The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the SDP-Plus structure determination package supplied by the Enraf-Nonius Corp. The zirconium atom was located in an origin-removed Patterson synthesis. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinements. The function minimized in the least-squares runs was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, $w = \sigma^{-2}(F_o)$. The scattering factors were taken from the compilation of Cromer and Waber[43a] and the anomalous dispersion terms from that of Cromer.[43b] During the refinement process we detected the disorder in the neopentyl group about the pseudomirror of the metallacyclic ring. Atoms C(1), C(3), and C(4), common in both orientations, were fully weighted. The C(2), C(5), and C(6) pairs were shown to be equally populated about the pseudomirror by occupancy factor refinement. The majority of hydrogen atoms were located. The positions of all H atoms other than those attached to C(1) were idealized with a C–H distance of 0.95 Å, and these atoms were included as a fixed contribution with $B_H = 5.0$ Å^2 and the appropriate occupancy factor. The highest peaks of residual electron density in a final difference Fourier synthesis are ca. 0.4 e Å^{-3} and correspond approximately to the expected H atom positions about C(1). These H atoms were not refined or included because of the proximity of the disordered atoms C(2A) and C(2B). Least-squares refinements converged to the values shown in Table III, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$.

Acknowledgment. Several of us (F.M.H., S.M.C., and J.S.) acknowledge support for this work given by the National Institutes of Health and the National Science Foundation. T.H.T. thanks L. Lardear for skilled technical assistance, Dr. F. N. Tebbe for invaluable, discussions, and Prof. L. Messerle for communication of results prior to publication.

Registry No. **2a**, 79061-88-4; **2b**, 79061-85-1; Cp_2ZrHCl, 79061-85-1; diisobutylneohexenylaluminum, 61382-44-3; dimethylneohexenylaluminum, 71058-46-3.

Supplementary Material Available: Non-hydrogen atom thermal parameters (Table V) and idealized H atom positions (Table VI), and a view of disordered neopentyl group (Figure 2) (6 pages); a listing of observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead.

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(42) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1976**, *6*, 197.

(43) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.28B; (b) Table 2.3.1.

Communications

Cationic Phosphonium Carbyne and Bis(phosphonium) Carbene Tungsten Complexes: $[Tp'(OC)_2WC(PMe_3)_n][PF_6]$ (n = 1, 2)

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Summary: Cationic phosphonium carbyne and bis(phosphonium) carbene complexes $[Tp'(OC)_2WC(PMe_3)_n][PF_6]$ (n = 1, 2) (Tp' = $[HB(N_2C_3Me_2H)_3]^-$, hydridotris(3,5-dimethylpyrazolyl)borate) have been prepared. The bis(phosphonium) carbene complex (n = 2) has been structurally characterized. The cationic carbyne complex reacts with MeLi or $K[HB(O\text{-}i\text{-}Pr)_3]$ to form $Tp'(OC)_2W{=}C(Me)PMe_3$ or $Tp'(OC)_2W{=}C(H)PMe_3$, respectively.

Angelici and co-workers have recently reported that carbyne–carbonyl coupling occurs when PEt_3 is added to $Tp(OC)_2W{\equiv}CSMe$ (Tp = $[HB(N_2C_3H_3)_3]^-$, hydridotris(pyrazolyl)borate) (1).[1] We wish to report formation of cationic phosphonium carbyne and bis(phosphonium)carbene tungsten complexes from reaction of the sterically congested analogue of 1, $Tp'(OC)_2W{\equiv}CSMe$ (Tp' = $[HB(N_2C_3Me_2H)_3]^-$, hydridotris(3,5-dimethylpyrazolyl)borate) (2),[2] with excess PEt_3 and PMe_3, respectively. These reactions resemble those of $Tp'(OC)_2Mo{\equiv}CCl$ recently reported by Lalor and co-workers where Cl^- is the leaving group in nucleophilic displacement reactions (eq 1).[3,4]

$$Tp'(OC)_2M{\equiv}CX + Nu \rightarrow [Tp'(OC)_2M{\equiv}CNu]^+ + X^- \qquad (1)$$

Excess PEt_3 reacts slowly with 2 in CH_2Cl_2 at room temperature to replace the reagent dicarbonyl IR pattern (1975 (s), 1880 (vs) cm^{-1}) with higher energy absorptions (2020 (s), 1935 (vs) cm^{-1}). Slow addition of Et_2O precipitates white byproducts which include the $[MePEt_3]^+$ cation.[5] Further addition of Et_2O to the filtrate precipitates an orange solid which can be recrystallized from CH_3CN/H_2O with added $[NH_4][PF_6]$ to produce low yields (20%) of $[Tp'(OC)_2W{\equiv}CPEt_3][PF_6]$ (**3**) as air-stable, red-orange crystals. Informative NMR features[6] include a 2:1 ratio of pyrazolyl environments in the ^1H NMR, J_{HP} coupling constants suggestive of a PR_4^+ moiety rather than $M{-}PR_3$,[7] and a singlet in the ^{31}P spectrum at +30.1 ppm

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(1) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1986**, *5*, 2481.

(2) **2** was prepared by using the reported procedure for **1**: Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983.

(3) Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1984**, 75.

(4) Angelici and co-workers have demonstrated that SMe^- is a good leaving group in the reactions of nucleophiles with thiocarbene complexes: Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489. Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1018. Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1583.

(5) The $[MePEt_3]^+$ cation was identified by comparison of its IR and ^1H NMR spectra with those of an authentic sample of $[MePEt_3][I]$.

(6) ^1H NMR (CD_2Cl_2): δ 6.07 (s, 2 H, Tp'C*H*), 5.86 (s, 1 H, Tp'C*H*), 2.49 (s, 6 H, Tp'CH_3), 2.42 (s, 6 H, Tp'CH_3), 2.40 (s, 3 H, Tp'CH_3), 2.33 (s, 3 H, Tp'CH_3), 2.2 (d of q, 6 H, $P(CH_2CH_3)_3$, $^2J_{HP}$ = 12.1 Hz, $^3J_{HH}$ = 7.6 Hz), 1.35 (d of t, 9 H, $P(CH_2CH_3)_3$, $^3J_{HP}$ = 19.0 Hz, $^3J_{HH}$ = 7.6 Hz).

(7) Schmidbaur, H.; Tronich, W. *Chem. Ber.* **1968**, *101*, 595. Weigart, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 4940. Kreissl, F. R.; Stuckler, P.; Meineke, E. W. *Chem. Ber.* **1977**, *110*, 3040.

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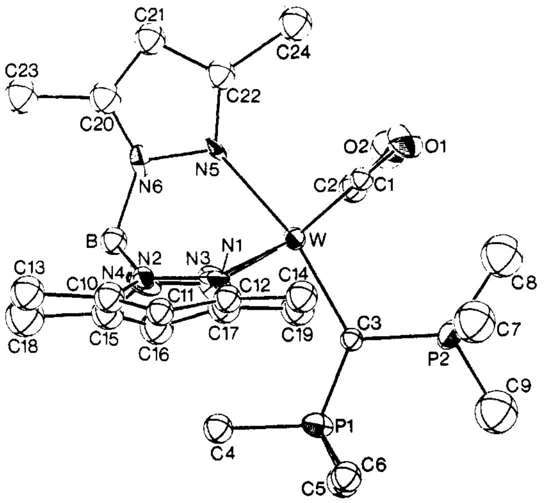
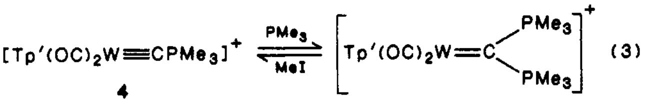


Figure 1. An ORTEP diagram of **5**, with $[PF_6]^-$ omitted. Selected bond distances (Å) and angles (deg): $W-C_3$, 2.11 (1); C_3-P_1, 1.75 (2); C_3P_2, 1.77 (1); $W-C_3-P_1$, 126.2 (8); $W-C_3-P_2$, 119.3 (8); $P_1-C_3-P_2$, 114.5 (8); dihedral angles, $P_1-C_3-W-N_1$, 45.0; $P_1-C_3-W-N_3$, 40.8.

with $^2J_{PW} = 150$ Hz (for ^{183}W with $I = {}^1/_2$, 14% abundant).

Reaction of **2** with excess PMe_3 under the same conditions follows a somewhat different course, presumably passing through the PMe_3 analogue of **3**, $[Tp'(OC)_2W{\equiv}CPMe_3]^+$ (**4**), along the way (eq 2 and 3). The resulting

$$\underset{\mathbf{2}}{\mathrm{Tp'(OC)_2W{\equiv}CSMe}} + \mathrm{PR_3} \rightarrow \underset{\substack{\mathbf{3},\ \mathrm{R = Et}\\ \mathbf{4},\ \mathrm{R = Me}}}{[\mathrm{Tp'(OC)_2W{\equiv}CPR_3}]^+} \qquad (2)$$



$$\underset{\mathbf{4}}{[\mathrm{Tp'(OC)_2W{\equiv}CPMe_3}]^+} \underset{\mathrm{MeI}}{\overset{\mathrm{PMe_3}}{\rightleftharpoons}} \underset{\mathbf{5}}{\left[\mathrm{Tp'(OC)_2W{=}C}\begin{matrix}\mathrm{PMe_3}\\ \mathrm{PMe_3}\end{matrix}\right]^+} \qquad (3)$$

green CH_2Cl_2 solution exhibits IR absorptions at 1910 and 1785 cm^{-1}, well below frequencies of the carbyne complexes. Workup with $[NH_4][PF_6]$ as for **3** produces an air-stable, green crystalline solid (80% yield based on reacted **2**) with ν_{CO} bands at 1885 (vs) and 1770 (s) cm^{-1}. A crystal structure has confirmed the identity of this product as the bis(phosphonium) carbene derivative **5**.[8] In solution, carbene **5** is in facile equilibrium with carbyne **4**: addition of PMe_3 drives conversion to the carbene while addition of MeI quantitatively yields the carbyne complex as $[PMe_4][I]$ precipitates (eq 3).[9]

The structure of **5**[11] reveals the dominant steric role of the three 3-methyl substituents in restricting access to the metal center which promotes ligand-based chemistry (see Figure 1). Differences in chemistry observed with Tp and Tp′ complexes have previously been rationalized on the basis of steric effects.[12] The tungsten atom in **5** lies within 0.08 Å of the plane defined by the three 3-methyl groups. The W=C distance of 2.11 (1) Å is appropriate for a metal–carbon double bond [$(dmpe)(Me_3CC)(Me_3CCH_2)W{=}CHCMe_3$, 1.94 Å;[13] $Cp(OC)_2(I)W{=}CH(C_6H_4Me\text{-}4)$, 2.05 Å;[14] $Cp_2W{=}CHPh$, 2.05 Å;[15] $(OC)_5W{=}CPh_2$, 2.15 Å[16]].

Rotation around the W=C bond of **5** is slow on the NMR time scale. The ^{31}P spectrum exhibits an AB pattern near 36 ppm with $^2J_{PP} = 78$ Hz, and the carbene carbon appears as a doublet of doublets at 168 ppm in the ^{13}C spectrum ($^1J_{CP} = 28, 9$ Hz).[17] This heteroatom carbene is unusual in that no lone pair electrons are available to stabilize the three-coordinate carbon; hence increased W=C double-bond character is expected relative to carbenes containing OR, NR_2, and SR substituents.

The $W{=}C(PMe_3)_2$ unit carries formal plus charges on the two PMe_3 groups; electron counting is simpler for the hypothetical $:H^-$ analogue of the $:PMe_3$ derivative: $[Tp'(OC)_2W{=}CH_2]^-$. Thus **5** is a six-coordinate 18-electron relative of the $[Cp(OC)_2Fe{=}CH_2]^+$ series[18] and differs significantly from the seven-coordinate $[Cp(OC)_2LM{=}CH_2]^+$ group 6 cations reported previously.[19] The only other bis(ylide) carbene complex of which we are aware was prepared from $(OC)_5W(THF)$ and $Ph_3P{=}C{=}PPh_3$.[20] The $(OC)_5WC(PPh_3)_2$ product constitutes a 20-electron complex (cf. the hypothetical $[(OC)_5W{=}CH_2]^{2-}$ ion) where the three-coordinate carbon can be considered a stabilized carbanion rather than a carbonium ion.

The facile carbene–carbyne equilibrium between **4** and **5** suggests that **4** might react with other nucleophiles to form new carbene derivatives. Preliminary reactions with MeLi and $K[HB(O\text{-}i\text{-}Pr)_3]$ indicate neutral carbenes **6** and **7** indeed form (eq 4).[21] The carbene methyl group of **6**

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(8) Room-temperature conversion of **2** to **5** in CH_2Cl_2 requires 3–4 days. The reaction occurs more rapidly by stirring 250 mg (0.42 mmol) of **2** in CH_3CN with 3–5 equiv of PMe_3 and 2 equiv of $[NH_4][PF_6]$ in a 65 °C oil bath for ~24 h. Addition of H_2O to the green reaction mixture followed by stirring in an ice water bath results in formation of a green microcrystalline solid. The solid is filtered in air and washed with H_2O and Et_2O to yield 330 mg of **5** (93% based on millimoles of **2**).

(9) **4** is prepared by reacting excess MeI with **5** in CH_2Cl_2 at room temperature. When the reaction is complete (as judged by IR in the ν_{CO} region), the solution is concentrated and filtered in air to remove $[PMe_4][I]$. The filtrate is evaporated to dryness, and the product is recrystallized from CH_3CN/H_2O with added $[NH_4][PF_6]$ to give an air-stable orange solid. IR (CH_2Cl_2): ν_{CO} 2015, 1935 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.07 (s, 2 H, Tp′C*H*), 5.87 (s, 1 H, Tp′C*H*), 2.48 (s, 6 H, Tp′CH_3), 2.41 (s, 9 H, Tp′CH_3), 2.33 (s, 3 H, Tp′CH_3), 1.94 (d, 9 H, $P(CH_3)_3$, $^2J_{HP} = 13.7$ Hz). $^{13}C\{^1H\}$ NMR (CD_2CN_2): δ 253.4 (s, $WCP(CH_3)_3$),[10] 223.3 (s, WCO, $^1J_{CW} = 170$ Hz), 12.0 (d, $P(CH_3)_3$, $^1J_{CP} = 51$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 16.7 (s, $WCP(CH)_3)_3$, $^2J_{PW} = 147$ Hz).

(10) The only other "phosphinomethylidyne" species of which we are aware, $[(PMe_3)_2Cl_2W{\equiv}CPMe_3]_2$, prepared by Schrock and co-workers, also has a singlet carbyne ^{13}C signal. Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476.

(11) The crystal studied was monoclinic with space group $P2_1/c$ and unit cell dimensions $a = 10.875$ (6) Å, $b = 14.272$ (9) Å, $c = 23.824$ (10) Å, $\beta = 96.24$ (4)°, and Z = 4. One molecule of CH_3CN was located in the asymmetric unit. Data were collected on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation). Of 6438 reflections collected, 2974 reflections with $I > 2\sigma(I)$ were used in structure refinement. All carbon atoms and the PF_6^- were refined isotropically, with the remaining non-hydrogen atoms refined anisotropically, resulting in final agreement indices of $R = 7.9\%$ and $R_w = 6.1\%$. Disorder in the PF_6^- was resolved by assigning 12 fluorine positions with multiplicity varying from 0.3 to 0.7 and isotropic temperature factors ranging from 2.9 to 13.1.

(12) Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M.; Ruhl, B. *J. Chem. Soc., Chem. Commun.* **1983**, 55. Schoenberg, A. R.; Anderson, W. P. *Inorg. Chem.* **1972**, *11*, 85.

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(14) Howard, J. A. K.; Jeffrey, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A.; Stringer, A. *Inorg. Chim. Acta* **1985**, *100*, 23.

(15) Marsella, J. A.; Folting, K.; Huffman, J. C. Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.

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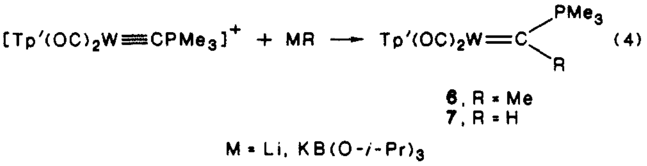
(17) ^1H NMR (CD_2Cl_2): δ 5.98 (s, 2 H, Tp′C*H*), 5.93 (s, 1 H, Tp′C*H*), 2.59 (s, 6 H, Tp′CH_3), 2.44 (s, 3 H, Tp′CH_3), 2.33 (s, 3 H, Tp′CH_3), 1.81 (s, 6 H, Tp′CH_3), 2.12 (d, 9 H, $P(CH_3)_3$, $^2J_{HP} = 11.2$ Hz), 1.14 (d, 9 H, $P(CH_3)_3$, $^2J_{HP} = 11.5$ Hz). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 258.3 (t, WCO, $^3J_{CP} \simeq 7$ Hz, $^1J_{CW} = 168$ Hz), 168.0 (dd, W=C, $^1J_{CP} = 28, 9$ Hz), 20.0 (d, $P(CH_3)_3$, $^1J_{CW} = 56$ Hz), 15.2 (d, $P(CH_3)_3$, $^1J_{CP} = 54$ Hz). $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ 36 (AB pattern, $^2J_{PP} = 78$ Hz). All NMR spectra of **5** were obtained on sealed samples containing a small amount of PMe_3 (see eq 3).

(18) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *Ibid.* **1980**, *102*, 1203.

(19) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

(20) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F. *J. Organomet. Chem.* **1973**, *47*, 391.



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

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′CH_3), 2.32 (s, 6 H, Tp′CH_3), 2.14 (s, 3 H, Tp′CH_3), 1.96 (s, 6 H, Tp′CH_3), 1.20 (d, 3 H, CH_3, $^3J_{HP}$ = 24 Hz), 1.16 (d, 9 H, P(CH_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′CH_3), 2.34 (s, 6 H, Tp′CH_3), 2.15 (s, 3 H, Tp′CH_3), 2.00 (s, 6 H, Tp′CH_3), 1.00 (d, 9 H, P(CH_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(*C*H$_3$)$_3$, $^1J_{CP}$ = 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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(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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