation by addition of cold pentane and analyzed by NMR spectroscopy. The ^{11}B NMR spectra show a broad signal characteristic of poly(aminoborane) centered at around $\delta -5 \text{ ppm}$. Size exclusion chromatographic (SEC) analysis of this material supports the formation of a low-molecular-weight polymer ($M_n = 4,200\text{--}7,800 \text{ g mol}^{-1}$, $D = 1.3\text{--}2.4$). Of note, higher molecular weights and polymer yields were obtained in reactions in the presence of KOtBu that show full conversion within several minutes (see Supporting Information for details). Although complex **8** is much less active and productive, these findings are in accordance with a recently reported catalyst system consisting of a Ru(II) aminophosphine dichloride precatalyst that is activated with a well-defined amount of KOtBu .^[46,47] In general, fast dehydrogenation of the amine borane leads to the accumulation of the reactive aminoborane monomer $\text{H}_2\text{B=NMeH}$, which in turn leads to a higher degree of polymerization due to the direct correlation between the rates of propagation/termination.^[47]

All complexes studied herein are suited as precatalysts for the catalytic dehydrocoupling of amine boranes, giving cyclic borazanes as main products. Similarly as reported by us before for Co and Rh complexes that possess a pyrazole-based PNN(H) ligand, it must be noted that changing the nature of the aminophosphine ligand from the well-established bis(phosphinoethyl)amine PN(H) P pincer ligand ($i\text{-Pr}_2\text{PCH}_2\text{CH}_2\text{NH}$) to a related imidazole-based PN(H)N ligand results in loss of selectivity for the poly(aminoborane) with only the Ru complex giving comparably small amounts of a low-molecular weight polymer.

3. Conclusion

In summary, we have systematically studied the coordination chemistry of two imidazolylphosphine-based tridentate ligands at Rh, Ir, and Ru. In all complexes, hydrogen bonding of the chloride ligand present in the secondary coordination sphere and

facial coordination of the pincer ligand produce systems that resemble Weller's highly active Rh(I) PN(H)P catalyst system. Evaluation of these potentially metal-ligand cooperative species as precatalysts for the dehydrocoupling of amine boranes shows that all complexes are active for dehydrogenation. However, Rh and Ir PN(H)N complexes show no selectivity for the desired poly(aminoborane), producing mainly linear and cyclic oligomers. In contrast, base activation of a related Ru PN(H)N complex generates a highly active system that produces low-molecular-weight poly(aminoboranes) in addition to linear and cyclic oligomers. NMR spectroscopic analysis of this catalyst system shows degradation into a well-known Ru(II) dihydride through loss of the PN(H)N ligand. We are currently investigating the application of the complexes presented here for related (de)hydrogenation reactions and are working on the development of further potentially cooperative systems for the activation of amine boranes.

Supporting Information

The authors have cited additional references within the Supporting Information.^[48–50] The Supporting Information includes experimental, spectroscopic, and crystallographic details as well as details of amine borane dehydrocoupling experiments. Deposition Numbers 2433124–2433131 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe <http://www.ccdc.cam.ac.uk/structures.uk>.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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