TECHNISCHE UNIVERSITÄT WIEN
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Dissertation

Synthesis and Characterization of Pyrrole-Based Group IV PNP Pincer Complexes

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Doktors der technischen Wissenschaften (Dr. techn.)

unter Leitung von

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Wien, im Februar 2022

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Table of Content

Abstract

The activation of small molecules such as N_2, CO, H_2 or CO_2 is a fundamental subfield in organometallics chemistry. In the case of N_2 activation group IV metals are known for their unique coordination modes of dinitrogen. One of the most important aspects in this research field is the choice of the ancillary ligand fine-tuning, the steric and electronic parameters of the complexes, which bind N_2 in various modes. In the last decades it has been proven that amidophosphines are well suited for this task, due to the combination of the hard anionic nitrogen donor in combination with the soft phosphine moiety.

This work focuses on the development, synthesis and characterization of group IV metal complexes as well as the functionalization of these for desired N_2 activation. In this context a PNP pincer type ligand based on the pyrrole scaffold was chosen. The complexation was achieved upon utilization of $MCl_4{\cdot}2THF$ (M = Ti, Zr, Hf) as well as the less common $M(NR_2)_4$ (R = Me, Et) precursor. In course of the work, it became apparent that silyl reagent such as TMS-X (X = Cl, Br, I, N_3) were suitable for targeted functionalization.

Therefore, it was possible to isolate the corresponding chloride complexes by the utilization of $MCl_4{\cdot}2THF$. In case of Titanium, mono nuclear complexes were achieved. Interestingly, zirconium- and hafnium-based organometallics form chloride bridged binuclear complexes. The functionalization with the silyl reagents proofed to be challenging for zirconium and hafnium congeners.

In contrast, the obtained amido complexes, achieved by conversion of the ligand with $M(NR_2)_4$, showed a broader functionalization spectrum with silyl reagents. Among these transformations, it was possible to isolate rare examples of anionic zirconium and hafnium bromide complexes. In general, the heavier group IV metals proofed to be more suitable in functionalization with silyl reagents.

Unfortunately, N_2 activation mediated by the newly synthesized complexes could not be achieved by the utilization of different strong reducing agents (KC_8, Na, NaHg). The rigidity of the utilized PNP ligand was signed to be the limiting factor for this transformation. Within this context, a novel PNP-based ligand was designed and potential synthetic routes towards the desired compound were investigated.

Kurzfassung

Ein integraler Teilbereich der metallorganischen Chemie ist die Aktivierung von kleinen Molekülen wie etwa N_2, CO, H_2 oder CO_2. Im Falle der N_2-Aktivierung nehmen die frühen Übergangsmetalle, wie die Gruppe IV, aufgrund ihrer einzigartigen Koordinationseigenschaften eine spezielle Rolle ein. Einer der wichtigsten Aspekte ist die Wahl des Liganden, da sterische und elektronische Parameter des Komplexes modifiziert werden können um N_2 binden zu können. Hierbei hat sich in den letzten Jahrzenten die Verwendung von Amidophosphinen als Liganden etabliert. Grund dafür ist die Kombination des harten, anionischen Stickstoff- und des weichen Phosphordonors.

Diese Arbeit konzentriert sich sowohl auf die Entwicklung, Synthese und Charakterisierung von Gruppe IV Metallkomplexen als auch weitere Funktionalisierungen dieser für eine mögliche N_2-Aktivierung. Als Ligand hierfür wurde ein PNP Pincer Ligand mit einem Pyrrol Grundgerüst gewählt. Für die Komplexbildung wurde sowohl $MCl_4 \cdot 2THF$ (M = Ti, Zr, Hf) als auch die weniger üblichen $M(NR_2)_4$ (R = Me, Et) verwendet. Durch den Einsatz von Silylreagenzien TMS-X (X = Cl, Br, I, N_3) waren nachfolgende Funktionalisierungen möglich.

So konnten mit $MCl_4 \cdot 2THF$ die entsprechenden Chloridkomplexe isoliert werden. Interessanter Weise kam es im Falle von Zirkonium und Hafnium zur Bildung von binuklearen Komplexen, welche über zwei Chloridliganden überbrückt sind. Die Umsetzung mit Silylreagenzien erwies sich bei den Chloridkomplexen als problematisch, da lediglich eine Umsetzung der schwereren Gruppe IV Metalle mit TMS-I möglich war.

Die durch die Umsetzung mit $M(NR_2)_4$ erhaltenen Amido-Komplexe zeigten generell ein höheres Ausmaß an Funktionalisierungsmöglichkeiten mit Silylreagenzien. So konnte unter anderem seltene Beispiele für anionische Zirkonium- sowie Hafniumbromid Komplexe erhalten werden.

Die Aktivierung von N_2 mit den hergestellten Komplexen mittels starker Reduktionsmittel (KC_8, Na, NaHg) führte lediglich zur Zersetzung der Komplexe. Es erwies sich, dass das gewählte Ligandensystem zu starr für die Aktivierung von elementarem Stickstoff ist. In weiterer Folge wurde ein neuer PNP-Ligand entworfen und diverse Syntheserouten zu diesem untersucht.

Aim of the Thesis

The activation of N_2 using transition metals is still an emerging field in the organometallic chemistry. Within this field group IV metals display unique coordination modes of the N_2 unit. Whether a coordination of N_2 occurs is strongly dependent on the selected ligand. Consequently, the investigation of new ligands suited for group IV metals is desirable.

Figure 1. Schematic amidophosphine ligand and utilized precursor.

In this respect, the aim of this thesis was the investigation of the synthesis and characterization of novel group IV metals complex bearing amidophosphine ligands, which are suitable for N_2 activation. This shall be achieved by the examination of an monoanionic PNP pincer type ligand with the typical precursors MCl_4·2THF (M = Ti, Zr, Hf) and the less common $M(NR_2)_4$ (R = Me, Et) (Figure 1). Upon further functionalization, potential candidates for N_2 activation shall be introduced.

1 Introduction

Transition metal complexes are indispensable in many fields of chemistry, e.g., organic chemistry, polymer chemistry or biochemistry. Besides the utilization in unique reactions (e.g., coupling reactions, hydrogenations), organometallic complexes can provide fundamental understanding to a manifold of processes in industry as well as in nature.

In the last 70 years the development of group IV metals complexes has become very prominent and manifold. In this context, the highly efficient Ziegler-Natta catalyst for the synthesis of High-Density Polyethylene (HDPE) was discovered in 1953. Since then, the system was continuously optimized and allows polymerization reactions with merely 1 ppm of catalyst.[1–4] Furthermore, in 1976 the first catalyst based on a metallocene was described by Kaminsky for the polymerization of ethylene.[5,6] Nowadays such systems are used for the synthesis of different polymers with a defined tacticity.[7]

In the 1980s the first application for asymmetric epoxidation was developed by Sharpless. Upon utilization of $Ti(OPr)_4$ and optical pure tartrates it was possible to epoxidize allylic alcohols in high yields and excellent enantioselectivity.[8] Based on these results the kinetic resolution was developed, which is important to receive enantiomerically pure products from a racemic mixture.[9–12] Likewise, group IV metal complexes are known for the activation of small molecules, especially for dinitrogen. Besides the pioneer studies on N_2 fixation,[13–18] the fundamental work of Chirik[19,20] and Fryzuk[21–23] has contributed to the understanding of fixation and coordination of dinitrogen, which is essential for enzymatic nitrogen fixation (nitrogenases).[24]

The following section will give an overview of complexation possibilities as well as functionalization methods of group IV metals and provides a selected overview of group IV N_2-complexes

1.1 Group IV Precursors

For the complexation of group IV metals with an ancillary ligand one shall distinguish between neutral and anionic ligands. Generally, anionic ligands are more used for early transition metals, because of their potential π-donor properties by providing high electron density to the electron-deficient transition metal typically being in high oxidation states.

The most common way to afford group IV complexes with an anionic ligand is deprotonation of the acidic site of the ligand, followed by addition of the corresponding MCl_4 (M = Ti, Zr, Hf) precursor.[25,26] However, this procedure is accompanied by several disadvantages. Due to the high Lewis acidity of the precursor, unexpected side reaction with the ligand backbone may occur. Furthermore, $ZrCl_4$ and $HfCl_4$ are solids and show low solubility in most organic solvents. To overcome this problem it is well established to use $MCl_4 \cdot 2R$ (R = Et_2O, THF) as more soluble precursors.[27,28] In addition to that, coordinated ether lowers the Lewis acidity significantly.

Another way to get access to group IV complexes is the conversion of alkylated $MX_{4-n}R_n$ (R = alkyl, X = NMe_2, Cl) precursors with the ligand, still being protonated.[29,30] These complexes can be easily prepared by treatment of the corresponding MCl_4 with lithium- or Grignard-reagents.[31] In case of neutral ligands, additional ligation occurs.[32] Hydrogenolysis of one or more alkyl groups, depending on the number of potential anionic sites, gives rise to the desired complexes. Noteworthily, most of these precursors are light sensitive and thermally unstable. Thus, they should be converted immediately after preparation.

In the last two decades the use of tetrakis(dialkylamido) group IV precursor $M(NR_2)_4$ (R = Me, Et, *i*Pr) has been established for the synthesis of group IV complexes. These dialkylamido compounds are commercially available or can be obtained by treatment of the corresponding metal chlorides with lithium dialkylamide.[33,34] Furthermore, these precursors are well known for chemical vapor deposition of group IV metal nitrides and nitride carbides, providing robust material layers.[35] Contrary to MCl_4 and $MCl_4 \cdot 2R$, $M(NR_2)_4$ have a substantially lower Lewis acidity. In case of an anionic ligand no deprotonation is necessary, since dialkylamido substituents represent an internal base.[36–40] The obtained group IV amido complexes can be easily transformed to their halogen congeners upon treatment with TMS-X (X = Cl, Br, I) or BX_3.[41,42] Hence, $M(NR_2)_4$ represents a good alternative for the synthesis of group IV metal complexes.

1.2 Group IV Complexes Supported by Polydentate Amidophosphine Ligands

As already mentioned, group IV metal complexes play an important role in the activation of small molecules and catalysis.[19,20,23] The reactivity of these complexes is influenced by the choice of the ancillary ligand. Thus, the design of the ligand plays an important role.

Early studies on group IV metal complexes mainly focused on cyclopentadienyl (Cp) and its derivatives as ligands.[18,43–46] In the last decades different polydentate amidophosphine ligands were reported for the synthesis of group IV metal complexes, to achieve unique reactivity.[47–49] The introduction of the hard amido donor enables the use of polydentate ligands which contains softer donors such as phosphines. Besides the higher possible diversity of this ligand type, the introduction of a phosphine moiety introduces the possibility of structural assignment by ^{31}P-NMR spectroscopy.

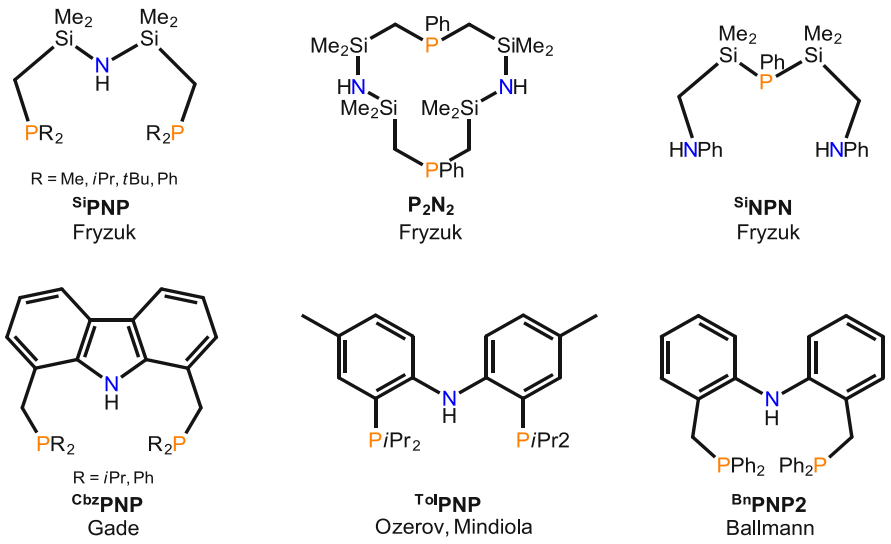
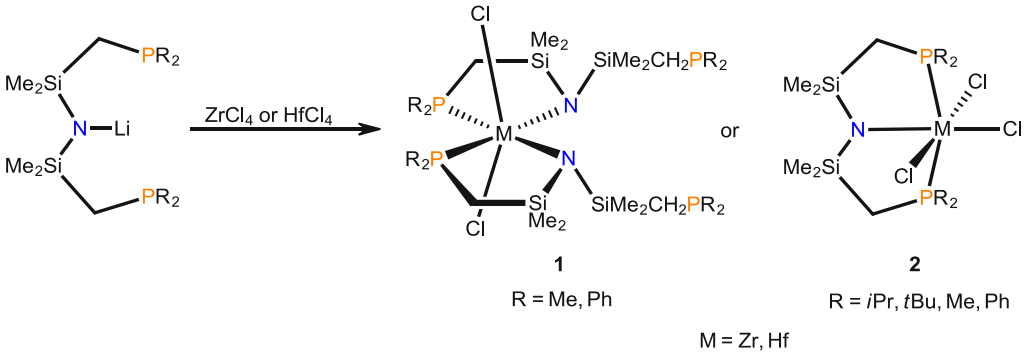


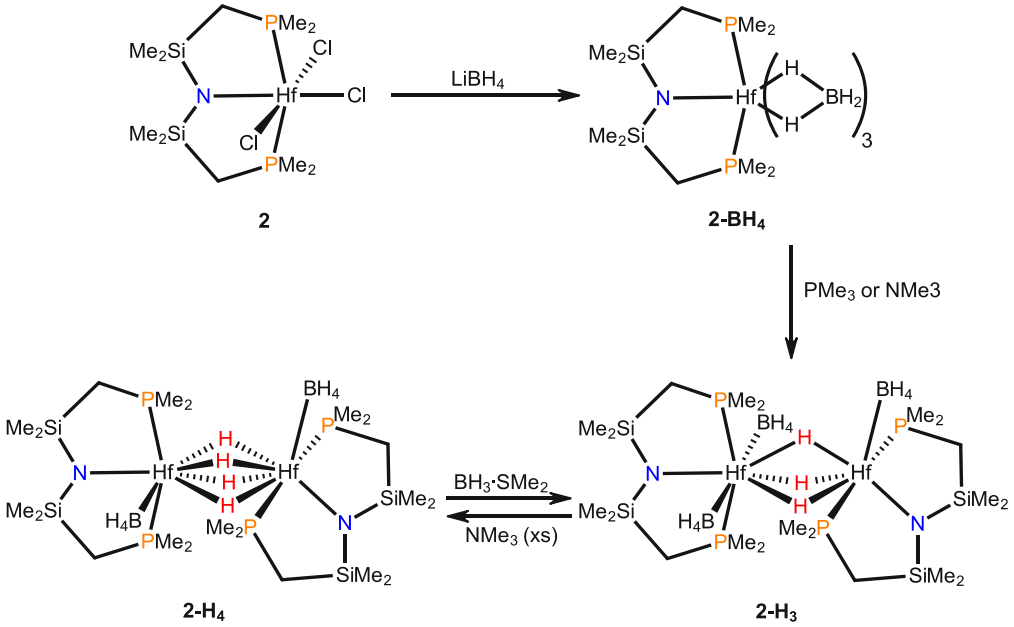
Figure 2. Selected amidophosphine ligands.

The ligands depicted in Figure 2 are selected examples of reported polydentate amidophosphine ligands known for the coordination of group IV metals.[50–53] The vast majority of these ligand types are tridentate ligands, which can coordinate in a meridional or facial fashion. Furthermore, they differ in the ring size of the formed metallacycle as well as in the number of anionic donors. In virtue of the simple modification possibilities these ligands can be easily adapted.



Scheme 1. Synthesis of zirconium and hafnium ^{Si}**PNP** complexes.

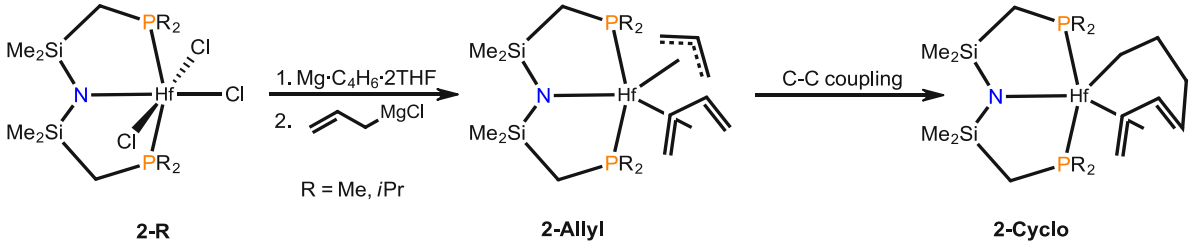
One of the first reported polydentate amidophosphine ligand for group IV metals was $N(SiMe_2CH_2PR)_2$ (R = Me, Ph, *i*Pr, *t*Bu) ^{Si}**PNP** as described by Fryzuk in 1983 as depicted in Scheme 1.[54] Prior to this report, the chemistry of group IV metals was dominated by Cp-based ligands. Due to the limited variation possibilities of Cp ligands, Fryzuk designed ^{Si}**PNP** to extend the potential coordination chemistry of the titanium group. In case of lithiated ^{Si}**PNP-Me** or ^{Si}**PNP-Ph**, MCl_4 (M = Zr, Hf) is converted to the corresponding $[M(^{Si}PNP)_2Cl_2]$ complexes **1**, where only one phosphine donor is coordinated to the metal center. However, when the ligand was added in higher dilution $[M(^{Si}PNP)Cl_3]$ **2** is formed. The use of bulkier substituents on the phosphine donor, such as *i*Pr or *t*Bu, solely $[M(^{Si}PNP)Cl_3]$ **2** was generated.[55]



Scheme 2. Synthesis of hafnium polyhydride complexes.

First investigation of the novel complexes **2** revealed the formation of several hydride species. Treatment of the Hf congener **2-Me** with $LiBH_4$ in toluene results in the formation the ninefold coordinated $[Hf(^{Si}PNP)(\mu^2\text{-}BH_4)_3]$ **2-BH$_4$**, wherein one BH_4 group is *trans* to the amide and two

cis to the amide. Although no crystal structure was obtained, the spectroscopic data confirmed the bidentate coordination mode of the BH_4 group. In order to obtain a classical hydride complex, **2-BH4** was treated with Lewis bases such as PMe_3 or NMe_3. However, treatment of **2-BH4** with PMe_3 or NMe_3 did not afford the expected mononuclear hydride complex (Scheme 2). Instead the binuclear $[Hf(^{Si}PNP)(BH_4)_3]_2(\mu\text{-}H)_3$ **2-H3** is formed, containing three bridging hydrides. Interestingly, treatment with less basic amines such as pyridine did not cleave the BH_4-unit. If an excess of NMe_3 is added to **2-H3** the binuclear complex $[Hf(^{Si}PNP)(BH_4)]_2(\mu\text{-}H)_4$ **2-H4** is obtained. Addition of $BH_3{\cdot}SMe_2$ to **2-H4** resulted in the regeneration of **2-H3**. These results were entirely different to known Cp systems at that time.[55]

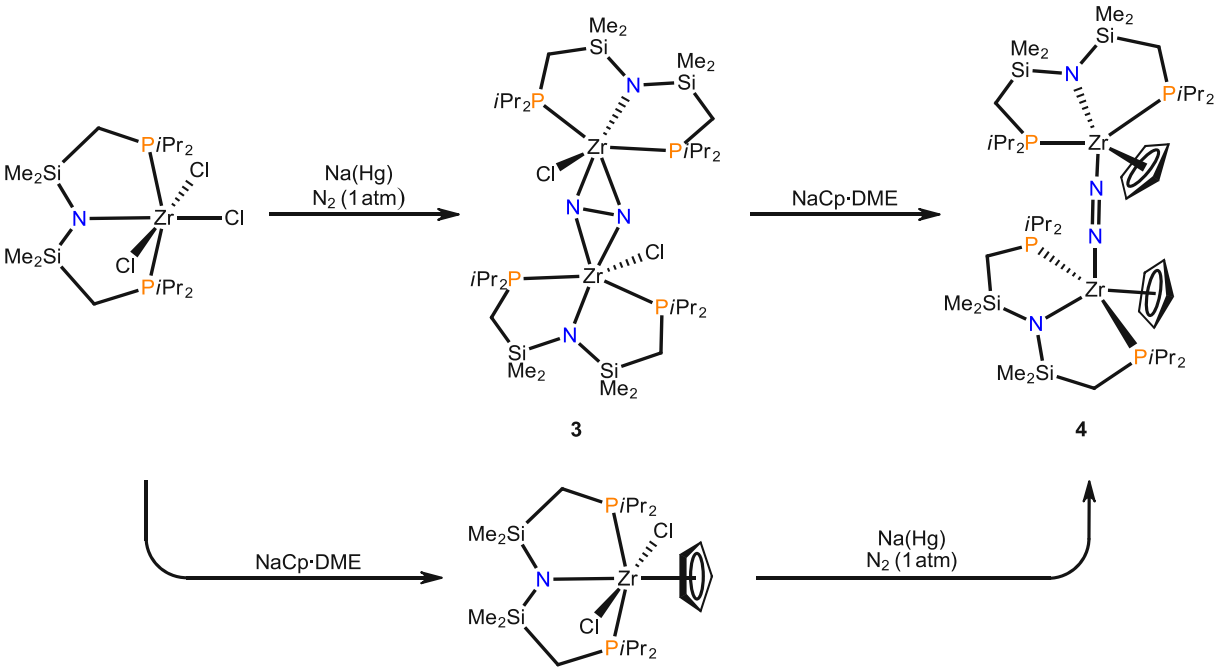


2-R **2-Allyl** **2-Cyclo**

Scheme 3. Synthesis of **2-Cyclo**.

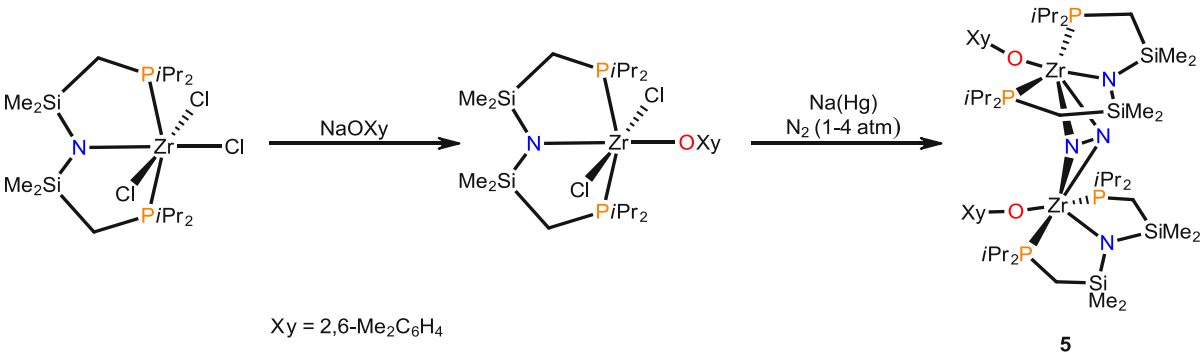
Based on the work of the known complex $[Zr(C_5H_5)(allyl)(\eta^4\text{-butadien})]$, the alkylated $[Hf(^{Si}PNP)(\mu^4\text{-}C_4H_4)(\mu^3\text{-}C_3H_5]$ **2-Allyl** was isolated upon treatment of the Hf congener **2-Me** and **2-*i*Pr** with Mg-butadiene, followed by addition of allylmagnesium chloride (Scheme 3). Interestingly, **2-Allyl** undergoes a C-C coupling to the cyclometaled $[Hf(^{Si}PNP)(\mu^5\text{-}C_7H_{11}]$ **2-Cyclo** after several hours, which was not observed for $[Zr(C_5H_5)(allyl)(\eta^4\text{-butadien})]$.[56] This C-C coupling only occurs, when allyl is used for the alkylation. When **2-Me** and **2-*i*Pr** are treated with Mg-butadiene followed by addition of phenyllithium or neopentyllithium, the corresponding alkylated complexes were obtained.[57] Notably, no C-C coupling was observed in these compounds.

One of the most inspiring results on the influence of the ancillary ligand was reported by Fryzuk in 1993. Upon reduction of $[Zr(^{Si}PNP)Cl_3]$ with sodium amalgam in presence of N_2 $[Zr(^{Si}PNP)Cl]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **3** was isolated, wherein the N_2 is coordinated in a side-on fashion. The N-N unit with a bond length of 1.548(7) Å was the longest reported at that time, and can be considered as a N_2^{4-} unit. Furthermore, **3** was the first well defined d-block metal complex with a side-on coordinated dinitrogen ligand as depicted in Scheme 4.[58]



Scheme 4. Conversion of $[Zr(PNP)Cl]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **3** to $[Zr(PNP)(C_5H_5)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **4**.

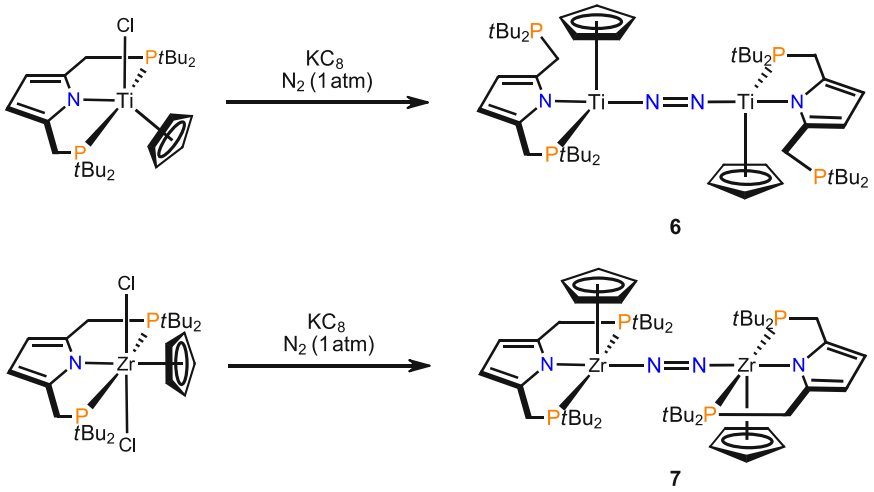
Hydrogenation of **3** resulted in the liberation of hydrazine. Interestingly, exchanging one chloride with a Cp-ligand changed the coordination mode of N_2 to the bridged end-on $[Zr(PNP)(C_5H_5)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **4**, which could also be obtained by treatment of **3** with NaCp·DME followed by reduction with sodium amalgam in presence of dinitrogen. This transformation showed the possibility to rearrange a side-on N_2 to an end-on unit.[22]



Scheme 5. Synthesis of $[Zr(PNP)(OXy)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **5**.

Computational examinations suggested that the presence of a π-donor ligand promote side-on coordination of N_2. In order to prove this thesis, $[Zr(PNP)Cl_3]$ was treated with different anionic ligands, such as alkoxides or amides. Hence $[Zr(PNP)(OXy)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **5** could be isolated as a mixture of two stereoisomers, from which the major species could be isolated as deep blue solid. The N-N bond length of 1.528 Å does not significantly differ from the N-N bond length of **3**. As can be seen in Scheme 5, the N_2 unit of **5** exhibits a hinged or bent geometry. This

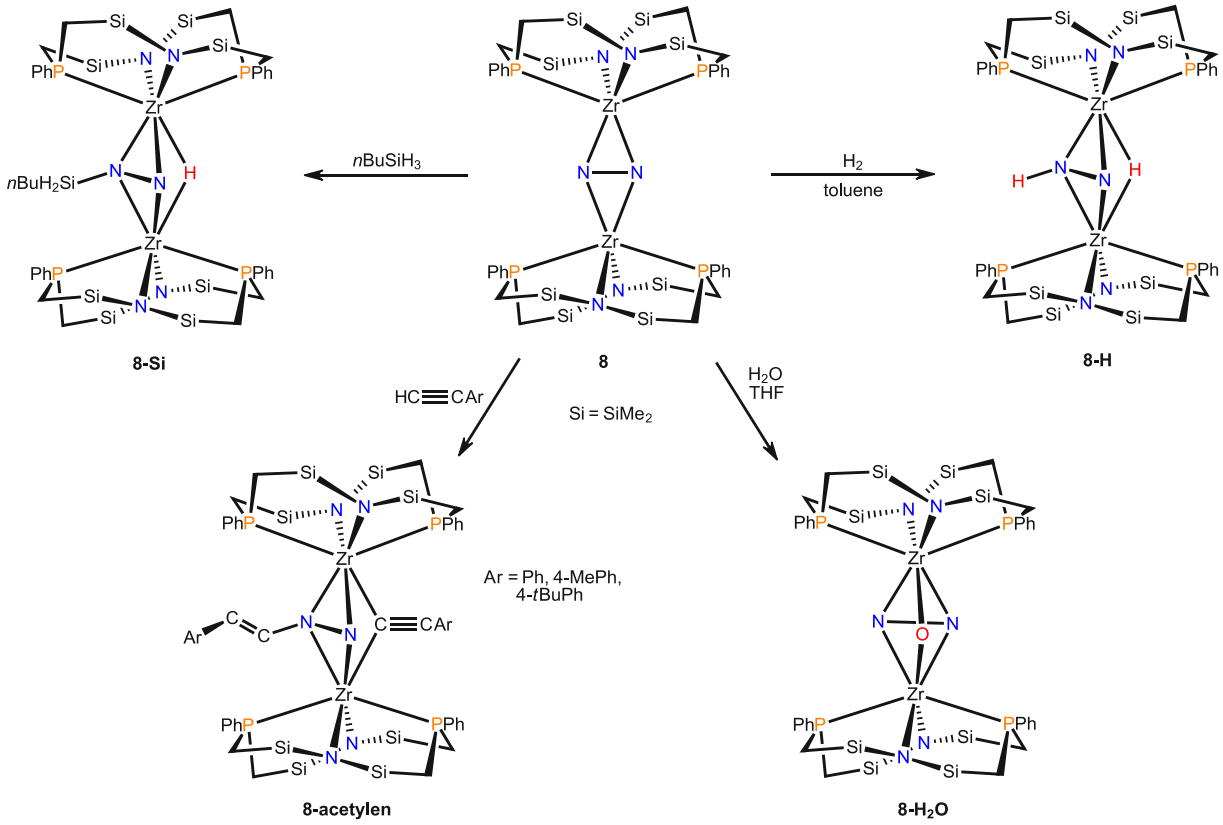
result shows that substitution of one chloride by another hard, anionic ligand, such as alkoxides, does not dramatically change the coordination mode of the N_2 unit in comparison to Cp. Further congeners of $[Zr(PNP)(OXy)Cl_2]$ with $^{-}OtBu$, $^{-}OCHPh$, $^{-}NPh_2$ instead of ^{-}OXy were synthesized. However, reduction under similar conditions failed.[59]



Scheme 6. Synthesis of $[Ti(PNP^{Pyr})(C_5H_5)]_2(\mu\text{-}\eta^1\text{:}\eta^1)\text{-}N_2$ **6** and $[Zr(PNP^{Pyr})(C_5H_5)]_2(\mu\text{-}\eta^1\text{:}\eta^1)\text{-}N_2$ **7**.

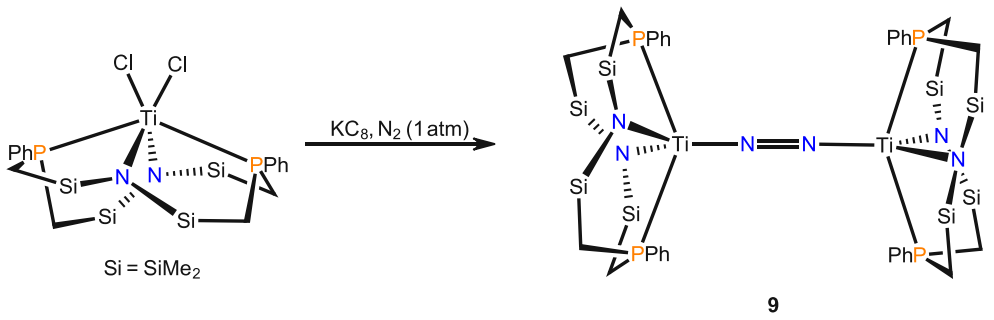
In 2018, Nishibayashi adapted this concept, by employing an anionic PNP pyrrole-based pincer ligand as it can be seen in Scheme 6. Thus, the synthesis of the Ti(III) $[Ti(PNP^{Pyr})Cl_2]$ and dinuclear zirconium $[Zr(PNP^{Pyr})Cl_2](\mu\text{-}Cl)_2$ complexes was reported. Attempts to activate N_2 by direct reduction of $[Zr(PNP^{Pyr})Cl_2](\mu\text{-}Cl)_2$ with KC_8 or NaHg (5%) and $[Ti(PNP^{Pyr})Cl_2]$ resulted in decomposition. However, when one chloride was substituted by Cp, followed by reduction, end-on bridged $[Ti(PNP^{Pyr})(C_5H_5)]_2(\mu\text{-}\eta^1\text{:}\eta^1)\text{-}N_2$ **6** and $[Zr(PNP^{Pyr})(C_5H_5)]_2(\mu\text{-}\eta^1\text{:}\eta^1)\text{-}N_2$ **7** were isolated. The N-N bond length in **6** and **7** are 1.247(3) Å and 1.287(4) Å, respectively. In presence of excess KC_8 and $[H(OEt_2)_2][BarF_4]$ these complexes were shown to catalyze the reduction of N_2 to NH_3.[26]

It should be noted that **3** showed high reactivity towards several reagents such as H_2, silanes and other small molecules. However, no pure material could be isolated in these transformations. It was proposed that the phosphine arms of ^{Si}**PNP** dissociate from Zr(IV), resulting in undesired side reactions. In an effort to suppress phosphine dissociation, the macrocyclic $\mathbf{P_2N_2}$ (P_2N_2 = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$) was synthesized and isolated as lithium salt.[49]



Scheme 7. Transformations of $[Zr(P_2N_2)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **8**.

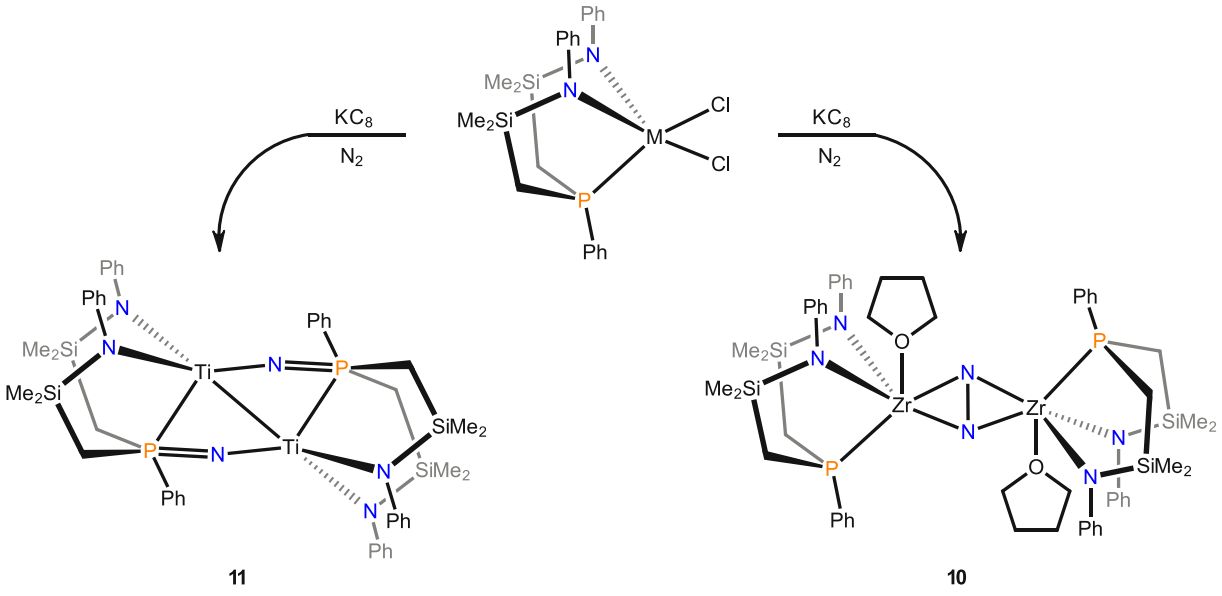
Reaction of the lithiated species with $ZrCl_4{\cdot}2THT$ (THT = tetrahydrothiophene) afforded $[Zr(P_2N_2)Cl_2]$, which could be reduced with KC_8 in presence of N_2 to obtain bridged side-on $[Zr(P_2N_2)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **8** (Scheme 7). The N_2 unit has a bond length of 1.465(19) Å and can be considered as N_2^{4-}. The higher stability of the macrocycle facilitated further reactions. Exposure to H_2 did not result in the formation of hydrazine, however $[Zr(P_2N_2)]_2(\mu\text{-H})](\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2H$ **8-H** was received upon addition of dihydrogen on the ligated N_2-unit and the metal centers. This N-H functionalization was the first report of such a transformation by addition of H_2 to a N_2 complex. Further stoichiometric functionalization of the N_2 unit revealed some interesting aspects. Treatment with *n*$BuSiH_3$ afforded $[Zr(P_2N_2)]_2(\mu\text{-H})](\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **8-Si**, upon formation of a N-Si bond.[21] Conversion with terminal aryl acetylenes resulted in the formation of $[Zr(P_2N_2)]_2(\mu\text{-C}{\equiv}\text{CAr})](\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2C{=}CAr$ **8-acetylene** (Ar = Ph, 4-MePh, 4-*t*BuPh).[60] When **8** was treated with H_2O, deprotonation occurred and the oxo bridged derivate $[Zr(P_2N_2)(O)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2H_2$ **8-H$_2$O** was afforded.[52]



Scheme 8. Synthesis of $[Ti(P_2N_2)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **9**.

The titanium congener showed an entirely, different reactivity (Scheme 8). Complex $[Ti(P_2N_2)Cl_2]$was received by reaction with $TiCl_4$ with the macrocyclic ligand. Upon reduction with KC_8 the bridged end-on $[Ti(P_2N_2)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **9** with a N-N bond length of 1.255(7) Å was afforded. However **9** showed a lack of reactivity towards H_2, silanes and alkynes.[61]

Besides the macrocyclic **P_2N_2** ligand different acyclic dianionic NPN ligands were synthesized by Fryzuk. It was expected that a phosphine donor between two anionic amido donors should reduce the tendency of phosphine dissociation as it was shown for the macrocyclic **P_2N_2** ligand.

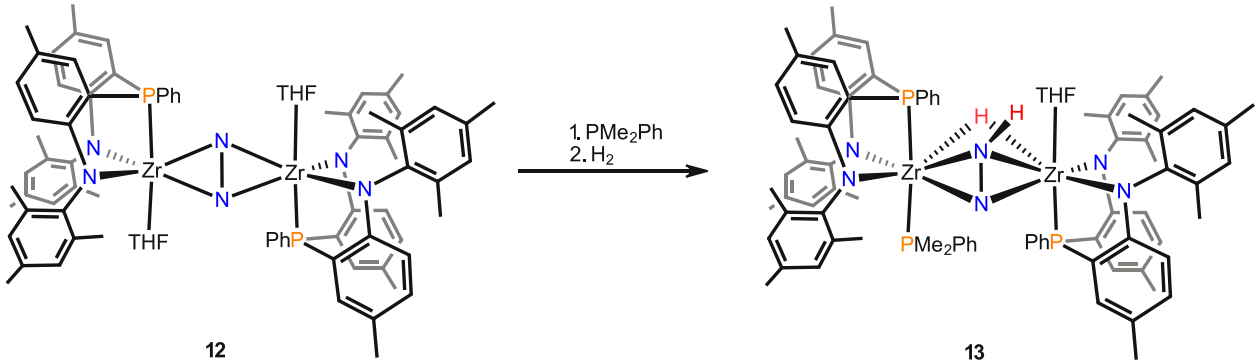


Scheme 9. Reduction of $[M(^{Si}PNP)MCl_2]$ (M = Zr, Hf) with KC_8.

The first reported NPN ligand was **^{Si}NPN** as shown in Scheme 9. The zirconium and titanium complexes $[M(^{Si}NPN)Cl_2]$ were prepared by reaction of **^{Si}NPN-Li** with the corresponding $MCl_4{\cdot}2THF$ (M = Ti, Zr) precursor. It was possible to isolate the bridged side-on $[Zr(^{Si}NPN)]_2(\mu\text{-}\eta^2\text{:}\eta^2)\text{-}N_2$ **10** by reduction of $[Zr(^{Si}NPN)Cl_2]$ with KC_8 in presence of N_2. With a N-N bond distance of 1.503(3) Å, the N_2 is highly activated and can be described as a N_2^{4-} unit. However, attempts to functionalize the N_2-moiety in **10** by addition of H_2, silanes or

alkynes were not successful. Reduction of [Ti(^{Si}NPN)Cl$_2$] with KC$_8$ in presence of N$_2$ did not result in the formation of a dinitrogen complex. Interestingly, the diphosphinimido complex [Ti(^{Si}NP(N)N)] **11** was isolated.[61]

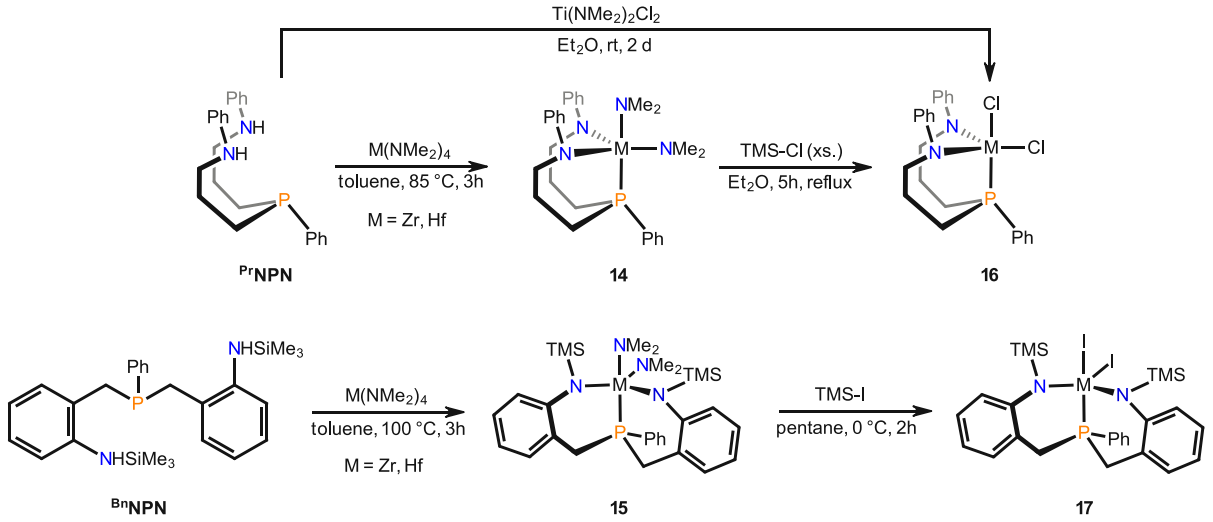
Further modifications of **^{Si}NPN** were done based on results of the investigation of this ligand with tantalum. Reaction of the side-on, end-on bridged [Ta(^{Si}NPN)]$_2$(μ- η^1:η^2)(μ-H)$_2$-N$_2$ with HBCy$_2$[62,63] and HAl*i*Bu$_2$[64] resulted in ligand rearrangements involving N-Si bond cleavage and phosphine oxidation. Hence different **NPN'** were synthesized in which the CH$_2$SiMe$_2$ linker were replaced by *ortho*-phenylene units. These linkers were chosen due to similar pK$_a$ values of aryl amines and silyl amines.



Scheme 10. Hydrogenation of complex [Zr(^{Mes}NPN')(THF)$_2$]$_2$(μ-η^2:η^2)-N$_2$ **12** in presence of PMe$_2$Ph.

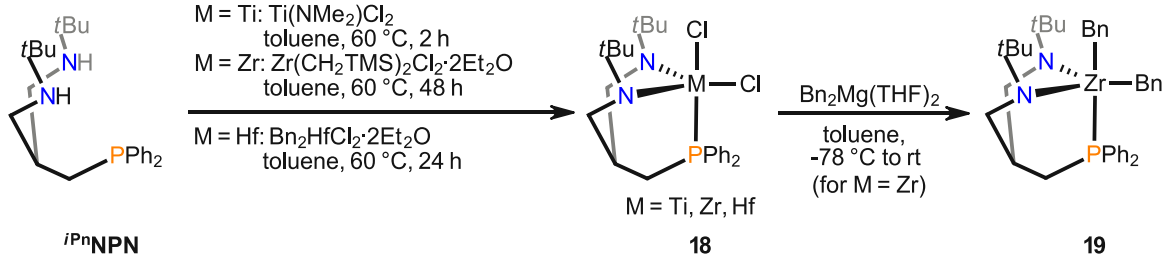
Reaction of **^{Mes}NPN'** with Zr(NMe$_2$)$_4$ followed by addition of TMS-Cl resulted in the formation of [Zr(^{Mes}NPN')Cl$_2$] (Scheme 10). Reduction with KC$_8$ in N$_2$ led to the formation of the expected bridged side-on [Zr(^{Mes}NPN')(THF)$_2$]$_2$(μ-η^2:η^2)-N$_2$ **12**, with a N-N bond length of 1.503(6) Å. In presence of H$_2$ **10** showed no reactivity. However, when THF is exchanged by PMe$_2$Ph addition of H$_2$ occurs to form [Zr(^{Mes}NPN')(PMe$_2$Ph)]$_2$(μ-η^2:η^2)-N$_2$H **13**.[65] Further modifications were done by substitution of the mesityl group with the less sterically demanding aryl groups 4-isopropylphenyl ^{iPr}NPN' and 4-methylphenyl ^{tol}NPN'. Both ligands showed a similar reaction pattern.[66]

Although the aforementioned dianionic NPN amidophosphine proved to be a suitable scaffold for group IV metals, only few works were accomplished on such systems. Ballmann reported the synthesis of three novel dianionic NPN ligands in 2016. Based on the studies of Fryzuk, and his own research on tripodal ligands, **^{Pr}NPN**, **^{Bn}NPN** and **^{iPn}NPN**, were employed for group IV metals, forming six-membered metallacyles.[67–69]



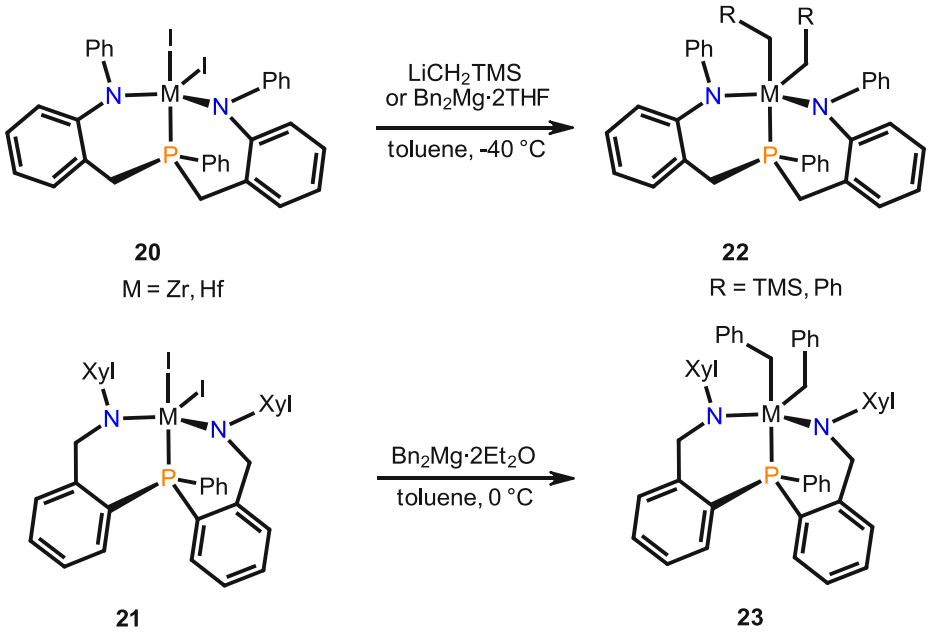
Scheme 11. Synthesis of [M(^{Pr}NPN)(NMe$_2$)$_2$] **14** and [M(^{Bn}NPN)(NMe$_2$)$_2$] **15** and further transformations.

In these studies different complexation methods were described. Therefore, **^{Pr}NPN** and **^{Bn}NPN** were converted to amido complexes [M(^{Pr}NPN)(NMe$_2$)$_2$] **14** and [M(^{Bn}NPN)(NMe$_2$)$_2$] **15** upon reaction with the corresponding M(NMe$_2$)$_4$ (M = Zr, Hf) (Scheme 11). The chloride species of **14** was obtained by treatment with an excess of TMS-Cl. Thus, complex [M(^{Pr}NPN)Cl$_2$] **16** could be isolated. In case of **15** this transformation was unsuccessful, however, the iodide species [M(^{Bn}NPN)I$_2$] **17** could be isolated upon addition of TMS-I. The titanium congener was only obtained for **^{Pr}NPN** by conversion with Ti(NMe$_2$)$_2$Cl$_2$ to [Ti^{Pr}NPN(NMe$_2$)$_2$].[70]



Scheme 12. Synthesis of [M(^{iPn}NPN)Cl$_2$] **18** and further alkylation.

Due to low solubility in most organic solvents, as well as little transformation possibilities, **^{iPn}NPN** was designed to circumvent these problems (Scheme 12). The corresponding halide complexes [M(^{iPn}NPN)Cl$_2$] **18** were isolated by protonolysis of Ti(NMe$_2$)$_2$Cl$_2$, Zr(CH$_2$TMS)$_2$Cl$_2$·2Et$_2$O and Bn$_2$HfCl$_2$·2Et$_2$O. Treatment with Bn$_2$Mg·2THF resulted in formation of [Zr(^{iPn}NPN)Bn$_2$] **19**, however, only in case of zirconium.[70]



20 M = Zr, Hf

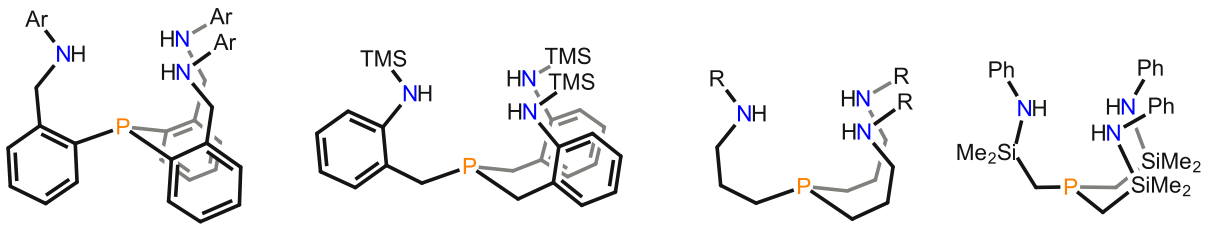
22 R = TMS, Ph

21

23

Scheme 13. Alkylation of [M(^{Ph}NPN)I$_2$] **20** and [M(^{Xyl}NPN)I$_2$] **21**.

Shortly after that, Ballmann reported on the syntheses of two dianionic NPN ligands ^{Ph}**NPN** and ^{Xyl}**NPN**, in order to increase thermal stability. Both ligands exhibit an alkyl group on the N-donor to avoid a N-Si bond cleavage (Scheme 13). The iodide complexes [M(^{Ph}NPN)I$_2$] **20** and [M(^{Xyl}NPN)I$_2$] **21** were afforded upon treatment with M(NMe$_2$)$_4$ (M = Zr, Hf) followed by reaction with TMS-I. The complexes **20** could be smoothly alkylated with LiCH$_2$TMS and Bn$_2$Mg·2THF to compounds [M(^{Ph}NPN)R$_2$] **22** (R = TMS, Ph). In case of **21** only the benzyl group could be introduced by reaction with Bn$_2$Mg·2Et$_2$O to form [M(^{Xyl}NPN)Bn$_2$] **23**.[71]



Ar = 3,5-Xylyl

^{Ph}**N$_3$P**

^{Bn}**N$_3$P**

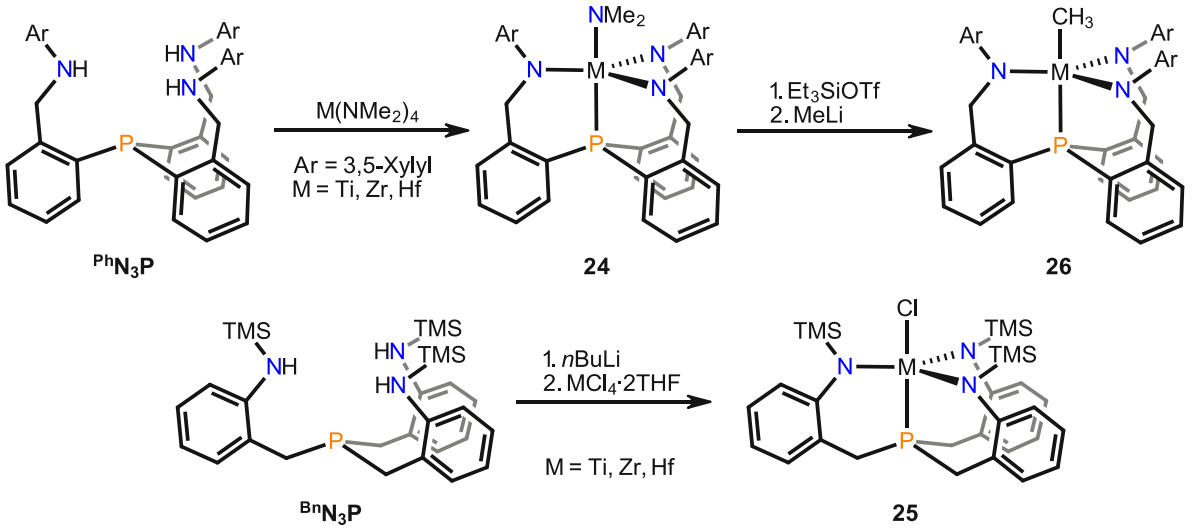
R = *i*Pr, *t*Bu, Ph

^{Pr}**N$_3$P**

^{Si}**N$_3$P**

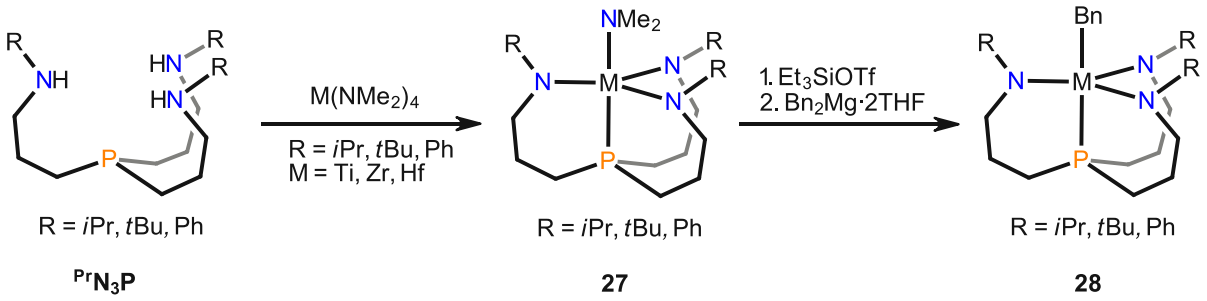
Figure 3. Different trisamidophosphine known for coordination to group IV metals.

In contradiction to dianionic amidophosphine ligands, trisamidophosphine were employed for the ligation of early transition metals within the last decade (Figure 3) In this context, the unique coordination modes can be described as “closed cages” or *endo* conformation. Due to high flexibility the trisamidophosphines can also function as tridentates, whereby one amido or the central phosphine is not coordinated to the metal center. In the latter case, the obtained complex is described as *exo* conformation.[72–75]



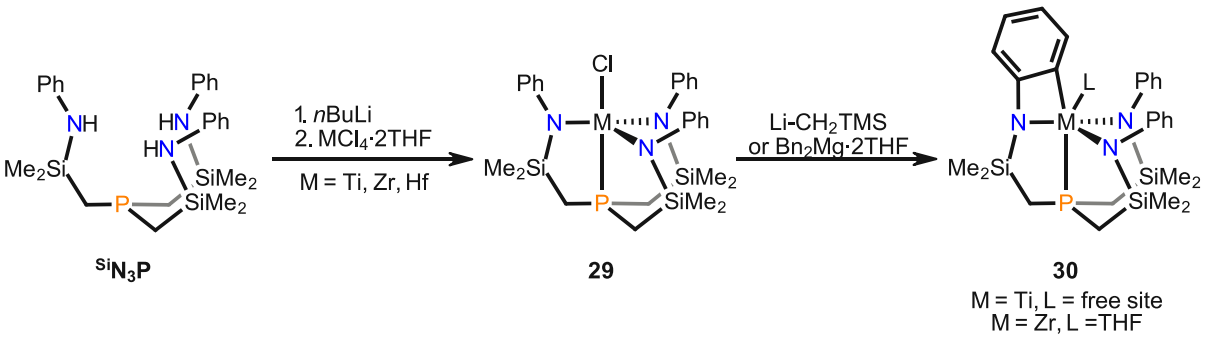
Scheme 14. Synthesis of [M(^{Ph}N$_3$P)(NMe$_2$)] **24**, [M(^{Bn}N$_3$P)Cl] **25** and [M(^{Ph}N$_3$P)Me] **26**.

In case of ^{Ph}**N$_3$P** and ^{Bn}**N$_3$P** complexation with M(NMe$_2$)$_4$ or deprotonation of the ligand followed by addition of MCl$_4$·2THF (M = Ti, Zr, Hf) resulted in the formation of complexes [M(^{Ph}N$_3$P)(NMe$_2$)] **24** and [M(^{Bn}N$_3$P)Cl] **25** in *endo* conformation (Scheme 14). Transformation of **24** to the analogous chloride species *via* addition of TMS-Cl led to decomposition. However, the triflate complex could be isolated upon addition of Et$_3$SiOTf. Consecutive treatment with MeLi allowed the isolation of the methylated complex [M(^{Ph}N$_3$P)Me] **26**.[67,76]



Scheme 15. Synthesis of [M(^{Pr}N$_3$P)(NMe$_2$)] **27** and [M(^{Pr}N$_3$P)Bn] **28**.

In contrast to the aforementioned ligands, ^{Pr}**N$_3$P** has a flexible alkyl linkage, which may lead to *exo*-coordination. However, the flexible linker solely provide a *endo*-coordiantion (Scheme 15). Thus, ^{Pr}**N$_3$P** could be converted to the amido complex [M(^{Pr}N$_3$P)(NMe$_2$)] **27** (M = Ti, Zr, Hf). Similar to **20**, the alkylated compound [M(^{Pr}N$_3$P)Bn] **28** was isolated by treatment with Et$_3$SiOTf, followed by addition of Bn$_2$Mg·2THF.[68]



$^{Si}N_3P$ **29** **30**

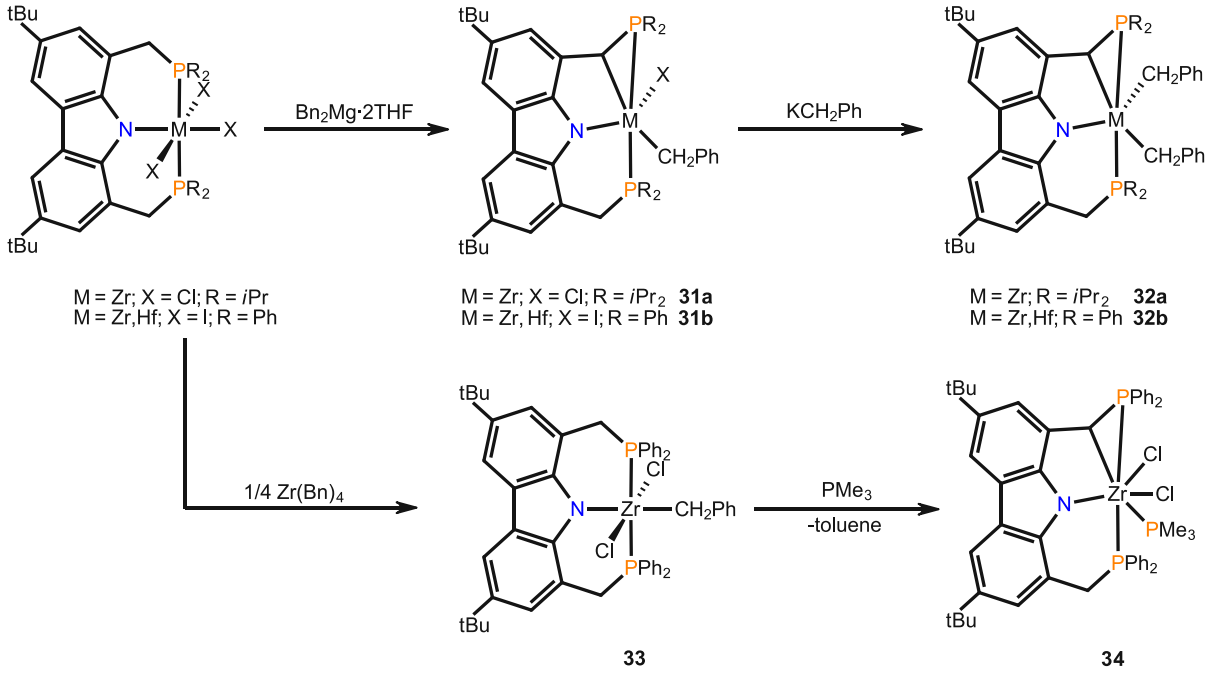
M = Ti, L = free site
M = Zr, L =THF

Scheme 16. Synthesis of [M($^{Si}N_3P$)Cl] **29** and [M($^{Si}N_3P$)(N-Ph)(L)] **30**.

Interestingly **$^{Si}N_3P$**, which would feature three strained five membered metallacycles, showed *endo* configuration upon coordination. The silicon atom on each arm was chosen in respect to an elongated Si-N bond compared to Si-C bond as well as the Thorpe-Ingold effect of the $SiMe_2$ units. Hence the chloride [M($^{Si}N_3P$)Cl] **29** was isolated upon deprotonation of **$^{Si}N_3P$** with *n*BuLi followed by addition of MCl_4·2THF (M = Ti, Zr, Hf). In case of Ti and Zr congeners further transformation were done including treatment with Li-CH_2TMS and Bn_2Mg·2THF, respectively. Interestingly, no alkyl complex was observed (Scheme 16). Surprisingly, C-H activation of the phenyl ring occurred under cyclometallation, yielding [M($^{Si}N_3P$)(N-Ph)(L)] **30** (M = Ti, L =free site; M = Zr, L = THF).[69] In this context, C-H activation by group IV metals is not a unique behavior of complexes bearing the **$^{Si}N_3P$** ligand.

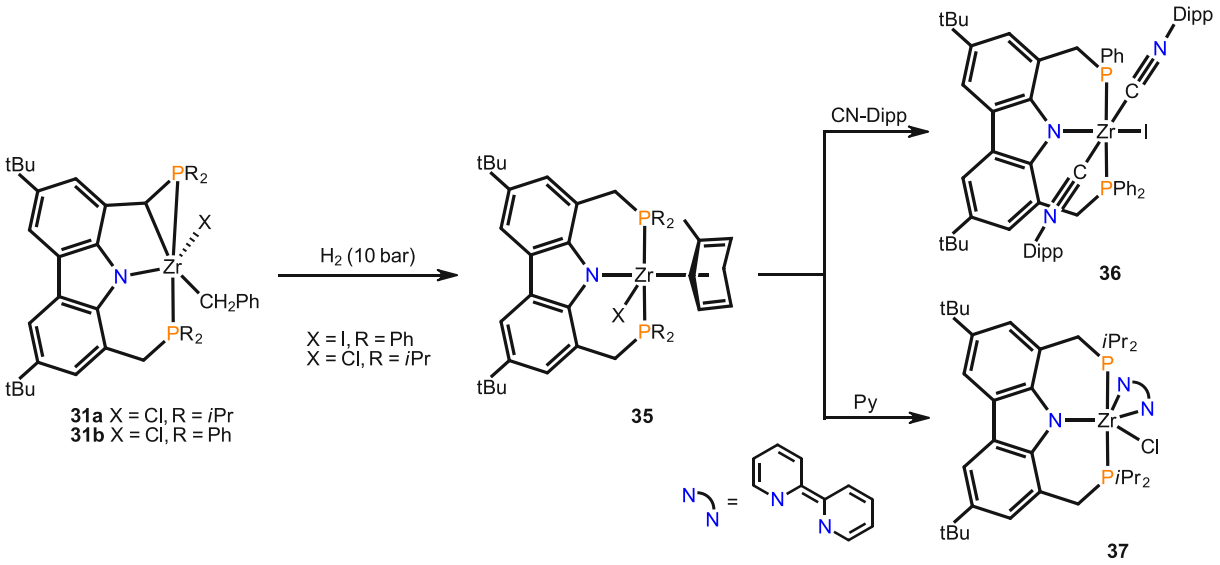
In 2015 Gade and co-workers reported on the syntheses of group IV transition metal complexes supported by the **^{Cbz}PNP** ligand, wherein the CH_2 linker undergoes C-H activation. In this work the chloride species [M($^{Cbz}PNP^{R}$)Cl_3] (M = Ti, Zr, Hf, R = *i*Pr, Ph) were obtained, upon treatment of deprotonated **^{Cbz}PNP** with corresponding precursor $TiCl_4$·2THF and MCl_4 (M = Zr, Hf). Subsequent transformation to the corresponding iodide species was achieved upon treatment with an excess of TMS-I.

Originally inspired by the isolation of group IV alkylidene complexes, different approaches for alkylation were conducted.[77,78] In case of titanium, alkylidene complex [Ti(^{Cbz}PNP)(CHPh)X)] could be observed upon treatment of [Ti(^{Cbz}PNP)X] (X = Cl, I) with Bn_2Mg·2THF. Utilization of Bn_2Mg·2THF for the alkylation of zirconium and hafnium congeners resulted in the formation of the cyclometalated complexes [Zr($^{Cbz}PNP^{iPr}$-CH)(Bn)Cl] **31a** and [M($^{Cbz}PNP^{Ph}$-CH)(Bn)I] **31b** (M = Zr, Hf) (Scheme 17).



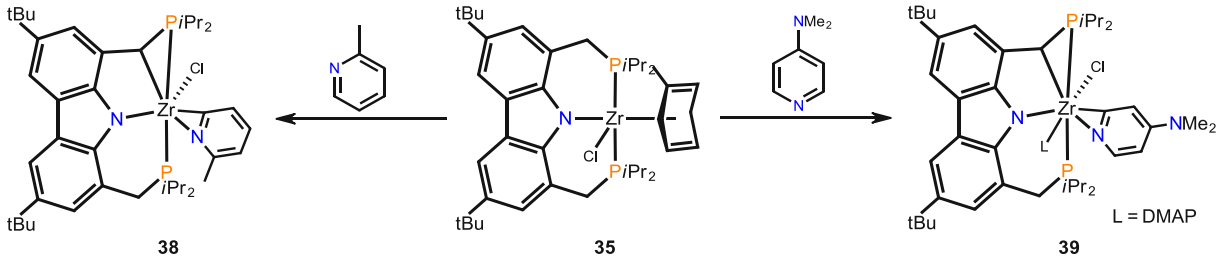
Scheme 17. Alkylation of hafnium and zirconium ^{Cbz}PNP complexes.

Both complexes could be transformed to the dialkylated [Zr(^{Cbz}PNP^{iPr}-CH)Bn$_2$] **32a** and [M(^{Cbz}PNP^{Ph}-CH)Bn$_2$] **32b** upon addition of KCH$_2$Ph. Further investigations on these systems revealed, that cyclometalation could be suppressed by the utilization of Zr(Bn)$_4$. Thus, monoalkylated [Zr(^{Cbz}PNP^{Ph})(Bn)Cl$_2$] **33** was afforded by treatment of complex [Zr(^{Cbz}PNP^{Ph}Cl$_3$] with 0.25 equivalent Zn(Bn)$_4$. Upon heating X with PMe$_3$ one methylene linker is deprotonated and the cyclometalated [Zr(^{Cbz}PNP^{Ph}-CH)(PMe$_3$)Cl$_2$] **34** is formed upon release of toluene.[79]



Scheme 18. Hydrogenolysis of [Zr(^{Cbz}PNP^{iPr}-CH)(Bn)Cl] **31a** and [Zr(^{Cbz}PNP^{Ph}-CH)(Bn)I] **31b**.

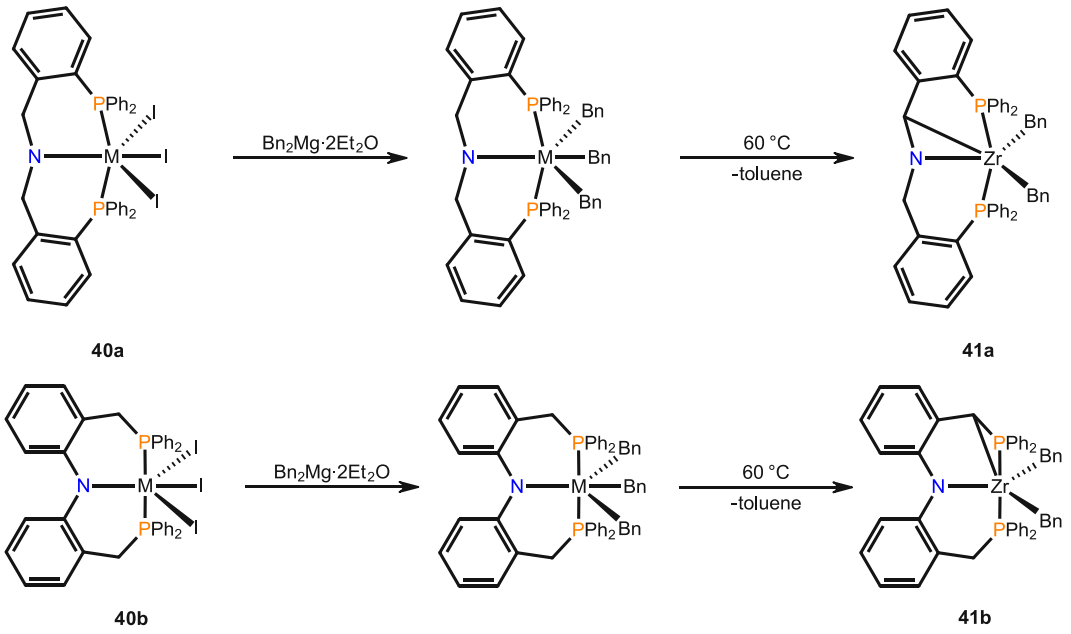
In presence of 10 bar H_2 complexes **31a** and the zirconium congener of **31b** undergo hydrogenolysis under formation of an η^6-arene complex [Zr(^{Cbz}PNP^{R})(η^6-tol)X] **35** (X = I for R = Ph, X = Cl for R = *i*Pr$_2$), whereby the tolyl ring adopts a puckered arrangement (Scheme 18). Although **35** is formally a Zr(IV) species, it can be considered as a Zr(II) synthon, which can be obtained by substitution of the η^6-arene moiety. Thus, the Zr(II) species could be isolated by reaction of **35** (X = I, R = Ph) with 2,6-diisopropylphenyl isocyanide (CNDipp), yielding [Zr(^{Cbz}PNP^{Ph})(CNDipp)$_2$Cl] **36**. Complex **35** (X = Cl, R = *i*Pr) was shown to react cleanly with *para*-substituted pyridines to afford the corresponding species [Zr(^{Cbz}PNP^{iPr})(Bpy)Cl] **37** through reductive coupling.[51]



Scheme 19. Conversion of [Zr(^{Cbz}PNP^{iPr})(η^6-tol)Cl] **35** with different pyridine derivatives.

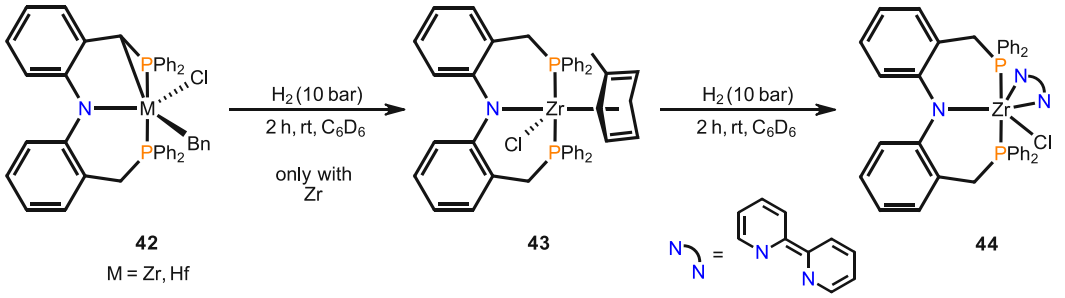
The conversion of **37** (X = I, R = *i*Pr) with 2-, 3- and 4-picoline and different *para*-substituted pyridines (e.g., CF_3, CN, OMe, NMe_2) revealed, that dehydrogenative coupling is favored if the pyridine derivates are electron-rich. Interestingly, 2-picoline and 4-(dimethylamino)pyridine (DMAP) undergo cyclometallation with **35** to give [Zr(^{Cbz}PNP^{iPr})(NC_5H_3R)Cl] **38** (R = CH_3) and **39** (R = NMe_2), which was considered as a possible transition state of the dehydrogenative coupling. Thus, it was suggested that the ligand backbone contributes in dehydrogenative coupling of pyridines by initial C-H activation of one pyridine molecule. However, deuterium labeling experiments excluded such a cyclometallation step involving the PNP ligand backbone. This result was confirmed by reaction of **35** with isoquinoline, which resulted in coupling without loss of H_2. DFT calculation suggested, that the reaction proceeds *via* an initial *syn* C-C coupling step of pyridine.[41]

Furthermore, Ballmann reported on the synthesis of zirconium and hafnium complexes with more flexible ligands such as **^{Bn}PNP1** and **^{Bn}PNP2,** which were considered as possible ancillary ligands for M^{II} (M = Zr, Hf) synthons. The corresponding iodide complexes [M(^{Bn}PNP1)I_3] **40a** and [M(^{Bn}PNP2)I_3] **40b** were obtained by heating the ligand in presence of the amido precursors M(NMe_2)$_4$ (M = Zr, Hf) followed by treatment with TMS-I.



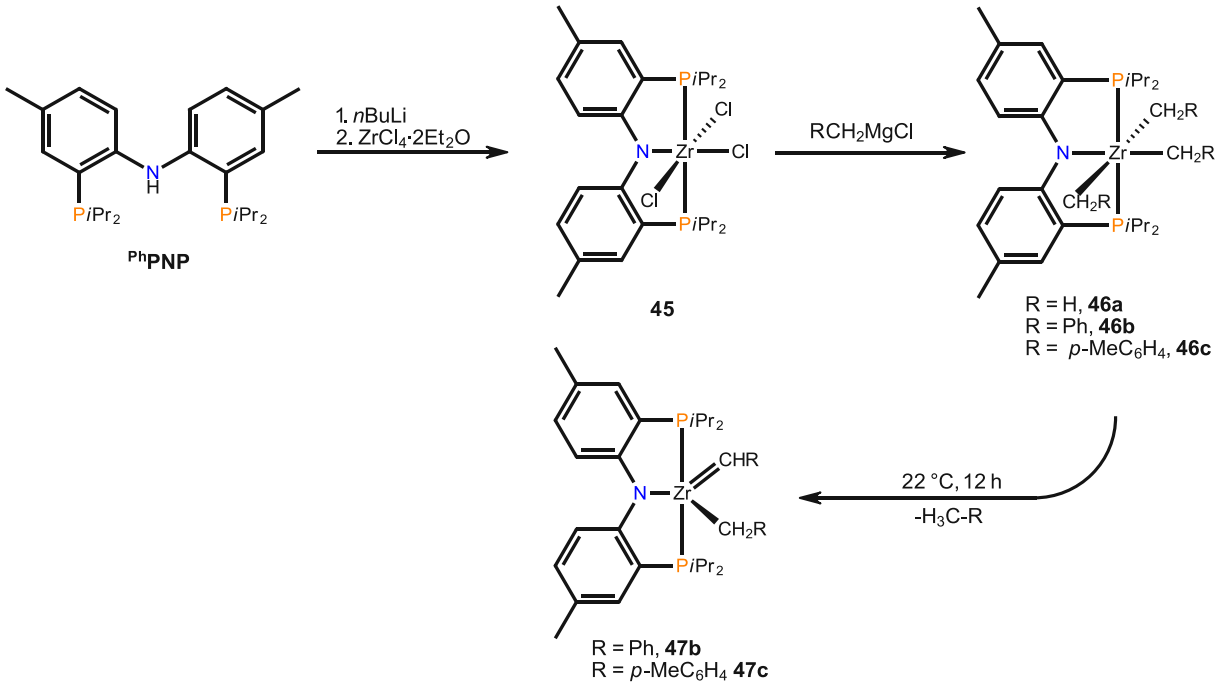
Scheme 20. Synthesis of [Zr(^{Bn}PNP1-CH)Bn$_2$] **41a** and [Zr(^{Bn}PNP2-CH)Bn$_2$] **41b**.

In contrast to [M(^{Cbz}PNP)Cl$_3$] (M = Ti, Zr, Hf), the alkylation of **40a** and **40b** with Bn$_2$Mg·2THF resulted in the formation of the tri-alkylated species [M(^{Bn}PNP1)Bn$_3$] and [M(^{Bn}PNP2)Bn$_3$] (Scheme 20). Thermolysis of zirconium homologues afforded the cyclometalated species [Zr(^{Bn}PNP1-CH)Bn$_2$] **41a** and [Zr(^{Bn}PNP2-CH)Bn$_2$] **41b**. However, hydrogenation of **41a** and **41b** led to formation of undefined mixtures.



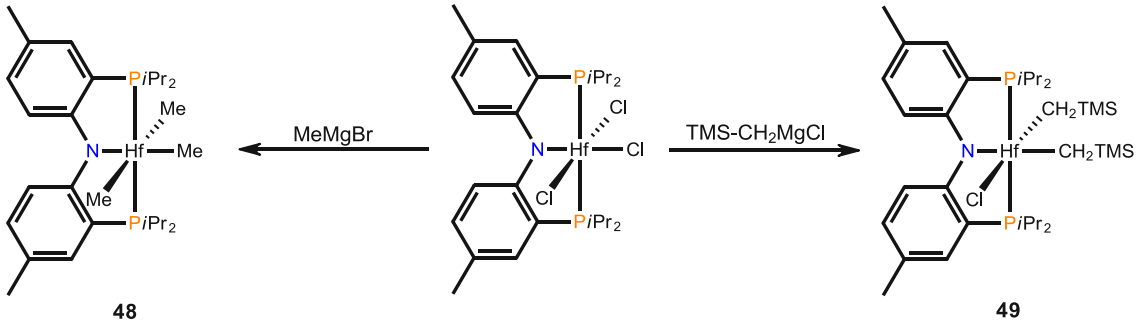
Scheme 21. Synthesis of [Zr(^{Bn}PNP2)(BPy)Cl] **44**.

Since hydrogenolysis was not possible, the monoalkylated complexes [M(^{Bn}PNP2-CH)(Bn)Cl] **42** (M = Zr, Hf) were synthesized, which are similar to **31a** and **31b**. Pressurizing **42** with H$_2$ led to the targeted [Zr(^{Bn}PNP2)(η^6-tol)Cl] **43**, however, only with the zirconium congener (Scheme 21). In analogues to **35,** complex **43** undergoes a dehydrogenative C-C coupling in presence of pyridine to form the corresponding bipyridine complex [Zr(^{Bn}PNP2)(BPy)Cl] **44**.[50]



Scheme 22. Synthesis and functionalization of [Zr(^{Tol}PNP)Cl$_3$) **45**.

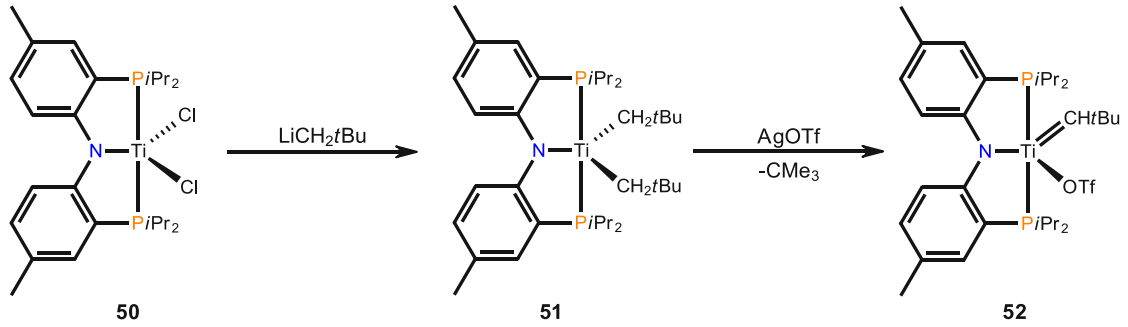
In regard to group IV alkylidene complexes, Ozerov employed ^{Tol}**PNP** in 2004. Complex [Zr(^{Tol}PNP)Cl$_3$) **45** was received by conversion of the lithiated ^{Tol}**PNP** with ZrCl4·2Et$_2$O (Scheme 22). Treatment of **45** with RCH$_2$MgCl (R = H, Ph, *p*-MeC$_6$H$_4$) led to the formation of the corresponding alkyl complexes [Zr(^{Tol}PNP)(CHR)] **46a-c**. While **46a** was thermally stable, **46b** and **46c** slowly underwent α-H abstraction at room temperature to form the desired alkylidene complexes **47b** and **47c**.[25]



Scheme 23. Alkylation of complex [Hf(^{Tol}PNP)Cl$_3$].

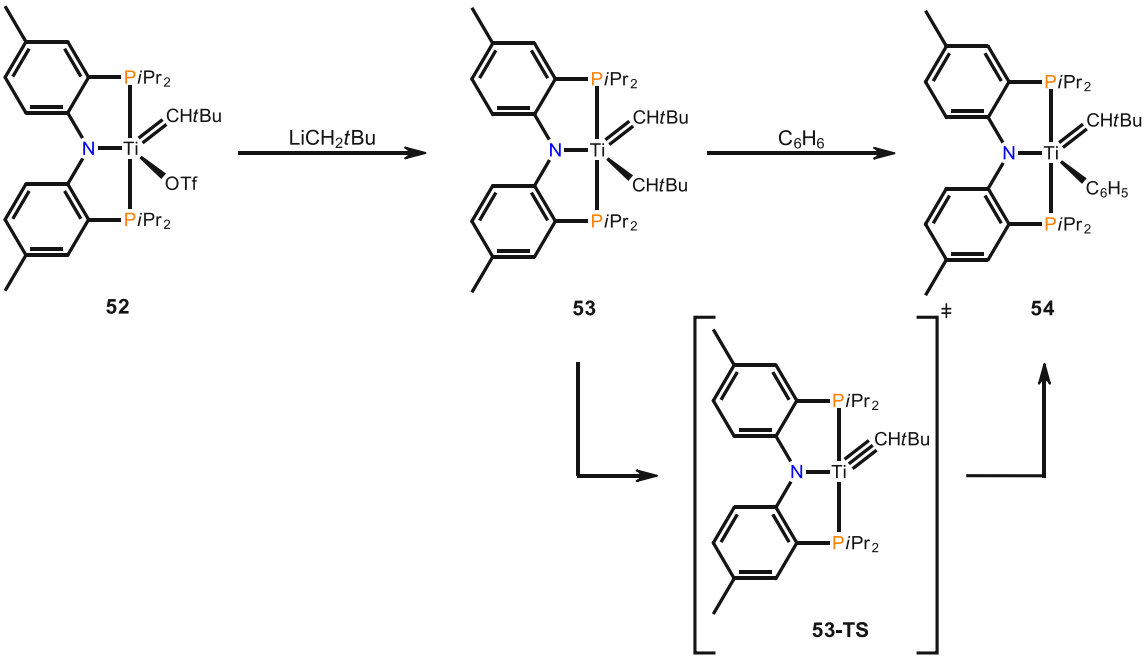
Interestingly, the Hf congener of ^{Ph}**PNP** showed a strikingly different behavior. Conversion of [Hf(^{Tol}PNP)Cl$_3$] with 3 equivalents of MeMgBr resulted in formation of [Hf(^{Tol}PNP)Me$_3$] **48**. However, when 3 equivalents of the bulkier alkylation reagent TMS-CH$_2$MgCl were used decomposition occurred (Scheme 23). If 2.5 equivalents of TMS-CH$_2$MgCl were utilized, the dialkylated [Hf(^{Tol}PNP)(CH2-TMS)$_2$Cl] **49** was obtained. Attempts to promote α-H abstraction

thermally, photolytically or chemically by using Lewis acids or bases resulted in formation of multiple products.[27]



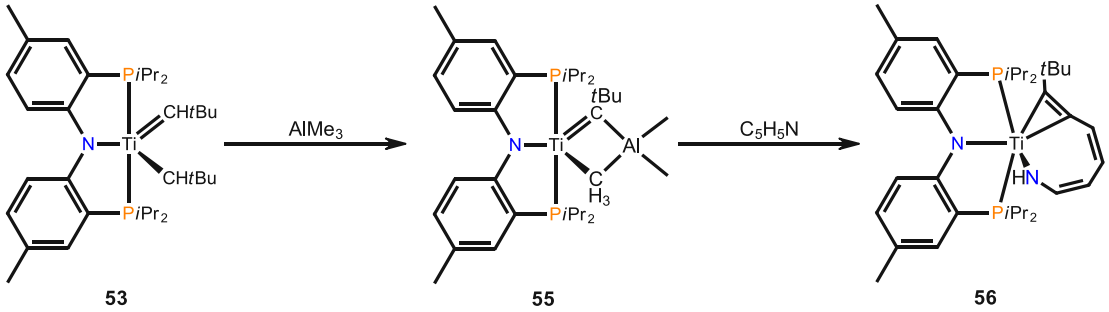
Scheme 24. Synthesis of [Ti(^{Tol}PNP)Cl$_2$] **50** and further alkylation.

In 2005, Mindiola reported on the synthesis of the titanium congener [Ti(^{Tol}PNP)Cl$_3$]. Alkylation proved to be more difficult in comparison to the zirconium and hafnium complexes. Treatment of [Ti(^{Tol}PNP)Cl$_3$] with Grignard reagents led to undesired reactions instead of alkylation (Scheme 24). This difference between the reactivities of **45** and [Ti(^{Tol}PNP)Cl$_3$] was explained by the general higher reduction potential of titanium complexes compared to zirconium and hafnium complexes. In order to avoid the reductive pathway [Ti(^{Tol}PNP)Cl$_2$] **50** was synthesized, by reaction of the lithiated ^{Ph}**PNP** with TiCl$_3$·3THF. Complex **50** could be transformed to [Ti(^{Tol}PNP)(CH$_2$*t*Bu)$_2$] **51** upon treatment with neopentyllithium. Treatment with AgOTf afforded alkylidene complex [Ti(^{Tol}PNP)(CH*t*Bu)OTf] **51** by single electron oxidization.[80]



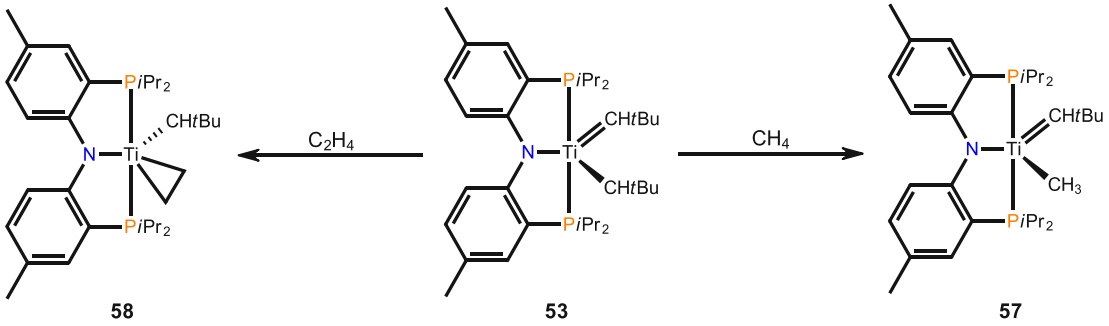
Scheme 25. Synthesis of [Ti(^{Tol}PNP)(CH*t*Bu)(CH$_2$*t*Bu)] **53** and formation of [Ti(^{Tol}PNP)(CH*t*Bu)(C$_6$H$_5$)] **54**.

Later on, Mindiola reported on substitution of the triflate group by -CH_2tBu to afford [Ti(^{Tol}PNP)(CH*t*Bu)(CH_2tBu)] **53** (Scheme 25). It seemed that **53** is the kinetic product, since it reacts with benzene in several hours to give [Ti(^{Tol}PNP)(CH*t*Bu)(C_6H_5)] **54** in quantitative yield. It was proposed that **53** undergoes rapid α-H abstraction under simultaneous elimination of CH_3tBu to form the alkylidene [Ti(^{Tol}PNP)(C*t*Bu)] **53-TS**. Consecutive C-H activation of benzene gave **54**. This conclusion was supported by different labeling and thermolysis experiments as well as computational studies.[81]



Scheme 26. Synthesis of [Ti(^{Tol}PNP)(CH*t*Bu)Al(CH_3)$_3$] **55** and [Ti(^{Tol}PNP)(C*t*Bu)CC_4H_4NH] **56.**

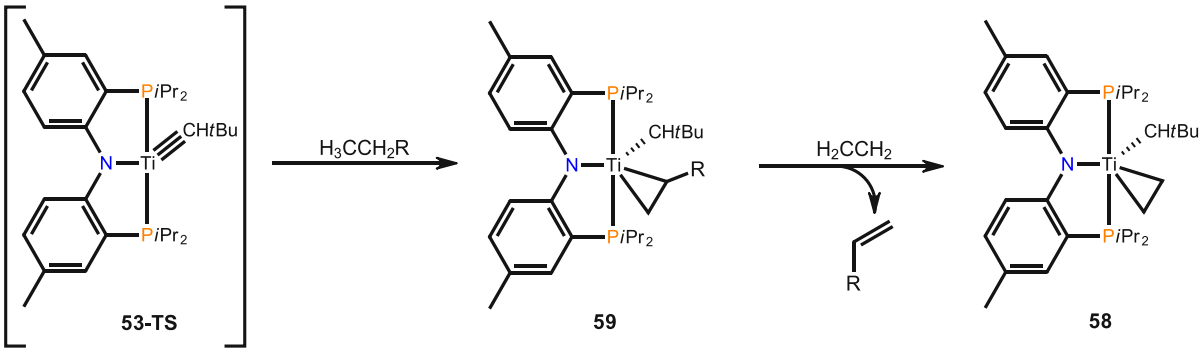
Attempts to stabilize **53-TS** by $AlMe_3$ as Lewis acid led to the isolation of compound [Ti(^{Tol}PNP)(CH*t*Bu)Al(CH_3)$_3$] **55**, which undergoes a ring opening of N-heterocycles such as pyridines or chinolins (Scheme 26). Thus, [Ti(^{Tol}PNP)(C*t*Bu)CC_4H_4NH] **56** was isolated by addition of pyridine.[82,83]



Scheme 27. Treatment [Ti(^{Tol}PNP)(CH*t*Bu)(CH_2tBu)] **53** with methane and ethane.

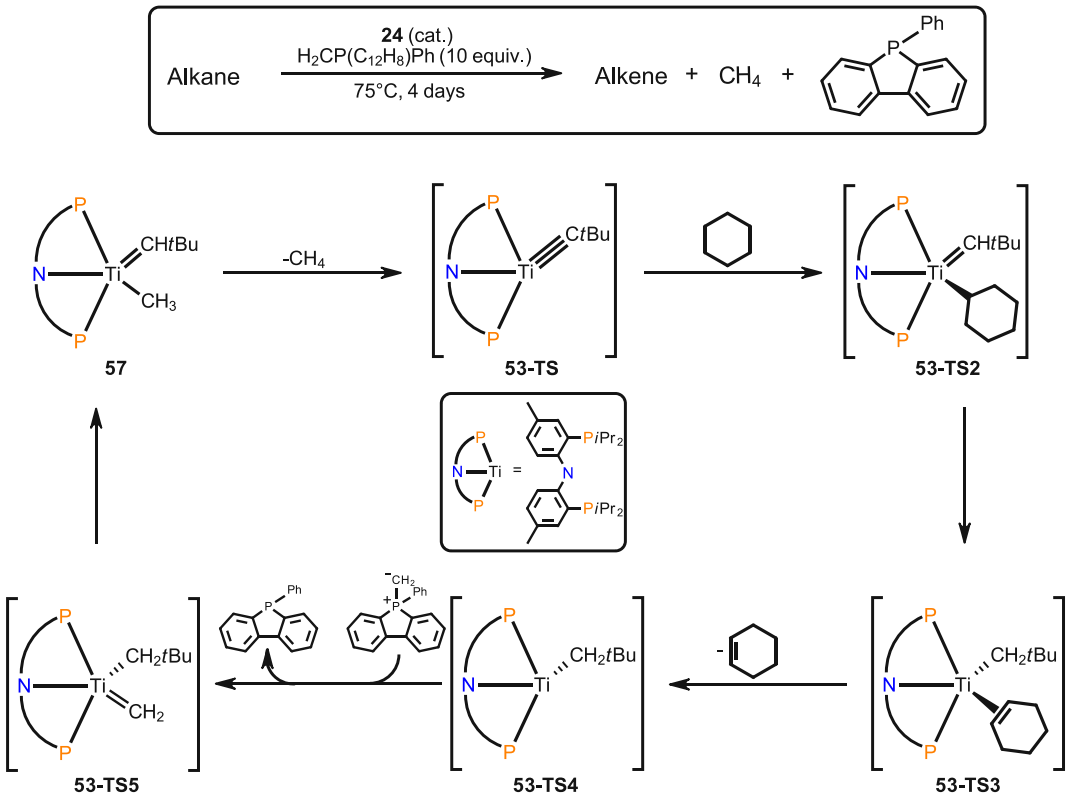
When **53** was treated with cyclohexane the corresponding [Ti(^{Tol}PNP)(CH*t*Bu)(C_6H_{11})] was formed. However, this complex was unstable and decomposed to unidentified products upon release of cyclohexene. Computational studies estimated that methane should be a suitable substrate for **53-TS**. Thus, **53** was exposed to CH_4 under 80 bar to form [Ti(^{Tol}PNP)(CH*t*Bu)(CH_3)] **57** (Scheme 27). Interestingly, the methyl group can undergo slow exchange with the neopentylidene ligand *via* a possible titanium methylidene species.[78] In presence of ethane the η^2-ethylene compound [Ti(^{Tol}PNP)(CH*t*Bu)(H_2CCH_2)] **58** was formed

by a stepwise double α,β C-H activation process. Treatment with an amine led to the release of ethene by dehydrogenation.[84] In conclusion **53** proved to be a potential synthon for C-H activation of alkanes, followed by a dehydrogenation to the corresponding alkenes. By combining of this results Mindiola developed a concept to dehydrogenate alkanes to alkenes for C_4 to C_8 employing **53**.



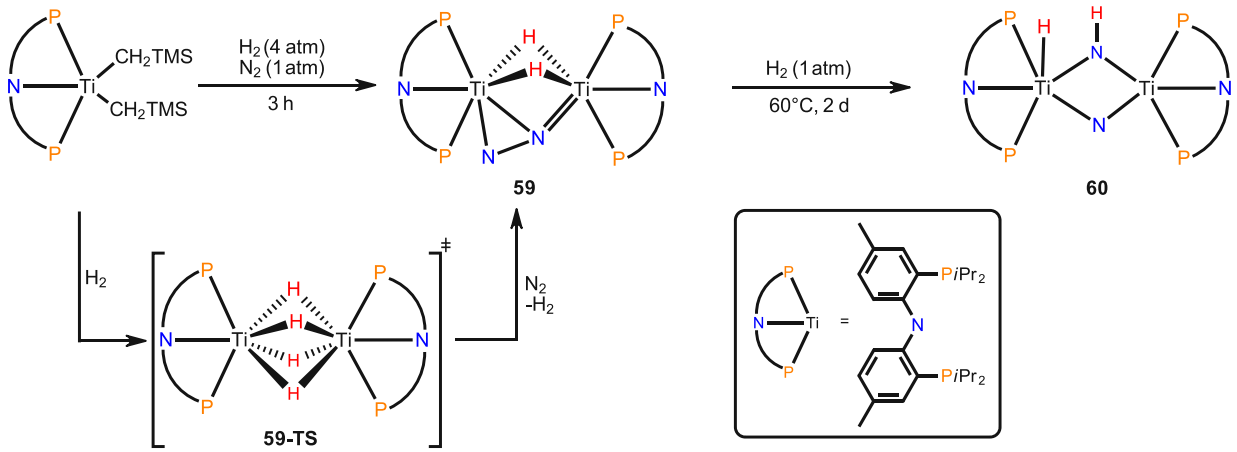
Scheme 28. Conversion of an alkane to alkene by complex **53-TS**.

Treatment of **53-TS** with an alkane H_2CCH_2R (R = CH_3, CH_2CH_3, *n*Pr, *n*Bu, *n*Pentyl, *n*Hexyl) at room temperature led to the formation of the cyclometalated species [Ti(^{Tol}PNP)(CH*t*Bu)(η^2-H_2CCHR)] **59**. Exposure of **59** to ethylene resulted in the release of the corresponding alkene H_2C=CHR. Thereby generating complex **58** (Scheme 28).[85]



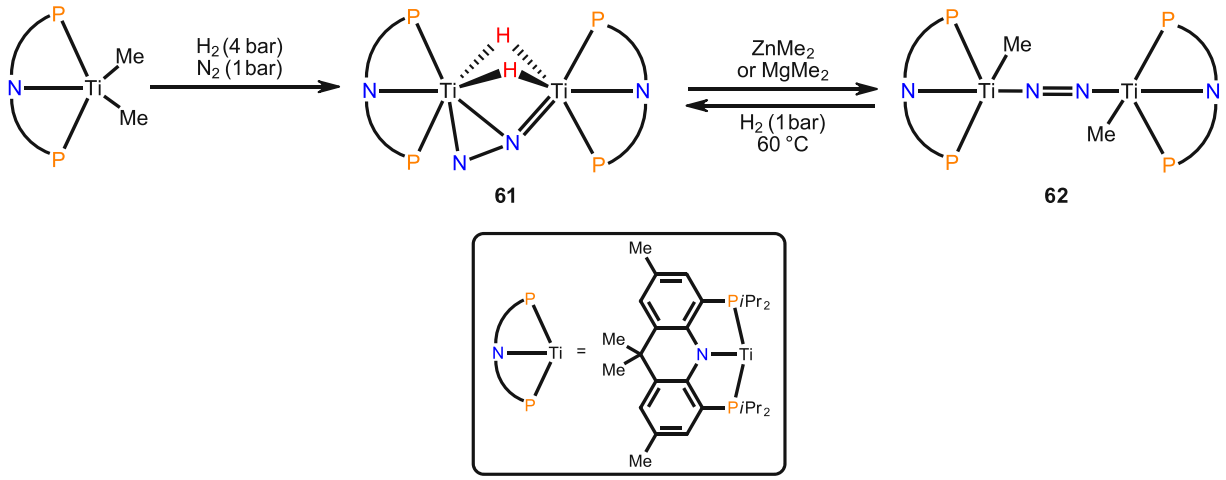
Scheme 29. Catalytic cycle for alkane dehydrogenation by complex **57**.

In 2017, Mindiola improved this concept to establish a catalytic protocol. Based on previous studies about the use of the ylide H_2CPPh_3 in presence of **57**[86], the novel ylide $H_2CP(C_{12}H_8)Ph$, which acts as a methylene transfer agent was used. The proposed catalytic cycle for cyclohexane is depicted in Scheme 29. In the first step CH_4 is eliminated under α-H abstraction to **53-TS**. Alkylidene **53-TS** then activates cyclohexane to form **53-TS2**, which undergoes β-H abstraction under formation of cyclohexene adduct **53-TS3**. Elimination of cyclohexene results in the formation of **53-TS4**. In the following, a CH_2 group of the $H_2CP(C_{12}H_8)Ph$ ylide is transferred to give **53-TS5**. The tautomerization of **53-TS5** leads to **57** and closes the catalytic cycle. Thus, it was possible to dehydrogenate linear alkanes from C_4 to C_8 as well as cyclohexane and cyclooctane to the corresponding terminal alkenes with catalyst **57** and 10 equivalents of $H_2CP(C_{12}H_8)Ph$ at 75 °C.[87]



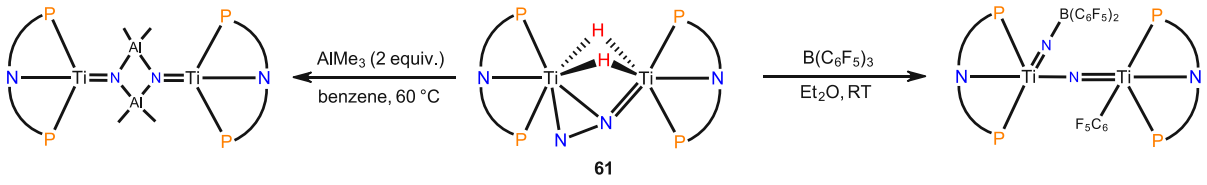
Scheme 30. Synthesis of $[Ti(^{Tol}PNP)]_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2)\text{-}N_2$ **59**.

Noteworthily, the aforementioned complexes also can be utilized in the activation of N_2. Recently, Hou and co-workers reported on the synthesis of a titanium N_2 complex, in which N_2 has the rare end-on/side-on coordination mode. $[Ti(^{Tol}PNP)]_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2)\text{-}N_2$ **59** could be isolated upon hydrogenolysis of the alkylated $[Ti(^{Tol}PNP)(CH_2TMS)_2)]$ in presence of N_2 within 3 hours (Scheme 30). Surprisingly no reducing agent is required for N_2 activation. Inspired by the work of Fryzuk it was proposed that the hydrogenolysis forms the poly hydride complex **59-TS**.[88,89] Subsequent exposure to N_2 resulted in an N_2 activation *via* reductive elimination of H_2. Therefore, **59-TS** itself can be considered as the reducing agent. Heating **59** under H_2 atmosphere resulted in the formation of imido/nitride/hydrido $[Ti(^{Tol}PNP)(\mu^2\text{-}NH)(\mu^2\text{-}N)H]$ **60**.[90]



Scheme 31. Synthesis of [Ti(PNP^{Acr})]$_2$(μ-H)$_2$(μ-η^1:η^2)-N$_2$ **61** and conversion with ZnMe$_2$.

Very recently, Hou and co-workers reported on the synthesis of [Ti(PNP^{Acr})]$_2$(μ-H)$_2$(μ-η^1:η^2)-N$_2$ **61** with an acridine-based PNP pincer ligand. The synthesis was achieved by hydrogenolysis of [Ti(PNP^{Acr})Me$_2$] with H$_2$ (4 bar) in presence of N$_2$ (1 bar) in hexane (Scheme 31). The coordinated N$_2$ possess a side-on/end-on configuration with an N-N bond length of 1.296(3) Å. Treatment of **61** with ZnMe$_2$ or MgMe$_2$ resulted in the formation of the end-on bridged complex [Ti(PNP^{Arci})Me$_2$]$_2$(μ-η^1:η^1)-N$_2$ **62**. **61** could be regenerated by exposure of **62** to H$_2$ (1 bar) at 60 °C. The regeneration of **61** demonstrated, that the coordination mode of the N$_2$ unit can be switched by hydride/alkyl exchange at the Ti center.



Scheme 32. Conversion of [Ti(PNP^{Acr})]$_2$(μ-H)$_2$(μ-η^1:η^2)-N$_2$ **61** with AlMe$_3$ and B(C$_6$F$_5$)$_3$.

Besides this transformation **61** was studied in respect to its reactivity towards AlMe$_3$, B(C$_6$F$_5$)$_3$, PhSiH$_3$ or HBpin. In all cases cleavage of the N-N bond occurred *via* reductive elimination of H$_2$ (Scheme 32).[91]

2 Results and Discussion

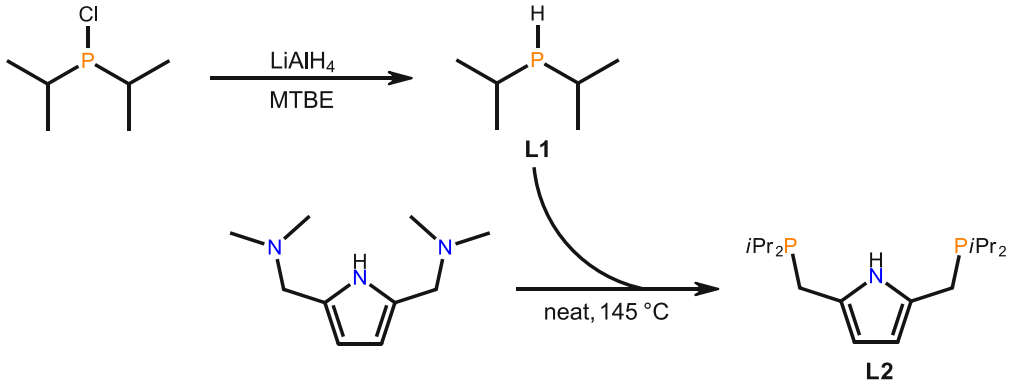
As shown in the section before about the synthesis of group IV metal complexes and further transformation, the choice of the ligand and precursor is important. Little changes of the system may influence the reactivity drastically.

Amidophosphines as ligands take a special role for the syntheses of group IV complexes. The hard amido functionality in combination with a polydentate coordination minimizes the dissociation of the soft phosphine donor. In this work a PNP pincer type ligand with a pyrrole scaffold bearing two phosphine donor was employed, which is well suited for the implementation of group IV metals (Figure 4). Besides the typically known chloride precursor MCl_4·2THF (M = Ti, Zr, Hf), the tetrakisamido $M(NMe_2)_4$ (M = Ti, Zr) and $Hf(NEt_2)_4$ were used for the complexation.

Figure 4. Used Ligand and Precursors.

The following section describes the synthesis of group IV metal complexes with different precursors. Further transformations should lead to complexes, which are capable of activation of N_2. Furthermore, the chemical properties of the novel complexes will be presented and discussed.

2.1 Synthesis of PNP-*i*Pr Ligand



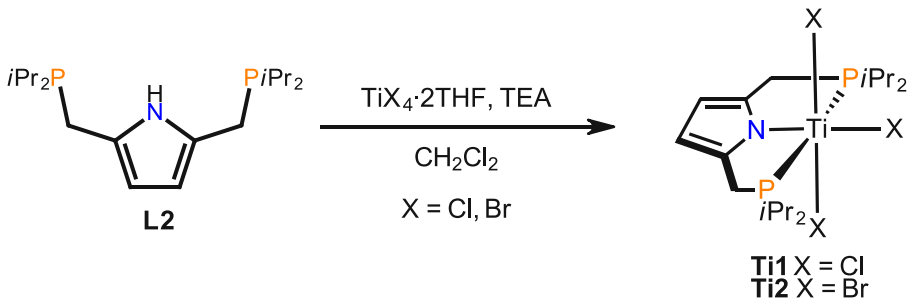
Scheme 33. Synthesis of PNP-*i*Pr **L2**.

The synthesis of the desired PNP-ligand was achieved *via* a two-step protocol. In the first step, diisopropylphopshine **L1** was synthesized from the commercially available chlorophosphine building block (Scheme 33). This transformation was done similar to the protocol of Goldman, however, some modifications were introduced. Methyl *tert*-Butyl ether (MTBE) was utilized as solvent instead of Et_2O due to more efficient separation from the product upon distillation. Furthermore, solely 0.5 equiv. of $LiAlH_4$ as reductant were required to afford full conversion within a few hours. This represents only 1.2 equiv. of hydride-donor in comparison to approx. 8 equiv. as reported in the literature.[92] The lower amount of $LiAlH_4$ resulted in less formation of aluminum salts upon addition of water during work up and therefore resulted in more convenient product isolation.

In the second step, the targeted ligand **L2** was received *via* nucleophilic substitution of dimethylamine groups in bis(dimethylaminomethyl)pyrrole by phosphorous moieties.[93] This reaction was conducted 140 °C for 48 h under solvent free conditions, yielding 76% **L2** as orange oil.

2.2 Titanium PNP Complexes

In order to get synthetic entrance to titanium(IV) complexes, **L2** was treated with $TiCl_4$·2THF in presence of NEt_3 in CH_2Cl_2. Delightfully, complex [Ti(PNP-*i*Pr)Cl_3] **1** was obtained as highly moisture sensitive dark red powder in 80% yield within 10 minutes. The reaction also can be performed in toluene, however, the reaction time increases to 3 hours (Scheme 34). Another approach represents the deprotonation of **L2** with *n*BuLi in THF, followed by addition of $TiCl_4$·2THF. However, this reaction pathway results in the formation of several unidentified side products, therefore resulting in a significantly lower yield.



Scheme 34. Synthesis of complex **Ti1** and **Ti2**.

$^{31}P\{^1H\}$-NMR analysis revealed a single signal at 81.4 ppm, suggesting a pincer-type coordination mode. In addition to that, the molecular structure of **Ti1** was confirmed by X-ray

analysis. The crystal structure of **Ti1** displays a distorted octahedral geometry with bond angles of 149.19(4)° (P1-T1-P2) and 160.60(9)° (N1-Ti1-Cl3). The torsion angle of the phosphine arms out of the pyrrole plane represents a rational value for the determination of the tension in such a rigid system. The determination of the torsion angle is depicted in Figure 9 (right). This results in an average torsion angle of 26.85° in **Ti1**. With a Ti1-N1 distance of 2.062 Å is in the range of such system.[94]

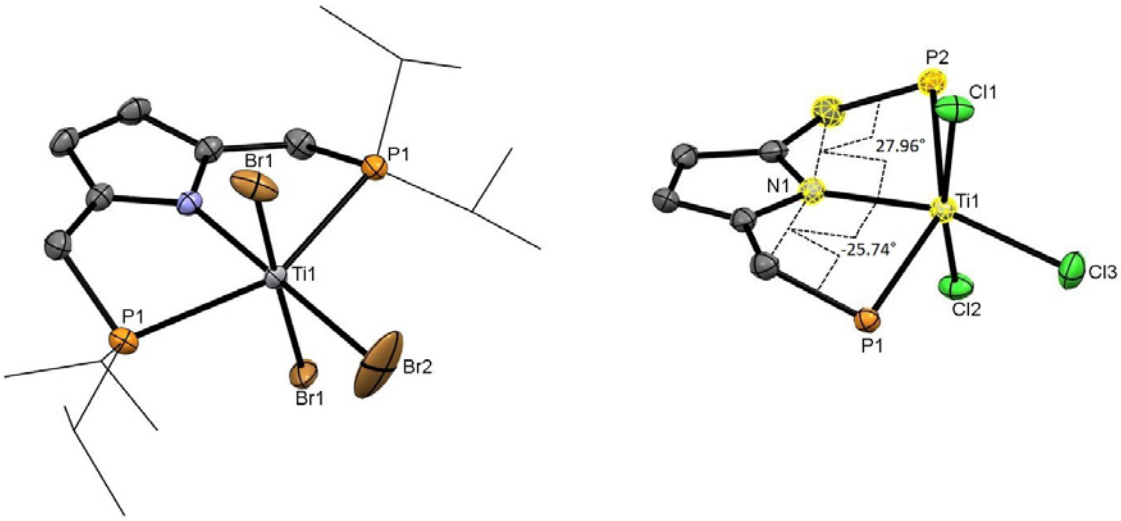
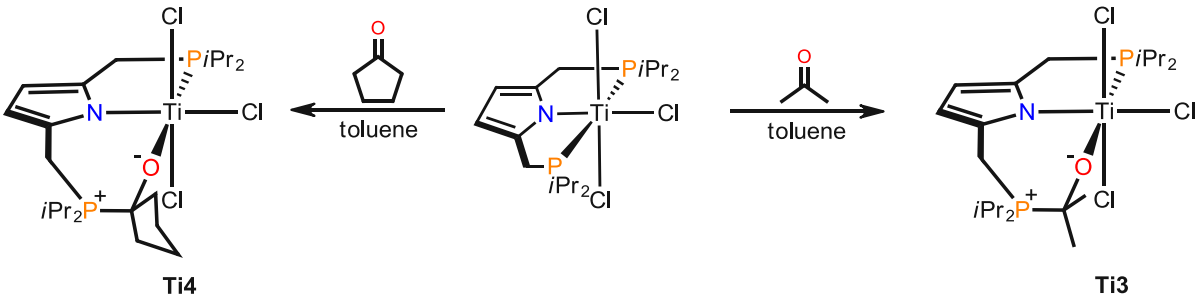


Figure 5. ORTEP view of [Ti(PNP-*i*Pr)Cl_3] **Ti1** (right) and [Ti(PNP-*i*Pr)Br_3] **Ti2** (left). showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Ti1 2.062(4), P1-Ti1 2.572(3), P2-Ti1 2.594(3), P1-Ti1-P2 149.19(4), N1-Ti1-Cl3 160.60(9) for **Ti1** and N1-Ti1 2.064, P1-Ti1 2.616, N1-Ti1-Br2 180.00, P1-Ti1-P1 151.54 for **Ti2**.

The bromide congener [Ti(PNP)Br_3] **Ti2** could be obtained similarly to **Ti1** by treatment of **L2** with $TiBr_4$·2THF. Thus, **Ti2** could be isolated as orange powder in 80% yield. Single crystals were obtained by storing a saturated CH_2Cl_2 of **Ti2** at -30 °C. The solid-state structure of **Ti2** displays a distorted octahedral geometry with characteristic angles of 159.35° (N1-Ti1-Br1) and 151.54° (P1-Ti1-P1). The N1-Ti1 distance of 2.064 Å is similar to complex **Ti1**. The torsion angle of 24.29° suggests that the bromide system is less strained than the chloride species. Interestingly, the phosphine signal in $^{31}P\{^1H\}$-NMR is shifted to 88.6 ppm. Attempts to afford complex **Ti2** upon halogenide exchange in **Ti1** with TMS-Br resulted in decomposition of the complex. Furthermore, the treatment of **Ti1** or **Ti2** with TMS-I resulted in the formation of various unidentified products. Thus, a iodine congener of **Ti1** (or **Ti2**) could not be isolated.



Scheme 35. Synthesis of complex **Ti3** and **Ti4**.

In virtue of the known oxyphilic character of titanium compounds complex **Ti1** and **Ti2** were treated with different alcohols and ketones (Scheme 35). However, in presence of MeOH and *t*BuOH solely decomposition of the starting material occurred. Interestingly, in presence of a ketone complex **Ti1** forms an internal salt. Thus, treatment of **Ti1** with one equivalent of acetone or cyclopentanone at room temperature afforded [Ti(PNO)Cl_3-acetone] **Ti3** and[Ti(PNO)Cl_3-cyclopentanone] **Ti4** in quantitative yield as a pale red solids within 10 minutes. Crystals suitable for X-Ray diffraction for both complexes were obtained by layering a saturated CH_2Cl_2 solution of **Ti3** or **Ti4** with *n*-pentane.

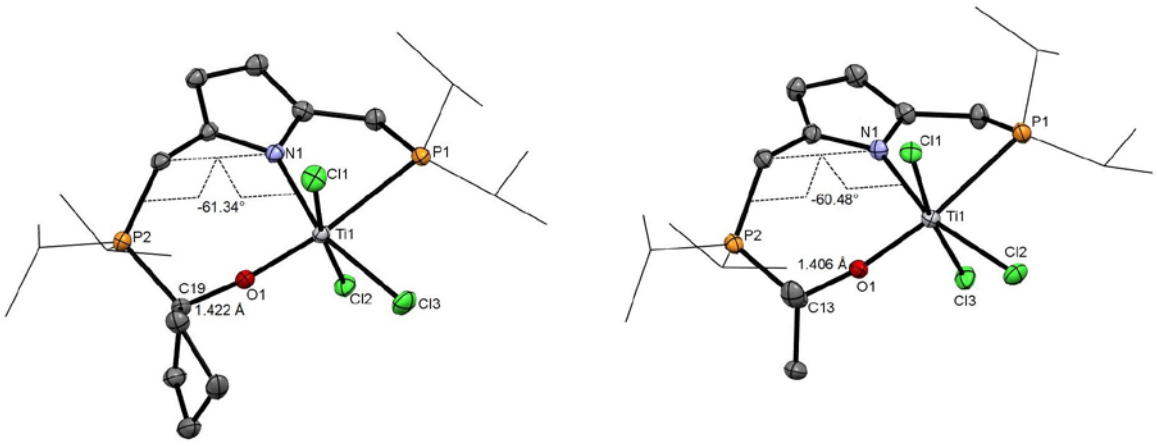


Figure 6. ORTEP view of [Ti(PNO)Cl_3-acetone] **Ti3** (right) and [Ti(PNO)Cl_3-cyclopentanone] **Ti4** (left) showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Ti1 2.064, P1-Ti1 2.660, O1-Ti1 1.778, C13-O1 1.406, P1-Ti1-O1 165.78, N1-Ti1-Cl2 162.92 for complex **Ti3** and N1-Ti1 2.076, P1-Ti1 2.670, O1-Ti1 1.792, C19-O1 1.422, P1-Ti1-O1 165.99, N1-Ti1-Cl2 161.70 for complex **Ti4**.

The refined molecular structure unambiguously revealed that both complexes have a distorted octahedral geometry with bond angles of 162.92° (N1-Ti1-Cl2) and 165.78° (P1-Ti1-O1) for **Ti3** and of 161.70° (N1-Ti1-Cl2) and 165.99° (P1-Ti1-O1) for **Ti4**. The torsion angle out of the pyrrole plane of the phosphonium arm is 60.48° and 61.34°, respectively. The bond distance of 1.406 Å (C13-O1) for **Ti3** and 1.422 Å (C19-O1) for **Ti4** are almost the same and correspond to a single bond (Figure 6).[95] $^{31}P\{^1H\}$-NMR analysis revealed two phosphorus signals at 40.9

and 25.2 ppm for **Ti3** and 35.4 and 31.8 ppm for **Ti4**. The ^{1}H-NMR of **Ti3** exhibits two singlets at 1.88 and 1.86 ppm which can be assigned to the CH_3 groups of the inserted acetone. Surprisingly, when more than one equivalent of acetone or cyclopentanone is used no further insertion takes place, even if the reaction mixture is heated to reflux for several hours.

Interestingly, the observed ketone insertion only occurs if the ketone contains an α-hydrogen. When **Ti1** is treated with hexamethyl acetone or benzophenone no reaction took place. In addition to that *in situ* NMR-spectroscopic experiments on the behaviour of **Ti1** in presence of other reagents bearing an electrophilic carbon such as aldehydes, nitriles and carbodiimide were conducted. Thus, **Ti1** was treated with one equivalent, two equivalents and an excess of benzaldehyde, acetonitrile and diisopropylcarbodiimide. In presence of one equivalent of benzaldehyde two phosphorus signals at 36.4 and 34.8 ppm were detected in ^{31}P{^{1}H}-NMR. However, after a few minutes the observed complex decomposed to several undefinable species. If two equivalents or an excess of benzaldehyde was utilized a mixture of different inseparable products was obtained. When **Ti1** was treated with acetonitrile or diisopropylcarbodiimide no reaction took place.

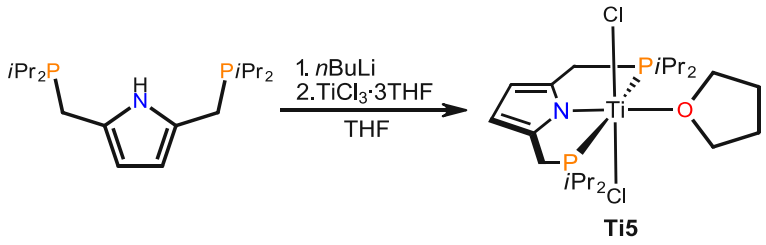
Since activation of dinitrogen from the atmosphere was targeted, complexes **Ti1** and **Ti2** were treated with 4.4 equivalents of different reducing agents in various solvents under 1 to 4 bar N_2 for 12 h at room temperature (Table 1). However, apart from not-coordinated ligand, no tractable product was obtained.

Table 1. Reducing agents and solvents for N_2 activation.

Entry	Reducing Agent	Solvent
1	KC_8	toluene
2	KC_8	THF
3	NaHg (5%)	toluene
4	NaHg (5%)	THF
5	Mg	toluene
6	Mg	THF

Due to unsuccessful activation of elemental nitrogen upon direct reduction of **Ti1** and **Ti2**, complexes containing alkyl ligands were envisioned to achieve the desired transformation. A consecutive hydrogenolysis should form a bridged polyhydride complex, which may activate N_2 as shown by Hou.[90,91] However, attempts to alkylate **Ti1** and **Ti2** directly with MeLi, neopentyllithium or phenyl lithium failed. It was supposed that the high reducing property of lithium reagents would lead to reductive decomposition.[31] Therefore, the corresponding

Grignard reagents were used. Unfortunately, no tractable material could be isolated. Another possibility to obtain alkylated group IV complexes is the utilization of alkylated precursors. Therefore $Ti(CH_2TMS)_4$ was synthesized upon adding $LiCH_2TMS$ to a solution of $TiCl_4 \cdot 2THF$ in toluene at -78 °C under light exclusion. This precursor was isolated as orange oil in 62% yield. The obtained precursor was reacted with **L2** at room temperature for 24 hours in toluene under light exclusion. Interestingly, no reaction was observed.



Ti5

Scheme 36. Synthesis of complex **Ti5**.

An alternative approach to afford titanium complexes for dinitrogen activation was incorporation of titanium in the oxidation state +III. For this purpose, the commercially available $3TiCl_3 \cdot AlCl_3$ was converted with THF in toluene to isolate $TiCl_3 \cdot 3THF$ as turquoise solid.[96] Upon conversion with the lithiated ligand **L2** in THF, the paramagnetic 13 electron complex [Ti(PNP-*i*Pr)Cl_2(THF)] **Ti5** was afforded as pink powder in 65% yield (Scheme 36). Interestingly, the usage of triethylamine as base was not successful. The solution magnetic moment of 1.8(1) μ_B (CH_2Cl_2, Evans method) of **Ti5** is in agreement with one unpaired electron.[97,98]

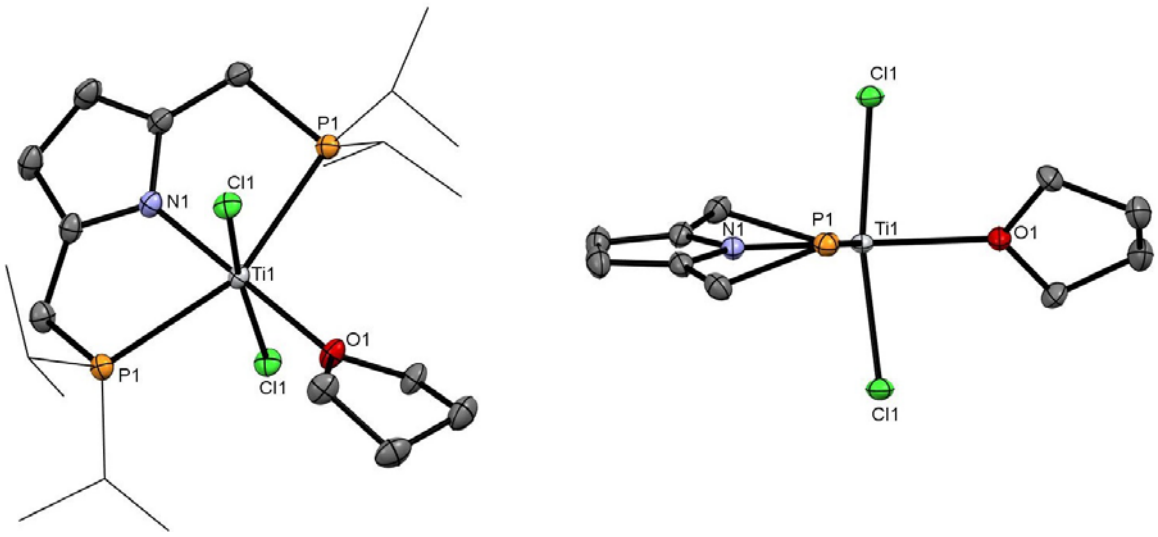
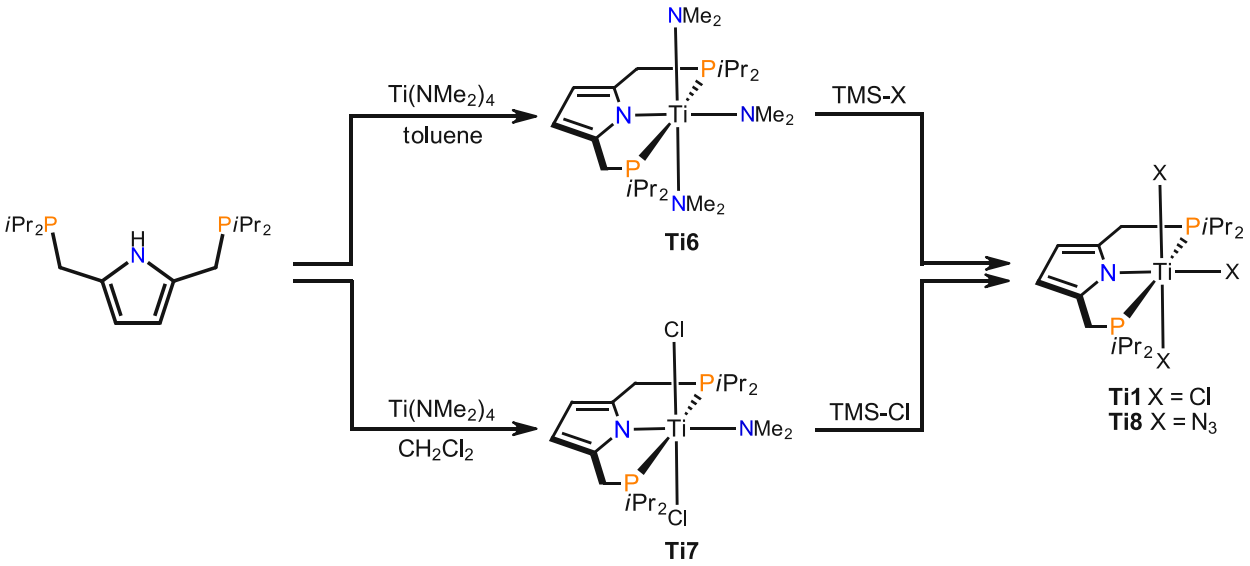


Figure 7. ORTEP view of [Ti(PNP-*i*Pr)Cl_2(THF)] **Ti5** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Ti1 2.057, P1-Ti1 2.066, P1-Ti1-P1 155.31, N1-Ti1-O1 180.00.

Crystals suitable for X-Ray analysis were obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. The solid-state structure of **Ti5** can be described as distorted octahedral with a coordinated THF molecule *trans* to the pyrrole nitrogen with a perfect linear angle of 180.00° (N1-Ti1-O1) and the two chloride ligands *trans* to each other with a bond angle of 155.32° (P1-Ti1-P1). The bond distance of N1-Ti1 with 2.057 Å and P1-Ti1 with 2.066 Å are in good agreement for a similar system (Figure 7).[99] With a torsion angle of 20.01° the phosphine arms are significantly less bent out of the pyrrole plane than in complexes **Ti1** and **Ti2**. A similar complex was reported by Nishibayashi with PNP-*t*Bu resulting in formation of [Ti(PNP-*t*Bu)Cl_2]. Contrary to **Ti5** no THF coordinates to the titanium center, probably due to the more steric demanding *t*Bu groups on the phosphines.[26]

In analogy to **Ti1** complex **Ti5** was treated with 1, 2 equivalents and an excess of acetone. In contrast to **Ti1** no insertion of ketone occurred. This fact may be a result of the lower strained ligand as well as the higher electron density on the metal center.

In order to achieve N_2 activation, it was attempted to alkylate **Ti5**, as reported by Hou and co-workers.[90,91] However the alkylation with MeLi, PhLi, Li-CH_2TMS, MeMgBr, BnMgBr and TMS-CH_2MgBr as well as the exchange of one chloride ligand with a Cp ligand led to decomposition of the complex. The direct reduction of **5** with 4.4 equivalents of different reducing agents in various solvents under N_2 atmosphere, as depicted in Table 1, also afforded no tractable material.



Scheme 37. Synthesis of titanium PNP complexes **Ti1**, **Ti6**, **Ti7** and **Ti8**.

Another strategy to afford Ti(IV) complexes, is the utilization of the amido-precursor $Ti(NMe_2)_4$. The targeted amido complex was considered to allow more functionalization

possibilities in contrast to the halide congeners upon treatment with trimethylsilyl reagents. Thus, [Ti(PNP-*i*Pr)(NMe_2)$_3$] **Ti6** was afforded by stirring **L2** with one equivalent Ti(NMe_2)$_4$ in toluene at 80 °C for 48 hours. After removal of the solvent the amido complex was isolated as red oil in quantitative yield, which could not be crystallized (Scheme 37). The $^{31}P\{^1H\}$-NMR of the obtained oil exhibits one signal at 6.2 ppm and one at 0.5 ppm. One may suggest that the latter signal might be attributed to the free ligand. However, it is supposed that a dynamic equilibrium between coordination and decoordination of one phosphine arm is responsible for the signal at 0.5 ppm. This assumption is supported by the corresponding proton-NMR spectrum, due to lack of signal for the NH of the pyrrole ring.

DFT calculations were performed to support the assumption of a possible equilibrium. As it is shown in Figure 8 the **κ²** coordination mode is significantly favored. Thus, one phosphine arm of the κ³ complex **PNP-Ti(κ³)** dissociates through **PNP-Ti (TS)** with a barrier of $\Delta G^{\ddagger}$ = 4.9 kcal/mol, leading to the κ² complex **PNP-Ti(κ²)**, which is energetically more favorable by 17.3 kcal/mol in comparison to κ³. Although these calculations favor κ²coordination in **Ti6** the actual equilibrium in solution is underscored, as supported by spectroscopic data.

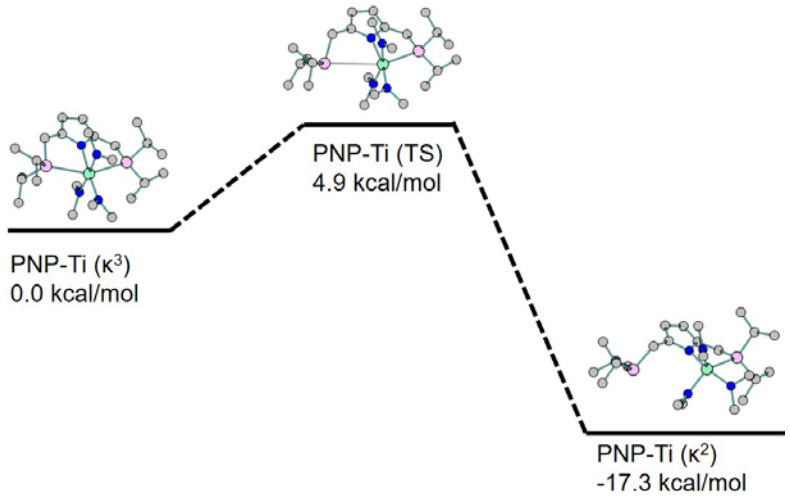


Figure 8. Calculated free energies (kcal/mol) of κ³ vs. κ² coordinated complex **Ti6**.

Interestingly, when **L2** is converted with 2 equivalents of Ti(NMe_2)$_4$ in CH_2Cl_2 at 40 °C, a brown solid is obtained with a single phosphorous signal at 54.0 ppm in $^{31}P\{^1H\}$-NMR. Crystals for X-Ray diffraction could be obtained by storing a saturated solution of the product kept at -20 °C. The single crystal analysis revealed that [Ti(PNP-*i*Pr)(NMe_2)Cl_2] **Ti7** was formed instead of **6**. The solid-state structure of **Ti7** can be described as a distorted octahedron with the chloride *trans* to each other and the dimethylamido *trans* to the pyrrole scaffold (Figure 9). The bond distance of Ti1-N1 with 2.144 Å is significantly longer than the T1-N1

distance of **1**, which is in agreement with the higher π acidity of a chloride ligand compared to an amido ligand. This effect is also apparent in the slightly longer T1-P1 bond distance of 2.088 Å. The torsion angle of the phosphine arms is with 23.70° lower than for trichloride complex **Ti1**. The N1-Ti1-N2 angle is perfectly linear with 180.00° and P1-Ti1-P2 is 150.58°.

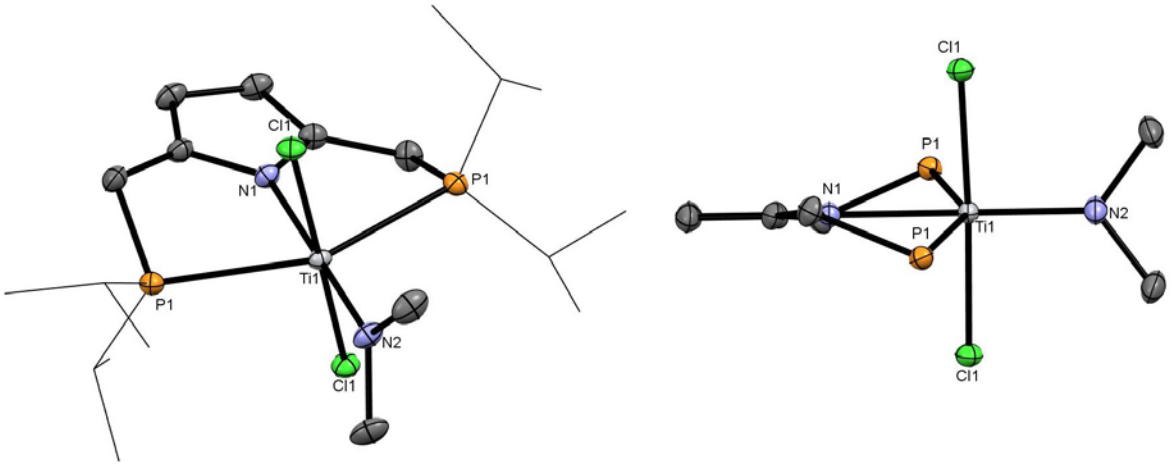


Figure 9. ORTEP view of [Ti(PNP-*i*Pr)(NMe_2)Cl_2] **Ti7** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Ti1 2.144(4), P1-Ti1 2.088, P1-Ti1-P1 150.85, N1-Ti1-N2 180.00.

Fascinated by these findings, further investigations on the halide-source in **Ti7** were conducted. In order to test whether halide-impurities in the reaction vessels are responsible for the formation of **Ti7**, **Ti6** was stirred with an excess of LiCl in refluxing toluene and THF. Surprisingly, no amido substitution took place under these conditions. However, when **6** was stirred in CH_2Cl_2 with an extra equivalent of $Ti(NMe_2)_4$, complex **Ti7** was quantitatively formed. It seems that the high Lewis acidity of $Ti(NMe_2)_4$ is required for this transformation and CH_2Cl_2 represent the halide source.

Inspired by various reports of Ballmann further transformations of **Ti6** were conducted by utilization of different TMS-X (X = Cl, Br, I, CN, N_3) agents.[50,71] Thus, complex **Ti1** can be obtained by conversion of **6** with 6 equivalents of TMS-Cl within 12 hours. Noteworthily, it is essential to use an excess of TMS-Cl in order to shift the equilibrium in the reaction mixture. Usage of only 3 equivalents resulted in a mixture of **Ti1** and the dichloride species **Ti7**. Prolonged reaction time and higher reaction temperatures did not result in higher yields. Unfortunately, treatment of **Ti6** with TMS-Br, TMS-I or TMS-CN led to no tractable material. When **Ti6** is converted with TMS-N_3 the azido complex [Ti(PNP-*i*Pr)(N_3)$_3$] **Ti8** is afforded in low purity (Scheme 37). However, any attempts to receive a pure product were unsuccessful.

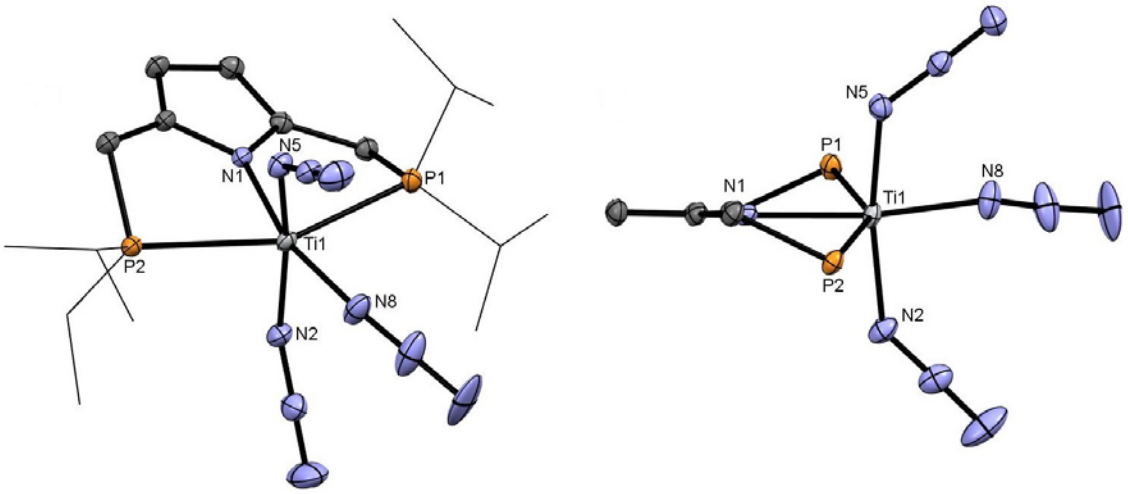


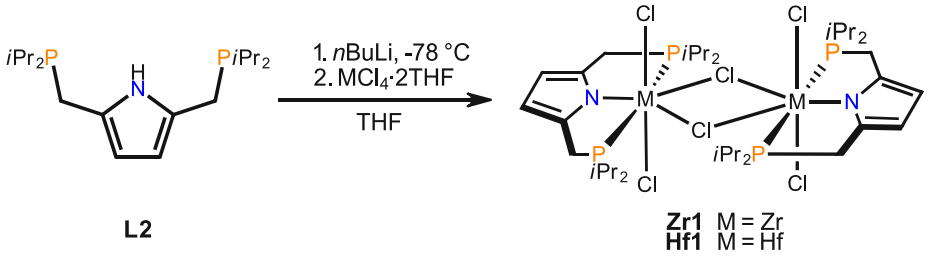
Figure 10. ORTEP view of [Ti(PNP-*i*Pr)(N_3)$_3$] **Ti8** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Ti1 2.059, P1-Ti1 2.578, P2-Ti1 2.581, N2-Ti1 1.971, N5-Ti1 1.997, N8-Ti1 2.000, P1-Ti1-P2 150.36, N1-Ti1-N8 165.08.

Fortunately, single crystals suitable for X-Ray analysis were obtained by storing a saturated solution of the crude product in *n*-pentane at -20 °C. The $^{31}P\{^{1}H\}$ exhibits a single signal at 63.1 ppm. The complex adopts a distorted octahedral geometry with bond angles of 165.08° (N1-Ti1-N8) and 150.36° (P1-Ti1-P2) (Figure 10). The averaged torsions angle of the phosphine arms out of the pyrrole plane is 25.94°, which is in the range of **Ti1**. The bond distances of N2-Ti1 of 1.971 Å, N5-Ti1 of 1.997 Å and N8-Ti1 of 2.000 Å are in good agreement with literature known titanium azide complexes.[100,101]

2.3 Zirconium and Hafnium PNP Complexes

Since N_2 activation with titanium complexes bearing PNP-*i*Pr was not possible, the focus was shifted to zirconium and hafnium-based organometallics. Although the reduction of zirconium and hafnium is more difficult, due to the required higher reducing power. This aspect may lead to increased stability, which is crucial for dinitrogen activation.[19,102]

Treatment of PNP-*i*Pr **L2** with *n*BuLi at -78 °C in THF and subsequent addition of MCl_4·2THF (M = Zr, Hf) afforded the dinuclear complexes [Zr(PNP-*i*Pr)Cl_2(μ-Cl)$_2$]$_2$ **Zr1** and [Hf(PNP-*i*Pr)Cl_2(μ-Cl)$_2$]$_2$ **Hf1** as beige solids with yields of 76% and 80%, respectively (Scheme 38). The $^{31}P\{^1H\}$-NMR shows a single peak at 42.8 ppm for the zirconium congener and one peak at 40.2 ppm for the hafnium congener. When **L2** is treated with MCl_4·2THF in presence of TEA both complexes are formed, however, with some unidentified side products, therefore lowering the yield. In contrast to the report by Nishibayashi full conversion could be achieved within 1 hour in higher yields. This may be attributed to the higher solubility of the employed precursors in THF in comparison to MCl_4 in toluene.[26]



Scheme 38. Synthesis of complex **Zr1** and **Hf1**.

For the hafnium congener suitable crystals for the X-Ray analysis were obtained by layering a saturated solution of **Hf1** in CH_2Cl_2 with *n*-pentane (Figure 11). Although only crystals in low quality were achieved for X-Ray measurement, the solid state structure clearly shows that **10** adopts a dinuclear structure, in which the Hf atoms are bridged by two chloride ligands. The coordination mode can be described as distorted pentagonal bipyramidal, with phosphines, nitrogen and the bridging chlorides in the equatorial plane and the remaining two chloride ligand in the axial positions. The bond distances between the pyrrole nitrogens and the hafnium centers are 2.188 Å and 2.196 Å and are not significantly longer than those of the reported [Zr(PNP-*t*Bu)Cl_2(μ-Cl)$_2$]$_2$.[26] The averaged torsion angle 31.94° is significantly higher compared to the aforementioned titanium congeners. This may be attributed to the higher ion radius of the hafnium center in comparison to titanium.

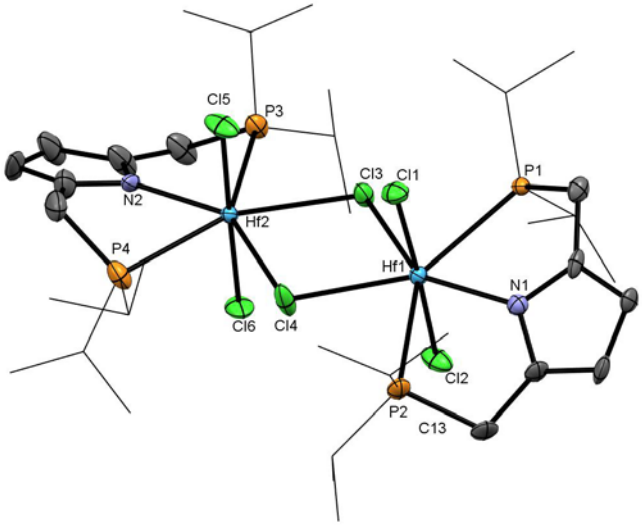
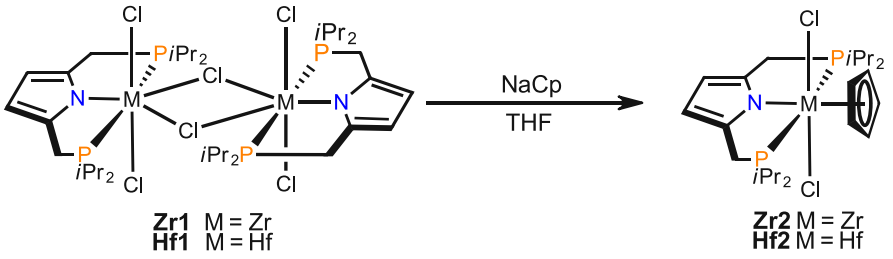


Figure 11. ORTEP view of [Hf(PNP-*i*Pr)Cl_2(μ-Cl)$_2$]$_2$ **Hf1** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Hf1 2.188, N2-Hf2 2.196, P1-Hf1 2.739, P2-Hf1 2.742, P3-Hf2 2.750, P4-Hf2 2.753, P1-Hf1-P2 140.89, P3-Hf2-P4 140.68.

Attempts to prepare the corresponding dinitrogen complexes upon reaction of **Zr1** and **Hf1** with 4.4 equivalent NaHg (5%), KC_8 and Na in various solvents at room temperature under 1 to 4 bar N_2 only afforded no tractable materials.

In order to overcome decomposition of these complexes, Cp was introduced to these systems as a more sterically demanding ligand. Hence **Zr1** and **Hf1** were treated with NaCp in THF at room temperature resulting in a color change of the reaction mixture from orange to dark red (Scheme 39). Upon work up, the mononuclear complexes [Zr(PNP-*i*Pr)Cl_2(Cp)] **Zr2** and [Hf(PNP-*i*Pr)Cl_2(Cp)] **Hf2** were obtained as beige solids in 90% and 93% yield, respectively.



Scheme 39. Synthesis of complex **Zr2** and **Hf2**.

Both complexes were characterized by multinuclear NMR-spectroscopy. Complex **Zr2** and **Hf2** both exhibit a triplet resonance at 6.70 (J_{HP} = 1.2 Hz) and 6.40 ppm (J_{HP} = 1.1 Hz) assignable to the Cp ligand in ^{1}H-NMR. The ^{31}P{^{1}H}-NMR resonances arise at 36.2 and 37.8 ppm, respectively.

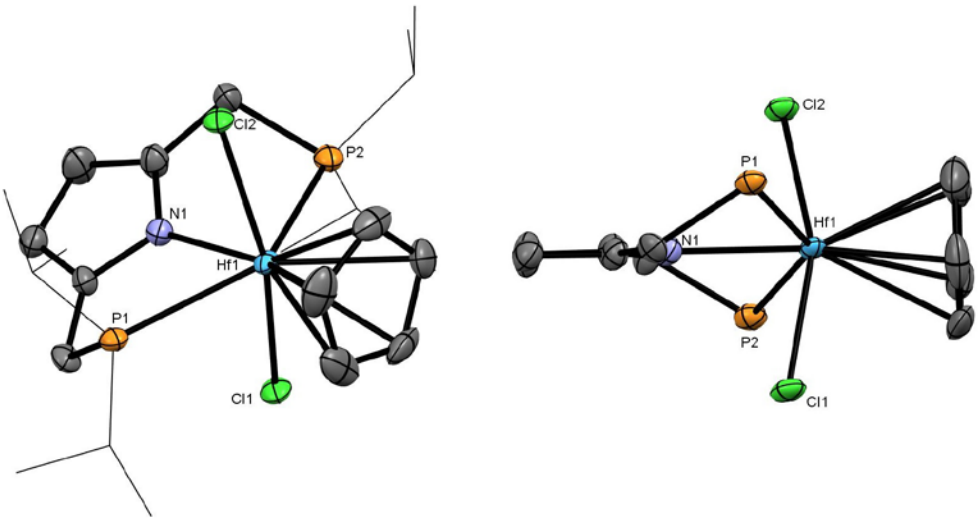
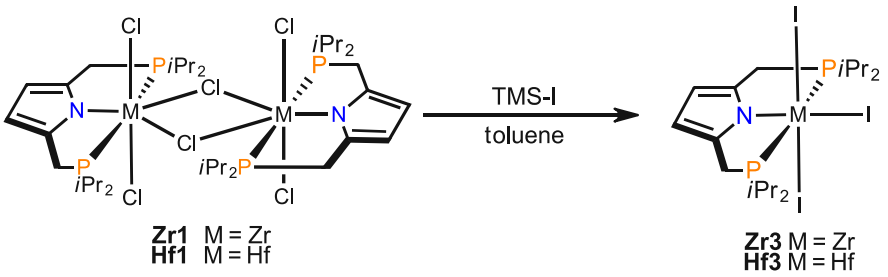


Figure 12. ORTEP view of [Hf(PNP-*i*Pr)Cl$_2$Cp] **Hf2** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Hf1 2.228, P1-Hf1 2.744, P2-Hf1 2.765, Cl1-Hf1 2.483, Cl2-Hf1 2.476, P1-Hf1-P2 139.42, Cl1-Hf1-Cl2 160.09, N1-Hf1-Cl2 80.43, N1-Hf1-Cl2 79.72.

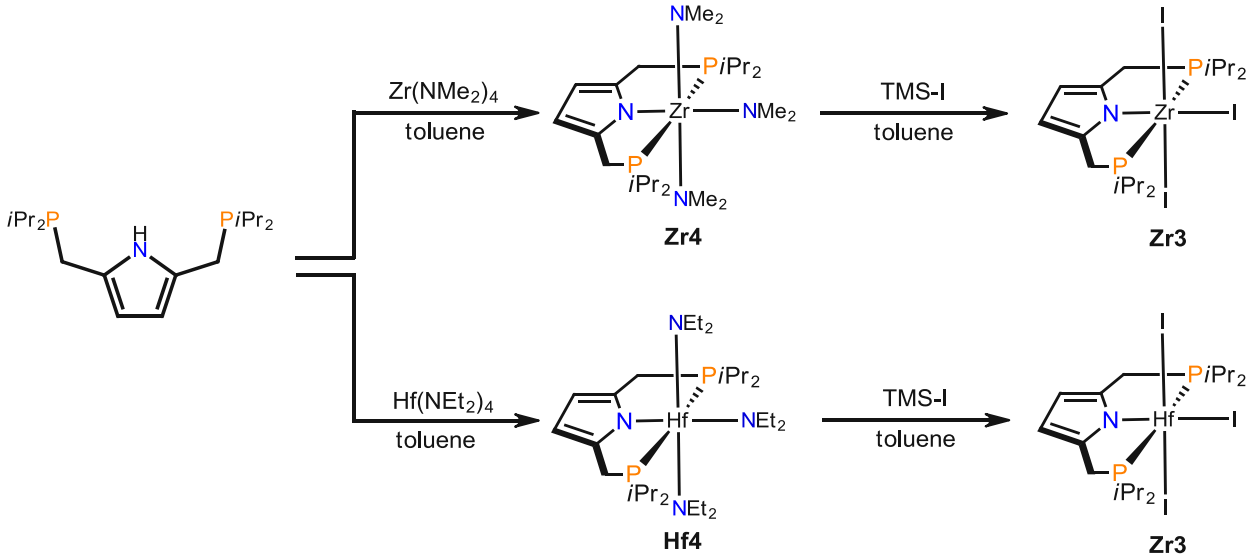
Suitable crystals for X-Ray analysis for **Hf2** were grown from saturated CH_2Cl_2 solution layered with *n*-pentane. The coordination sphere can be described as distorted octahedral with bond angles of 139.42° (P1-Hf1-P2), 160.09° (Cl1-Hf1-Cl2) and an essentially linear angle 179.74° (N1-Hf1-Cp) (Figure 12). Like in **Hf1** the N1-Hf1 bond distance is with 2.228 Å in the range of the zirconium congener of PNP-*t*Bu.[26] The Cp ligand is coordinated *trans* in respect to the pyrrole N as well as both chlorides are arranged *trans* to each other. The phosphine arms are bent in average 32.71° out if the pyrrole plane. Particularly interesting is that the chlorides are bent with bond angles of 80.43° (N1-Hf1-Cl2) and 79.72° (N1-Hf1-Cl2) towards the pyrrole scaffold.



Scheme 40. Synthesis of complex **Zr3** and **Hf3**.

Unfortunately, it was not possible to activate elemental nitrogen under similar conditions to **Zr1** and **Hf1**. Due to the lack of nitrogen activation of these complexes, further functionalizations were considered. Based on literature about the generally more active iodide species in N_2 activation, it was attempted to obtain the iodide congeners of **Zr2** and **Hf2** by treatment with TMS-I.[103] However, only unidentified compounds were afforded.

When **Zr1** and **Hf1** were treated with 30 equivalents of TMS-I the mononuclear compounds [Zr(PNP-*i*Pr)I_3] **Zr3** and [Hf(PNP-*i*Pr)I_3] **Hf3** were formed within 2 hours in 78% and 87% isolated yield (Scheme 40). Unfortunately, several inseparable side products were formed. Furthermore, it has to be noted that 30 equivalents TMS-I are required in this transformation. If less equivalents were used the reaction time increased to 12 hours and more side products were formed. Both complexes were characterized by NMR spectroscopy. In $^{31}P\{^1H\}$-NMR the complex signals arise at 56.5 for **Zr3** and 62.3 ppm for **Hf3**. Compared to the chloride congeners the signals of the iodide complexes are shifted to high field. Therefore, one may presume that **Zr3** and **Hf3** are mononuclear complexes.



Scheme 41. Synthesis of complexes **Zr3** and **Hf3** *via* complexes **Zr4** and **Hf4**.

Since the transformation of **Zr1** and **Hf1** to the iodide complexes **Zr3** and **Hf3** was associated with the formation of inseparable byproducts, amido precursor $Zr(NMe_2)_4$ and $Hf(NMe_2)_4$ were utilized to overcome this problem. Thus, **L2** was stirred with $Zr(NMe_2)_4$ and $Hf(NEt_2)_4$ at 120 °C in toluene for 48 hours resulted in the formation of complex [Zr(PNP-*i*Pr)$(NMe_2)_3$] **Zr4** and [Hf(PNP-*i*Pr)$(NEt_2)_3$] **Hf4** as red oils (Scheme 41). In the case of the zirconium congener the conversion as well as the yield was quantitative. Interestingly, only 80% conversion of the hafnium analogues was achieved. Due to similar solubility properties of the precursor $Hf(NEt_2)_4$, **Hf4** and the ligand further purification was not possible. However, it turned out, that further transformations could be carried out with crude **Hf4**. The structure of complexes **Zr4** and **Hf4** were confirmed by ^1H and $^{31}P\{^1H\}$-NMR. The $^{31}P\{^1H\}$-NMR exhibits a signal at 13.4 ppm for **Zr4** and at 9.2 ppm for **Hf4**. The ^1H-NMR of **Zr4** shows no signal for the pyrrole proton. In the case of the hafnium congener **Hf4** the proton of the pyrrole is still present as well as the characteristic signals of the ethyl groups of the precursor $Hf(NEt_2)_4$.

When **Zr4** and **Hf4** were treated with 3.5 equivalents of TMS-I in toluene the corresponding iodide analogues **Zr3** and **Hf3** are afforded within 1 hour. Due to no side product formation **Zr3** and **Hf3** were isolated in 90% and 84% yield as orange and pale pink solid. In the case of **Hf4** the inseparable $Hf(NEt_2)_4$, is converted to HfI_4, which readily precipitates in toluene. Therefore, HfI_4 could be separated by extraction of the crude product with toluene. For the Hf congener **Hf4** single crystals for X-Ray analysis could be isolated by layering a saturated CH_2Cl_2 with *n*-pentane. The molecular structure confirmed the assumption, that the iodide species **Zr3** and **Hf3** are mononuclear complexes.

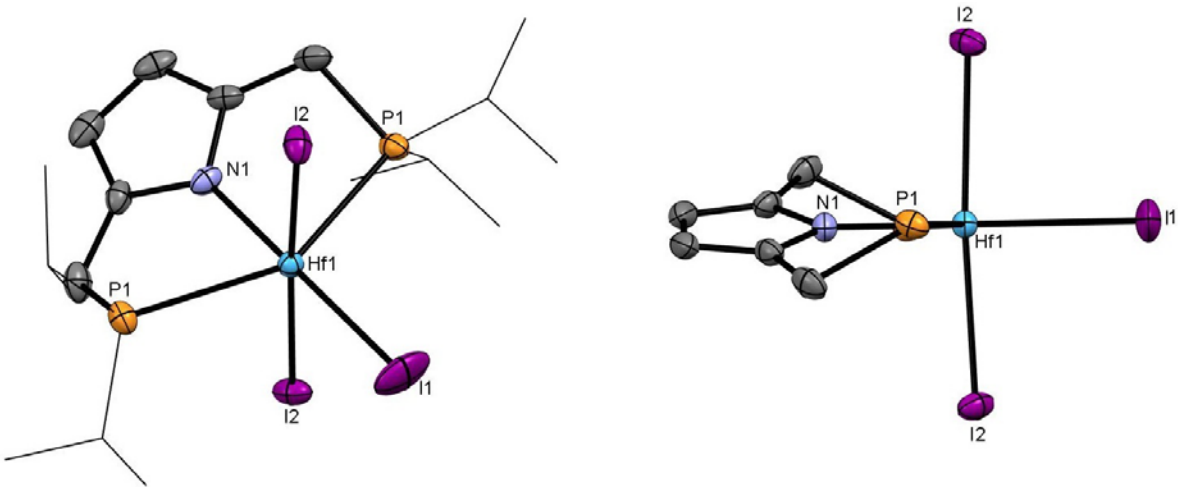
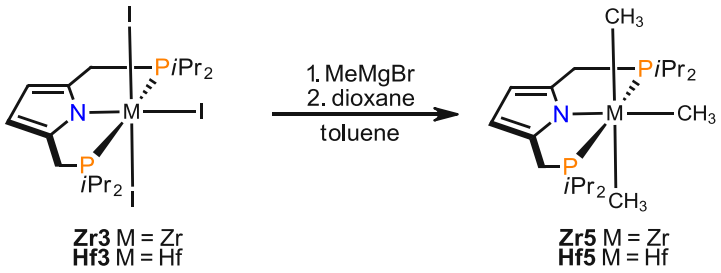


Figure 13. ORTEP view of [Hf(PNP-*i*Pr)I_3] **Hf3** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Hf1 2.142, P1-Hf1 2.737, I1-Hf1 2.805, I2-Hf1 2.792, P1-Hf1-P1 145.21, N1-Hf1-I1 180.00.

The coordination sphere of **Hf3** can be described as a distorted octahedron around the metal center with bond angles of 180.00° (N1-Hf1-I1) and 145.21° (P1-H1-P1). The ancillary ligand coordinates in a meridional fashion and is in equatorial plane with I1 (Figure 13). With a torsion angle of 29.93° the iodide species has a lower tension than **Hf1** and **Hf2**. The bond distance of N1-Hf1 with 2.142 Å is significantly shorter than for the chloride analogue **Hf1**. Furthermore the Hf-I average bond distances is 2.799 Å and is therefore significantly longer than the Hf-Cl distance in **Hf1**.

Attempts to activate dinitrogen in presence of 4.4 equivalent KC_8, NaHg (5%), $NaC_{10}H_8$, Na-sand and Mg in toluene or THF at 1 to 4 bar N_2 led to decomposition of **Zr3** and **Hf3**. Therefore, it was attempted to obtain the iodide congener of **Hf2** by conversion of **Zr3** and **Hf3** with NaCp in THF. However, no tractable material could be isolated in these transformations.



Zr3 M = Zr
Hf3 M = Hf

Zr5 M = Zr
Hf5 M = Hf

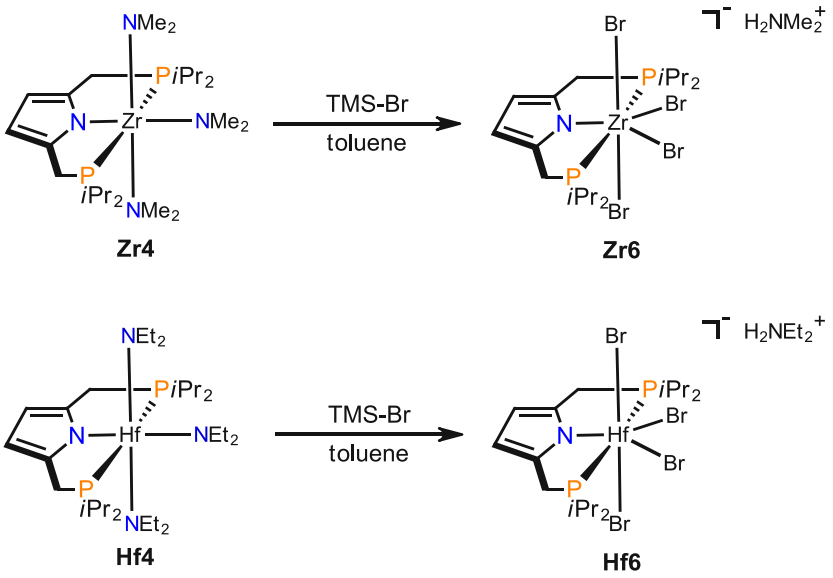
Scheme 42. Synthesis of complex **Zr5** and **Hf5**.

Since no N_2 activation of **Zr3** and **Hf3** was not possible it was considered to synthesize the corresponding alkyl complexes. Due to the knowledge of a possible reduction by using lithium reagents, alkylation was achieved by the use of Grignard reagents. The addition of MeMgBr to a solution **Zr3** or **Hf3** in toluene resulted in a brightening of the reaction mixture. Directly after the addition of the Grignard reagent, 6 equivalents of dioxane were utilized to precipitate the formed magnesia salts. Upon filtration and evaporation of the solvent the alkylated complexes [Zr(PNP-*i*Pr)Me_3] **Zr5** and [Hf(PNP-*i*Pr)Me_3] **Hf5** were obtained as orange oils in 80% and 82% yield, respectively (Scheme 42). The addition of dioxane seems to be crucial to separate the formed magnesia salts. Furthermore, it is vital to employ toluene as solvent. When THF or diethyl ether were utilized, fast decomposition of the formed complexes occurred, due to a presumable higher reduction potential of Grignard reagents in ethereal solvents.

Both complexes were characterized by NMR spectroscopy. The phosphine signals for **Zr5** and **Hf5** are located at 27.9 and 30.8 ppm in $^{31}P\{^1H\}$-NMR. In ^1H and $^{13}C\{^1H\}$-NMR the CH_3 groups on the metal center arise at 1.04 (t, J_{PH} = 3.8 Hz) and 51.7 ppm for **Zr5** and 0.74 (t, J_{PH} = 3.9 Hz) and 59.4 (t, J_{CP} = 6.4 Hz) for **Hf5**. This shifts are in good agreement with similar systems.[25,27]

Surprisingly, the alkylation of **Zr3** and **Hf3** only took place with MeMgBr. Attempts to introduce bulkier groups such as benzyl or CH_2TMS resulted in decomposition of these complexes. This result was also described by Ozerov for a similar system.[27]

The hydrogenolysis of **Zr5** and **Hf5** upon treatment with H_2 at 1 or 4 bar in THF or toluene resulted in decomposition of the alkylated complexes. This may be attributed to low stability of the *in situ* formed polyhydride complex. Therefore the reaction was carried out in presence of 1 bar nitrogen and 1 or 4 bar H_2 in order to capture dinitrogen. However, no defined complex could be isolated.



Scheme 43. Synthesis of complex **Zr6** and **Hf6**.

Since nitrogen activation was neither possible with the iodide nor the alkylated species, the bromide congeners were targeted. Contrary to expectations, when **Zr4** and **Hf4** are treated with 3.5 equivalents TMS-Br, no mononuclear bromide complexes are formed. Interestingly, the anionic complex [Zr(PNP-*i*Pr)Br$_4$][H$_2$NMe$_2$] **Zr6** and [Hf(PNP-*i*Pr)Br$_4$][H$_2$NMe$_2$] **Hf6** were afforded as salmon colored solid in 80% and 81% yield (Scheme 43). Both complexes are highly moisture and oxygen sensitive. The ^{1}H-NMR exhibits a singlet at 7.64 ppm for **Zr6** and 7.66 ppm for **Hf6** which corresponds to the ammonium protons. In ^{31}P{^{1}H}-NMR the complex signal arise at 39.7 and 49.9 ppm, respectively. Single crystals suitable for X-Ray analysis were afforded for **Zr6** by layering a saturated CH_2Cl_2 solution with *n*-pentane and storage at -20 °C in a freezer. The molecular structure confirmed the presence of an anionic complex. The coordination sphere can be described as distorted capped octahedral with the PNP-*i*Pr ligand and two bromide ligands in the equatorial plane.

As can be seen in Figure 14 the anionic complex is under high tension. This can be derived from the long N1-Br1 bond distance of 2.251 Å as well as the high torsion angle of the phosphine of 35.01°. Additionally, the observation of an organometallic zirconate is rare. So far most zirconate and anionic hafnium complexes are described as a transition state or as an internal salt.[104–110]

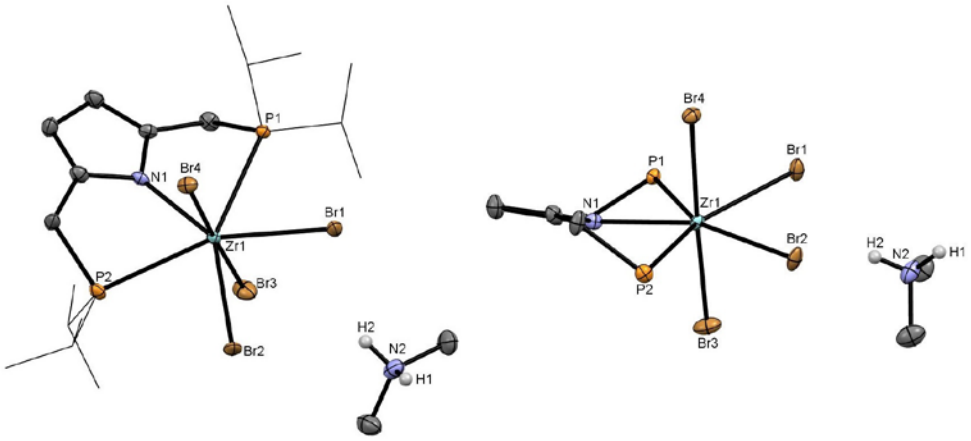
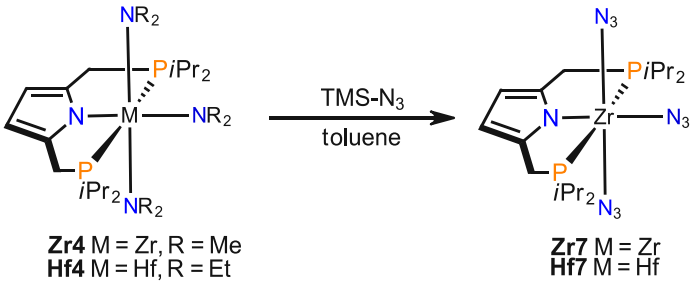


Figure 14. ORTEP view of [Zr(PNP-*i*Pr)Br$_3$][H$_2$NMe$_2$] **Zr6** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): N1-Zr1 2.251, P1-Zr1 2.772, P2-Zr1 2.785, Br11-Zr1 2.776, Br2-Zr1 2.735, Br3-Zr1 2.587, Br4-Zr1 2.632, P1-Zr1-P2 135.34, Br3-Zr1-Br4 177.53.

In virtue of the better functionalization of the amido complexes [Zr(PNP-*i*Pr)(NMe$_2$)$_3$] **Zr4** and [Hf(PNP-*i*Pr)(NEt$_2$)$_3$] **Hf4** with TMS-X (X = N$_3$, CN, OTf) reagents in comparison to the titanium congener, further investigations were conducted. Treatment of **Zr4** and **Hf4** with 3.5 equivalents of TMS-N$_3$ afforded the corresponding azide complexes [Zr(PNP-*i*Pr)N$_3$] **Zr7** and [Zr(PNP-*i*Pr)N$_3$] **Hf7** as orange solids in 51% and 65% yield, respectively (Scheme 44).



Scheme 44. Synthesis of complex **Zr7** and **Hf7**.

Although this transformation also takes place with **Ti6**, the use of zirconium and hafnium led to higher selectivity in the investigated reaction. Hence **Zr7** and **Hf7** could be isolated in moderate yield in pure form. Both complexes were characterized by NMR studies. The complex signal arises at 38.5 for **Zr7** and at 40.5 ppm for **Hf7** in $^{31}P\{^{1}H\}$-NMR. Therefore, the formation of an anionic complex or a disubstituted complex can be excluded. Although treatment of **Zr4** and **Hf4** with TMS-X reagents leads to more selective reactions, isolation of the corresponding complexes offer transformation with TMS-CN or TMS-OTf was not achieved.

2.4 Ligand Modification

In comparison to systems reported by Gade[51,79], Mindiola[80,85,111] or Fryzuk[61,65,66] the chosen ligand **L2** seems to be more rigid, which resulted in highly strained complexes. This fact may be problematic for further transformations or reactions, such as N_2 activation. In order to circumvent this problem, it was intended to expand the linker by one carbon unit. Therefore, a six membered cyclometalated ring would be obtained upon complexation, which would decrease the ring strain.

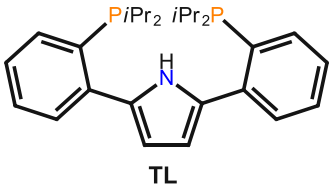
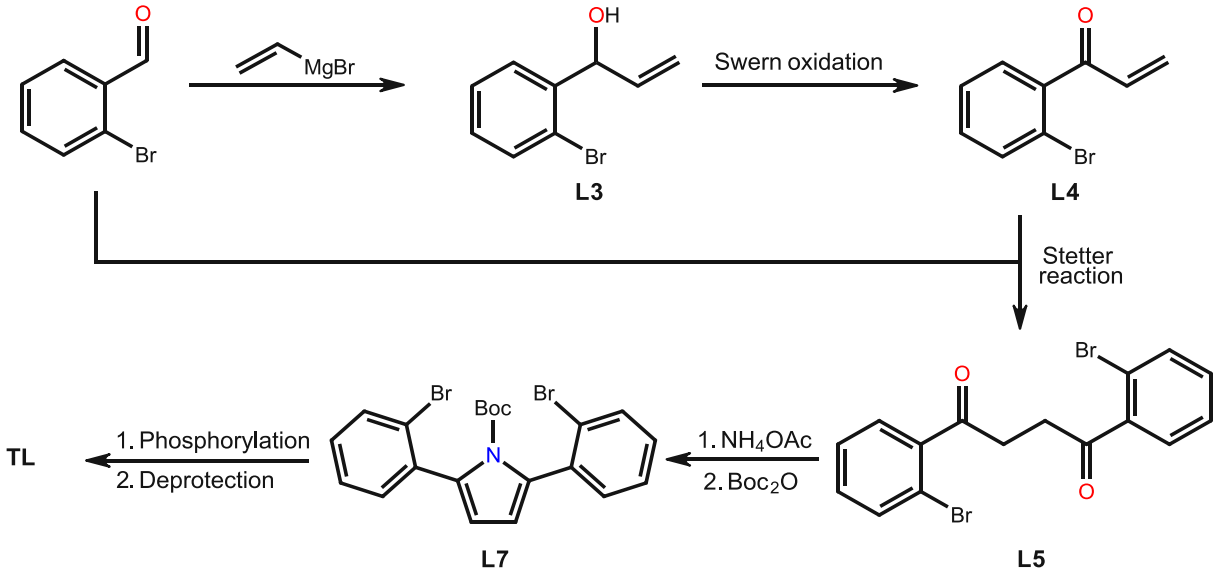


Figure 15. Pyrrole ligand with expanded linkers.

Based on the work of Gade[51,79] and Ballmann[50] it was planned to substitute the CH_2 linker of PNP-*i*Pr$_2$ **L2** by a phenyl linker. In the case of an alkyl linker C-H activation may occur upon coordination or functionalization. The targeted ligand **TL** is depicted in Figure 15**.**



Scheme 45. Planed synthetic route to achieve **TL**.

For the synthesis of the ligand **TL** three strategies were considered. In the first synthetic route, depicted in Scheme 45, **TL** should be obtained *via* a 1,4-diketone, bearing two phenyl rings containing a bromide. Upon a Paal-Knorr pyrrole synthesis the corresponding pyrrole should be isolated. The phosphine should be introduced by phosphorylation with *n*BuLi or a Grignard reaction.

2-Bromobenzaldehyde represents the starting material, which was converted with vinylmagnesiumbromide in THF at 0 °C to form 1-(2-bromophenyl)prop-2-en-1-ol **L3**. The product could be directly isolated upon quenching the reaction mixture with water followed by extraction with Et_2O, yielding 95% **L3** as a pale yellow liquid.

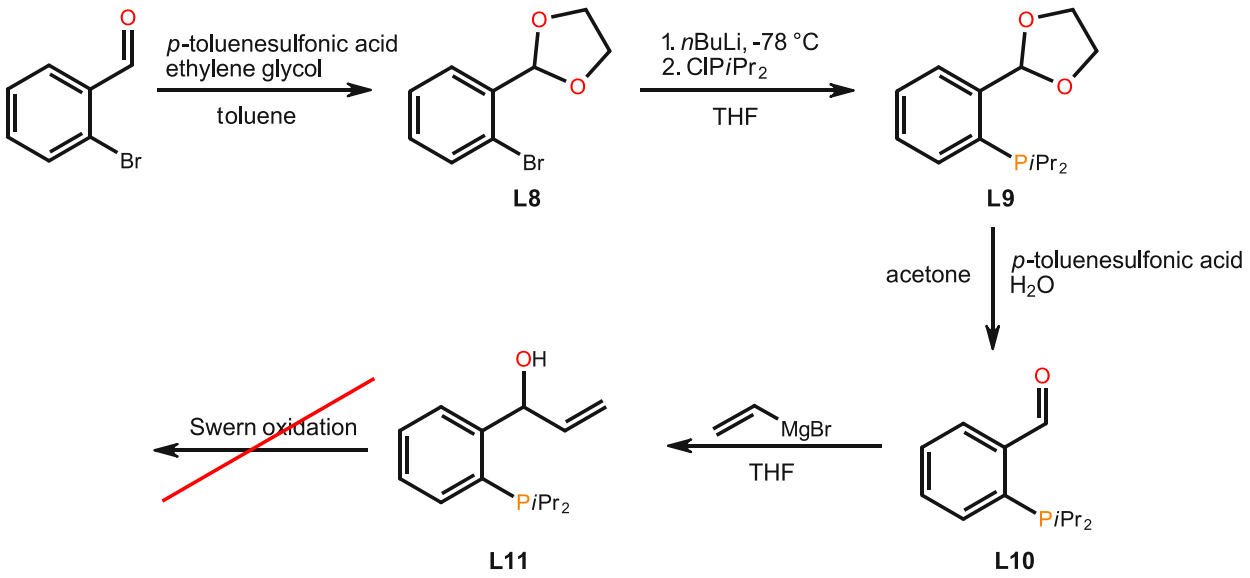
The ketone 1-(2-Bromophenyl)-2-propen-1-on **L4** could be obtained by Swern oxidation in 70%. It has to be mentioned, that a strict temperature/time protocol has to be used to achieve high yields. Furthermore, **L4** is light- and temperature sensitive and has to be stored in the freezer.

The 1,4-diktone could be obtained by a Stetter reaction. Thus 1,4-bis(2-bromophenyl)-1,4-butandione **L5** was afforded by stirring **L4** with 5-(2-hydroxyl)-2,3,4-trimethylthiazonium iodide and 2-bromobenzaldehyde in EtOH at 70 °C. Upon work up, **L5** was obtained as yellow oil in 81% yield. If the reaction is carried out in DMF as solvent, as reported in the literature, neither the reaction time is shorter nor the yield better.[112]

The next step was the formation of the pyrrole ring. This was achieved by cyclization of **L5** with NH_4OAc and two drops glacial acetic acid in EtOH at 80 °C for 18 hours. Pouring the reaction mixture on ice followed by extraction with EtOAc, gave the crude product as yellow oil. Purification by column chromatography afforded 2,5-bis(2-Bromphenyl)-1*H*-pyrrol **L6** as colorless oil, which was solidified upon storing in the freezer at -30 °C.

Prior to phosphorylation, the NH functionality had to be protected. A Boc group was introduced, by conversion of **L6** with Boc_2O and DMAP, as catalyst, in MeCN. After stirring for 3 hours at room temperature **L7** could be isolated as colorless solid with a yield of 94%. Interestingly protection attempts with silyl groups, such as TMS-Cl or TBDMS-Cl, resulted in no conversion.

Next, **7** was treated with 2.2 equivalent or 4.4 equivalents of *n*BuLi or *t*BuLi in THF at -78 °C. The addition of Cl*i*Pr_2 should provide **TL**. However, the desired compound was not formed. Another approach was the formation of Grignard reagent of **L7** followed by the addition of Cl*i*Pr_2. However, no tractable material could be isolated in all of the above mentioned cases.



Scheme 46. Second synthetic route.

Since the phosphorylation of **7** was not possible, it was planned to introduce the phosphine moiety at the beginning of the synthesis. Therefore a synthetic route, depicted in Scheme 46, was investigated, in which the building block **L4** would already contain the phosphine group.

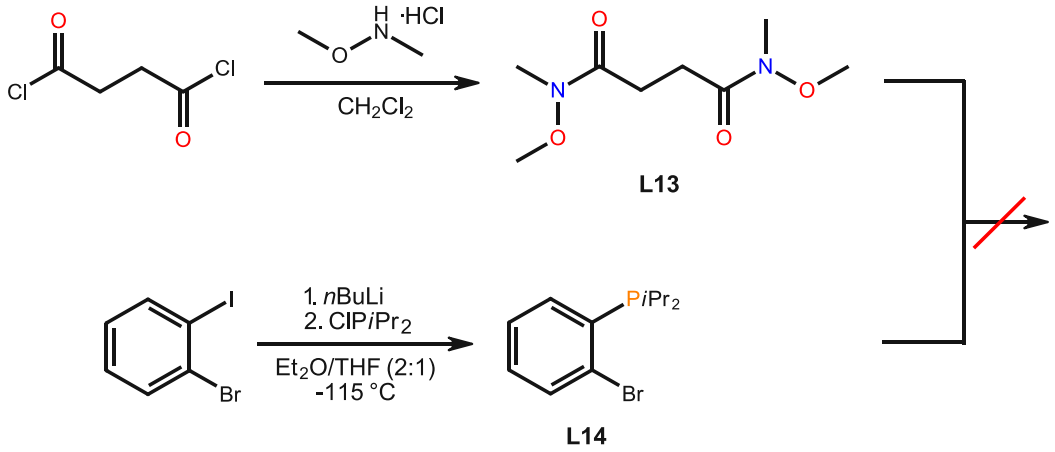
The first step was to protect the aldehyde with ethylene glycol. Therefore 2-bromobenzaldehyde was treated with *p*-toluenesulfonic acid and ethylene glycol. After work up, 2-(2-bromophenyl)-1,3-dioxolane **L8** was obtained as colorless liquid in 96% yield.

For phosphorylation, **L8** was lithiated with 1 equivalent of *n*BuLi at -78 °C in THF. Subsequent addition of Cl*P*i*P*r$_2$ afforded (2-diisopropylphosphinophenyl)-1,3-dioxolane **L9** in 88% yield.

In the following, **L9** was deprotected upon refluxing with a catalytic amount of *p*-toluenesulfonic acid and water in acetone. Therefore 2-(diisopropylphosphino)benzaldehyde **L10** was isolated as yellow crystals in 95% yield. In the next step, the conversion of **L10** with vinylmagnesiumbromide was achieved similar to the synthesis of **L3**. Hence 1-(2-diisopropylphosphinphenyl)prop-2-en-1-ol **L12** was afforded as pale yellow liquid in 97% yield.

The next step was the oxidation of the secondary alcohol to ketone by Swern oxidation. This was done similarly to the synthesis of **L4**. However, instead of the formation of the carbonyl the corresponding phosphine oxide was formed.

A completely different approach was to start from a 1,4-diketone building block. For this reason the following route was examined (Scheme 47).



Scheme 47. Synthesis *via* diketone building block.

In this route two different compounds were synthesized, which should be combined to the phosphorylated diketone of **L5**. In order to achieve the 1,4-diketone synthon, the Weinreb amide *N,N'*-dimethoxy-*N,N'*-dimethylsuccinamide **L13** was utilized. **L13** was obtained upon conversion of succinyl chloride with *N,O*-dimethylhydroxylaminhydrochloride and pyridine. **L13** was isolated in 88% yield as white solid.[113]

The second building block was (2-bromophenyl)diisopropylphosphine **L14**. This compound was obtained by lithiation of 1-iodo-2-bromobenzene with 1.03 equivalent *n*BuLi in a THF/Et_2O mixture at -115 °C. The addition of Cl*i*Pr_2 led to the formation of **L14** in an isolated yield of 90%. For this synthesis low temperature is crucial as well as the slow addition of *n*BuLi and Cl*i*Pr_2. If the temperature is above -100 °C and the addition of the reagents is too fast, benzyne radical is formed, which is indicated by a red coloring of the reaction mixture. The benzyne radical leads to the formation of undesired side products, which results in a significantly lower yield.[114]

Both building blocks could be synthesized in good yields. Unfortunately, the conversion to the corresponding phosphorylated diketone **L5** failed. It was intended to convert the corresponding Grignard reagent of **L14** with **L13**.Thus **L14** was treated with Mg in THF, resulted in a coloring of the solution. After refluxing for 3 hours, **L13** dissolved in THF was added dropwise at 0 °C. After work up a yellow oil was obtained. However, no tractable material could be isolated. Another approach was the lithiation of **L14** in THF with *n*BuLi at -78 °C followed by a dropwise addition to a THF solution of **L13**. Like in the case of the conversion with the Grignard reagent no product was formed.

3 Conclusion

In sum a set of new group IV metal complexes could be synthesized supported by a pyrrole-based PNP ligand (**L2**). For complexation the corresponding metal halide precursors MCl_4·2THF (M = Ti, Zr, Hf), $TiCl_3$·3THF and $TiBr_4$·2THF as well as the amido precursors $M(NMe_2)_4$ (M = Ti, Zr) and $Hf(NEt_2)_4$ were utilized.

Thus, [Ti(PNP-*i*Pr)Cl_3] **Ti1** and [Ti(PNP-*i*Pr)Br_3] **Ti2** could be isolated upon conversion of **L2** with TiX_4·2THF (X = Cl, Br) and TEA as base. In presence of ketones **Ti2** was converted to internal salts. Therefore [Ti(PNO)Cl_3-acetone] **Ti3** and Ti(PNO)Cl_3-cyclopentanone] **Ti4** were received by treatment of **Ti1** with acetone or cyclopentanone. When **L2** was treated with $Ti(NMe_2)_4$ in toluene [Ti(PNP-*i*Pr)$(NMe_2)_3$] **Ti6** could be isolated. If the reaction was carried out in CH_2Cl_2 and a second equivalent of $Ti(NMe_2)_4$ the dichloride species [Ti(PNP-*i*Pr)$(NMe_2)Cl_2$] **Ti7** was formed. The addition of TMS-Cl to **Ti6** and **Ti7** resulted in the formation of **Ti1**. The azide complex [Ti(PNP-*i*Pr)$(N_3)_3$] **Ti8** was afforded by addition of TMS-N_3 to **Ti6**.

When **L2** was reacted with MCl_4·2THF (M = Zr, Hf) the corresponding dinuclear complexes [M(PNP-*i*Pr)$Cl_2(\mu\text{-}Cl)_2]_2$ **Zr1** and **Hf1** were afforded. Further transformations were done by treatment with NaCp and TMS-I to give [M(PNP-*i*Pr)Cl_2(Cp)] **Zr2** and **Hf2** as well as iodide complexes [M(PNP-*i*Pr)I_3] **Zr3** and **Hf3**. Delightfully,**Zr3** and **Hf3** could be alkylated to [M(PNP-*i*Pr)Me_3] **Zr5** and **Hf5** by addition of MeMgBr. According to the synthesis of **6** the corresponding amido complexes [Zr(PNP-*i*Pr)$(NMe_2)_3$] **Zr4** and [Hf(PNP-*i*Pr)$(NEt_2)_3$] **Hf4** were afforded. Utilization of different TMS-X (X = I, N_3) reagents led to the formation of **Zr3** and **Hf3** as well as [M(PNP-*i*Pr)N_3] **Zr7** and **Hf7**. Instead of the expected tribromide the zirconate [Zr(PNP-*i*Pr)Br_4][H_2NMe_2] **Zr6** and [Hf(PNP-*i*Pr)Br_4][H_2NEt_2] **Hf6** were obtained upon treatment with TMS-Br.

Dinitrogen activation was conducted with selected complexes. Unfortunately, no N_2-ligated complexes could be observed. It is proposed that the ligand architecture is too rigid for this challenging transformation. Thus, it was attempted to synthesize **TL**, wherein the linkers are expanded by one carbon unit. Unfortunately, all attempts to synthesize **TL** were unsuccessful.

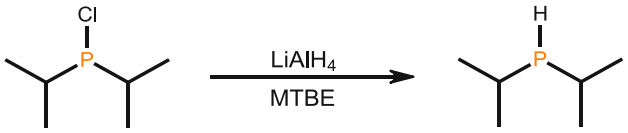
Although no N_2 activation was not possible with the chosen ligand system, this work introduced new strategies for the synthesis of group IV metal complexes including the synthesis of a rare example of a zirconate complex. Thus, this work contributes to gain further insights in the coordination chemistry of group IV complexes.

4 Experimental

General Information. All reactions were performed under inert atmosphere of argon using Schlenk techniques or in a MBraun inert-gas glovebox, unless otherwise noted. The solvents were purified according to standard procedures.[115] The deuterated solvents were purchased from Aldrich and dried over 3 Å molecular sieves. All starting materials are known compounds and were used they were purchased. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra were recorded on Bruker AVANCE-250, AVANCE-400 and AVANCE-600 spectrometers. ^{1}H and $^{13}C\{^{1}H\}$-NMR spectra were reference internally to residual portio-solvent and solvent resonance, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). $^{31}P\{^{1}H\}$-NMR spectra were referenced externally to H_3PO_4 (85%) (δ = 0 ppm). Single crystals suitable for X-Ray analysis were measured on a Bruker SMART-CCD area diffractometer system with a Mo-K α-radiation and a graphite monochromator. The data were processed with the SADABS[116] algorithm and the crystale stuctures were solved and refined with SHELXTL software suite.[117] All calculations were performed with the BP86 approach to density functional theory (DFT), the def2-SVP basis set for the light atoms C,P,N,H and the def2-TZVP basis set for Titanium.

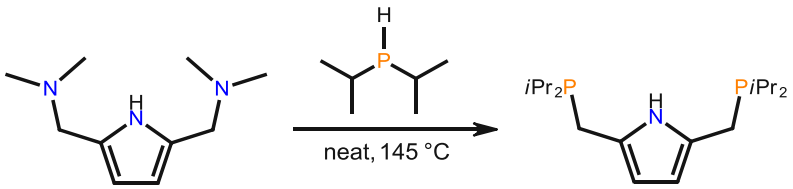
4.1 Synthesis of PNP-*i*Pr

Diisopropylphosphine (L1)



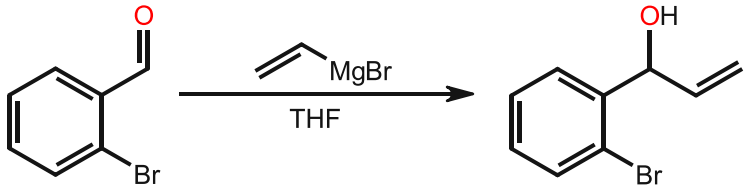
To a suspension of $LiAlH_4$ (700 mg, 124 mmol, 0.5 equiv.) in MTBE (50 mL) Cl*i*Pr$_2$ (6.00 mL, 38 mmol) was added dropwise over a period of 5 minutes at 0 °C. The solution was stirred for 20 minutes at rt. Upon filtration of the solid the solvent was distilled off. Distillation of the crude product (b.p.: 119 °C, 1 bar) yielded the product as colorless liquid (3.22 g, 72%). ^{1}H NMR (250 MHz, C_6D_6, 25 °C) δ = δ 3.27 (t, *J* = 6.0 Hz, 0.5H, PH), 2.50 (t, *J* = 6.0 Hz, 0.5H, PH), 1.91 – 1.66 (m, 2H, C*H*CH$_3$), 1.09 – 0.91 (m, 12H,, CHC*H$_3$*). $^{13}C\{^{1}H\}$ NMR (63 MHz, C_6D_6, 25 °C) δ = 23.5 (d, *J* = 6.4 Hz), 22.4 (d, *J* = 20.4 Hz), 21.1 (d, *J* = 9.6 Hz).$^{31}P\{^{1}H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ = -16.5.[118]

PNP-*i*Pr$_2$ (L2)



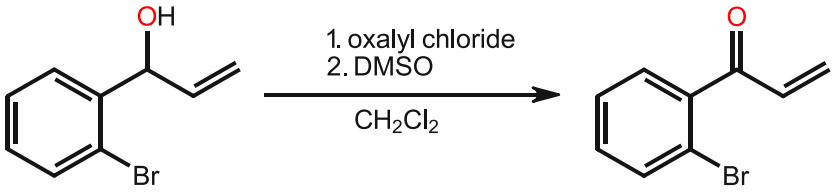
A mixture of **L1** (1.17 g, 9.90 mmol, 2.3 equiv.) and 2,5-bis(dimethylaminomethylene)pyrrole (780 mg, 4.3 mmol) was placed in a capped microwave vial (20 mL) and stirred for 2 d at 145 °C. The reaction mixture was allowed to cool to rt and the crude product was filtered through a pad of silica gel. The pad was rinsed with *n*-pentane (4 mL). The solvent was evaporated to yield the product as orange oil (1.16 g, 76%). ^{1}H NMR (250 MHz, C_6D_6, 25 °C) δ = 6.00 (d, *J* = 2.7 Hz, 2H, Pyr^{3,5}), 2.57 (s, 4H, CH_2), 1.66 – 1.45 (m, 4H, C*H*CH$_3$), 1.05 – 0.84 (m, 24H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (63 MHz, C_6D_6, 25 °C) δ = 135.7 (d, *J* = 20.8 Hz, C_q, Pyr^{2,5}), 107.7 (d, *J* = 5.0 Hz, Pyr^{3,4}), 24.3 (d, *J* = 14.9 Hz, CH_2), 20.5 (d, *J* = 14.6 Hz, *C*HCH$_3$), 19.6 (d, *J* = 10.8 Hz, CH*C*H$_3$). ^{31}P{^{1}H} NMR (101 MHz, C_6D_6, 25 °C) δ = 0.4.[119]

1-(2-Bromophenyl)prop-2-en-1-ol (L3)



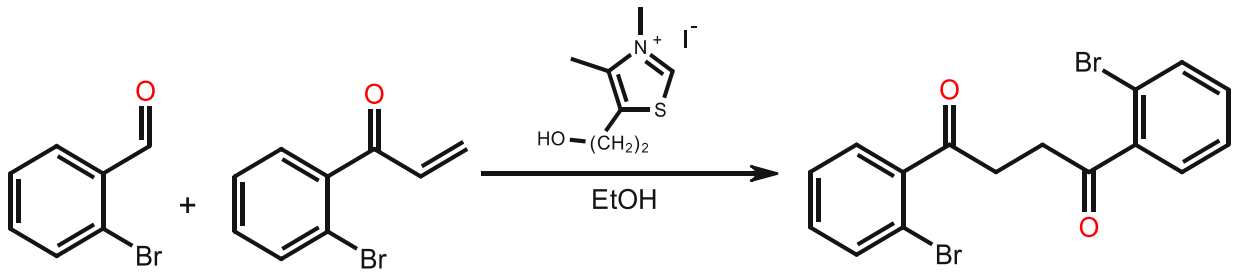
A solution of 2-bromobenzaldehyde (7.0 g, 37.8 mmol) in THF was treated with vinylmagnesiumbromide (45.40 mL, 1 M in THF, 45.40 mmol, 1.2 equiv.) at 0 °C within 5 minutes. Then the reaction mixture was stirred for 3 h at rt. After adding a saturated NH_4Cl solution (60 mL), the product was extracted with Et_2O (4 x 40 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was isolated as pale yellow liquid. (7.66 g, 95%).^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C) δ = 7.55 (ddd, *J* = 9.3, 7.9, 1.5 Hz, 2H), 7.36 (td, *J* = 7.4, 0.9 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.3, 1.8 Hz, 1H), 6.03 (ddd, *J* = 17.2, 10.4, 5.4 Hz, 1H), 5.60 (d, *J* = 5.4 Hz, 1H), 5.39 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.23 (dt, *J* = 10.4, 1.4 Hz, 1H), 2.48 (s, 1H, OH).^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2 20 °C) δ = 142.5, 139.4, 133.5, 129.9, 128.7, 128.6, 123.2, 116.0, 74.1.

1-(2-Bromophenyl)-2-propen-1-one (L4)



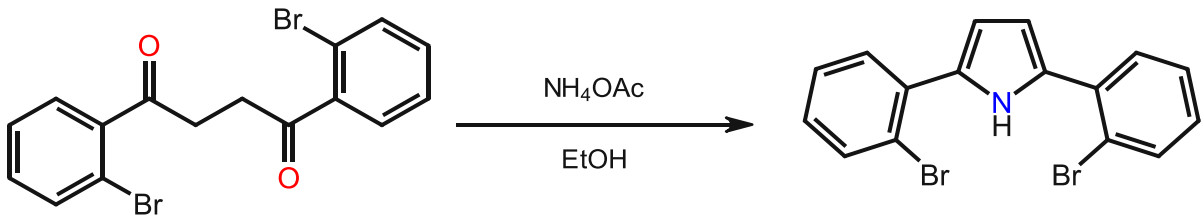
A solution of oxalyl chloride (3.1 mL, 36 mmol, 1.1 equiv.) in CH_2Cl_2 was treated dropwise with DMSO (5.13 mL, 72 mmol, 2.2 equiv.) in CH_2Cl_2 (30 mL) within 15 minutes. **L3** (7.0 g, 33 mmol) in DCM (55 mL) was added in a period of 15 minutes. During the addition a white precipitate was formed. The reaction mixture was stirred 40 minutes at -65 °C until the gas evolve ended. Then TEA (20 mL) was added and the reaction mixture was allowed to reach rt. Upon adding H_2O (250 mL) the reaction mixture was extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were dried over Na_2SO_2 and the solvent was removed. The crude product was purified by silica gel chromatography (120 g, CH_2Cl_2/PE 1:2, R_f = 0.3) yielding the product as colorless oil (4.85 g, 70%). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C) δ = 7.70 – 7.56 (m, 1H), 7.53 – 7.23 (m, 3H), 6.72 (dd, *J* = 17.5, 10.6 Hz, 1H), 6.18 – 5.96 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 20 °C) δ = 195.7, 141.0, 136.9, 134.2, 133.2, 132.3, 129.9, 128.1, 120.0.

1,4-Bis(2-bromophenyl)-1,4-butandione (L5)



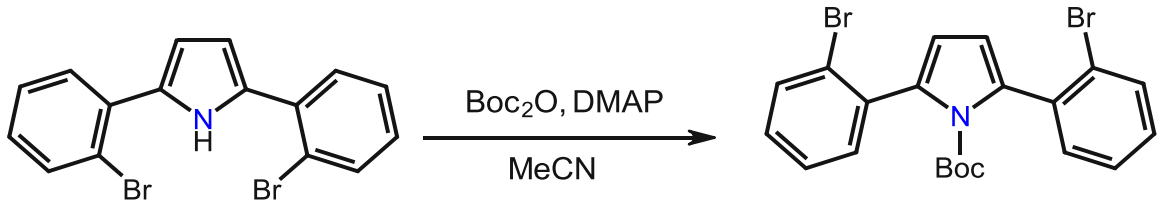
A solution of 5-(2-hydroxyl)-2,3,4-trimethylthiazonium iodide (1.31 g, 4.6 mmol, 0.2 equiv.), 2-bromobenzaldehyde (5.10 g, 28 mmol, 1.2 equiv.) **L4** (4.85 g, 23 mmol, 1.2 equiv.) and TEA (0.465 mL, 4.6 mmol, 0.2 equiv.) in EtOH (20 mL) were stirred for 12 h at 70 °C. After cooling the reaction mixture to rt the solution was treated with H_2O (40 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by silica gel chromatography (PE/EE 9:1, R_f = 0.14) yielding a yellow oil (8.91 g, 81%).[120]

2,5-Bis(2-brompphenyl)-1*H*-pyrrole (L6)



A solution of **L5** (4.00 g, 10.1 mmol) in EtOH (20 mL) and NH_4OAc (3.27 g, 42.4 mmol, 4.2 equiv.) and glacial acetic acid (2 drops) were refluxed for 18 h. The reaction mixture was poured on ice and extracted with EtOAC (3 x 40 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by silica gel chromatography (CH_2Cl_2/PE 1:2, R_f =0.3) forming a colorless oil which was put in the freezer at -30 °C overnight. The product was obtained as white solid (2.94 g, 78%). ^{1}H NMR (600 MHz, CD_2Cl_2, 20 °C) δ = 9.72 (s, 1H, NH), 7.67 (dd, *J* = 8.1, 1.3 Hz, 2H, Ph^3), 7.60 (dd, *J* = 7.8, 1.7 Hz, 2H, Ph^6), 7.38 (ddd, *J* = 7.8, 7.3, 1.3 Hz, 2H, Ph^4), 7.15 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 2H, Ph^5), 6.67 (d, *J* = 2.7 Hz, 2H, $Pyr^{3,4}$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 20 °C) δ = 134.9, 133.6 (C_q), 131.8 (C_q), 130.9, 128.9, 128.6, 120.5 (C_q), 111.4 ($Pyr^{3,4}$).

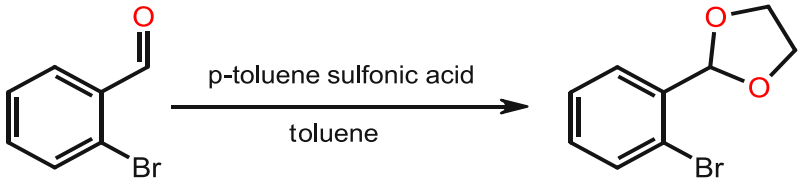
2,5-Bis(2-bromophenyl)-1-Boc-pyrrole (L7)



To a solution of **L6** (0.380 g, 1.01 mmol) and DMAP (0.0185 g, 0.15 mmol, 0.15 equiv.) in MeCN (10 mL) Boc_2O (0.259 mL, 1.21 mmol, 1.2 equiv.) was added at rt resulting in an orange color change. After three hours the reaction was complete (TLC: CH_2Cl_2/PE 1:2, R_f = 0.3). Upon evaporation of the solvent the residue was redissolved in CH_2Cl_2 (20 mL) and 1N HCl (25 mL) was added to. After separation of the phases, the aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (2 x 40 mL), dried over Na_2SO_4 and the solvent was evaporated. After solidification by storing the orange oil at -30 °C in a freezer the product was obtained as pale orange solid (0.450 g, 94%). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C)δ = 7.62 (ddd, *J* = 8.0, 1.2, 0.4 Hz, 2H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 7.38 (td, *J* = 7.4, 1.2 Hz, 2H), 7.25 (ddd, *J* =

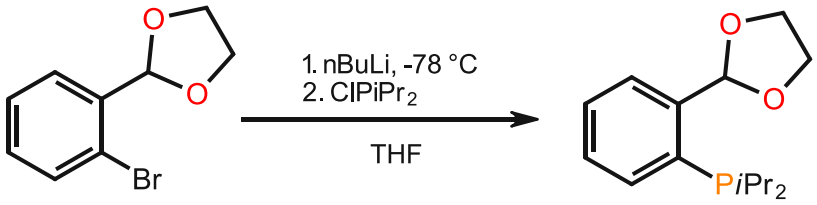
8.0, 7.3, 1.9 Hz, 2H), 6.21 (s, 2H, Pyr^{3,4}), 1.11 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C) δ = 149.2, 137.5, 134.8, 132.8, 132.4, 129.9, 127.8, 126.0, 84.1, 27.7.

2-(2-Bromophenyl)-1,3-dioxolane (L8)



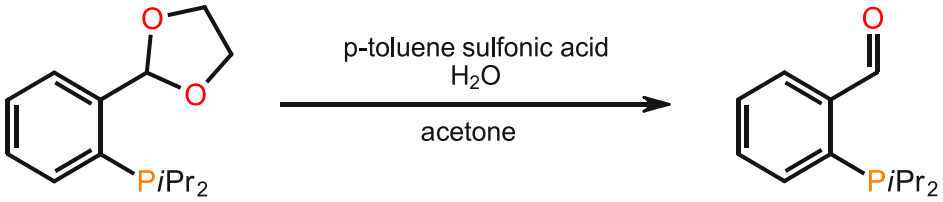
A 10 mL Dean-Stark apparatus was charged with 2-bromobenzaldehyde (10 g, 54 mmol), *p*-toluene sulfonic acid (0.206 g, 1.08 mmol, 2 mol%), ethylene glycol (3.80 mL, 67.6 mmol, 1.25 equiv.) and toluene (50 mL). The mixture was refluxed for 12 h under continuous removal of water. The reaction mixture was allowed to reach rt. Upon addition of aqueous NaOH solution (10%, 40 mL) the phases were separated and the aqueous phase was extracted with toluene (2 x 20 mL). The combined organic layers were dried over Na_2SO_4. After evaporation of the solvent the product was obtained as colorless oil yielding (11.87 g, 96%)[121]

(2-Diisopropylphosphinophenyl)-1,3-dioxolane (L9)



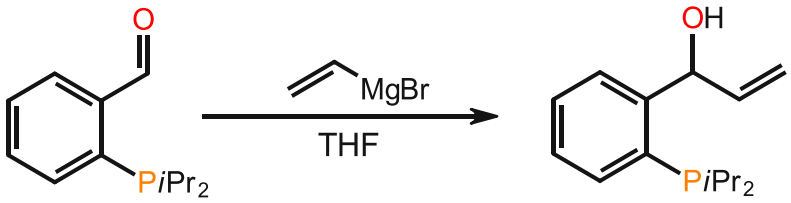
To a solution of 2-(2-bromophenyl)-1,3-dioxolane **L8** (5 g, 21.83 mmol) in THF (50 mL) *n*BuLi (13.6 mL, 1.6 M in *n*-hexane, 21.83 mmol) was added dropwise at -78 °C. Upon stirring for one hour Cl*i*Pr$_2$ (3.5 mL, 21.83 mmol) was added. The reaction mixture was allowed to reach rt. After stirring for 2 h the solvent was removed under vacuum. The sticky white residue was redissolved in Et_2O (40 mL) and degassed water (20 mL) was added. After phase separation, the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The product was obtained as colorless solid (5.11 g, 88%).[121]

2-(Diisopropylphosphino)benzaldehyde (L10)



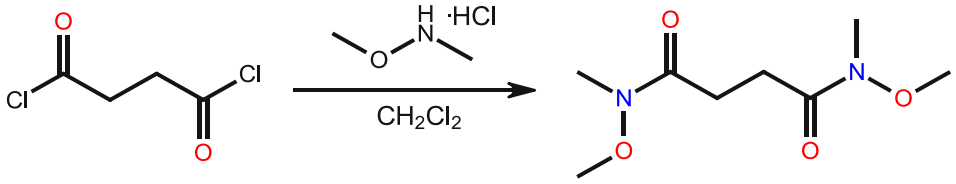
A solution of **L9** (5.11 g, 19.21 mmol), *p*-toluene sulfonic acid (0.330 g, 1.92 mmol, 0.1 equiv.) and degassed H_2O (20 mL) in acetone (100 mL) was refluxed for 12 h under Ar-atmosphere. The reaction mixture was allowed to reach rt and all volatiles were evaporated. Followed by addition of toluene (30 mL) and degassed H_2O (30 mL). After stirring for 30 minutes, the organic layer was separated and the aqueous layer was extracted with toluene (2 x 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under vacuum giving a bright yellow oil which was solidified kept at -30 °C. Recrystallization of the crude product with Et_2O afforded yellow crystals (4.05 g, 95%).[122]

1-(2-Diisopropylphosphinphenyl)prop-2-en-1-ol (L12)



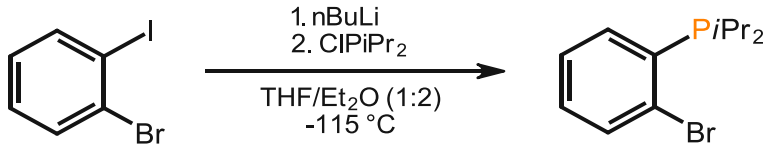
A solution of **L10** (4.05 g, 18.22 mmol) in THF (60 mL) was treated with vinylmagnesiumbromide (18.22 mL, 1 M in THF, 21.87 mmol, 1.2 equiv.) at 0 °C within 5 minutes. After stirring for 3 h at rt a saturated NH_4Cl solution (30 mL) was added. The crude product was extracted with Et_2O (4 x 50 mL). The combined organic layers were dried over Na_2SO_4. Upon evaporation of the solvent giving the product as pale yellow liquid (4.42 g, 97%). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C) δ = 7.43 – 7.33 (m, 2H, Ph), 7.27 (tdd, *J* = 7.7, 1.5, 0.6 Hz, 1H, Ph), 7.19 (td, *J* = 7.4, 1.5 Hz, 1H, Ph), 6.09 – 5.95 (m, 1H, C*H*-OH), 5.30 – 5.21 (m, 1H, C*H*=CH_2), 5.12 – 5.04 (m, 2H, C*H*=CH_2), 2.64 (s, 1H, O*H*), 2.12 – 1.92 (m, 2H, C*H*CH_3), 1.06 (ddd, *J* = 15.1, 10.5, 7.0 Hz, 6H, CHC*H*$_3$), 0.80 (ddd, *J* = 12.1, 7.0, 3.8 Hz, 6H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 20 °C) δ = 150.5 (d, *J* = 22.3 Hz), 141.6, 134.8 (d, *J* = 19.9 Hz), 133.5 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 1.1 Hz), 127.8, 114.7 (d, *J* = 1.3 Hz), 73.2 (d, *J* = 24.5 Hz), 25.3 (t, *J* = 11.9 Hz), 21.0 (dd, *J* = 19.0, 7.3 Hz), 20.3 (dd, *J* = 10.3, 8.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 20 °C) δ = -7.6.

_N,N'_-Dimethoxy-_N,N'_-dimethylsuccinamide (L13)



A solution of *N,O*-dimethylhydroxylaminhydrochloride (13.2 g, 136 mmol, 2.1 equiv.) and succinyl chloride (10 g, 65 mmol) in CH_2Cl_2 (300 mL) were treated with pyridine (22.90 mL, 284 mmol, 4.4 equiv.) at 0 °C. During the addition a precipitate was formed and the solution becomes pale rosa. The reaction mixture was allowed to reach rt. After stirring for 12 h the reaction mixture was treated with a saturated $NaHCO_3$ solution (100 mL) resulting in a dissolving of the precipitate. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 60 mL). The combined organic layers were washed with 1N HCl (2 x 130 mL) and dried over Na_2SO_4. After evaporation of the solvent the product was obtained as colorless solid (11.60 g, 88%). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C) δ = 3.72 (s, 6H, OCH_3), 3.15 (s, 6H, NCH_3), 2.72 (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C) δ = 174.1 (C_q), 61.9 (CH_3O), 32.8 (CH_3N), 27.1 (CH_2).[113]

(2-Bromophenyl)diisopropylphosphine (L14)

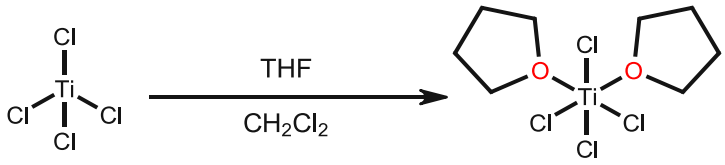


To a solution of 1-iod-2-bromobenzene (3.00 g, 10.6 mmol) in THF/Et_2O (45 mL, 1:2) *n*BuLi (6.83 mL, 1.6 M in *n*-hexane, 10.9 mmol, 1.03 equiv.) was added dropwise at -115 °C within 90 minutes. During addition a white precipitate was formed and the suspension becomes peach colored. After complete addition the reaction mixture was treated dropwise with Cl*i*Pr$_2$ (1.77 mL, 11.1 mmol, 1.05 equiv.) within 45 minutes. During addition of Cl*i*Pr$_2$ the color of the suspension has to stay peach colored. After addition was completed, the reaction mixture was allowed to reach rt and stirred for 12 h. The solvent was evaporated and the white residue was treated with toluene (40 mL) and filtered over a pad of silica gel. Upon evaporation of the solvent the product was obtained as colorless viscous oil (2.61 g, 90%).^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ =: 7.45 (ddd, *J* = 8.0, 3.1, 1.3 Hz, 1H), 7.11 (dt, *J* = 7.6, 1.4 Hz, 2H), 6.92 (td, *J* = 7.4, 1.3 Hz, 1H), 6.73 (td, *J* = 7.6, 1.7 Hz, 1H), 1.89 (p, *J* = 7.0 Hz, 2H, C*H*CH_3), 1.07 (dd, *J*

= 14.2, 7.0 Hz, 6H, CHC*H*$_3$), 0.87 (dd, *J* = 11.9, 7.0 Hz, 6H, CHC*H*$_3$).^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 20 °C) δ = 138.6 (d, *J* = 22.7 Hz, C_q), 134.8, 134.3 (d, *J* = 32.2 Hz, C_q), 134.2 (d, *J* = 3.1 Hz), 130.8, 127.3, 25.0 (d, *J* = 16.0 Hz, *C*HCH$_3$), 20.6 (d, *J* = 18.8 Hz, CH*C*H$_3$), 20.1 (d, *J* = 11.7 Hz, CH*C*H$_3$).^{31}P{^{1}H} NMR (162 MHz, C_6D_6,20 °C) δ = 8.9.[114]

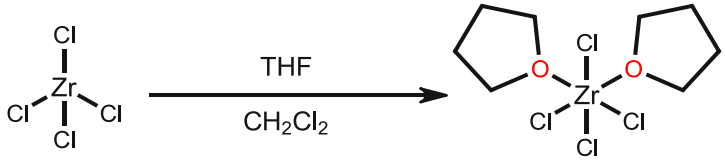
4.2 Synthesis of Group IV Precursor

$TiCl_4$·2THF



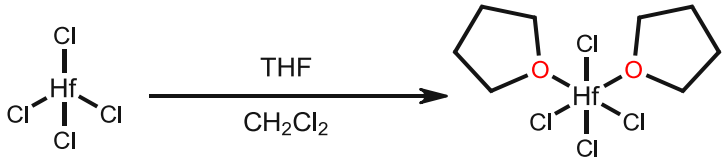
A solution of $TiCl_4$ (5 g, 26.4 mmol) in CH_2Cl_2 (40 mL) was treated with THF (8.11 mL, 100 mmol, 3.8 equiv.) at 0 °C. During the addition a yellow precipitate was formed. After stirring for 15 minutes, *n*-pentane (20 mL) was added and the suspension was stored in a freezer at -30 °C for 1 h. The solvent was decanted and the yellow residue was washed with *n*-pentane (20 mL). The product was obtained as yellow powder (7.70 g, 86%).[123]

$ZrCl_4$·2THF



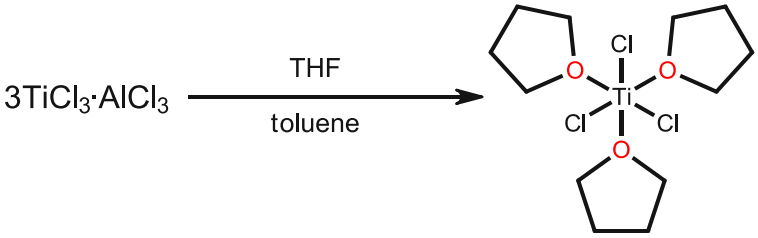
To a suspension of $ZrCl_4$ (5 g, 21.4 mmol) in CH_2Cl_2 (40 mL) THF (6.60 mL, 81.5 mmol, 3.3 equiv.) was added at 0 °C. After stirring the suspension for 3 d the solvent was decanted and washed with *n*-pentane (20 mL). The product was isolated as white powder (7.28 g, 90%).[123]

$HfCl_4$·2THF



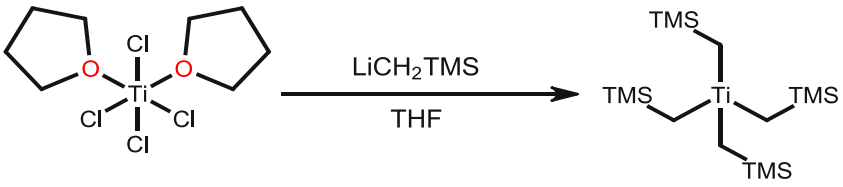
This precursor was prepared analogously to **23** and **24** with $HfCl_4$ (5 g, 15.6 mmol) and THF (4.80 mL, 59.3 mmol, 3.8 equiv.) yielding the product as white powder (6.30 g, 87%).

$TiCl_3$·3THF



A red suspension of $3TiCl_3 \cdot AlCl_3$ (2 g, 10 mmol) in toluene (5 mL) was treated with THF (20 mL). During the addition the suspension became turquoise. After stirring for 12 h at 80° C the solvent was decanted and washed with *n*-pentane (2 x 15 mL). The product was obtained as blue powder (2.58 g, 68%). $\mu_{eff} = 1.8$ (1) μ_B[124]

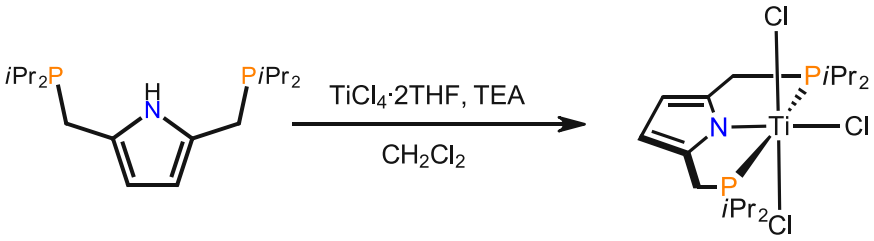
$Ti(CH_2TMS)_4$



A solution of $TiCl_4 \cdot 2THF$ (205 mg, 0.6 mmol) in toluene (5 mL) was treated with $LiCH_2TMS$ (2.46 mL, 1 M in THF, 2.50 mmol, 4 equiv.) at -78 °C under light exclusion. During the addition the solid dissolved completely and the solution became green. After stirring for 2 h at -78 °C the solution was orange and was allowed to reach rt. Upon stirring for 4 h the reaction mixture was filtered through a syringe filter (PTFE, 0.2 µm) and the solvent was evaporated. The product was obtained as an orange oil (159 mg, 62%)[125]

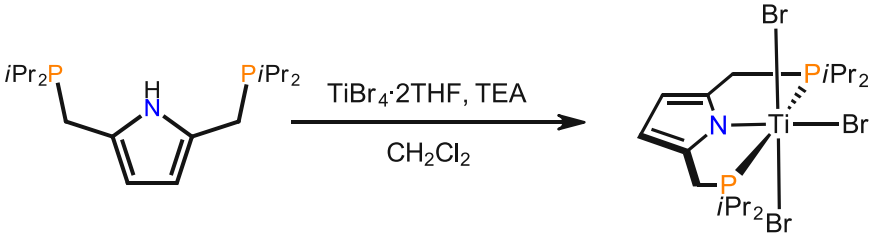
4.3 Synthesis of Ti PNP Pincer complexes

[Ti(PNP-*i*Pr)Cl$_3$] (Ti1)



A solution with PNP-Pyrrole **L2** (200 mg, 0.61 mmol) and TEA (12.7 mL, 0.61 mmol) in CH_2Cl_2 (5 mL) was treated with $TiCl_4$·2THF (0.204 g, 0.61 mmol). The solution immediately becomes dark reddish. Upon stirring for 10 minutes all volatiles were evaporated. The residue was taken up in toluene (10 mL) and filtered through a pad of celite® and all volatiles were removed under reduced pressure. Upon washing of the oily brown residue with *n*-pentane (2 x 10 mL) the product was obtained as dark red powder (236 mg, 80%). Single crystals for X-ray diffraction measurement could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ = 5.69 (s, 2H, Pyr^{3,4}), 3.38 – 3.33 (m, 4H, CH_2), 2.58 – 2.31 (m, 4H, C*H*CH$_3$), 1.45 – 1.16 (m, 24H, CHC*H$_3$*). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25 °C) δ = 141.3 (t, *J* = 6.2 Hz, C_q, Pyr^{2,5}), 105.6 (t, *J* = 4.2 Hz, Pyr^{3,4}), 27.7 (t, *J* = 6.3 Hz, *C*HCH$_3$), 27.2 (dd, *J* = 10.8, 9.4 Hz, CH_2), 27.2 (d, *J* = 9.4 Hz, CH_2), 19.4 (CH*C*H$_3$), 19.2 (CH*C*H$_3$). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 25 °C) δ = 81.4.

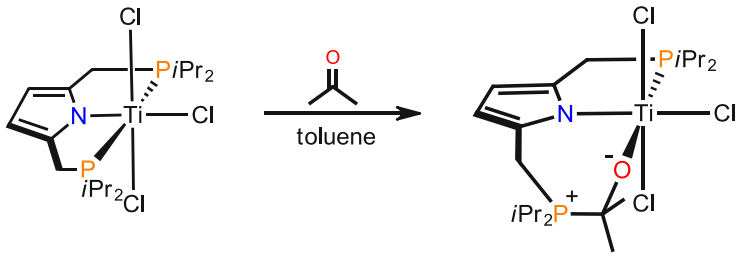
[Ti(PNP-*i*Pr)Br$_3$] (Ti2)



To a solution of PNP-Pyrrole **L2** (200 mg, 0.61 mmol) and TEA (12.7 mL, 0.61 mmol) in CH_2Cl_2 (5 mL) $TiBr_4$·2THF (312 mg, 0.61 mmol) was added, resulting in a dark red colored solution. After stirring for 10 minutes all volatiles were evaporated. The residue was taken up in toluene (10 mL) and filtered through a pad celite® and all volatiles were removed under reduced pressure. Upon washing with *n*-pentane (2 x 10 mL) the product was obtained as orange powder (300 mg, 80%). Single crystals for X-ray diffraction measurement could be obtained

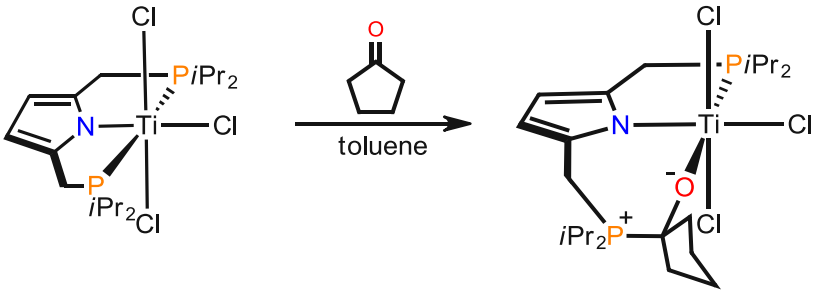
by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ = 5.72 (s, 2H, Pyr^{3,4}), 3.41 – 3.35 (m, 4H, CH_2), 2.62 – 2.36 (m, 4H, C*H*CH$_3$), 1.46 – 1.15 (m, 24H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25 °C) δ = 143.2 (C_q, Pyr^{2,5}), 106.6 (t, *J* = 4.1 Hz, Pyr^{3,4}), 29.0 (*C*HCH$_3$), 28.2 (CH_2), 20.0 (CH*C*H$_3$), 19.8 (CH*C*H$_3$). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 25 °C) δ = 88.7.

[Ti(PNO-*i*Pr)Cl$_3$] (Ti3)



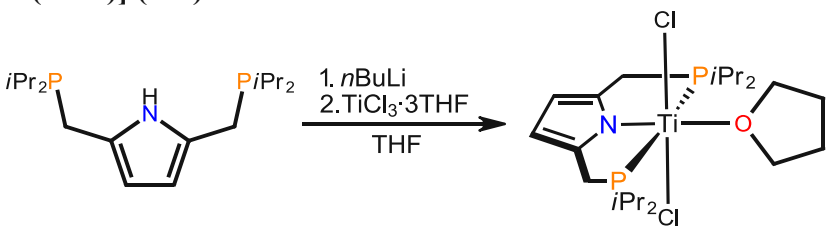
[Ti[PNP-*i*Pr)Cl$_3$] **Ti1** (100 mg, 0.21 mmol) was dissolved in toluene (5 mL) and acetone (15.3 µL, 0.21 mmol) was added. Upon stirring for 10 minutes all volatiles were evaporated. The residue was washed with *n*-pentane yielding the product as pale red powder (110 mg, 97%). Single crystals for X-Ray diffraction measurement could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ = 5.82 (bs, 1H, Pyr^{3,4}), 5.67 (bs, 1H, Pyr^{3,4}), 4.18 (bs, 1H, CH_2), 3.88 (bs, 1H, CH_2), 3.21 (d, *J* = 7.2 Hz, 2H, CH_2), 2.81 – 2.61 (m, 3H, C*H*CH$_3$), 2.56 – 2.40 (m, 1H, C*H*CH$_3$), 1.88 (s, 3H, C*H*$_3$CC*H*$_3$), 1.86 (s, 3H, C*H*$_3$CC*H*$_3$), 1.47 – 1.42 (m, 12 H, C*H*$_3$CHC*H*$_3$), 1.33 – 1.28 (m, 12H, C*H*$_3$CHC*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25 °C) δ = 141.0 (dd, *J* = 7.8, 3.7 Hz, Pyr^{2,5}), 125.4 (dd, *J* = 10.7, 2.8 Hz, Pyr^{2,5}), 111.6 (d, *J* = 8.5 Hz, Pyr^{3,4}), 103.3 (dd, *J* = 6.9, 2.8 Hz, Pyr^{3,4}), 88.6 (dd, *J* = 46.3, 8.8 Hz, CH$_3$*C*CH$_3$), 28.6 (d, *J* = 5.1 Hz, *C*H$_3$C*C*H$_3$), 26.8 (d, *J* = 17.3 Hz, CH_2P), 26.0 (d, *J* = 8.4 Hz, *C*HP$^+$), 22.7 (d, *J* = 32.8 Hz, *C*HP), 19.8 *C*H$_3$CHCH$_3$, CH_2P^+), 18.0 (d, *J* = 3.8 Hz, *C*H$_3$CH*C*H$_3$, CH_2P^+), 17.5 (vd, *J* = 3.6 Hz, *C*H$_3$CH*C*H$_3$, CH_2P^+) ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 25 °C) δ = 40.9, 35.2.

[Ti(PNO-*i*Pr)Cl$_3$] (Ti4)



This complex was prepared analogously to **Ti3** with cyclopentanone (18.4 µL, 0.21 mmol) yielding a pale red powder (116 mg, 97%).Single crystals for X-Ray measurements could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C) δ = 5.77 (s, 1H, Pyr^{3,4}), 5.64 (s, 1H, Pyr^{3,4}), 4.11 (bs, 1H, CH_2), 3.19 (d, *J* = 7.6 Hz, 1H, CH_2), 2.87 (d, *J* = 10.5 Hz, 2H, CH_2), 2.78 – 2.61 (m, 2H, CH_3CHCH_3), 2.54 – 2.45 (m, 2H, CH_3CHCH_3), 2.32 (bs, 2H,$CCH_2CH_2CH_2CH_2$), 2.12 (bs, 2H, $CCH_2CH_2CH_2CH_2$), 1.94 (bs, 2H, $CCH_2CH_2CH_2CH_2$), 1.88 (bs, 2H, $CCH_2CH_2CH_2CH_2$), 1.56 – 1.18 (m, 24H, CH_3CHCH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 141.2 (dd, *J* = 8.2, 3.9 Hz, Pyr^{2,5}), 126.4 (d, *J* = 11.6 Hz, Pyr^{2,5}), 111.8 (d, *J* = 8.5 Hz, Pyr^{3,4}), 103.3 (dd, *J* = 7.1, 2.5 Hz, Pyr^{3,4}), 98.2 (dd, *J* = 48.3, 8.3 Hz, CH_2CCH_2), 39.0 ($CCH_2CH_2CH_2CH_2$), 26.4 (d, *J* = 17.4 Hz, CH_2), 25.9 (d, *J* = 8.7 Hz, CH_3CCH_3), 24.0 ($CCH_2CH_2CH_2CH_2$), 23.9 ($CCH_2CH_2CH_2CH_2$), 23.7 ($CCH_2CH_2CH_2CH_2$), 23.4 ($CCH_2CH_2CH_2CH_2$, CH_3CCH_3) , 23.0 ($CCH_2CH_2CH_2CH_2$), 19.8 (d, *J* = 11.4 Hz, $CHCH_3$), 18.0 (d, *J* = 3.7 Hz, $CHCH_3$), 17.7 (d, *J* = 3.5 Hz, $CHCH_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 20 °C) δ = 35.4, 31.8.

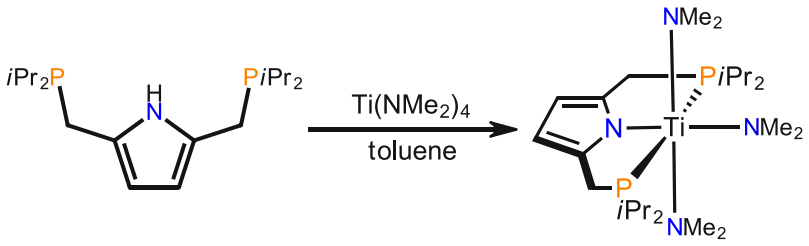
[Ti(PNP-*i*Pr)Cl$_2$(THF)] (Ti5)



A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) in THF (8 mL) was treated with *n*BuLi (0.382 mL, 1.6 M in hexane, 0.61 mmol) at -78 °C. Upon stirring for 30 minutes at this temperature and 30 minutes at rt $TiCl_3$·3THF (204 mg, 0.54 mmol, 0.9 eq) was added. The reaction mixture was stirred for 12 h at rt. All volatiles were removed under reduced pressure. The residue was resolved in toluene (5 mL) and filtered through a pad of celite® upon evaporation of the solvent. By washing the residue with *n*-pentane (2 x 10 mL) the product was obtained as pink powder (210 mg, 65%). Single crystals for X-ray diffraction measurement

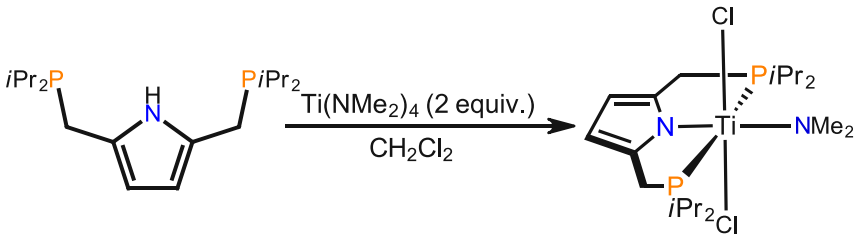
could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. μ_{eff} = 1.8(1) μ_B(CH_2Cl_2, Evans method)

[Ti(PNP-*i*Pr)(NMe$_2$)$_3$] (Ti6)



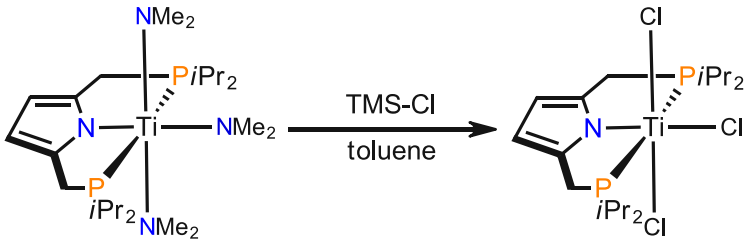
A solution of PNP-*i*Pr **L2** (100 mg, 0.31 mmol) and $Ti(NMe_2)_4$ (71 µL, 0.31 mmol) in toluene (4 mL) was stirred for 2 d at 80 °C. By removing all volatiles under reduced pressure, the product was obtained as red oil as a mixture of κ^2 and κ^3 coordinated complex. For clarity only κ^3 coordinated signals are given. ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ = 6.42 (s, 2H, Pyr^{3,4}), 3.14 (s, 18H, NCH_3), 2.82 – 2.77 (m, 4H, CH_2) 1.90 – 1.64 (m, 4H, C*H*CH_3), 1.08 (dd, *J* = 7.1, 3.6 Hz, 12H, CHC*H*$_3$), 1.05 (dd, *J* = 7.1, 2.3 Hz, 12H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C) δ = 136.7 (d, *J* = 12.4 Hz, C_q, Pyr^{2,5}), 107.7 (d, *J* = 4.9 Hz, Pyr^{3,4}), 44.6 (CH_3), 24.8 (d, *J* = 11.7 Hz, CH_2), 24.3 (d, *J* = 14.8 Hz, *C*HCH_3), 20.4 (d, *J* = 14.8 Hz, CH*C*H$_3$), 19.5 (d, *J* = 10.6 Hz, CH*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C) δ = 6.2, 0.4.

[Ti(PNP-*i*Pr)(NMe)Cl$_2$] (Ti7)



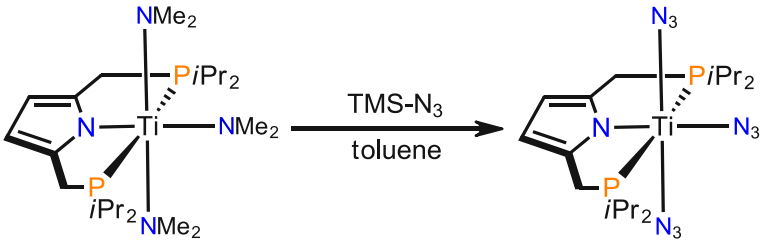
A solution of PNP-*i*Pr **L2** (100 mg, 0.31 mmol) and $Ti(NMe_2)_4$ (142 µL, 0.62 mmol, 2 equiv.) in CH_2Cl_2 (5 mL) was stirred for 12 h at rt. After removing all volatiles under reduced pressure the product was obtained as brown solid (140 mg, 92%). Single crystals for X-ray diffraction measurement could be obtained by storing a saturated *n*-pentane solution kept at -20 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 6.40 (Pyr^{3,4}) 3.13 – 3.04 (m, 4H, CH_2), 2.50 (s, 6H, NC*H*$_3$), 1.88-1.60 (m, 4H, C*H*CH_3), 1.45 – 1.15 (m, 24H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 135.2 (Pyr^{2,5}), 105.9 (Pyr^{3,4}), 44.5 (CH_3), 24.8 (CH_2), 20.2 (CH*C*H$_3$), 18.4 (CH*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C) δ = 54.0.

[Ti(PNP-*i*Pr)Cl$_3$ (Ti1) with Ti6



A solution of PNP-*i*Pr **L2** (100 mg, 0.31 mmol) and Ti(NMe$_2$)$_4$ (71 µL, 0.31 mmol) in toluene (4 mL) was stirred for 2 d at 80 °C. All volatiles were removed under reduced pressure. The red oily residue was redissolved in toluene (5 mL) and TMS-Cl (0.231 mL, 1.83 mmol, 6 equiv.) was added. The reaction mixture was stirred for 12 h at rt. All volatiles were removed under reduced pressure and the crude product was washed with *n*-pentane (3 x 7 mL) to obtain the product as dark red powder (82 mg, 55%).

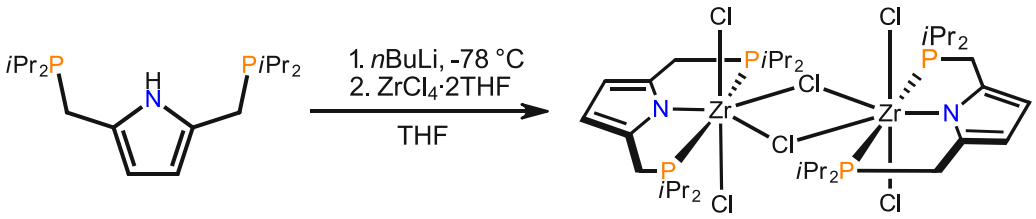
[Ti(PNP-*i*Pr)(N$_3$)$_3$] (Ti8)



A solution of PNP-*i*Pr **L2** (100 mg, 0.31 mmol) and Ti(NMe$_2$)$_4$ (71 µL, 0.31 mmol) in toluene (4 mL) was stirred at 80 °C for 2 d. All volatiles were removed under reduced pressure and the red oily residue was redissolved in toluene (5 mL). TMS-N$_3$ (242 µL, 1.84 mmol, 6 equiv.) was added to the reaction mixture. During addition a precipitate appeared and the pale red solution becomes dark red. Upon stirring for 2 h at rt the reaction mixture was filtered through a syringe filter (PTFE, 0.2 µm). All volatiles were removed under reduced pressure. Due to good solubility of the formed complex in *n*-pentane and Et$_2$O no further work up was possible. A small amount of the complex could be obtained as dark red crystals (suitable for X-ray measurement) by storing a saturated *n*-pentane solution in the freezer at -20 C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C) δ = 5.93 (s, 2H, Pyr^{3,4}), 2.86 – 2.74 (m, 4H, CH$_2$), 1.81 – 1.68 (m, 4H, C*H*CH$_3$), 0.94 – 0.81 (m, 12H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 25 °C) δ = 137.2 (d, *J* = 6.0 Hz, C$_q$, Pyr^{4,5}), 105.3 (t, *J* = 4.1 Hz, Pyr^{3,4}), 25.0 (t, *J* = 6.2 Hz, CH$_2$), 23.4 (d, *J* = 15.2 Hz, *C*HCH$_3$), 18.1 (d, *J* = 19.4 Hz, *C*HCH$_3$). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 25 °C) δ = 63.1.

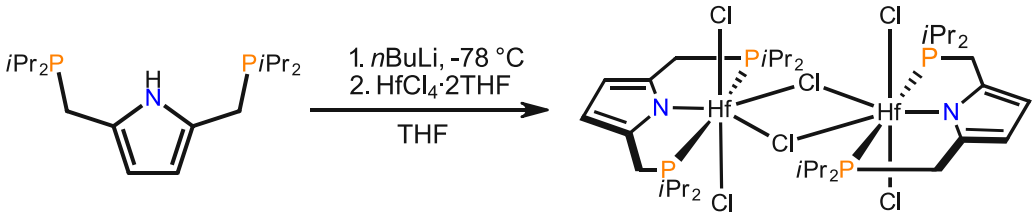
4.4 Synthesis of Zr and Hf PNP Pincer Complexes

[Zr(PNP-*i*Pr)Cl$_2$(μ-Cl)$_2$]$_2$ (Zr1)



A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) in THF (8 mL) was treated with *n*BuLi (419 µL, 1.6 M in *n*-hexane, 0.67 mmol, 1.1 equiv.) at -78 °C. After stirring for 30 minutes at this temperature the reaction mixture was allowed to reach rt and stirred for further 30 minutes. $ZrCl_4$·2THF (219 mg, 0.58 mmol, 0.95 equiv.) was added. Upon stirring for 1 h, all volatiles were removed under reduced pressure and the orange oily residue was redissolved in toluene (10 mL). The orange solution was filtered through a syringe filter (PTFE, 0.2 µm), which was washed with toluene (2 x 8 mL). After evaporation of the solvent, the residue was washed with *n*-pentane (3 x 10 mL) until the washing phase was colorless. The product was obtained as beige powder (230 mg, 76%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 5.85 (s, 2H, Pyr^{3,4}), 3.29 – 3.22 (m, 4H, CH_2), 2.40 – 2.24 (m, 4H, C*H*CH$_3$), 1.42 – 1.28 (m, 12H, CHC*H*$_3$), 1.23 – 1.09 (m, 12H, CHC*H*$_3$).^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 138.3 (C$_q$, Pyr^{2,5}), 107.2 (Pyr^{3,4}), 25.0 (CH_2), 19.2 (*C*HCH$_3$), 18.3 (CH*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C) δ = 40.2.

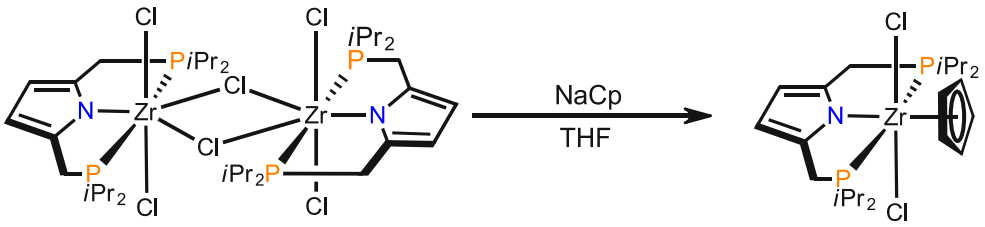
[Hf(PNP-*i*Pr)Cl$_2$(μ-Cl)$_2$]$_2$ (Hf1)



This complex was prepared analogously to **Zr1** with PNP-*i*Pr **L2** (200 mg, 0.61 mmol), *n*BuLi (419 µL, 1.6 M in hexane, 0.67 mmol, 1.1 equiv.), and $HfCl_4$·2THF (283 mg, 0.58 mmol, 0.95 equiv.) yielding the product as beige powder (298 mg, 80%). Single crystals for X-Ray diffraction measurement could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ = 5.86 (s, 2H), 3.28 (s, 4H), 2.34 (bs, 4H), 1.39 – 1.31 (m, 12H), 1.18 (bs, 12H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25 °C) δ = 137.9

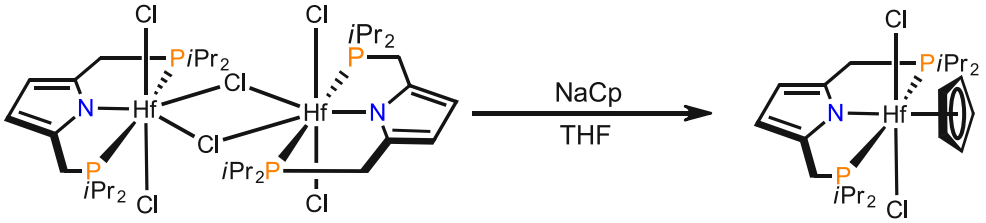
(C_q, Pyr^{2,5}), 107.7 (Pyr^{3,4}), 24.9 (*C*HCH$_3$), 21.0 (CH$_2$), 19.3 (CH*C*H$_3$), 18.4 (CH*C*H$_3$). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 25 °C) δ = 42.8.

[Zr(PNP-*i*Pr)Cl$_2$(Cp)] (Zr2)



To a solution of **9** (100 mg, 0.095 mmol) in THF (6 mL) NaCp (79.5 µL, 2.4 M in THF, 0.19 mmol, 2 equiv.) was added at rt. During the addition of NaCp the solution immediately became dark red. Upon stirring for 1 h, the solvent was evaporated and the residue was redissolved in toluene (10 mL). The solution was filtered through a syringe filter (PTFE, 0.2 µm). Upon evaporation of the solvent and washing of the residue with *n*-pentane (2 x 10 mL) afforded the product as brown powder (95 mg, 90%).^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ = 6.70 (t, *J* = 1.2 Hz, 5H, Cp), 5.78 (s, 2H, Pyr^{3,4}), 3.20 – 3.14 (m, 4H, CH$_2$), 2.34 – 2.26 (m, 4H, C*H*CH$_3$), 1.32 – 1.28 (m, 12H, CHC*H$_3$*), 1.28 – 1.23 (m, 12H, CHC*H$_3$*). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2 25 °C) δ = 135.0 (t, *J* = 4.3 Hz, C_q, Pyr^{2,5}), 115.6 (Cp), 105.8 (t, *J* = 4.5 Hz, Pyr^{3,4}), 25.5 (t, *J* = 5.9 Hz, C*H*CH$_3$), 25.3 (dd, *J* = 9.5, 8.0 Hz, CH$_2$), 19.6 (d, *J* = 7.9 Hz, CH*C*H$_3$). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 25 °C) δ = 36.2.

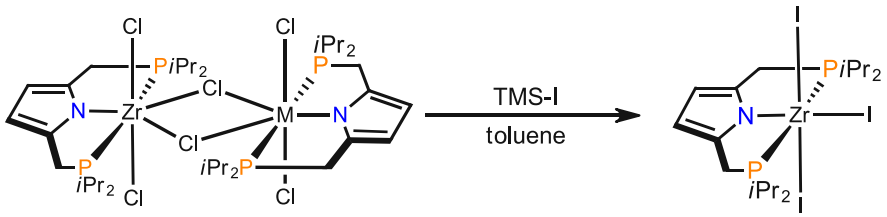
[Hf(PNP-*i*Pr)Cl$_2$(Cp)] (Hf2)



This complex was prepared analogously to **Zr2** with [Hf(PNP-*i*Pr)Cl$_2$(µ-Cl)$_2$]$_2$ **10** (250 mg, 0.20 mmol) and NaCp (170 µL, 2.4 M in THF, 0.40 mmol, 2 equiv.) yielding the product as beige powder (243 mg, 93%). Single crystals for X-Ray diffraction measurement could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ = 6.40 (t, *J* = 1.1 Hz, 5H, Cp), 5.64 (s, 2H, Pyr^{3,4}), 3.11 – 3.00 (m, 4H, CH$_2$), 2.25 – 2.16 (m, 4H, C*H*CH$_2$), 1.19 – 1.15 (m, 12H, CHC*H$_3$*), 1.15 – 1.11 (m, 12H, CHC*H$_3$*).^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25 °C) δ = 134.9 (t, *J* = 4.2 Hz, C_q, Pyr^{2,5}), 114.0 (Cp), 106.2 (t, *J* = 4.4 Hz, Pyr^{3,4}), 25.5 (t, *J* = 6.8 Hz, *C*HCH$_3$), 25.1 (d, *J* = 8.9 Hz, CH$_2$), 25.0

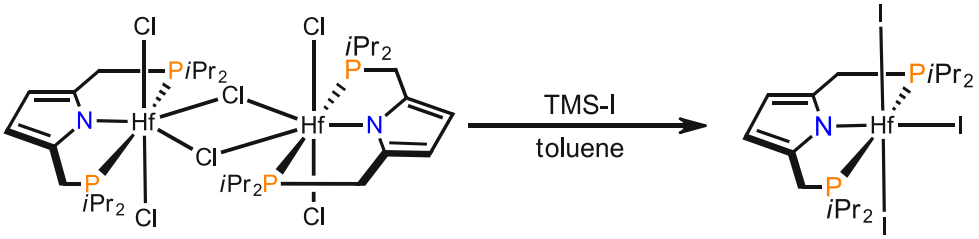
(d, J = 9.0 Hz, CH_2), 24.2 (d, 13.5 Hz, $CHCH_3$), 19.6 ($CHCH_3$).$^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 25 °C) δ = 37.8.

[Zr(PNP-*i*Pr)I$_3$] (Zr3) with Zr1



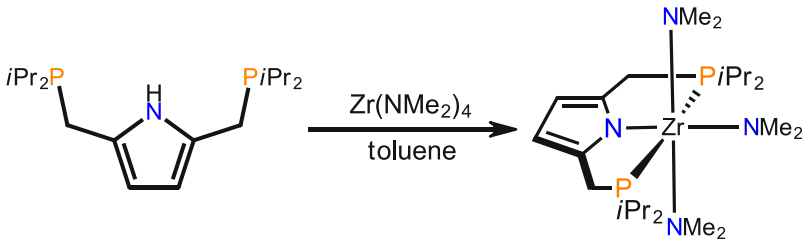
To a solution of **Zr1** (100 mg, 0.095 mmol) in toluene (10 mL) TMS-I (407 µL, 2.86 mmol, 30 equiv.) was added at rt and stirred for 1 h. During addition the solution became orange and a precipitate was formed. The solution was decanted and the remaining residue was extracted three times with toluene (10 mL). The organic layers were combined and all volatiles were removed under reduced pressure. The orange residue was washed with *n*-pentane (3 x 10 mL) yielding the product as orange powder (120 mg, 78%)

[Hf(PNP-*i*Pr)I$_3$] (Hf4) with Hf1



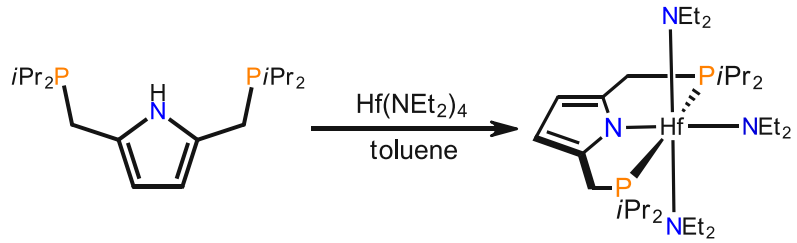
A solution of **Hf1** (100 mg, 0.082 mmol) in toluene (5 mL) was treated with TMS-I (249 µL, 2.5 mmol, 30 equiv.). After stirring for 1 h the orange solution was decanted. The remaining solid was extracted with toluene (10 mL). The organic layers were combined and all volatiles were removed under reduced pressure. The orange residue was washed with *n*-pentane (3 x 10 mL) to afford the product as pale pink powder (57 mg, 87%).

[Zr(PNP-*i*Pr)(NMe$_2$)$_3$] (Zr4)



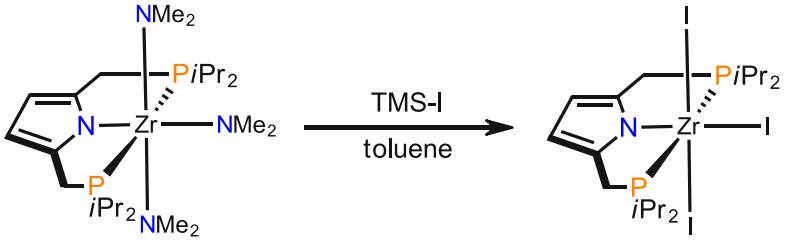
A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) and Zr(NMe$_2$)$_4$ (0.164 mg, 0.61 mmol) in toluene (4 mL) was stirred at 120 °C for 72 h. The reaction mixture was allowed to reach rt and all volatiles were removed under reduced pressure to yield the product as red oil (335 mg, 100%) ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C) δ = 6.19 (s, 2H, Pyr^{3,4}), 3.11 (s, 18H, NMe$_2$), 2.90 (d, *J* = 2.4 Hz, 4H, CH$_2$), 1.75 – 1.58 (m, 4H, C*H*CH$_3$), 1.18 – 0.91 (m, 24H, CHC*H$_3$*). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 25 °C) δ = 136.4 (d, *J* = 8.5 Hz, C$_q$, Pyr^{2,5}), 107.3 (dd, *J* = 3.9, 1.8 Hz, Pyr^{3,4}), 45.0 (NCH$_3$), 26.9 (d, *J* = 3.5 Hz, CH$_2$), 24.3 (d, *J* = 5.5 Hz, *C*HCH$_3$), 21.1 (d, *J* = 10.0 Hz, CH*C*H$_3$), 19.9 (d, *J* = 2.6 Hz, CH*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 25 °C) δ = 13.4.

[Hf(PNP-*i*Pr)(NEt$_2$)$_3$] (Hf4)



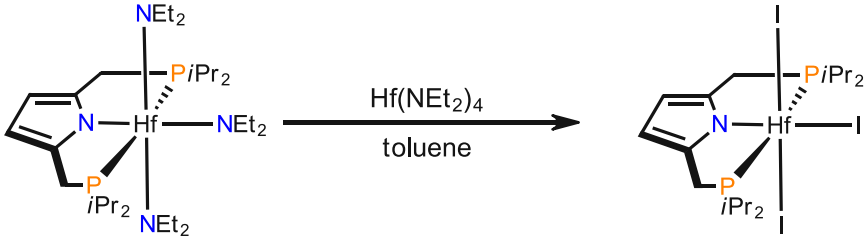
A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) and Hf(NMe$_2$)$_4$ (228 µL, 0.61 mmol) in toluene (4 mL) was stirred at 120 °C for 48 h. The reaction mixture was allowed to reach rt and all volatiles were removed under reduced pressure. Due to similar solubility behavior of Hf(NEt$_2$)$_4$, **L2** and the product no further work up was possible. The crude product was obtained as a red oil with a purity of about 80% (quantified by NMR). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C) δ = 6.38 (s, 2H, Pyr^{3,4}), 3.51 (q, *J* = 7.0 Hz, 8H, C*H$_2$*CH$_3$), 3.36 (q, *J* = 7.0 Hz, 4H, C*H$_2$*CH$_3$), 1.89 – 1.69 (m, 4H, CH$_3$C*H$_2$*CH$_3$), 1.19 – 1.01 (m, 52H, C*H$_3$*CH$_2$C*H$_3$*, CH$_2$C*H$_3$*).^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 25 °C) δ = 136.9 (d, *J* = 9.7 Hz, Pyr^{2,5}), 109.7 (dd, *J* = 8.0, 1.4 Hz, Pyr^{3,4}), 43.5 (*C*H$_2$CH$_3$), 43.2 (*C*H$_2$CH$_3$), 24.3 (d, *J* = 14.9 Hz, *C*HCH$_3$), 20.6 (d, *J* = 9.6 Hz, *C*H$_3$CH$_2$CH$_3$, *CH$_2$CH$_3$*), 20.2 (d, *J* = 7.8 Hz, *C*H$_3$CH$_2$*C*H$_3$, CH$_2$*C*H$_3$), 16.9 (*C*H$_3$CH$_2$*C*H$_3$, CH$_2$*C*H$_3$), 16.2 (*C*H$_3$CH$_2$*C*H$_3$, CH$_2$*C*H$_3$).^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 25 °C) δ = 9.2.

[Zr(PNP-*i*Pr)I$_3$] (Zr3)



A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) and Zr(NMe$_2$)$_4$ (163 mg, 0.61 mmol) in toluene (8 mL) was stirred at 120 °C for 72 h. The reaction mixture was allowed to reach rt and TMS-I (280 µL, 2.1 mmol, 3.5 equiv.) was added. During the addition an orange precipitate was formed. After stirring for 1 h at rt all volatiles were removed under reduced pressure and the residue was washed with *n*-pentane (3 x 10 mL). The product was isolated as orange powder (440 mg, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 5.88 (s, 2H, Pyr^{3,4}), 3.48 – 3.32 (m, 4H, CH_2), 2.63 – 2.48 (m, 4H, C*H*CH$_3$), 1.45 – 1.18 (m, 24H, CHC*H$_3$*). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 139.1 (t, *J* = 5.3 Hz, Pyr^{2,5}), 108.6 (t, *J* = 4.3 Hz, Pyr^{3,4}), 27.2 (t, *J* = 7.0 Hz, *C*HCH$_3$), 26.7 (t, *J* = 9.9 Hz, CH_2), 20.1 (CH*C*H$_3$), 19.7 (CH*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C) δ = 56.5.

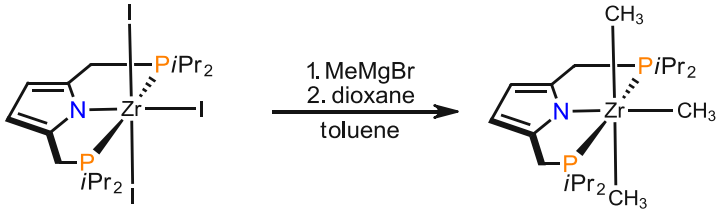
[Hf(PNP-*i*Pr)I$_3$] (Hf4)



A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) and Hf(NMe$_2$)$_4$ (228 µL, 0.61 mmol) in toluene (4 mL) was stirred at 120 °C for 48 h. The reaction mixture was allowed to reach rt and TMS-I (291 µL, 2.14 mmol, 3.5 equiv.) was added. During the addition an orange precipitate was formed (HfI$_4$ from the not converted Hf(NEt$_2$)$_4$). The suspension was filtered through a syringe filter (PTFE, 0.2 µL) and washed with toluene (3 x 10 mL). All volatiles were removed under reduced pressure and the residue was washed with *n*-pentane (3 x 10 mL). The product was obtained as pale pink powder (0.454 g, 84%).Single crystals for X-Ray measurements could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane ^{1}H NMR (400 MHz, CH_2Cl_2, 25 °C) δ = 5.84 (s, 2H, Pyr^{3,4}), 3.56 – 3.40 (m, 4H, CH_2), 2.73 – 2.49 (m, 4H, CHC*H$_3$*), 1.38 (ddt, *J* = 10.2, 7.1, 3.6 Hz, 24H, CHC*H$_3$*). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 139.0

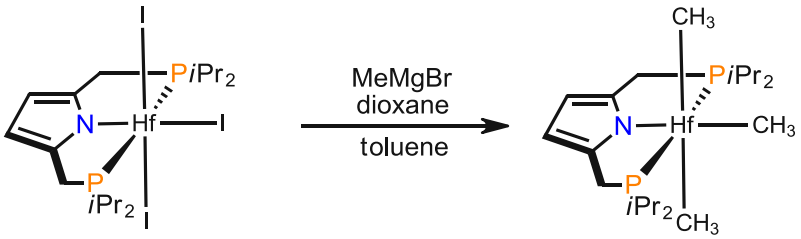
(t, J = 4.8 Hz, Pyr^{2,5}, C_q, Pyr^{2,5}), 109.4 (t, J = 4.3 Hz, Pyr^{3,4}), 27.5 (t, J = 9.9 Hz, CH_2), 27.2 (t, J = 8.2 Hz, CHCH$_3$), 20.1 (d, J = 6.4 Hz, CHCH$_3$).^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C) δ = 62.3.

[Zr(PNP-*i*Pr)Me$_3$] (Zr5)



A suspension of [Zr(PNP-*i*Pr)I$_3$] **Zr3** (60 mg, 0.075 mmol) in toluene (5 mL) was treated with MeMgBr (161 µL, 1.4 M in THF/toluene (1:4), 0.23 mmol, 3 equiv.) at rt. During the addition the suspension dissolved and the color of the solution became brighter. Dioxane (116 µL, 1.35 mmol, 6 equiv.) was added for precipitation of the formed magnesia salts. Upon stirring for 1 h all volatiles were evaporated under reduced pressure and the white residue was redissolved in *n*-pentane (5 mL). The reaction mixture was filtered through a syringe filter (PTFE, 0.2 µL) to afford a pale orange solution. After evaporation of the solvent the product was obtained as orange oil (28 mg, 80%).^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ = 6.26 (d, J = 0.9 Hz, 2H, Pyr^{3,4}), 2.90 (d, J = 6.1 Hz, 4H, CH_2), 1.94 (dq, J = 14.4, 7.2 Hz, 2H, CHCH$_3$), 1.04 (t, J = 3.8 Hz, 9H, Zr-CH$_3$), 0.99 (dd, J = 13.6, 7.1 Hz, 12H, CHCH_3), 0.92 (dd, J = 12.8, 7.1 Hz, 12H, CHCH_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 136.6 (t, J = 6.3 Hz, C_q, Pyr^{4,5}), 107.0 (t, J = 4.3 Hz, Pyr^{3,4}), 51.7 (Zr-CH$_3$), 23.9 – 23.4 (m, CH_2), 23.3 – 23.0 (m, CHCH$_3$), 18.3 (d, J = 7.4 Hz, CHCH$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C) δ = 27.9.

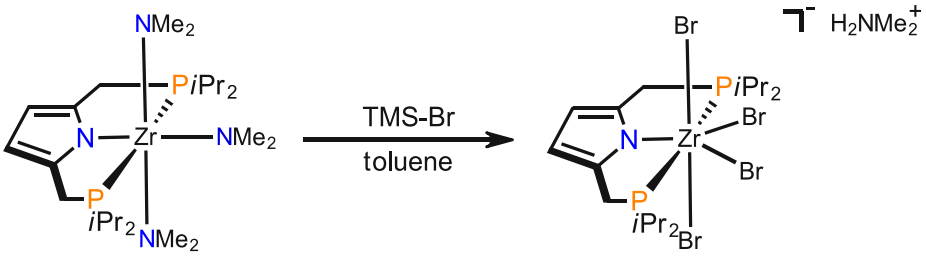
[Hf(PNP-*i*Pr)Me$_3$] (Hf5)



This complex was prepared analogously to **Zr5** with [Hf(PNP-*i*Pr)I$_3$] **Hf3** (60 mg, 0.067 mmol), MeMgBr (145 µL, 1.4 M in THF/toluene (1:4), 0.20 mmol, 3.5 equiv.) and dioxane (35 µL,0.41 mmol, 6 equiv.) yielding the product as orange oil (31 mg, 82%).^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ = 6.24 (s, 2H, Pyr^{3,4}), 2.93 (d, J = 5.6 Hz, 4H, CH_2), 2.05 – 1.88 (m, J = 7.2 Hz, 4H, CHCH$_3$), 1.02 – 0.86 (m, 24H, CHCH_3), 0.74 (t, J = 3.9 Hz, 9H, Hf-

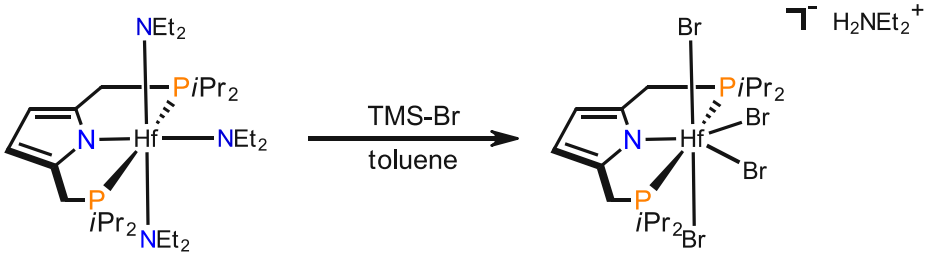
CH_3).$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ = 136.5 – 136.1 (m, $Pyr^{2,5}$), 106.8 – 106.6 (m, $Pyr^{3,4}$), 59.4 (t, *J* = 6.4 Hz, Hf-CH_3), 22.6 (d, *J* = 7.1 Hz, CH_2), 22.3 (d, *J* = 10.1 Hz, C*H*CH_3), 17.6 (dt, *J* = 18.1, 1.2 Hz, CH*C*H_3). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C) δ = 30.8.

[Zr(PNP-*i*Pr)Br$_4$][H$_2$NMe$_2$] (Zr6)



A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) and $Zr(NMe_2)_4$ (163 mg, 0.61 mmol) was stirred at 120 °C for 72 h. The reaction mixture was allowed to reach rt and TMS-Br (282 µL, 2.1 mmol, 3.5 equiv.) was added. After 5 minutes an orange precipitate was formed. All volatiles were removed under reduced pressure and the residue was washed with *n*-pentane (4 x 10 mL). The product was obtained as salmon colored powder (383 mg, 80%). Single crystals for X-Ray diffraction measurement could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 7.64 (bs, 2H, *H*$_2$NMe$_2$), 5.90 (s, 2H, $Pyr^{3,4}$), 3.27 (d, *J* = 6.4 Hz, 4H, CH_2), 2.94 (s, 6H, Zr-N-CH_3), 2.58 – 2.40 (m, 4H, C*H*CH_3), 1.34 (dd, *J* = 13.5, 7.2 Hz, 12H, CHC*H*$_3$), 1.24 (dd, *J* = 12.0, 7.1 Hz, 12H, CHC*H*$_3$).$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 137.6 (t, *J* = 5.6 Hz, C_q, $Pyr^{2,5}$), 106.3 ($Pyr^{3,4}$), 36.2 (Zr-N-CH_3), 24.9 (t, *J* = 5.2 Hz), 21.4 (*C*HCH_3), 18.9 (CH*C*H_3), 18.0 (CH*C*H_3).$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C) δ = 39.7.

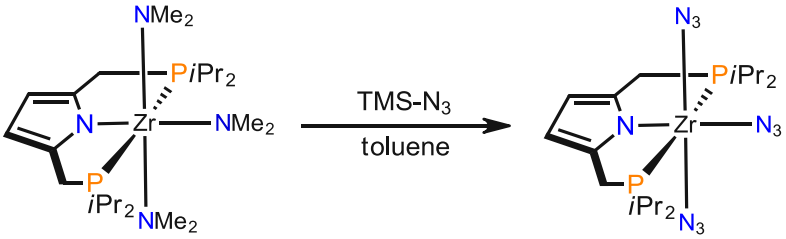
[Hf(PNP-*i*Pr)Br$_4$][H$_2$NMe$_2$] (Hf6)



A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) and $Hf(NEt_2)_4$ (228 µL, 0.61 mmol) in toluene (4 mL) was stirred at 120 °C for 48 h. The reaction mixture was allowed to reach rt and TMS-Br (282 µL, 2.12 mmol, 3.5 equiv.) was added. During the addition the orange colored solution became more intensive and a precipitate was formed. After stirring for 1 h at rt, the precipitate

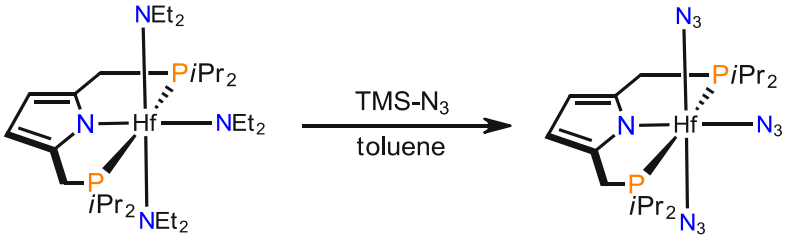
was filtered through a syringe filter (PTFE, 0.2 µl) and washed with toluene (3 x 10 mL). All volatiles were removed under reduced pressure. After washing of the residue with *n*-pentane (10 mL) yielded the product as salmon colored powder (390 mg, 81%). Single crystals for X-Ray measurements could be obtained by layering a saturated CH_2Cl_2 solution with *n*-pentane. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 7.66 (bs, 2H, H_2NEt_2) 5.86 (s, 2H, Pyr^{3,4}), 3.38 – 3.34 (m, 2H, CH_2P), 3.30 (q, *J* = 7.4 Hz, 4H, NCH_2CH_3), 2.59 – 2.44 (m, 4H, $CHCH_3$), 1.46 (t, *J* = 7.3 Hz, 6H, NCH_2CH_3), 1.39 – 1.22 (m, 24H, $CHCH_3$).^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 138.4 (C_q, Pyr^{2,5}), 108.2 (Pyr^{3,3}), 42.5 (NCH_2CH_3), 25.8 (t, *J* = 7.6 Hz, $CHCH_3$), 24.7 (CH_2P), 19.7 ($CHCH_3$), 19.3 ($CHCH_3$), 11.5 (NCH_2CH_3).^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C) δ = 49.9.

[Zr(PNP-*i*Pr)(N$_3$)$_3$] (Zr7)



A solution of PNP-*i*Pr **L2** (200 mg, 0.61 mmol) and $Zr(NMe_2)_4$ (163 mg, 0.61 mmol) in toluene (8 mL) was stirred at 120 °C for 72 h. The reaction mixture was allowed to reach rt and TMS-N_3 (142 µL, 2.1 mmol, 3.5 equiv.) was added. During addition an orange precipitate was formed. Upon stirring for 1 h all volatiles were removed under reduced pressure. The residue was redissolved in toluene (5 mL) and filtered through a syringe filter (PTFE 0.2 µm) followed by evaporation of the solvent. The orange residue was digested in *n*-pentane (10 mL) to precipitate the product. Upon decantation of the solvent and washing the residue with *n*-pentane (4 x 10 mL) yielded the product as orange powder (170 mg, 51%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 5.72 (s, 2H, Pyr^{3,4}), 3.01 (d, *J* = 6.3 Hz, 4H, CH_2), 2.26 – 2.11 (m, 4H, $CHCH_3$), 1.24 (dd, *J* = 14.2, 7.1 Hz, 12H, $CHCH_3$), 1.05 (dd, *J* = 12.2, 7.1 Hz, 12H, $CHCH_3$). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 137.7 (C_q, Pyr^{2,5}), 107.0 (Pyr^{3,4}), 24.9 (t, *J* = 5.5 Hz, $CHCH_3$), 18.8 (CH_3), 18.2 (CH_3). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C) δ = 38.5.

[Hf(PNP-*i*Pr)(N$_3$)$_3$] (Hf7)



This complex was prepared analogously to **Zr7** with PNP-*i*Pr **L2** (100 mg, 0.31 mmol), Hf(NEt$_2$)$_4$ (114 mg, 0.31 mmol) and TMS-N$_3$ (142 µL, 1.07 mmol, 3.5 equiv.) yielding the product as orange powder (126 mg, 65%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 5.83 (s, 2H, Pyr^{3,4}), 3.12 (s, 4H, C*H*$_2$), 2.39 – 2.23 (m, 4H, C*H*CH$_3$), 1.38 – 1.28 (m, 12H, CHC*H*$_3$), 1.19 – 1.09 (m, 12H, CHC*H*$_3$).^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ = 137.5 (C$_q$, Pyr^{2,5}) 107.6(Pyr^{3,4}), 24.8 (t, *J* = 6.3 Hz, *C*HCH$_3$), 21.8 (d, *J* = 19.5 Hz), 20.8 – 20.4 (m), 20.2 (d, *J* = 14.3 Hz), 19.4 (d, *J* = 10.4 Hz, CH$_2$), 18.7(CH*C*H$_3$), 18.2 (CH*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C) δ = 40.5.

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6 List of Abbreviations

Ac	acetate
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
Bu	butyl
***n*BuLi**	*n*-butyllithium
Cp	cyclopentadienyl
DMAP	dimethylaminopyridine
DME	dimethoxyethane
DMF	dimethylformamide
Et	ethyl
Et_2O	diethyl ether
equiv.	equivalent
Me	methyl
MTBE	methyl *tert*-butyl ether
MeCN	acetonitrile
NMR	nuclear magnetic resonance
TBDMS	*tert*-butyldimethylsilyl ether
Tf	triflate
THF	tetrahydrofuran
TMS	trimethylsilyl
ppm	parts per million
Xy	xylene

7 Curriculum Vitae

Personal Data

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Education

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PhD student at the Institute of Applied Synthetic Chemistry (IAS)
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B.Sc. Technical Chemistry
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September 2000 - June 2008

Higher secondary school BRG Stockerau
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Experience

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Project assistant (FWF Österreich) at VTU

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University Assistant for academic research and teaching in student laboratories

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March 2015 -January 2017

Tutor in synthetic chemistry student laboratory

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Languages

- German: Mother tongue
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Technical Skills

- Laboratory: Extended experience in synthesis of organic and organometallic compounds under air and moisture free conditions with Schlenk technique and glovebox; Characterization of organic and organometallic compounds *via* TLC, HPLC, GC, NMR (multinuclear spectroscopy and Evans method), IR, EPR, X-Ray single crystal analysis.
- Computational: Extended experience in different softwares for chemical research, including, ChemDraw, ChemDoodle, MestreNova, TopSpin, APEX II, ShelXle; Extended experience in Microsoft Office (Word, Excel, PowerPoint)

8 Conference Contributions

Poster-Presentation: 34th Congress Organometallic Chemistry Group (GEQO) in Girona, Spain ”New PCP Pincer Pyrimidine Complexes with non-precious Metals” (2016)

Poster-Presentation: 17th Austrian Chemistry Days in Salzburg, Austria “New PCP Pincer Pyrimidine Complexes with non-precious Metals” (2017)

Poster-Presentation: 10th Workshop Inorganic Chemistry in Graz, Austria “New PCP Pincer Pyrimidine Complexes with non-precious Metals” (2018)

Poster-Presentation: 5th CHAOS-Meeting International Conference of Organometallics Chemistry (ICOMC) in Florence, Italy “Synthesis of New Anionic-PNP Ti(IV) and Ti(III) Pincer Complexes” (2018)

Poster-Presentation: 28th International Conference of Organometallics Chemistry (ICOMC) in Florence, Italy “Synthesis of New Anionic-PNP Ti(IV) and Ti(III) Pincer complexes” (2018)

Poster-Presentation: 18th Austrian Chemistry Days in Linz, Austria “Synthesis of New Anionic-PNP Ti(IV) and Ti(III) Pincer Complexes” (2019)