Pentamethylcyclopentadienyl Zirconium and Hafnium Polyhydride Complexes: Synthesis, Structure, and Reactivity†

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The half-sandwich zirconium and hafnium *N*,*N*-dimethylaminopropyl complexes Cp*M-[$(CH_2)_3NMe_2$]Cl_2 (Cp* = η^5-C_5Me_5, M = Zr, **1**; Hf, **2**) and Cp*M[$(CH_2)_3NMe_2$]$_2$Cl (M = Zr, **3**; Hf, **4**) were synthesized by mono- or dialkylation of Cp*MCl_3 with the corresponding alkyllithium and Grignard reagents. Hydrogenolysis of the monoalkyl species resulted in the formation of the polyhydride complexes Cp*$_3M_3(\mu$-H$)_4(\mu$-Cl$)_2Cl_3$ (M = Zr, **5**; Hf, **6**) and Cp*MCl_3. A crystal structure determination of Cp*$_3Hf_3H_4Cl_5$ (**6**) revealed a fully asymmetric trinuclear structure with three widely differing Hf···Hf distances. Reaction of Cp*$_3M_3H_4Cl_5$ with PMe_3 resulted in fragmentation of the cluster and ligand redistribution to give Cp*MCl_3-(PMe_3) and the dimeric hydride complexes Cp*$_2M_2(\mu$-H$)_3Cl_3$(PMe_3) (M = Zr, **7**; Hf, **8**), structurally characterized for M = Zr. The trinuclear polyhydride Cp*$_3Hf_3H_4Cl_5$ reacts with 2,6-xylylisocyanide to give three distinct products, a μ-enediamide complex, [Cp*$HfCl_2]_2[\mu$-xyNCH=CHNxy] (**11**, xy = 2,6-dimethylphenyl), which was structurally characterized, an imido complex, [Cp*Hf(μ-Nxy)Cl]$_2$ (**12**), and an azaallyl species, Cp*Hf(η^3-CH_2CHNxy)Cl_2 (**13**). The reactivity of **6** can be interpreted as proceeding through initial cleavage of the trinuclear complex into the fragments "Cp*$_2Hf_2(\mu$-H$)_3Cl_3$" and "Cp*$HfHCl_2$", followed by the separate reactivity of these fragments.

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Introduction

Group 4 metal metallocene hydride species are used for stoichiometric[1] as well as catalytic[2] reductions of organic substrates. The synthesis and organometallic chemistry of these metallocene hydrides have been investigated quite extensively, especially for zirconium.[3−6] In contrast, relatively little is known on the synthesis and chemisty of non-metallocene group 4 metal hydrides.[7−11] We expect interesting structural and reactive chemistry of highly electron-deficient group 4 metal polyhydride species and tried to devise a synthesis route to access mono(pentamethylcyclopentadienyl) group 4 metal polyhydrides of the type Cp*MH_nCl_{3-n} (Cp* = η^5-C_5Me_5).

The synthesis of group 4 metal hydrides is usually performed either by reaction of metal halide species with boron hydrides or trialkyl tin hydrides or by hydrogenolysis of metal alkyl species. The first route has led to a number of interesting mixed group 4 metal−boron polyhydride species,[7] but it is difficult to obtain boron-free compounds. A range of polynuclear mixed hydrido-

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halide zirconium species were obtained by reaction of zirconium halides with trialkyl tin hydrides in the presence of phosphines.[11] Most of these are structurally derived from an octahedral hexametallic framework, with central or bridging hydrides. Hydrogenolysis of simple mono(pentamethyl)cyclopentadienyl group 4 metal alkyl species such as $Cp^*M(CH_3)_nCl_{3-n}$ has not yielded well-defined products so far, producing mostly poorly soluble materials.[10] Only when bulky phosphido ligands are used in the starting materials were complexes such as $\{Cp^*Hf(R)[\mu\text{-}P^tBu_2](\mu\text{-}H)\}_2$ (R = Cl, Me) obtained.[10b]

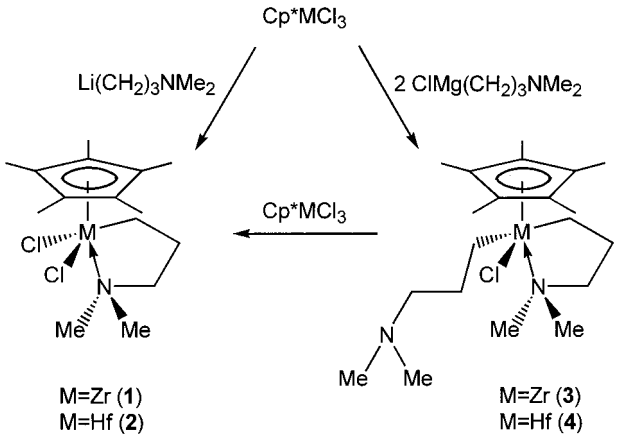
The observation, made previously in our group, that hydrogenolysis of the hafnium 2,3-dimethyl-1,3-butadiene complex $Cp^*Hf(C_6H_{10})Cl$ yielded a soluble, well-defined tetrameric hydride, $[Cp^*Hf(H)_2Cl]_4$,[12] suggested that the nature of the hydrocarbyl precursor is of crucial importance for the formation of well-defined soluble polyhydride species. We therefore investigated the synthesis and hydrogenolysis of mono(pentamethylcyclopentadienyl) zirconium and hafnium *N*,*N*-dimethylaminopropyl complexes. It was expected that the amine substituent on the alkyl group would ensure the monomeric nature of the starting hydrocarbyls and provide (transient) stabilization of the hydride species generated upon hydrogenolysis. Here we describe the synthesis of the alkyl compounds $Cp^*M[(CH_2)_3NMe_2]_nCl_{3-n}$ (M = Zr, Hf; n = 1, 2) and their use in generating well-defined polyhydride complexes. The reactivity of these species with trimethylphosphine and 2,6-xylylisocyanide is also described. A part of this study has been communicated previously.[13]

Results and Discussion

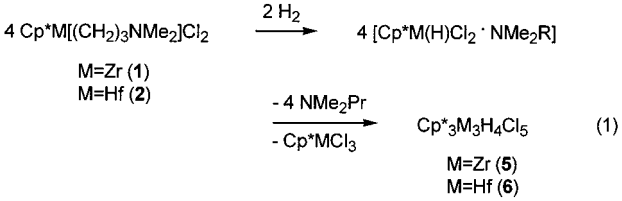
Synthesis of Zirconium and Hafnium *N*,*N*-Dimethylaminopropyl Complexes. The monoalkyl complexes $Cp^*M[(CH_2)_3NMe_2]Cl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$, M = Zr, **1**; Hf, **2**) were obtained in 65% isolated yield from the reaction of Cp^*MCl_3 with 1 equiv of $Li(CH_2)_3NMe_2$ in THF (Scheme 1). The dialkyl complexes $Cp^*M[(CH_2)_3NMe_2]_2Cl$ (M = Zr, **3**; Hf, **4**) were most conveniently prepared by the reaction of Cp^*MCl_3 with 2 equiv of the corresponding Grignard reagent $ClMg(CH_2)_3NMe_2$ (Scheme 1). Mixtures of the monoalkyl and dialkyl complexes were obtained when the alkyl-lithium reagent was used. The monoalkyl zirconium complex **1** was also obtained in high yield from a ligand redistribution reaction between the dialkyl complex **3** and Cp^*ZrCl_3.

The ^{1}H NMR spectra of the monoalkyl complexes **1** and **2** each show a single resonance for the NMe_2 group, which does not show coalescence broadening even down to −60 °C. This indicates either a pseudo trigonal-bipyramidal geometry of the complex with C_s symmetry or a very rapid rotation and inversion of the NMe_2 group on the NMR time scale. The IR spectra of the dialkyls **3** and **4** show a ν_{CH} absorption around 2760 cm^{-1}, indicative of a noncoordinated NMe_2 group,[14] which is absent in the IR spectra of the monoalkyls **1** and **2**. This suggests that in all the alkyl complexes **1**−**4** only one dimethylaminopropyl group is chelating. At 20 °C the ^{1}H NMR spectra of the dialkyls **3** and **4** are indicative of a symmetrically averaged structure, but at −60 °C the fluxionality is frozen out completely for the Hf dialkyl complex **4**. All α-methylene protons are inequivalent at that temperature, and the NMe_2 resonance is split into three resonances in a 3:3:6 ratio. At this temperature the fluxionality in the Zr complex **3** is not yet completely frozen out. From the coalescence temperatures for one of the MCH_2 groups the energy of activation $\Delta G^{\ddagger}_{Tc}$ of this process was estimated to be 43.9 ± 0.2 kJ mol^{-1} (at T_c = −46 ± 1 °C) for **3** and 45.8 ± 0.6 kJ mol^{-1} (at T_c = −36 ± 1 °C) for **4**.[15] These NMR data indicate that in the dialkyl species only one dimethylaminopropyl group is chelating at a time, which is consistent with the IR data.

Scheme 1



Hydrogenolysis of the Monoalkyl Complexes 1 and 2. Reaction of the monoalkyl complexes **1** and **2** with H_2 (benzene-d_6 solvent) at ambient temperature and pressure resulted in clear, pale yellow solutions. Monitoring the reactions by ^{1}H NMR spectroscopy revealed gradual formation of free (*n*-propyl)dimethylamine, Cp^*MCl_3, and a polyhydride species with three inequivalent Cp* groups and four inequivalent hydrides (compounds **5**, **6**, eq 1). For Zr, the reaction takes about



24 h at ambient temperature to go to completion; for Hf about 48 h. The hydride resonances for the Zr compound are found at δ 4.23, 3.92, 2.96, and 0.88 ppm;

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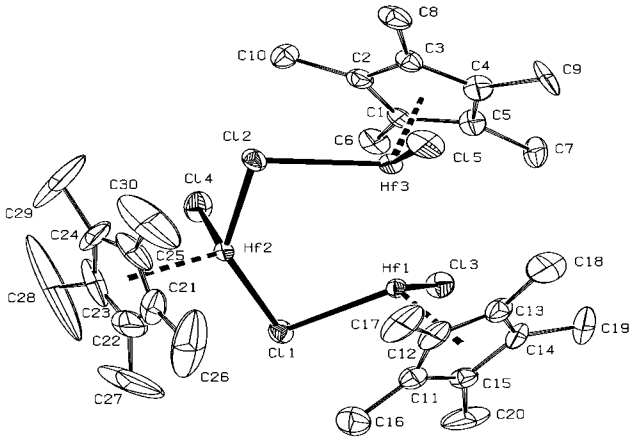

Figure 1. Molecular structure of $Cp^*_3Hf_3(\mu\text{-}H)_4(\mu\text{-}Cl)_2Cl_3$ (**6**).

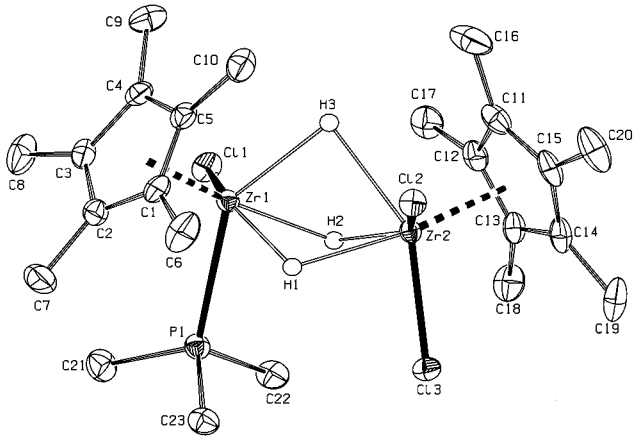

Figure 2. Molecular structure of $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (**7**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $Cp^*_3Hf_3(\mu\text{-}H)_4(\mu\text{-}Cl)_2Cl_3$ (6)

Hf(1)···Hf(2)	3.241(6)	Hf(1)−Cl(1)−Hf(2)	77.71(7)
Hf(2)···Hf(3)	3.721(7)	Hf(2)−Cl(2)−Hf(3)	94.93(10)
Hf(1)···Hf(3)	3.061(6)	Cl(1)−Hf(1)−Cl(3)	79.24(9)
Hf(1)−av C(Cp)	2.473	Cl(1)−Hf(2)−Cl(2)	143.11(9)
Hf(2)−av C(Cp)	2.472	Cl(1)−Hf(2)−Cl(4)	89.91(10)
Hf(3)−av C(Cp)	2.484[a]	Cl(2)−Hf(2)−Cl(4)	92.18(10)
Hf(1)−Cl(1)	2.648(3)	Cl(2)−Hf(3)−Cl(5)	93.59(10)
Hf(2)−Cl(1)	2.516(3)		
Hf(2)−Cl(2)	2.536(3)		
Hf(3)−Cl(2)	2.514(3)		
Hf(1)−Cl(3)	2.470(3)		
Hf(2)−Cl(4)	2.394(3)		
Hf(3)−Cl(5)	2.399(3)		

[a] The largest being 2.524 and the smallest 2.459 Å.

for the Hf congener at δ 9.17, 8.46, 7.71, and 4.63 ppm, with each resonance integrating as a single hydride. On the basis of the NMR data, as well as elemental analysis and X-ray diffraction data for the compound with M = Hf (vide infra), these products are formulated as $Cp^*_3M_3H_4Cl_5$ (M = Zr, **5**; Hf, **6**).

Warming the solutions of the polyhydrides in the NMR spectrometer reveals that the compounds $Cp^*_3M_3H_4Cl_5$ **5** and **6** show complicated fluxional behavior. Initially, the two upfield Cp* signals coalesce into a single resonance (around 40 °C). At about 70 °C the third Cp* signal also broadens significantly, but the full fast exchange limit could not be reached for either compound (100 °C). The three downfield hydride resonances also collapse, and at elevated temperature the upfield hydride signal broadens as well.

From reactions on a 1.5−2.5 mmol scale (toluene solvent) the polyhydrides could be isolated as crystalline material by slow diffusion of pentane or hexane into the solution. It proved difficult to obtain the Zr derivative **5** analytically pure due to cocrystallization of Cp^*ZrCl_3. A structural characterization of **5** was hampered by facile loss of cocrystallized solvent from the crystal lattice, rendering the material unsuitable for X-ray analysis. In contrast, the Hf analogue **6** was isolated analytically pure in 80% yield from this procedure, and suitable crystals were obtained for an X-ray structure determination.

The crystal structure of **6** (Figure 1, pertinent interatomic distances and angles in Table 1) reveals a triangular trinuclear arrangement, with each Hf atom bearing one η^5-Cp* ligand and one terminal chloride. Two sides of the cluster, Hf(1)Hf(2) and Hf(2)Hf(3), are bridged by one chloride ligand. The three metal−metal distances are all quite different, Hf(2)···Hf(3) being the longest, 3.721(7) Å (with a bridging chloride), and Hf(1)···Hf(3) the shortest, 3.061(6) Å (without bridging chloride). Unfortunately, the hydrides could not be located from the difference Fourier map, but the structural features and the spectroscopic data of **6** allow us to make a proposal for their positions (see below for a more detailed description of the structure).

Reaction of 5 and 6 with PMe_3. Reaction of the trinuclear hydrides **5** and **6** with an excess of the Lewis base PMe_3 was found to induce fragmentation of the trinuclear core and ligand redistribution to yield a mixture of a dinuclear hydrido complex, $Cp^*_2M_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (M = Zr, **7**; Hf, **8**), and $Cp^*MCl_3(PMe_3)$ (M = Zr, **9**; Hf, **10**; eq 2). The complexes **7** and **8** were obtained analytically pure by crystallization from diethyl ether.

$$3\ Cp^*_3M_3H_4Cl_5 + 5\ PMe_3 \longrightarrow \begin{matrix} \text{M=Zr (5)} \\ \text{M=Hf (6)} \end{matrix} \quad \begin{matrix} 4\ Cp^*_2M_2H_3Cl_3(PMe_3) \\ \text{M=Zr (7)} \\ \text{M=Hf (8)} \end{matrix} + \begin{matrix} Cp^*MCl_3(PMe_3) \\ \text{M=Zr (9)} \\ \text{M=Hf (10)} \end{matrix} \qquad (2)$$

At −30 °C the ^{1}H NMR spectrum of **7** (toluene-d_8 solvent) shows three separate hydride resonances at δ 4.73, 4.44, and 2.97 ppm. For the Hf congener **8** two of the hydride resonances overlap at δ 9.15 ppm in addition to a resonance at δ 7.67 ppm. Upon warming the solution of **7** to 75 °C, the hydride resonances coalesce into one single resonance at 4.09 ppm, but the two Cp* resonances remain inequivalent, indicating that Cl/PMe_3 exchange between the metal centers does not take place at a significant rate and that the observed fluxional process corresponds to a rotation around the metal−metal axis. For the Hf analogue **8** similar behavior is seen, although this process appears to be substantially slower, as even at 100 °C the fast exchange limit for the hydride resonances had not been reached.

A crystal structure determination of the Zr complex **7** reveals that the compound is dinuclear, with one Cp^*ZrCl_2 fragment and one $Cp^*ZrCl(PMe_3)$ fragment bridged by three hydrides that could be located from the difference Fourier analysis (Figure 2, pertinent

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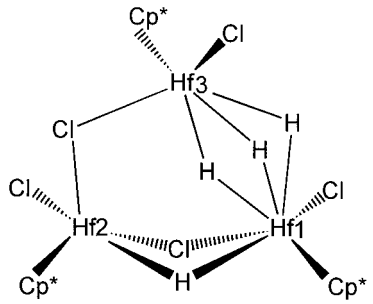
Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (7)

Zr(1)···Zr(2)	3.126(1)	Zr(1)−H(1)−Zr(2)	104.1(19)
Zr(1)−av C(Cp)	2.508	Zr(1)−H(2)−Zr(2)	103.2(14)
Zr(2)−av C(Cp)	2.510	Zr(1)−H(3)−Zr(2)	85.9(17)
Zr(1)−Cl(1)	2.470(1)	P(1)−Zr(1)−Cl(1)	86.06(3)
Zr(2)−Cl(2)	2.456(1)	Cl(2)−Zr(2)−Cl(3)	101.77(3)
Zr(2)−Cl(3)	2.452(1)		
Zr(1)−P(1)	2.744(1)		
Zr(1)−H(1)	1.92(3)		
Zr(1)−H(2)	2.00(3)		
Zr(1)−H(3)	2.24(5)		
Zr(2)−H(1)	2.04(4)		
Zr(2)−H(2)	1.98(3)		
Zr(2)−H(3)	2.35(5)		

interatomic distances and angles in Table 2). As is expected for a $(\mu\text{-H})_3$ dimer,[16] the Zr(1)···Zr(2) distance of 3.126(1) Å is considerably shorter than the 3.460 Å in the $(\mu\text{-H})_2$ complex $[(\eta^5\text{-}C_5H_4Me)_2ZrH(\mu\text{-H})]_2$.[4f] The Cp*, Cl, and PMe_3 ligands adopt a nearly eclipsed configuration around the Zr···Zr axis, with relatively small torsion angles P(1)−Zr(1)−Zr(2)−Cl(3) = −11.34(3)°, CT(1)−Zr(1)−Zr(2)−Cl(2) = 6.29(3)°, and Cl(1)−Zr(1)−Zr(2)−CT(2) = 28.38(3)° (with CT(*x*) being the centroid of the Cp* ligand on the Zr(*x*) atom). The three hydride ligands take up positions staggered relative to the other ligands.

Structural Relationship between $Cp^*_3M_3H_4Cl_5$ and $Cp^*_2M_2H_3Cl_3(PMe_3)$. A comparison of the available structural data on $Cp^*_3Hf_3H_4Cl_5$ (**6**) and $Cp^*_2Zr_2H_3Cl_3(PMe_3)$ (**7**) allows for a proposal for the location of the hydrides in **6**. As mentioned above, in the crystal structure determination of the trinuclear hafnium hydride **6** the hydrides themselves could not be located. Nevertheless, it may be observed that the shortest metal−metal distance in **6**, Hf(1)···Hf(3) (3.061(6) Å), is not bridged by a chloride ligand and is close to the Zr(1)···Zr(2) distance (3.126(1) Å) in the $Zr(\mu\text{-H})_3Zr$ dimer **7**. Therefore, it seems reasonable to propose that Hf(1) and Hf(3) are connected by three bridging hydrides. The two remaining Hf···Hf sides in triangular **6** are each bridged by one chloride. The Hf(2)···Hf(3) distance of 3.721(7) Å is quite long and close to the intermetallic distances observed in $Hf(\mu\text{-Cl})_2Hf$ units (3.9−4.0 Å).[17] It seems unlikely that Hf(2) and Hf(3) are bridged by a hydride as well as a chloride ligand. The Hf(1)···Hf(2) distance of 3.241(6) Å is much closer to known intermetallic distances in $Hf_2(\mu\text{-H})_2$ units, for example, the Hf···Hf distance of 3.397 Å in the $Hf(\mu\text{-H})_2Hf$ dimer $[Cp^*Hf(^i\text{Pr-DAB})(\mu\text{-H})]_2$ (^{i}Pr-DAB = *N*,*N*′-diisopropyl-1,4-diaza-1,3-butadiene).[18] It thus seems possible that Hf(1) and Hf(2) in **6** are bridged by one chloride and one hydride. This would lead to a proposed structure for **6** as shown in Scheme 2. The Hf(1)−Cl(3) bond is the longest of the three $Hf-Cl_{terminal}$ bonds, and the Cl(1)−Hf(1)−Cl(3) and Cg−Hf(1)−Cl(3) angles are the smallest of the $Cl_{bridging}-Hf-Cl_{terminal}$ and Cg−Hf−$Cl_{terminal}$ angles. This indicates that Hf(1) has a higher coordination number than the other two Hf centers, in agreement with the proposed structure.

Scheme 2



6

The proposed structure for the trinuclear species $Cp^*_3M_3(\mu\text{-H})_4(\mu\text{-Cl})_2Cl_3$ (**5**, **6**) can also shed light on the formation of the dinuclear hydrides $Cp^*_2M_2(\mu\text{-H})_3Cl_3(PMe_3)$ (**7**, **8**) and $Cp^*MCl_3(PMe_3)$ (**9**, **10**) upon reaction of **5** or **6** with the Lewis base PMe_3. The side of the trinuclear cluster that is bridged only by a single chloride ligand is likely to be the "weakest link" in the cluster and most susceptible to attack by a Lewis base. Cleavage of the cluster in this position can lead to formation of $Cp^*_2M_2(\mu\text{-H})_3Cl_3(PMe_3)$, one of the observed products, and "Cp^*MHCl_2". The latter is the same species that was presumed to be generated in the reaction of the monoalkyl complexes $Cp^*M[(CH_2)_3NMe_2]Cl_2$ with H_2 and that was found to rearrange to give the trinuclear hydride cluster and Cp^*MCl_3. The latter will bind PMe_3 to generate $Cp^*MCl_3(PMe_3)$, the other observed product in the reaction of **5** and **6** with PMe_3.

Reaction of 6 with 2,6-Xylylisocyanide. Isocyanides are Lewis bases, but are also known to insert readily into early transition metal hydride bonds.[19] As described above, the trinuclear polyhydrides **5** and **6** were found to fragment and redistribute readily upon reaction with the Lewis base trimethylphosphine. To study the relation between the Lewis base-induced fragmentation and the reactivity of the hydride functionalites, the reactivity of **6** toward 2,6-xylylisocyanide was investigated.

The reaction of the trinuclear Hf-hydride **6** with 2,6-xylylisocyanide was studied by ^{1}H NMR (benzene-d_6 solvent) and was found to give full conversion of **6** when 2.7−3 equiv of isocyanide per trinuclear cluster are used. In the course of the reaction several transient intermediates can be observed (vide infra), but eventually the reaction yields three end-products (Scheme 3), one of which is poorly soluble and crystallizes from the solution. This product was identified as the dimeric μ-enediamide complex $[Cp^*HfCl_2]_2[\mu\text{-xyNCH=CHNxy}]$ (**11**, xy = 2,6-dimethylphenyl) by an X-ray structure determination (Figure 3, pertinent interatomic distances and angles in Table 3). The Hf atoms have a three-legged piano-stool configuration. The Hf−N distance is relatively short at 2.039(3) Å (indicating substantial π-donation from the amide nitrogen),[20] and the enediamide ligand is planar with an *E*-configuration around the CH=CH double bond (1.343(5) Å). This product can be considered to derive from reaction of the isocyanide with "$Cp^*Hf(H)Cl_2$", one of the fragments proposed to

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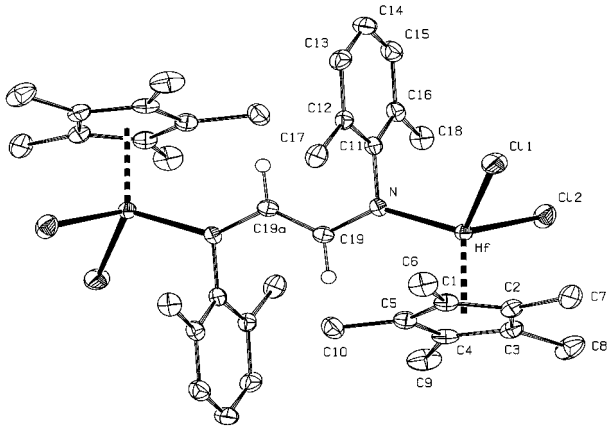

Figure 3. Molecular structure of $[Cp^*HfCl_2]_2[\mu$-(xyNCH=CHNxy)] (**11**).

Scheme 3

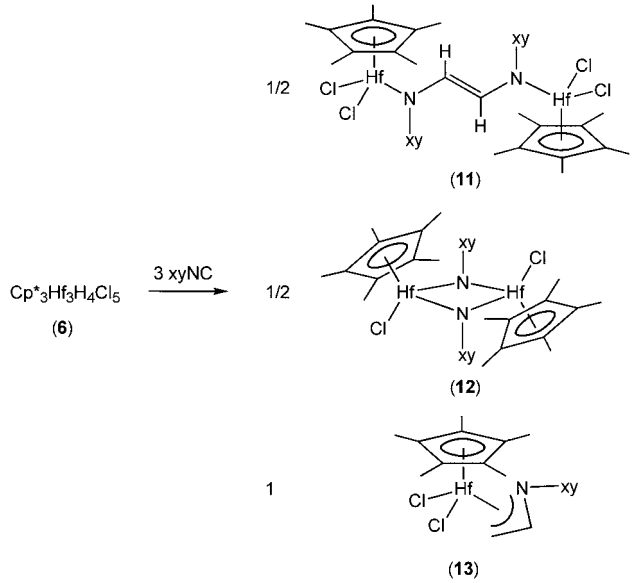

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Cp^*HfCl_2]_2[\mu$-(xyNCH=CHNxy)] (11)

Hf−C1	2.471(4)	Hf−N−C11	108.9(2)
Hf−C2	2.470(3)	Hf−N−C19	136.8(3)
Hf−C3	2.483(4)	C11−N−C19	114.3(3)
Hf−C4	2.485(4)	Cl1−Hf−Cl2	100.87(4)
Hf−C5	2.493(4)	Cl1−Hf−N	109.02(10)
Hf−Cl1	2.376(12)	Cl2−Hf−N	104.89(9)
Hf−Cl2	2.374(12)		
Hf−N	2.039(3)	Hf−N−C11−C16	93.3(3)
N−C11	1.446(5)	C11−N−C19−C19a	−6.2(5)
N−C19	1.417(5)		
C19−C19a	1.343(5)		

be produced by the cleavage of **6** with a Lewis base, by insertion of isocyanide into the Hf−H bond and subsequent iminoformyl C,C-coupling.

The other two end-products could be crudely separated by pentane extraction, as one of these products is considerably less soluble than the other. The least soluble product was obtained analytically pure by recrystallization from toluene. From its composition, solubility, and spectroscopic characteristics, this compound was identified as a dimeric imido complex, $[Cp^*Hf(\mu$-Nxy)Cl$]_2$ (**12**). Related compounds $[(C_5R_5)M(\mu$-NR′)Cl$]_2$ (M = Ti, Zr, Hf) have been prepared previously via various routes.[21] The pentane-soluble end-product could not be crystallized, but a combination of NMR spectroscopy and the product formation upon its reaction with ethanol suggested its formulation as an azaallyl complex, $Cp^*Hf(\eta^3$-$CH_2CHNxy)Cl_2$ (**13**). The ^{1}H NMR spectrum of **13** shows (in addition to the resonances of one Cp* group and one xylyl group) one resonance at δ 7.53 ppm (t, J 11.0 Hz, 1H, attached to one carbon with ^{13}C δ 137.62 ppm, d, J_{CH} 160.4 Hz) and one at δ 3.77 ppm (d, J 11.0 Hz, 2H, attached to one carbon with ^{13}C δ 88.24 ppm, t, J_{CH} 160.2 Hz). These spectroscopic characteristics are compatible with the presence of a (fluxional) trihapto *N*-xylyl-1-azaallyl ligand. Cooling a toluene-d_8 solution of **13** to −90 °C results in a splitting of the resonance at δ 3.77 ppm (the 1-azaallyl methylene group), although the resulting resonances are still broad at that temperature. The IR spectrum of **13** shows strong bands at 1600 and 1592 cm^{-1} that may be associated with the azaallyl moiety. The presence of a *N*-xylyl-1-azaallyl group in **13** is also suggested by the organic products formed in its reaction with an excess of ethanol: 2,6-dimethylaniline and 1,1-diethoxyethane (identified by GC/MS). These can be generated by protonation of the azaallyl group in **13** to give the imine xyN=CHMe, followed by alcoholysis of the latter.

From the observed product formation it thus seems that, after an initial C,C-coupling step, a cleavage of one of the N−C bonds occurs, resulting in one 1-azaallyl and one imido ligand. Cleavage of the N−C bond in a zirconium η^2-imine complex to give an imido species has been observed in the (TC-3,3)Zr[$(PhCH_2)_2$CN(2,6-$Me_2C_6H_3$)] system (TC-3,3 = tropocoronand ligand), leading to formation of the imido dimer $[(TC\text{-}3,3)Zr(\mu$-NAr$)]_2$.[22]

Reaction of 8 with 2,6-Xylylisocyanide. The products **12** and **13** as described above could derive from a reaction of two molecules of isocyanide with the "$Cp^*_2Hf_2(\mu$-$H)_3Cl_3$" fragment. Taken together with the observed formation of **11**, this seems to indicate that, like in the reaction with PMe_3, the reaction of **6** with isocyanide initially involves a specific cleavage of the cluster into a monohydride and a bimetallic trihydride fragment.

To test this hypothesis, we studied the reaction of the dimeric hafnium hydride **8** with 2,6-xylylisocyanide. In this reaction, the same intermediates could be observed by NMR as those that lead to the products **12** and **13** in the reaction of **6** with isocyanide, and the poorly soluble enediamide dimer **11** did not form in this case (Scheme 4). Of the observable intermediates (seen in the reactions of both **6** and **8** with isocyanide), the first one that is formed (**A**) is probably a (bimetallic) iminoformyl complex with composition $Cp^*_2Hf_2(xyCHN)H_2$-Cl_3, derived from the reaction of **8** with *one* molecule of isocyanide. The iminoformyl hydrogen resonance in **A** is found at δ 10.38 ppm with the two remaining hydride resonances at δ 3.43 and 2.15 ppm. By ^{1}H,^{1}H COSY NMR it was seen that these exhibit scalar coupling with each other, and the δ 2.15 ppm resonance also couples

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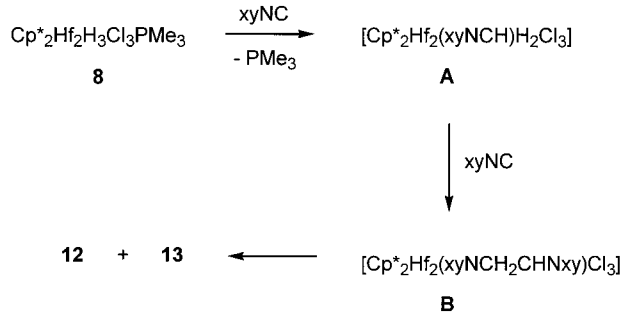
Scheme 4



weakly with the iminoformyl proton. In **A** there are two inequivalent Cp* ligands. The second intermediate (**B**) shows three proton resonances, one at δ 4.63 ppm, one at 4.47 ppm (both dd, J 6.2 and 9 Hz, and attached to a single carbon with ^{13}C δ 60.35 ppm), and one at δ 4.12 ppm (t, J 9 Hz, attached to a carbon with ^{13}C δ 56.68 ppm). This intermediate probably derives from a reaction of the iminoformyl intermediate **A** with a second molecule of isocyanide, involving transfer of the remaining hydrides to carbon and a C,C-coupling reaction to give a xyN−CH−CH_2−Nxy moiety. The intermediate **B** (Cp*$_2$Hf$_2$(xyCHCH_2Nxy)Cl$_3$) then apparently undergoes cleavage of the N−CH_2 bond to produce the imido and azaallyl final products **12** and **13**.

Conclusions

The hydrogenolysis of pentamethylcyclopentadienyl Zr and Hf *N*,*N*-dimethylaminopropyl dichloride complexes leads to the formation of a well-defined, crystallizable trinuclear hydride species, Cp*$_3$M$_3$(μ-H)$_4$(μ-Cl)$_2$Cl$_3$. The use of the *N*,*N*-dimethylaminopropyl group thus appears to aid the formation of this discrete species (unlike the ill-defined polymeric products produced upon hydrogenolysis of other Cp*M(alkyl)Cl$_2$ compounds), but the (*n*-propyl)dimethylamine itself is not incorporated into the final product. This principle should be more widely applicable in the synthesis of polynuclear polyhydrides of highly electron-deficient metal centers, and we are presently investigating the scope of this approach.

The highly asymmetric trinuclear structure of Cp*$_3$M$_3$(μ-H)$_4$(μ-Cl)$_2$Cl$_3$ is rather unusual, but probably represents the thermodynamically most stable structure, as the complex readily self-assembles in solution via ligand exchange reactions, eliminating a molecule of Cp*MCl$_3$. The reactivity of Cp*$_3$M$_3$(μ-H)$_4$(μ-Cl)$_2$Cl$_3$ studied so far (with PMe$_3$ and 2,6-xylylisocyanide) may be interpreted on the basis of its structure, where the cluster is initially attacked by Lewis basic substrates on the most "open" side of the M$_3$ triangle. The product formation is then dependent on the separate reaction pathways of the "Cp*$_2$M$_2$(μ-H)$_3$Cl$_3$" and "Cp*MHCl$_2$" fragments thus generated. The highly electron-deficient metal hydride species show a variety of reaction steps with 2,6-xylylisocyanide, inducing both C,C-coupling and C,N-cleavage processes.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Solvents were predried over Na wire, distilled from Na (toluene) or Na/K alloy (Et$_2$O, pentane, hexane, THF), and stored under nitrogen. Deuterated solvents (C$_6$D$_6$, C$_7$D$_8$, C$_4$D$_8$O; Aldrich) were vacuum transferred from Na/K alloy. Hydrogen gas (AGA 99.9%) and 2,6-xylylisocyanide (Fluka) were used as purchased. Cp*MCl$_3$ (M = Zr, Hf),[23] Li(CH_2)$_3$NMe$_2$,[24] and PMe$_3$[25] were synthesized according to published procedures. Me$_2$N(CH_2)$_3$MgCl was prepared in THF from the corresponding alkyl chloride. NMR spectra were recorded on Varian VXR 300 or Varian Unity 500 spectrometers. The ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (δ 0 ppm); J is reported in Hz. IR spectra were recorded from Nujol mulls between KBr disks on a Mattson-4020 Galaxy FT-IR spectrometer. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Found values are the average of at least two independent determinations.

Cp*Zr[(CH_2)$_3$NMe$_2$]Cl$_2$ (1). A mixture of **3** (0.35 g, 0.86 mmol) and Cp*ZrCl$_3$ (0.28 g, 0.84 mmol) was dissolved in 10 mL of toluene and stirred for 1 h at 20 °C. Concentrating and cooling the solution to −80 °C yielded 0.52 g (1.41 mmol, 84%) of colorless crystalline **1**. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 2.67 (m, 2H, NCH_2), 2.47 (s, 6H, NMe$_2$), 1.91 (s, 15H, C$_5$Me$_5$), 1.80 (m, 2H, −CH_2−), 0.69 (m, 2H, ZrCH_2). ^{13}C NMR (75.4 MHz, C$_6$D$_6$, 20 °C): δ 122.77 (s, Cp* C), 65.23 (t, J = 116.8, ZrCH_2), 63.06 (t, J = 135.8, NCH_2), 48.03 (q, J = 137.0, NMe$_2$), 26.73 (t, J = 126.6, −CH_2−), 12.18 (q, J = 127.0, Cp* Me). IR: 2710(vw), 1481(vw), 1390(m), 1262(vw), 1248(w), 1231(mw), 1166(m), 1099(m), 1048(m), 1008(vs), 979(s), 905(m), 872(m), 810(w), 773(vs), 723(mw), 640(vw), 593(w), 488(m), 356(mw) cm^{-1}. Anal. Calcd for C$_{15}$H$_{27}$NCl$_2$Zr: C, 46.98; H, 7.10; Cl, 18.49; Zr, 23.79. Found: C, 46.69; H, 7.08; Cl, 18.38; Zr, 23.73.

Cp*M[(CH_2)$_3$NMe$_2$]Cl$_2$ (M = Hf, 2; Zr, 1). Onto a mixture of solid Cp*HfCl$_3$ (1.71 g, 4.07 mmol) and Li(CH_2)$_3$NMe$_2$ (0.34 g, 3.65 mmol), which was frozen in liquid nitrogen, 10 mL of THF was condensed. The mixture was allowed to warm to room temperature, and after stirring for 1 h at room temperature the solvent was removed in vacuo. The white mixture was extracted twice with 20 mL of pentane. Concentrating the extract and cooling to −80 °C yielded 1.11 g (2.36 mmol, 65%) of white crystalline **2**. ^{1}H NMR (500 MHz, toluene-d_8, 0 °C): δ 2.52 (t, 2H, J = 7.0, NCH_2), 2.35 (s, 6H, NMe$_2$), 1.96 (s, 15H, C$_5$Me$_5$), 1.91 (m, 2H, −CH_2−), 0.57 (t, 2H, J = 8.0, HfCH_2). ^{13}C NMR (125.68 MHz, toluene-d_8, 0 °C): δ 120.91 (s, Cp* C), 64.44 (t, J = 114.4, HfCH_2), 63.69 (t, J = 135.8, NCH_2), 47.69 (q, J = 132.0, NMe$_2$), 25.17 (t, J = 125.9, −CH_2−), 11.93 (q, J = 126.7, Cp* Me). IR: 2726(m), 2672 (w), 1311(m), 1235(vw), 1169(s), 1155(sh), 1105(m), 1055(m), 1015(s), 974(s), 907(m), 891(w), 870(m), 808(w), 774(s), 723(vs), 593(mw), 488(m) cm^{-1}. Anal. Calcd for C$_{15}$H$_{27}$NCl$_2$Hf: C, 38.27; H, 5.78; N, 2.98; Cl, 15.06; Hf, 37.91. Found: C, 37.95; H, 5.77; N, 2.85; Cl, 14.92; Hf, 37.78.

The same procedure using Cp*ZrCl$_3$ (1.75 g, 5.26 mmol) yielded 1.35 g (3.52 mmol, 67%) of yellow crystalline Cp*Zr[(CH_2)$_3$NMe$_2$]Cl$_2$ (**1**).

Cp*M[(CH_2)$_3$NMe$_2$]$_2$Cl (M = Zr, 3; Hf, 4). At −30 °C, 3.5 mL of a 0.78 M solution of Me$_2$N(CH_2)$_3$MgCl in THF was added dropwise to a suspension of Cp*ZrCl$_3$ (0.31 g, 0.92 mmol) in 10 mL of Et$_2$O. The mixture was allowed to warm to room temperature, and after 3 h the solvent was pumped off. The pale yellow mixture was extracted twice with 30 mL of pentane. Concentrating the extract and cooling to −80 °C yielded 0.27 g (0.61 mmol, 67%) of pale yellow crystalline **3**, after a cold (−80 °C) washing with pentane. ^{1}H NMR (300

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(25) Prepared according to *Inorg. Synth.* **1989**, *26*, 7, using MeMgI instead of MeMgBr.

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MHz, toluene-d_8, −75 °C): δ 3.01 (s, 3H, NMe), 2.4 (br m, 6H, 3 CH_2), 2.22 (s, 6H, NMe_2), 2.0 (br m, 2H, CH_2), 1.88 (s, 15H, C_5Me_5), 1.83 (s, 3H, NMe), 0.54 (br m, 2H, $ZrCH_2$), −0.03 (br m, 1H, Zr−C*H*H), −0.35 (br d, 1H, J = 11.4, Zr−CH*H*). ^{13}C NMR (75.4 MHz, toluene-d_8, −65 °C): δ 119.74 (s, Cp* C), 67.57 (t, J = 136.4, NCH_2), 63.29 (t, J = 128.9, NCH_2), 59.95 (t, J = 128.9, $ZrCH_2$), 51.94 (t, J = 120.3, $ZrCH_2$), 50.70 (q, J = 132.9, NMe), 49.38 (q, J = 131.1, NMe), 46.14 (q, J = 131.2, NMe_2), 28.32 (t, J = 126.6, $-CH_2$-), 26.49 (t, J = 124.3, $-CH_2$-), 12.28 (q, J = 126.2, Cp* Me). IR: 2805(w), 2760(mw), 2705(w), 1390(mw), 1309(m), 1275(mw), 1251(s), 1223(w), 1198(s), 1167(mw), 1148(m), 1093(m), 1043(s), 1028(s), 1002(sh), 960(s), 896(s), 880(s), 843(s), 802(w), 774(s), 718(mw), 591(w), 568(m), 515(mw), 496(m), 467(w), 455(w), 420(m), 347(w) cm^{-1}. Anal. Calcd for $C_{20}H_{39}N_2ClZr$: C, 55.32; H, 9.05; Cl, 8.16; Zr, 21.01. Found: C, 55.21; H, 9.22; Cl, 7.62; Zr, 20.51.

The same procedure using Cp^*HfCl_3 (0.31 g, 0.74 mmol) yielded 0.20 g (0.38 mmol, 51%) of white crystalline $Cp^*Hf[(CH_2)_3NMe_2]_2Cl$ (**4**). ^{1}H NMR (500 MHz, toluene-d_8, −60 °C): δ 2.50 (br, 1H, −CH*H*′), 2.37 (s, 3H, NMe), 2.33 (br, 1H, N−CH*H*′), 2.32 (br, 1H, N−C*H*H′), 2.23 (s, 6H, NMe_2′), 2.15 (br, 1H, −C*H*H′), 1.97 (br, 1H, −CH*H*), 1.88 (br, 1H, −C*H*H), 1.84 (br, 1H, N−CH*H*), 1.83 (s, 15H, C_5Me_5), 1.80 (s, 3H, NMe), 1.59 (br, 1H, N−C*H*H), 0.65 (br, 1H, Hf−CH*H*), 0.48 (br, 1H, Hf−CH*H*′), 0.35 (br, 1H, Hf−C*H*H), 0.11 (br, 1H, Hf−C*H*H′). ^{13}C NMR (125.68 MHz, toluene-d_8, −60 °C): δ 118.97 (s, Cp* C), 70.09 (t, J = 117.2, $HfCH_2$′), 67.44 (t, J = 130.0, NCH_2′), 64.92 (t, J = 134.0, NCH_2), 54.98 (t, J = 114.7, $HfCH_2$), 47.95 (q, J = 136.8, NMe), 46.06 (q, J = 135, NMe_2+NMe), 29.36 (t, J = 123.3, CH_2′), 24.77 (t, J = 132.3, CH_2), 11.89 (q, J = 126.2, Cp* Me). With 2D NMR experiments (DQCOSY, HSQC, and NOESY) the different signals could be assigned to the various CH_2 groups. Resonances belonging to the nonchelating alkyl group are indicated by a prime (′). IR: 2817(w), 2765(m), 2705(vw), 1400(w), 1317(mw), 1302(w), 1277(vw), 1254(s), 1231(w), 1217(s), 1165(s), 1115(w), 1098(m), 1042(s), 1031(vw), 1007(s), 972(sh), 901(m), 851(s), 802(w), 762(s), 723(mw), 594(s), 552(m), 530(m), 482(m), 467(vw) cm^{-1}. Anal. Calcd for $C_{20}H_{39}N_2ClHf$: C, 46.06; H, 7.54; N, 5.37; Cl, 6.80; Hf, 34.23. Found: C, 45.90; H, 7.47; N, 5.29; Cl, 6.75; Hf, 34.05.

$Cp^*_3Zr_3(\mu\text{-}H)_4(\mu\text{-}Cl)_2Cl_3$ (5). A solution of **1** (0.95 g, 2.47 mmol) in 25 mL of benzene was stirred at room temperature in the dark under H_2 (1 atm) for several days. The clear yellow solution was concentrated, and slow diffusion of pentane into the solution produced large yellow crystals. The solvent was decanted, and the solid was dried in vacuo, yielding 0.515 g of material (approximately 1.8 mmol of Zr). The product thus obtained can contain varying amounts of Cp^*ZrCl_3 and is somewhat photosensitive, solutions turning green in daylight within an hour. The corresponding deuteride **5**-d_4 was obtained from a similar procedure using D_2. ^{1}H NMR (300 MHz, toluene-d_8, −50 °C): δ 4.23 (m, 1H, H_A), 3.92 (m, 1H, H_B), 2.96 (m, 1H, H_C), 2.21 (s, 15H, C_5Me_5), 2.10 (s, 15H, C_5Me_5), 1.86 (s, 15H, C_5Me_5), 0.88 (1H, H_D); hydride couplings: J_{AB} = 9.9, J_{AC} = 10.6, J_{BD} = 6.2, J_{AD} = 3.3, J_{CD} = 1.5, J_{BC} = 0 (determined by selective decoupling experiments). IR: 2710(vw), 1575*(br, vs), 1480(m), 1417(m), 1310*(br, mw), 1150*(w), 1105*(w), 1063(w), 1016(s), 926*(mw), 901*(mw), 855*(w), 806(vw), 592(w), 418(w), 369(s) cm^{-1}. The starred wavenumbers are shifted by a factor 1/(1.38−1.42) in the spectrum of **5**-d_4. No consistent elemental analyses could be obtained, due to the presence of varying amounts of cocrystallized Cp^*ZrCl_3 and interstitial benzene. Zr:Cl ratios between 1:1.7 and 1:2.0 were found.

$Cp^*_3Hf_3(\mu\text{-}H)_4(\mu\text{-}Cl)_2Cl_3$ (6). A solution of **2** (0.77 g, 1.64 mmol) in 10 mL of toluene was stirred at room temperature in the dark under H_2 (1 atm) for 2 days. The pale yellow solution was concentrated, and slow diffusion of 15 mL hexane into the solution gave 0.37 g (0.33 mmol, 80%) of white crystalline **6**. ^{1}H NMR (500 MHz, toluene-d_8, −60 °C): δ 9.17 (m, 1H, H_A), 8.46 (m, 1H, H_B), 7.71 (m, 1H, H_C), 4.63 (m, 1H, H_D), 2.26 (s, 15H, C_5Me_5), 2.14 (s, 15H, C_5Me_5), 1.90 (s, 15H, C_5Me_5); hydride couplings: J_{AB} = 8.3, J_{AC} = 8.9, J_{BD} = 4.3, J_{AD} = 2.1, J_{BC} = J_{CD} = 0 (determined by selective decoupling experiments). Anal. Calcd for $C_{30}H_{49}Cl_5Hf_3$: C, 32.10; H, 4.40; Cl, 15.79; Hf, 47.71. Found: C, 32.11; H, 4.28; Cl, 15.91; Hf, 47.42.

$Cp^*_2M_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (M = Zr, 7; Hf, 8). To a solution of **5** (0.249 g, 0.83 mmol Zr) in 10 mL of toluene was added 0.25 mL of PMe_3 (excess). After stirring for 20 h at 20 °C the solvent was evaporated and the residue was extracted with diethyl ether. After concentrating the extract, the solution was gradually (3 °C h^{-1}) cooled to −25 °C to produce analytically pure pale yellow crystalline **7** (0.101 g, 0.316 mmol Zr, 41%). Formation of $Cp^*ZrCl_3(PMe_3)$ (**9**) was observed by NMR (identified by comparison with an authentic sample, see below). The corresponding deuteride **7**-d_3 was obtained from a similar procedure using D_2. ^{1}H NMR (300 MHz, toluene-d_8, −30 °C): δ 4.73 (d, $^2J_{PH}$ = 12.1, t, $^2J_{HH}$ = 8, 1H, μ-H), 4.44 (d, $^2J_{PH}$ = 18.3, t, $^2J_{HH}$ = 8, 1H, μ-H), 2.97 (ps q, $^2J_{PH} \approx {}^2J_{HH}$ = 8, 1H, μ-H), 2.17 (s, 15H, C_5Me_5), 2.03 (s, 15H, C_5Me_5), 1.03 (d, $^2J_{PH}$ = 8.4, 9H, PMe_3). At 75 °C only one μ-H resonance is observed at 4.09 ppm (br, 3H). ^{31}P NMR (121.4 MHz, toluene-d_8, −30 °C, PMe_3-protons selectively decoupled): δ −18.1 (ddd, $^2J_{PH}$ = 18.3, 12.1, 8.3). At 75 °C a quartet is observed ($^2J_{PH}$ = 12.9). IR: 2710(vw), 1465*(vs sh), 1445*(vs), 1327*(m), 1285(m), 1148*(m), 1116*(mw), 1087(w), 1023(mw), 960 (s), 848(w), 780*(m), 765*(mw), 734(vw), 723(w), 413(vw), 366(m) cm^{-1}. The starred wavenumbers are shifted by a factor 1/(1.38−1.42) in the spectrum of **7**-d_3. Anal. Calcd for $C_{23}H_{42}Zr_2Cl_3P$: C, 43.28; H, 6.63; Cl, 16.66; Zr, 28.58. Found: C, 43.16; H, 6.66; Cl, 16.63; Zr, 28.46.

A similar procedure using **6** (0.22 g, 0.20 mmol) yielded 0.10 g (46%) of the Hf analogue **8**. ^{1}H NMR (300 MHz, toluene-d_8, 25 °C): δ 9.15 (m, 2H, μ-H), 7.67 (ps. q, $^2J_{PH} \approx {}^2J_{HH}$ = 7.6, 1H, μ-H), 2.23 (s, 15H, C_5Me_5), 2.11 (s, 15H, C_5Me_5), 1.08 (d, $^2J_{PH}$ = 8.3, 9H, PMe_3). IR: 2726(mw), 2679(vw), 1306(vw), 1289(w), 1204(m), 1173(m), 1094(mw), 1026(s), 964(vs), 856(w), 822(m), 812(m), 774(vw), 731(w), 723(w), 592(mw) cm^{-1}. Anal. Calcd for $C_{23}H_{42}Hf_2Cl_3P$: C, 33.98; H, 5.21; Hf, 43.91. Found: C, 34.06; H, 5.12; Hf, 43.71.

$Cp^*ZrCl_3(PMe_3)$ (9). At 20 °C, 0.5 mL of PMe_3 (excess) was added to a suspension of Cp^*ZrCl_3 (0.502 g, 1.51 mmol) in 20 mL of benzene. After stirring for 2 days a clear pale yellow solution had formed. After filtration and concentraation, pentane was condensed into the mixture, yielding 0.477 g (1.17 mmol, 77%) of crystalline **9**. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 1.97 (s, 15H, Cp*), 0.98 (d, $^2J_{PH}$ = 6.6, 9H, PMe_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): δ −23.13 (s, PMe_3). Anal. Calcd for $C_{13}H_{24}ZrCl_3P$: C, 38.19; H, 5.92; Cl, 26.01; Zr, 22.31. Found: C, 38.48; H, 5.98; Cl, 25.68; Zr, 22.29.

Reaction of 6 with 2,6-Dimethylxylylisocyanide on a Preparative Scale. To a solution of 2,6-xylylisocyanide (69.1 mg, 0.53 mmol) in 4.0 mL of toluene was added **6** (0.23 g, 0.20 mmol). The solution turned red immediately. After a few hours, crystals started to form. After 5 days at ambient temperature the solution was decanted and the crystals were washed with pentane. This gave 60 mg (0.058 mmol, 57%) of yellow crystalline $[Cp^*HfCl_2]_2[\mu$-(xyNCH═CHNxy)] (**11**). Anal. Calcd for $C_{38}H_{50}N_2Cl_4Hf_2$: C, 44.16; H, 4.88; N, 2.71. Found: C, 44.08; H, 4.92; N, 2.53. IR: 2725(mw), 2671(w), 2353(mw), 1307(mw), 1252(w), 1196(s), 1163(w), 1128(s), 1081(m), 1023(m), 982(w), 924(m), 897(vw), 859(s), 802(vw), 777(s), 722(s), 702(mw), 669(vw), 601(w), 573(vw), 517(m), 498(sh), 464(w), 450(w), 430(m) cm^{-1}. The compound is very poorly soluble in most solvents, precluding NMR spectroscopic characterization.

The volatiles of the mother liquor were evaporated, leaving a yellow-brown powder. This is a mixture of two compounds that could be crudely separated by extraction with pentane, one compound, $[Cp^*Hf(\mu\text{-}Nxy)Cl]_2$ (**12**), being less soluble in pentane than the other, $Cp^*Hf(\eta^3\text{-}CH_2CHNxy)Cl_2$ (**13**). Recrystallizing a portion of crude **12** from toluene yielded analytically pure material. ^{1}H NMR (500 MHz, C_6D_6, 25 °C):

Table 4. Crystallographic Data for $Cp^*_3Hf_3(\mu\text{-}H)_4(\mu\text{-}Cl)_2Cl_3$ (6), $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (7), and $[Cp^*HfCl_2]_2[\mu\text{-}(xyNCH{=}CHNxy)]$ (11)

	6	7	11
chem formula	$C_{30}H_{49}Cl_5Hf_3$	$C_{23}H_{42}Cl_3PZr_2$	$(C_{19}H_{25}Cl_2HfN)_2$
M_r	1122.45	638.36	1033.62
cryst syst	triclinic	monoclinic	triclinic
color, habit	white, plate	pale yellow, plate	orange, plate
size (mm)	0.12 × 0.38 × 0.48	0.18 × 0.25 × 0.30	0.06 × 0.24 × 0.56
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	9.029(1)	15.599(3)	9.451(1)
b (Å)	11.214(1)	11.203(3)	10.885(1)
c (Å)	17.449(2)	16.862(4)	11.774(1)
α (deg)	88.912(9)		116.363(6)
β (deg)	83.370(8)	103.27(2)	92.371(8)
γ (deg)	88.690(8)		113.232(8)
V (Å^3)	1754.2(3)	2868(1)	962.17(19)
Z	2	4	1
D_{calc} (g cm^{-3})	2.125	1.478	1.784
μ(Mo Kα) (cm^{-1})	92.5	10.6	57.0
F(000)	1060	1304	504
data collection			
temp (K)	130	130	130
θ range (deg)	1.17−27.5	1.24−28.0	2.00−27.0
ω scan width (deg)	0.90 + 0.34 tan θ	1.05 + 0.35 tan θ	0.90 + 0.34 tan θ
data collected (h,k,l)	−11:11, −14:0, −22:22	−20:20, −1:14, 0:22	0:12, −13:12, −15:15
min and max transm	0.0579, 0.4111		0.264, 0.717
no. of rflns collected	8737	8206	4442
no. of indpndt rflns	8065	6899	4183
observed rflns	7308 ($F_o \geq 4\sigma(F_o)$)	5557 ($I \geq 2.5\sigma(I)$)	3865 ($F_o \geq 4\sigma(F_o)$)
$R(F)$ (%)	5.89	3.4	2.18
$wR(F^2)$ (%)	15.6		5.61
GOF	1.013	2.045	1.046
weighting a,b	0.0924,49.26		0.0409,0.585
no. of params refined	358	432	308

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δ 7.22 (d, 4H, J = 7.3, *m*-Ar), 6.74 (t, 2H, J = 7.3, *p*-Ar), 2.78 (s, 12H, xy-Me), 1.71 (s, 30H, Cp*). ^{13}C NMR (125.68 MHz, C_6D_6, 25 °C): δ 148.05 (s, Ar C), 130.93 (s, Ar CMe), 128.59 (d, J = 157.9, Ar CH), 122.91 (d, J = 158.4, Ar CH), 121.16 (s, Cp* C), 24.06 (q, J = 124.2, xy-Me), 10.76 (q, J = 127.5, Cp* Me). IR: 2728(mw), 2670(w), 1588(m), 1253(m), 1186(s), 1165(sh), 1134(vw), 1104(s), 1027(m), 978(m), 957(sh), 916(m), 878(s), 803(w), 764(s), 739(s), 720(m), 612(m), 580(s), 542(m), 512(m), 488(m). Anal. Calcd for $C_{36}H_{48}N_2Cl_2Hf_2$: C, 46.16; H, 5.17; N, 2.99. Found: C, 46.23; H, 5.24; N, 2.97.

The azaallyl complex **13** could not be crystallized, but was characterized by NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 7.53 (t, 1H, J = 11.0, N−C*H*=CH$_2$), 7.0−6.9 (m, 3H, Ar), 3.77 (d, 2H, J = 11.0, N−CH=C*H*$_2$), 2.18 (s, 6H, xy-Me), 1.81 (s, 15H, Cp*). ^{13}C NMR (125.68 MHz, C_6D_6, 25 °C): δ 141.14 (s, Ar C), 137.65 (d, J = 160.4, N-*C*H=CH$_2$), 136.73 (s, Ar CMe), 129.59 (s, Ar CMe), 127.02 (d, J = 158.8, Ar CH), 119.97 (s, Cp* C), 88.24 (t, J = 160.2, N−CH=*C*H$_2$), 12.68 (q, J = 127.5, xy-Me), 11.43 (q, J = 128.1, Cp* Me). The remaining Ar CH signal is obscured by the solvent resonances. IR: 2731(s), 1600(s), 1592(s), 1555(m), 1339(vw), 1310(m), 1263(s), 1223(m), 1189(w), 1125(s), 1090(s), 1068(w), 1027(s), 975(s), 942(sh), 892(s), 871(w), 820(s), 768(s), 740(w), 720(w), 710(w), 651(s), 608(m), 594(w), 536(m), 495(s).

An aliquot of **13** was reacted with an excess of ethanol, and the products were analyzed by GC/MS (EI): m/z 117 (M−H) (1,1-diethoxyethane), m/z 121 (2,6-dimethylaniline), m/z 136 (1,2,3,4,5-pentamethylcyclopentadiene).

Reaction of 6 with 2,6-Dimethylxylylisocyanide on NMR Scale. To **6** (22 mg, 19.7 μmol) was added a solution of 2,6-dimethylxylylisocyanide (6.4 mg, 48.8 μmol) in 0.4 mL of C_6D_6. The red solution was transferred to an NMR tube (equipped with Teflon stopcock) and was monitored after 30 min, 6 h, 24 h, and 1 week. After a few hours crystals (of **11**) started to form in the tube. After 30 min intermediate **A** was observed. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 10.38 (d, J = 1.8, 1H, CH=N), 3.44 (d, J = 4.4, 1H, H), 2.48 (s, 3H, xy-Me), 2.34 (s, 3H, xy-Me), 2.15 (m, 1H, H), 1.90 (s, 15H, Cp*), 1.86 (s, 15H, Cp*). After 24 h intermediate **B** was predominant. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 7.0−6.8 (m, Ar), 4.63 (dd, J 6.2 and 9, 1H, NC*H*H), 4.48 (dd, J 6.2 and 9, 1H, NCH*H*), 4.12 (t, J 9, 1H, NCH), 2.16 (s, 6H, xy-Me), 2.10 (s, 6H, xy-Me), 1.81 (s, 15H, Cp*), 1.79 (s, 15H, Cp*). ^{13}C(APT) NMR (125.68 MHz, C_6D_6, 25 °C): δ 129.56 (Ar CH), 128.27 (Ar CH), 60.35 (NCH$_2$), 56.68 (NCH), 20.13 (xy Me), 18.99 (xy Me), 11.81 (Cp* Me), 11.50 (Cp* Me). The remaining Ar CH signals are obscured by the solvent resonances. The assignment for **B** was aided by ^{1}H,^{13}C HETCOR, and ^{13}C APT spectra. After 1 week, only the resonances of the end-products **12** and **13** were observed.

Reaction of 8 with 2,6-Dimethylxylylisocyanide on NMR Scale. To **8** (10.4 mg, 12.8 μmol) was added a solution of 2,6-dimethylxylylisocyanide (3.8 mg, 29.0 μmol) in 0.4 mL of C_6D_6. The yellow solution was transferred to an NMR tube (equipped with Teflon stopcock) and was monitored after 30 min, 6 h, 24 h, and 1 week. No crystallization occurred. In the spectra the formation of free PMe_3 was observed. The resonances of the intermediates **A** and **B** and the final products **12** and **13** are the same as for the reaction of **6** with 2,6-dimethylxylylisocyanide.

X-ray Structures. Suitable crystals of **6**, **7**, and **11** were glued on top of a glass fiber by using inert-atmosphere handling techniques and transferred into the cold nitrogen stream on an Enraf-Nonius CAD-4F diffractometer (graphite-monochromated Mo Kᾱ radiation, λ = 0.71073, $\Delta\omega$ = 0.90 + 0.34 tan θ). Accurate cell parameters and an orientation matrix were determined from the setting angles (SET4[26]) of 22 reflections in the ranges of 18.19° < θ < 20.62° (**6**), 16.85° < θ < 19.27° (**7**), and 16.65° < θ < 21.69° (**11**). Reduced cell calculations did not indicate any higher lattice symmetry.[27] Crystal data and details on data collection and refinement are presented in Table 4. Intensity data were corrected for Lorentz and polarization effects, and for absorption in the case of **6** and **11**. The structures were solved by Patterson methods and

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subsequent difference Fourier techniques (DIRDIF[28] in the case of **6** and **11**). All calculations for **6** and **11** were performed on a HP9000/735 computer with the program packages SHELXL[29] (least-squares refinements) and PLATON[30] (calculation of geometric data and the ORTEP illustrations). All calculations for **7** were performed on a CDC-Cyber 170/760 computer with the program packages XTAL[31] (least-squares refinements) and EUCLID[32] (calculation of geometric data and the ORTEP illustrations). For **6**, refinement was frustrated by a disorder problem: one of the three Cp* ligands is rotationally disordered; the electron density of the outer carbon atoms (C26−C30) appeared to be spread out. Attempts to refine a disorder model with discrete C-positions with fractional occupation in this region failed; so in the final refinement these atoms showed unrealistic displacement parameters. The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using hybridization at the C atom as appropriate with $U_{iso} = 1.5U_{equiv}$ of their parent atom, where values U_{equiv} are related to the atoms to which the H atoms are bonded. The methyl groups were refined as rigid groups, which were allowed to rotate free. The missing four hydride positions could not be located in the difference Fourier map. For **7** and **11**, refinement of the positions and anisotropic thermal parameters for the non-hydrogen atoms followed by difference Fourier synthesis resulted in the location of all hydrogen atoms of which the coordinates and isotropic thermal parameters were refined.

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Supporting Information Available: Tables showing details of crystal structure determinations, atom coordinates, equivalent isotropic displacement parameters, anisotropic thermal displacement parameters, bond lengths, angles, and hydrogen parameters for **6**, **7**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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