Organometallics **2003,** *22,* 615−617

Polynuclear Hafnium Polyhydrides with a 1,3-Butadiene-1,4-diyl Fragment from Hydrogenolysis of a Butadiene Alkyl Complex

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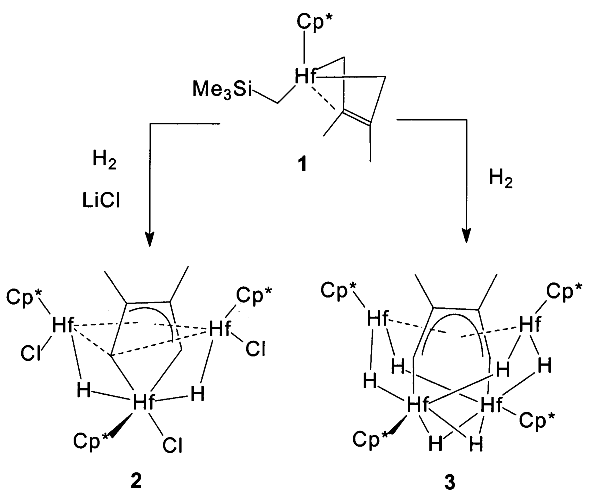
Received November 4, 2002

Summary: Hydrogenolysis of (η^5-C_5Me_5)*Hf(2,3-dimethyl-1,3-butadiene)*CH_2SiMe_3 *leads to the formation of the mixed-valence tetranuclear polyhydride* (η^5-C_5Me_5)$_4$$Hf_4$($\sigma^1$:$\sigma^1$:$\eta^4$:$\eta^4$-$C_6H_8$)($\mu$-H)$_6$, *with a central 2,3-dimethyl-1,3-butadiene-1,4-diyl fragment. The same reaction in the presence of LiCl gives chloride incorporation to yield the trinuclear species* (η^5-C_5Me_5)$_3$$Hf_3$($\sigma^2$:$\eta^4$:$\eta^4$-$C_6H_8$)($\mu$-H)$_2$$Cl_3$.

Electron-deficient monocyclopentadienyl polyhydrides of the heavier group 4 metals of the type (η^5-C_5R_5)-MH_nX_{3-n} (M = Zr, Hf) are expected to show interesting reactivity due to the combination of the high Lewis acidity of the metal center and the polar character of the metal−hydrogen bond, but they are relatively difficult to obtain as well-defined molecular species.[1] In previous work from our group it was shown that hydrogenolysis of the half-sandwich complexes Cp*M-(2,3-dimethyl-1,3-butadiene)Cl and Cp*M((dimethylamino)propyl)Cl_2 affords the polynuclear complexes [Cp*M(H)$_2$Cl]$_4$ and Cp*$_3$$M_3H_4Cl_5$, respectively (Cp* = η^5-C_5Me_5; M = Zr, Hf).[2,3] The reactivity of the latter species includes the insertion of unsaturated substrates into the M−H bonds, as well as C−C coupling and C−N cleavage reactions.[3,4] Here we describe attempts to obtain species of the type [Cp*HfH$_x$]$_n$ by hydrogenolysis of the diene alkyl complex Cp*Hf(2,3-dimethyl-1,3-butadiene)CH_2SiMe_3. Remarkably, this reaction yields polynuclear polyhydrides containing a central 2,3-dimethyl-1,3-butadiene-1,4-diyl fragment, as the result of double hydrogen atom abstraction from the diene ligand.

The 14-electron diene alkyl complex Cp*Hf(C_6H_{10})CH_2-$SiMe_3$ (**1**; C_6H_{10} = 2,3-dimethyl-1,3-butadiene) can be conveniently prepared by reaction of the readily available 16-electron THF adduct Cp*Hf(C_6H_{10})Cl.THF[5] with Me_3SiCH_2Li.[6] As **1** is a liquid at ambient temperature, initial experiments were performed with toluene solutions of **1** prepared in situ from the reagents mentioned above, from which the THF was removed by solvent evaporation followed by redissolution in toluene. This solution contains **1**, but in the presence of finely suspended LiCl. Hydrogenolysis of this solution at ambient temperature (6 bar of H_2, reaction time 5 days), followed by crystallization from toluene, afforded the trinuclear complex Cp*$_3$$Hf_3$($\sigma^2$:$\eta^4$:$\eta^4$-$C_6H_8$)($\mu$-H)$_2$$Cl_3$ (**2**; Scheme 1) in 64% yield as red-purple crystals containing 0.5 equiv of toluene. A structure determination of **2**[7] (Figure 1) revealed a triangular trinuclear arrangement of the metal atoms arranged around a central 2,3-dimethyl-1,3-butadiene-1,4-diyl fragment. This fragment is σ^2-bound to Hf(3) and η^4-bound to both Hf(1) and Hf(2).[8] The two hydrides bridge the Hf(1)/Hf(2)−Hf(3) sides of the triangle, and there is one terminal chloride on each Hf atom. The structure of **2** is similar to that of the compound Cp*$_3$$Hf_3$($\sigma^2$:$\eta^4$:$\eta^4$-$C_4H_4$)($\mu$-Cl)$_2$-$Cl_3$,[9] obtained by thermolysis of Cp*Hf(η^3-1-methallyl)-

Scheme 1



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(4) Substrates used include isonitriles,[3] nitriles, ketones, and CO: Visser, C.; Meetsma, A.; Hessen, B. Manuscript in preparation.

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(7) Crystal data for **2**: $C_{36}H_{55}Cl_3Hf_3 \cdot 0.5C_7H_8$, space group $P2_1/c$, monoclinic, a = 16.5994(9) Å, b = 11.2636(6) Å, c = 21.899(1) Å, β = 105.813(1)°, V = 3939.3(3) Å^3, Z = 4, T = 120(1) K, D_{calcd} = 1.982 g cm^{-3}, μ = 81.15 cm^{-1}, λ(Mo Kα) = 0.710 73 Å. A multiscan absorption correction was applied. Least-squares refinement with 9520 unique reflections and 501 parameters converged to a final $R_w(F^2) = 0.0774$ and $R(F) = 0.0321$ for 8371 reflections with $F_o \geq 4.0\sigma(F_o)$. The hydrides were located from the Fourier difference map, and their positional parameters were refined freely. The Cp* ligand attached to Hf(3) was disordered over two rotational orientations that were refined with a sof value of 0.516(8). The unit cell contains 0.5 molecule of toluene that is disordered over an inversion center.

(8) An inspection of the C−C distances within the C_6H_8 fragment in **2** suggests some localization of the π-electron density: C(31)−C(32) (1.503(3) Å) is significantly longer than C(32)−C(33) and C(33)−C(34) (1.433(3) and 1.437(3) Å, respectively).

10.1021/om020909l CCC: \$25.00
Publication on Web 01/17/2003

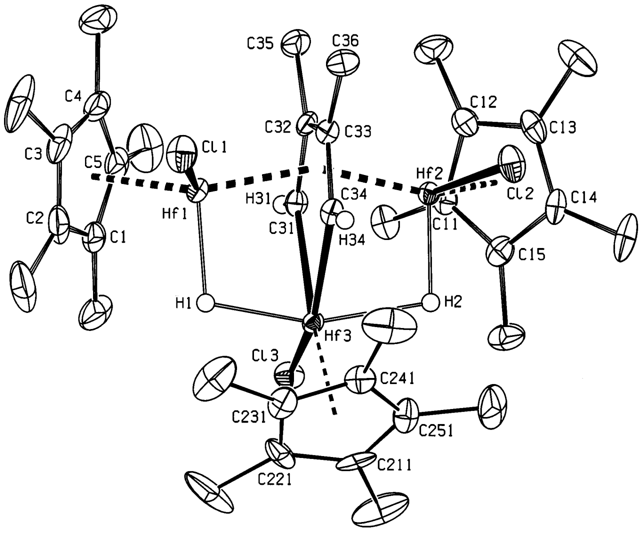

Figure 1. Molecular structure of **2** showing 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): Hf(1)···Hf(3) = 3.0466(3), Hf(2)···Hf(3) = 3.0438(3), Hf(3)−C(31) = 2.397(3), Hf−C(34) = 2.273(2), Hf(1)−C(31) = 2.357(3), Hf(1)−C(32) = 2.417(2), Hf(1)−C(33) = 2.486(3), Hf(1)−C(34) = 2.482(3), Hf(1)−Cl(1) = 2.429(2), Hf(3)−Cl(3) = 2.446(1), all Hf−H distances between 1.88(6) and 2.10(6); C(31)−Hf(3)−C(34) = 64.52(9).

Cl_2, with the differences that in the latter the butadienediyl fragment is unsubstituted and that there are two bridging chlorides instead of hydrides. The hydride-bridged Hf···Hf distances in **2** (3.0466(3) and 3.0438 Å) are noticeably shorter than the chloride-bridged Hf···Hf distances in $Cp^*{}_3Hf_3(C_4H_4)Cl_5$ (3.2261(9) and 3.2061(9) Å). As proposed for the latter compound, the structural and NMR spectroscopic features[10] of **2** suggest that the C_6H_8 fragment can be considered as a tetraanionic group, leading to a formal oxidation state of 4+ for all three Hf atoms.

The observed product formation is remarkable for two reasons. Even though the reaction is performed under 6 bar of hydrogen pressure, the product is effectively the result of a sequence that includes the dehydrogenation of a diene ligand. In addition, the incorporation of chloride into the product has to take place after initial hydrogenolysis. NMR experiments showed that under the applied conditions the alkyl complex **1** is formed quantitatively from $Cp^*Hf(C_6H_{10})Cl\cdot THF$ and the alkyllithium reagent, and, although the Cp*Hf to Cl ratio in **2** is the same as in $[Cp^*Hf(H)_2Cl]_4$ (the product of the hydrogenolysis of $Cp^*Hf(C_6H_{10})Cl^2$), none of the latter product could be identified in the reaction mixture. The formation of **2** has to follow a pathway that is quite different from the formation of $[Cp^*Hf(H)_2Cl]_4$, possibly involving Hf−H/Li−Cl salt metathesis (although the presence of LiH in the reaction mixture was not established).

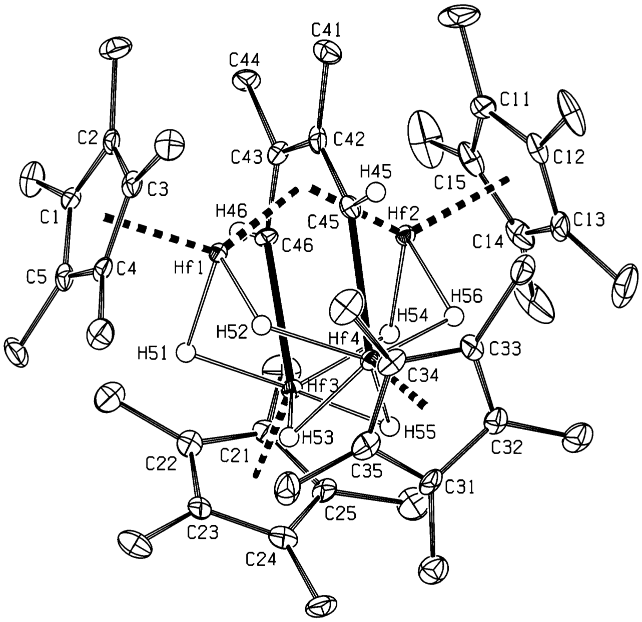

Figure 2. Molecular structure of **3** showing 50% probability ellipsoids. Selected interatomic distances (Å): Hf(1)···Hf(3) 3.0523(3), Hf(1)···Hf(4) = 3.0612(3), Hf(3)···Hf(4) = 2.8737(3), Hf(3)−C(46) = 2.475(5), Hf(4)−C(45) = 2.460(5), Hf(1)−C(45) = 2.306(5), Hf(1)−C(42) = 2.416(5), Hf(1)−C(43) = 2.413(5), Hf(1)−C(46) = 2.302(5), all Hf−H distances between 1.79(7) and 1.98(5).

Performing the hydrogenolysis of **1** in toluene solution, after it had been separated from the LiCl by pentane extraction, allowed the isolation of the tetranuclear polyhydride complex $Cp^*{}_4Hf_4(\sigma^1{:}\sigma^1{:}\eta^4{:}\eta^4\text{-}C_6H_8)(\mu\text{-}H)_6$ (**3**; Scheme 1) as deep red crystals in 44% yield. In this experiment the hydrogenolysis was performed at 20 bar of H_2 and 70 °C for 6 h. Compound **3** is also formed (more slowly) at lower temperatures and pressures, but isolated yields are then usually lower.[11] A structure determination of **3**[12] (Figure 2) revealed a tetranuclear butterfly arrangement of the four Hf atoms around a central 2,3-dimethyl-1,3-butadiene-1,4-diyl fragment. This fragment is σ^1-bound to Hf(3) and Hf(4) and η^4-bound to Hf(1) and Hf(2). Compound **3** contains six hydrides, four of which bridge the outside edges of the butterfly and the remaining two bridge the central Hf(3)···Hf(4) edge. The distances of Hf(1) and Hf(2) to Hf(3) and Hf(4) are all around 3.06 Å, comparable to those in **2**, but the Hf(3)···Hf(4) distance is substantially shorter at 2.8737(3) Å. To our knowledge this is the shortest Hf−Hf distance observed in molecular complexes of hafnium. For comparison, the intermetallic distances in the halide-bridged Hf(III) dimers Hf_2X_6-

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[9] Hessen, B.; Spek, A. L.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1058.

[10] NMR data for **2** are as follows. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 8.97 (s, 2H, HfH), 7.38 (d, J = 3.9 Hz, 1H, =CH−), 6.42 (d, J = 3.9 Hz, 1H, =CH−), 2.47 (s, 3H, CMe), 2.21 (s, 15 H, Cp*), 1.96 (s, 30H, Cp*), 1.85 (s, 3H, CMe). ^{13}C NMR (125.7 MHz, C_6D_6, 25 °C): δ 177.56 (d, J = 139 Hz, =CH−), 174.90 (d, J = 139 Hz, =CH−), 129.28 (s, *C*Me), 122.25 (s, *C*Me), 120.95 (s, Cp* C), 119.55 (s, Cp* C), 23.62 (q, J = 127 Hz, C*Me*), 20.15 (q, J = 127 Hz, C*Me*), 12.87 (q, J = 127 Hz, Cp* Me), 12.19 (q, J = 127 Hz, Cp* Me).

[11] Reaction of salt-free **1** with H_2 in the presence of powdered crystalline LiCl also yielded the chloride-free hydride **3** as the main product, suggesting that LiCl thus introduced is less reactive than finely divided LiCl generated in situ. Generation of **1** by reaction of $Cp^*Hf(C_6H_{10})Cl$ with Me_3SiCH_2Li in C_6D_6 followed by reaction with H_2 yielded the chloride-containing **2** as the only hydride product in the mixture, as seen by NMR spectroscopy.

[12] Crystal data for **3**: $C_{46}H_{74}Hf_4$, space group $P2_1/c$, monoclinic, a = 10.9467(5) Å, b = 17.1030(8) Å, c = 23.929(1) Å, β = 94.704(1)°, V = 4464.9(3) Å^3, Z = 4, T = 100(1) K, D_{calcd} = 1.995 g cm^{-3}, μ = 92.97 cm^{-1}, λ(Mo Kα) = 0.710 73 Å. A multiscan absorption correction was applied. Least-squares refinement with 9793 unique reflections and 747 parameters converged to a final $R_w(F^2) = 0.0593$ and $R(F) = 0.0318$ for 7609 reflections with $F_o \geq 4.0\sigma(F_o)$. The hydrides were located from the Fourier difference map, and their positional parameters were refined freely.

$(PR_3)_4$ range over 3.089−3.396 Å.[13] If the C_6H_8 fragment is counted again as a tetraanionic ligand, compound **3** could be considered as a $Hf^{III}{}_2Hf^{IV}{}_2$ mixed-valence complex. The diamagnetism of **3**, as seen by NMR, would then suggest a Hf(3)−Hf(4) single bond or a strong antiferromagnetic interaction between these centers. The NMR spectra of **3**[14] show two multiplets at δ 6.29 and 5.49 ppm in a 2:4 ratio for the hydrides and the C_6H_8 methyne carbons at remarkably high field (δ 115.0 ppm, J_{CH} = 145 Hz) compared to those in **2** (around δ 175.0 ppm). The σ^1:σ^1 bonding to two Hf atoms of the C_6H_8 fragment in **3** also results in an increase of the Hf−CH−CMe angles (around 144°; in **2** the angles are 123 and 130°) and significantly longer Hf−CH distances (2.475(5) and 2.460(5) Å) compared to **2** (2.397(3) and 2.273(2) Å).

It is clear that the arrangement of three or four metal centers around such a 1,3-butadiene-1,4-diyl group represents a thermodynamically quite stable structure. Still, it is remarkable that the complexes **2** and **3** are obtained in such relatively high isolated yields, considering the complicated pathways that would be required to assemble these multinuclear species from a simple monomeric starting material such as **1**. Although as yet it is impossible to give a complete description of the formation of these products, the reaction might be initiated by hydrogenolysis of the $Hf-CH_2SiMe_3$ bond in **1** to give a $Cp^*Hf(C_6H_{10})H$ intermediate. This may then undergo H_2 loss by abstraction of one of the diene methylene hydrogens, following a process similar to that observed by Bochmann et al. in the thermolysis of $[C_5H_3(SiMe_3)_2]Zr(C_6H_{10})Me$, from which the dimeric compound $\{[C_5H_3(SiMe_3)_2]Zr(\mu\text{-}C_6H_9)\}_2$ was isolated.[15] Repeating such a process could then lead to 1,4-deprotonation of the diene ligand to give the 1,3-butadiene-1,4-diyl fragment observed.

The relative ease of formation and the thermodynamic stability of polynuclear butadienediyl complexes make the Cp*Hf(diene)alkyl complexes with dienes that are unsubstituted on the 1,4-positions unsuitable for the generation of $[Cp^*HfH_x]_n$ complexes. On the other hand, they give access to entirely new types of polynuclear hydride species. We are presently exploring the reactivity of these complexes, as well as alternative routes to generate $[Cp^*HfH_x]_n$ compounds.

Acknowledgment. This work was supported by The Netherlands Foundation for Chemical Sciences (C.W.) with financial aid from The Netherlands Organization for Scientific Research (N.W.O.).

Supporting Information Available: Text giving full synthetic and characterization data for **2** and **3**. Text with details of the crystal structure determinations and tables with crystallographic data and thermal and positional parameters, bond lengths and angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] NMR data for **3** are as follows. ^1H NMR (300 MHz, C_7D_8, 25 °C): δ 6.29 (m, 2H, HfH), 5.49 (m, 4H, HfH), 4.93 (m, 2H, =CH−), 2.31 (s, 30 H, Cp*), 2.20 (s, 6H, CMe), 2.17 (s, 30 H, Cp*). ^{13}C NMR (75.4 MHz, C_7D_8, 25 °C): δ 116.35 (s, *C*Me), 115.02 (d, J = 145 Hz, =CH−), 114.64 (s, Cp* C), 112.56 (s, Cp* C), 25.59 (q, J = 127 Hz, C*Me*), 12.33 (q, J = 126 Hz, Cp* Me), 12.19 (q, 126 Hz, Cp* Me).

[15] Jimenéz Pintado, G.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1997**, 609.