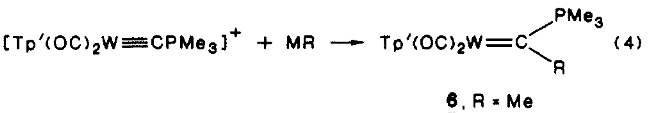

$$[Tp'(OC)_2W{\equiv}CPMe_3]^+ + MR \rightarrow Tp'(OC)_2W{=}C(PMe_3)(R) \quad (4)$$

6, R = Me
7, R = H

M = Li, KB(O-*i*-Pr)$_3$

appears as a doublet at 1.20 ppm ($^3J_{HP}$ = 24 Hz), and the carbene hydrogen of 7 appears as a doublet at 13.1 ppm ($^2J_{HP}$ = 20 Hz).[22] Only a single resonance is observed for each carbene substituent. Assuming a high W=C rotational barrier as in 5 would imply that only a single isomer is present. The absence of heteroatom stabilization in these low oxidation state tungsten carbenes and carbynes coupled with the ease of PMe$_3$ dissociation suggests an extensive carbene chemistry will be accessible in this system.

Acknowledgment. We thank Professor R. J. Angelici for kindly providing preprints concerning 1. The Department of Energy (85ER13430) is gratefully acknowledged for funding this research.

Supplementary Material Available: Tables of infrared and ^{1}H, ^{13}C, and ^{31}P NMR data for **3-7**, analytical data for **3**, **4**, and **7**, and X-ray data collection parameters, positional and thermal parameters, and bond distances and angles for **5** (15 pages). Ordering information is given on any current masthead page.

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[21] **6** is prepared at -78 °C by addition of ca. 1 equiv of MeLi to a THF solution of **4**. Evaporation of the solvent under vacuum, followed by extraction of the residue with Et$_2$O, gives a dark green solution which is subsequently evaporated to dryness and redissolved in C$_6$D$_6$. The product is sufficiently pure and stable for ^{1}H and ^{31}P NMR spectra but decomposes (in a sealed tube) over time hindering attempts to isolate **6** as a pure solid. NMR data for **6**: ^{1}H NMR (C$_6$D$_6$) δ 5.70 (s, 2 H, Tp'C*H*), 5.48 (s, 1 H, Tp'C*H*), 2.90 (s, 3 H, Tp'C*H*$_3$), 2.32 (s, 6 H, Tp'C*H*$_3$), 2.14 (s, 3 H, Tp'C*H*$_3$), 1.96 (s, 6 H, Tp'C*H*$_3$), 1.20 (d, 3 H, C*H*$_3$, $^3J_{HP}$ = 24 Hz), 1.16 (d, 9 H, P(C*H*$_3$)$_3$, $^2J_{HP}$ = 12 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 30.8 (s, br). **7** is prepared at -78 °C by addition of 1 equiv of K[HB(O-*i*-Pr)$_3$] to a THF solution of **4**. Evaporation of the solvent under vacuum followed by extraction of the product into Et$_2$O, and crystallization at 0 °C produces a 65% yield of **7** as a blue solid. NMR data for **7**: ^{1}H NMR (C$_6$D$_6$) δ 13.1 (d, 1 H, $^2J_{HP}$ = 20 Hz, $^2J_{HW}$ = 9 Hz) 5.70 (s, 2 H, Tp'C*H*), 5.47 (s, 1 H, Tp'C*H*), 2.90 (s, 3 H, Tp'C*H*$_3$), 2.34 (s, 6 H, Tp'C*H*$_3$), 2.15 (s, 3 H, Tp'C*H*$_3$), 2.00 (s, 6 H, Tp'C*H*$_3$), 1.00 (d, 9 H, P(C*H*$_3$)$_3$, $^2J_{HP}$ = 12 Hz); ^{13}C NMR (C$_6$D$_6$) δ 257.3 (d, W*C*O, $^3J_{CP}$ = 5 Hz, $^1J_{CW}$ = 170 Hz), 211 (dd, W*C*(H)P(CH$_3$)$_3$, $^1J_{CH}$ = 125 Hz, $^1J_{CP}$ = 30 Hz), 13.3 (d, P(CH$_3$)$_3$, $^1J_{CP}$ = 53 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 29.2 (s, $^2J_{PW}$ = 55 Hz).

[22] Other L$_n$MC(H)PR$_3$ complexes are known. See: Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* **1981**, *20*, 2466. Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1983**, *2*, 1336. Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289. Gell, K. I.; Schwartz, J. *Inorg. Chem.* **1980**, *19*, 3207. Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F.; Korte, W. D. *J. Am. Chem. Soc.* **1974**, *96*, 2847. Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744.

Reaction of $C_5(CH_3)_5Hf$(2,3-dimethyl-1,3-butadiene)Cl with Acetylene: Formation of an Asymmetric, Disubstituted 1,3-Dihafnacyclobutane

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Summary: Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl (Cp* = η^5-C$_5$Me$_5$) reacts with 1 mol of acetylene to form a disubstituted 1,3-dihafnacyclobutane complex, {Cp*Hf(Cl)-[μ-CHCHCH$_2$C(Me)=C(Me)CH$_2$]}$_2$, which was characterized by X-ray analysis (triclinic space group $P\bar{1}$, a = 8.446 (7) Å, b = 10.518 (2) Å, c = 10.792 (1) Å, α = 108.25 (1)°, β = 103.51 (3)°, γ = 103.66 (4)°, Z = 1). The Hf$_2$C$_2$ ring is asymmetrical, with two different Hf-C distances (2.246 (6) and 2.134 (5) Å). An agostic C-H→M interaction is present over the shorter Hf-C bond. The acetylene triple bond is reduced to a single bond (1.538 (6) Å), with one acetylene carbon bound to two Hf atoms and the other one to the two methylene carbon atoms of the former dimethylbutadiene ligand.

The electronically very unsaturated diene complex Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl[1] (1) (14 valence electrons) exhibits an unusual reactivity. Earlier we reported the formation of 1,2-dimethylcyclopentadiene and [Cp*Hf(O)Cl]$_n$ in the reaction with CO,[1a], which involves ring closure and complete fission of the CO bond. Here we wish to report the reaction of 1 with acetylene, leading to a substituted 1,3-dihafnacyclobutane type of complex. The product formation in this reaction differs considerably from that in the reaction of Cp$_2$M(diene) (M = Zr, Hf) complexes with mono- and disubstituted acetylenes. In the metallocene system either the diene ligand is displaced by two acetylene molecules to form metallacyclopentadienes[2] or insertion of one acetylene molecule into the diene-metal bond takes place to give η^3:η^1-heptadiene-1,6-diyl complexes.[3]

When a pentane solution of **1** is exposed to acetylene gas (1 mol/mol of Hf) at 20 °C, orange crystals slowly precipitate from the solution.[4] Elemental analysis[5] showed that the complex contains both the diene fragment and one acetylene molecule per Hf. The IR spectrum[6] of the product indicates the presence of a weakened C-H bond (ν_{CH} = 2660 cm^{-1}). An X-ray structure determination was undertaken[7] and revealed that the product is the dimeric {Cp*Hf(Cl)[μ-CHCHCH$_2$C(Me)=C(Me)CH$_2$]}$_2$ (**2**) (Figure 1), containing a planar, asymmetrical Hf$_2$C$_2$ ring. One carbon of the acetylene (C(11)) is asymmetrically bound to two Hf atoms, while the other (C(12)) is bound to the two methylene carbon atoms of the former 2,3-dimethylbutadiene ligand (C(13), C(18)). Thus by ring closure a (1,2-dimethylcyclopenten-3-yl)methylene ligand is formed. The former acetylene triple bond has been reduced to a

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[1] (a) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *Organometallics* **1983**, *2*, 1483. (b) Blenkers, J.; Hessen, B.; Van Bolhuis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 479.

[2] (a) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

[3] Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1982**, 1979.

[4] To a yellow solution of Cp*Hf(C$_6$H$_{10}$)Cl (0.317 g, 0.736 mmol) in 10 mL of pentane acetylene gas (0.745 mmol) was admitted at room temperature. After 14 h orange crystals had precipitated from a brown solution. The mother liquor was decanted, and the crystals were washed with pentane. Yield: 0.139 g (0.152 mmol, 41%) of {Cp*HfCl[μ-CHCHCH$_2$C(Me)=C(Me)CH$_2$]}$_2$. All manipulations were carried out by glovebox and vacuum line techniques.

[5] Anal. Calcd for C$_{36}$H$_{54}$Hf$_2$Cl$_2$: C, 47.27; H, 5.95; Cl, 7.75. Found: C, 47.16; H, 5.86; Cl, 7.76.

[6] IR (Nujol/KBr): 2735 (vw), 2660 (w, ν_{C-H}), 1498 (sh, w), 1489 (mw), 1456 (m, 1374 (s), 1299 (m), 1212 (w), 1040 (sh, w), 1024 (mw), 973 (vw), 888 (vw), 850 (w), 756 (mw), 614 (sh, w), 605 (s), 581 (s), 514 (mw), 450 (w) cm^{-1}.

[7] **2** crystallizes in the triclinic space group $P\bar{1}$ with (at 130 K) a = 8.446 (7) Å, b = 10.518 (1) Å, c = 10.792 (1) Å, α = 108.25 (1)°, β = 103.51 (3)°, γ = 103.66 (4)°, Z = 1. A total of 3847 reflections (3591 with $I \geq 3\sigma(I)$) were recorded. All hydrogen atoms were refined isotropically. R = 0.029 and R_w = 0.038 (w = 1).

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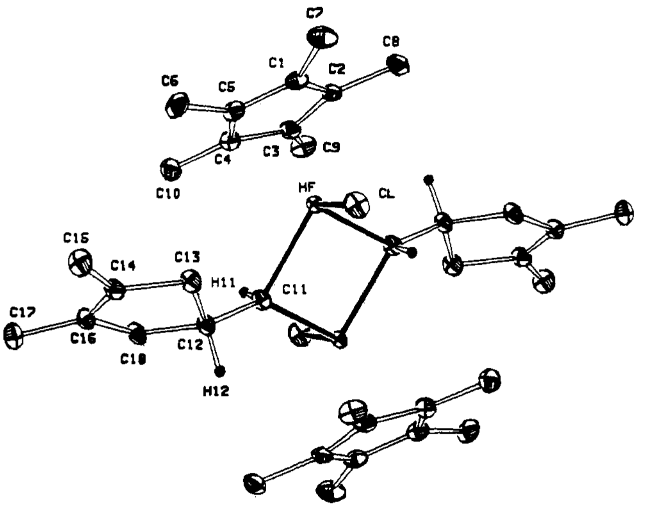
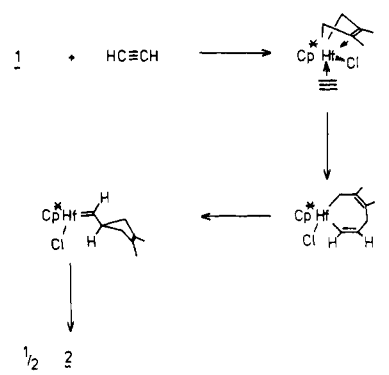


Figure 1. Molecular structure of $\{Cp^*Hf(Cl)[\mu\text{-}CHCHCH_2C(Me){=}C(Me)CH_2]\}_2$ (2). The only hydrogen atoms shown are from the former acetylene molecule. The molecule has a center of symmetry. Selected structural parameters (symmetry-related atoms are denoted by a prime): Hf–Cl = 2.393 (2) Å, Hf–C(11)′ = 2.134 (5) Å, Hf–C(11) = 2.246 (6) Å, C(11)–C(12) = 1.538 (6) Å, Hf–H(11)′ = 2.21 (11) Å, C(14)–C(16) = 1.336 (10) Å, ∠Hf–C(11)–Hf′ = 94.4 (2)°, ∠C(11)–Hf–C(11)′ = 85.6 (2)°, ∠Hf′–C(11)–H(11) = 87. (7)°.

single C–C bond (C(11)–C(12) = 1.538 (6) Å). The Hf_2C_2 unit shows several interesting features. The Hf_2C_2 ring is nearly rectangular (Hf–C(11)–Hf′ = 94.4 (2)°, C(11)–Hf–C(11)′ = 85.6 (2)°) with two different Hf–C distances, one of which (Hf–C(11) = 2.246 (6) Å) is quite normal for a Hf–C single bond[8] while the other (Hf–C(11)′ = 2.134 (5) Å) is significantly shorter, comparable to the Hf–C (ylide) bond in $Cp_2Hf(Et)CH{=}PPh_3$ (2.149 (6) Å) in which a considerable amount of Hf–C π-interaction is presumed.[9] The M–C bond sequence in the Hf_2C_2 ring is not unlike that of the Zr_2C_2 ring in the remarkable complex $[(C_5H_4Me)_2Zr]_2(\mu\text{-}C_2Ph)_2$ described by Erker et al.[10] The sharp Hf′–C(11)–H(11) angle (87 (7)°) and the Hf′–H(11) distance (2.21 (11) Å, the same as the Zr–H distance in the "agostic" complex $(C_5H_4Me)_2ZrCl(CH{=}CMe)Zr(C_5H_5)_2$[11]) make a C–H–Hf interaction likely. The ^{13}C NMR resonance[12] of the carbon atoms in the Hf_2C_2 ring is found at 190.9 ppm, i.e. at considerably lower field than in the dihafnacyclobutane $(Cp_2Hf)_2(\mu\text{-}CH_2)_2$ (149.6 ppm).[13] The small $^1J_{CH}$ of 94 Hz indicates that the C(11)–H(11) bond has a considerable amount of C 2p character. C(11) shows a large distortion from tetrahedral geometry (Hf′–C(11)–C(12) = 138.6 (5)°; Hf–C(11)–C(12) = 119.7 (4)°) with C(12) lying only 0.55 Å out of the Hf_2C_2 plane. The X-ray structure shows that the dimethylcyclopentenyl groups are forced into the diagonal plane between and parallel with the Cp* -rings. These steric requirements distort the geometry of C(12) (C(11)–C(12)–C(13) = 116.6 (5)°; C(11)–C(12)–C(18) = 115.6 (5)°). This is reflected in a decrease of $^1J_{CH}$ in the ^{13}C NMR spectrum for C(12) (δ 39.6 (d, 111 Hz)), and in this case it is unlikely that the metal atom exerts any influence (Hf′···H(12) = 3.45 (5) Å).

Scheme I



The mechanism of product formation in this reaction is not clear as yet, but one possible reaction sequence is given in Scheme I. It consists of initial coordination of the acetylene to Hf and insertion of the acetylene molecule in the Hf–diene bond to give a 3,4-dimethylhafnacyclohepta-3,6-diene. This could be followed by a ring contraction (formally a type of 1,3-shift) to a carbene species, which can then dimerize to the final product 2. Attempts to trap a possible carbene intermediate in the reaction mixture with, e.g., ketones, olefins, or substituted acetylenes have failed so far, as these reagents either react themselves with 1 or prevent the acetylene from reacting (possibly by blocking a coordination site).

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1, 106499-70-1; 2, 108150-65-8; HC≡CH, 74-86-2.

Supplementary Material Available: Tables of positional and thermal parameters for 2, crystallographic data, a list of interatomic distances and angles for 2, and a representation of the structure of 2 with all hydrogen atoms (8 pages); a listing of observed and calculated structure factors for 2 (17 pages). Ordering information is given on any current masthead page.

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[8] Typical values for Hf–C σ-bonds in Hf-alkyl compounds lie in the region of 2.23–2.29 Å. For example see: Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 750. Bristow, G. S.; Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1984**, 399 and ref 9.

[9] Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059.

[10] Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463.

[11] Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372.

[12] ^{13}C NMR of 2 (50.3 MHz, C_6D_6, 20 °C): 190.9 (d, 94 Hz, Hf_2CH), 131.3 (s, $=C$(Me)), 129.9 (s, $=C$(Me)), 120.4 (s, C_5Me_5), 51.9 (t, 133 Hz, CH_2), 51.4 (t, 129 Hz, CH_2), 39.6 (d, 111 Hz, CH), 13.8 (q, 125 Hz, $=C(CH_3)$), 12.1 ppm (q, 127 Hz, $C_5(CH_3)_5$).

[13] Van De Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *308*, 1.

Synthesis and X-ray Structure of a Bis(carboranyl)aluminate Derived from *nido*-$(2,7\text{-}C_2B_6H_8)^{2-}$

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Summary: Synthesis and characterization of $Na[Al(\eta^2\text{-}2,7\text{-}C_2B_6H_8)_2]$ (Na[**3**]) is described, and the results of a single-crystal X-ray structure determination for Na[**3**] are presented. The anion [**3**]$^-$ exists as enantiomers in the solid state. Variable-temperature ^1H and ^{11}B NMR studies indicate that in solution at room temperature this anion exhibits fluxional behavior such that its two enantiomeric forms rapidly interconvert.

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