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Synthesis, Reactions, and X-ray Crystal Structure Determination of $Cp_2Hf(isobutylene){\cdot}PMe_3$

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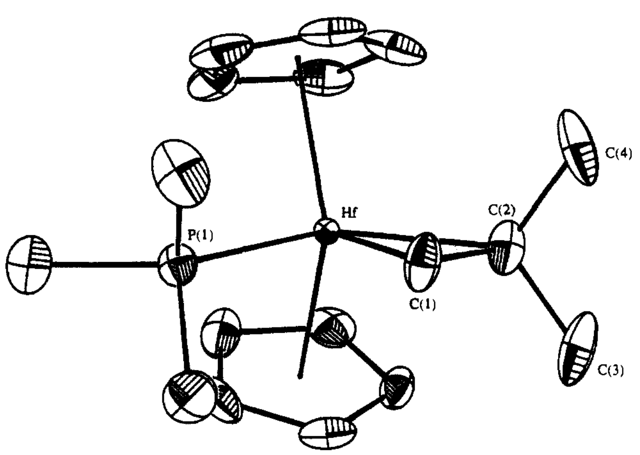
While the chemistry of zirconocene derivatives has been well-developed over the past few years,[2] a corresponding surge in the study of hafnocene compounds has not ensued.[3] As part of a study to probe the differences in structure and reactivity between complexes of these two elements, we now report the preparation and X-ray crystal structure determination of $Cp_2Hf(isobutylene){\cdot}PMe_3$. This constitutes the first structurally characterized olefin complex of hafnocene and, additionally, is the first group 4 complex of a 1,1-disubstituted olefin.[4]

Several years ago our group[5] and that of Negishi[6] reported that dibutylzirconocene (**1a**) rapidly eliminated butene at 0 °C and, in the presence of excess trimethylphosphine, produced **2a** in good yield (Scheme I). We have recently found, in contrast, that thermolysis of the hafnocene analogue **1b** at 80 °C was necessary for the conversion of **1b** to **2b**.[6] The harsh conditions required for this transformation, presumably a reflection of the comparatively strong Hf–C bond, caused noticeable decomposition to occur during the formation of **2b**. In order to decrease the temperature required to induce alkane elimination,[7] we prepared the unsymmetrical dialkylhafnocene **4**, via chloro-*tert*-butylhafnocene (**3**) (Scheme II). While the analogous zirconocene complex rearranges at low temperature to isobutylzirconocene chloride,[8,9] complex **3** is moderately stable in the solid state and in solution. Addition of 1 equiv of *n*-BuLi to **3** produces **4** in good yield. To our surprise, **4** is an isolable, moderately stable solid. Compound **4** can be conveniently prepared in >90% yield on a large scale (~8 g) by the sequential addition of *t*-BuLi and *n*-BuLi to hafnocene dichloride at −78 °C, followed by warming to room temperature. When **4** is heated at 45 °C for 21 h in the presence of excess trimethylphosphine, isobutylene complex **5** is produced in 20–40% isolated yield. In contrast, attempts to form the zirconium analogue of **5** have produced only the known[10d] dimeric Zr(III) complex, $\{(\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4))(Cp)Zr(PMe_3)\}_2$.

Recrystallization of **5** from hexane produced X-ray-quality crystals. The solid-state structure of **5** was determined by X-ray crystallography, and the ORTEP diagram, along with important bond lengths and angles, is shown in Figure 1. The C1–C2 bond distance of 1.46 (1) Å is essentially the same as that seen in zirconocene complexes of terminal alkenes[10] and clearly indicates that the complex is best described as a metallacyclopropane. Of considerable interest is that, within experimental error (3σ), the bond length of Hf–C1 (a primary carbon) is virtually identical with that of Hf–C2 (a tertiary carbon). This indicates that the strength of the Hf–C bond overwhelms any unfavorable steric interactions between C3 and C4 and the cyclopentadienyl groups.



Selected Bond Distances (Å)

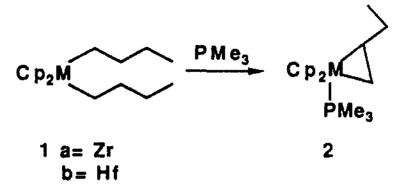
Hf	C(1)	2.316(8)
Hf	C(2)	2.368(9)
Hf	P(1)	2.653(2)
C(1)	C(2)	1.46(1)
C(2)	C(3)	1.52(1)
C(2)	C(4)	1.52(1)

Selected Bond Angles (°)

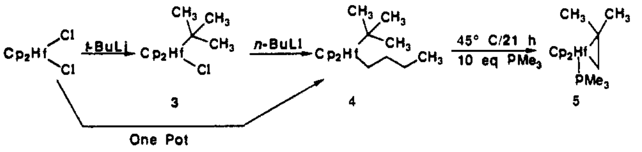
C(1)	Hf	C(2)	36.2(3)
C(1)	Hf	P(1)	72.6(2)
C(1)	C(2)	Hf	70.0(5)
C(2)	C(1)	Hf	73.9(5)
C(2)	Hf	P(1)	108.8(2)
C(4)	C(2)	C(3)	109(1)

Figure 1.

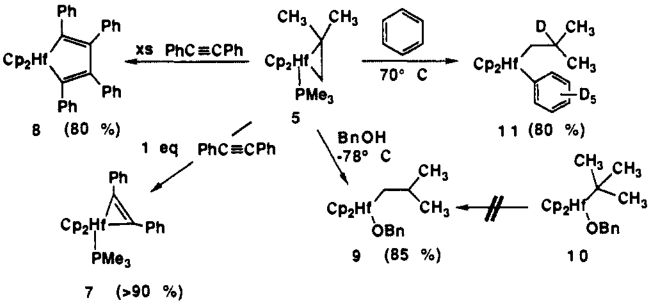
Scheme I



Scheme II



Scheme III



In solution, **5** is in equilibrium with a second, yet unidentified fluxional species, **6**. The ratio **5**:**6** is both temperature and con-

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[1] Camille & Henry Dreyfus Teacher-Scholar Awardee, 1989–1994; American Cancer Society Junior Faculty Research Awardee, 1987–1989; Eli Lilly Grantee, 1988–1990; Alfred P. Sloan Research Fellow, 1988–1990; Union Carbide Innovation Recognition Program Awardee, 1989.

[2] Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

[3] Cardin, D. J.; Lappert, M. F.; Raston, C. L. *The Chemistry of Organo-Zirconium and -Hafnium Compounds*; J. Wiley & Sons: New York, 1986.

[4] (a) Erker, G.; Czisch, P.; Kruger, C.; Wallis, J. *Organometallics* **1985**, *4*, 2059. (b) Erker, G.; Dorf, J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138. (c) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1989**, 852.

[5] Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544.

[6] (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Negishi, E.; Swanson, D. R.; Takahashi, T. *Chem. Lett.* **1987**, 623. (c) Negishi and co-workers have observed similar results: Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (d) Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521.

[7] Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

[8] (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113.

[9] Buchwald, S. L.; Barr, K.; Watson, B. T. Manuscript in preparation. This was expected on the basis of the work of Schwartz and co-workers: Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115.

[10] (a) Alt, H. G.; Denner, C. E.; Thewalt, J.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C85. (b) Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035. (c) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Kozawa, K.; Uchida, Y.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761. (d) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1986**, *310*, 27.

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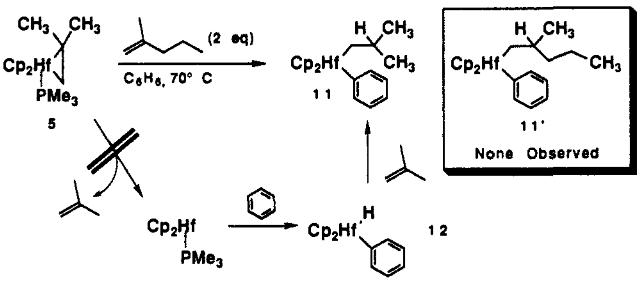
Scheme IV



centration dependent. We are continuing efforts to deduce the structure of **6**.[11]

As depicted in Scheme III, **5** participates in several interesting reactions. Treatment of **5** with 1 equiv of diphenylacetylene produces the alkyne complex **7** in good yield. Similarly, excess diphenylacetylene gives the known metallacycle **8**.[4b] Use of alkynes without aromatic groups gives slightly different results. Thus, **5**, upon exposure to a slight excess of 2-butyne, gives a ca. 3:1 ratio of the trimethylphosphine adduct of the hafnocene complex of 2-butyne and tetramethylhafnacyclopentadiene.[13] Complex **5** can be protonated[14] and participates in C–H bond activation reactions.[15] If **5** is allowed to react with a slight excess of benzyl alcohol, alkoxide **9** is produced. Of interest is that only the regioisomer shown is produced. That **9** is not formed by isomerization of its isomer **10** was shown by exposing **10**, independently prepared, to the reaction conditions used to convert **5** to **9**. When this protocol was used, no **9** was observed. This regiochemical outcome is consistent with the incoming alcohol approaching from the side of **5** away from the trimethylphosphine moiety (i.e., protonation presumably occurs faster than phosphine dissociation and probably requires coordination of the alcohol prior to proton transfer, or with protonation of the weakest and most electron rich Hf–C bond).

Unexpectedly, heating **5** at 70 °C in benzene causes C–H activation and produces complex **11** in good yield.[15] If this reaction is performed in neat C_6D_6, the deuterium ends up solely at the methine position. In order to probe whether the reaction of **5** with alcohols and with benzene involves a free (or PMe_3-bound) hafnocene intermediate,[16] the following experiments were performed. If **5** is heated in C_6H_6 in the presence of 2 equiv of 2-methyl-1-pentene, no incorporation of this olefin is seen in the product **11** (Scheme IV). Likewise, treatment of **5** with benzyl alcohol in the presence of 2 equiv of 2-methyl-1-pentene gives only regular product **9**, with no incorporation of the added olefin. In the reaction with benzene, if hydride **12** were an intermediate, it would be expected to hydrometalate the excess 2-methyl-1-pentene to produce **11′**. What these experiments show is that isobutylene is not lost to provide a free (or PMe_3-bound) hafnocene intermediate which reacts with benzene or benzyl alcohol to give the observed product. These experiments, as can be seen from the reactions with alkynes depicted above, however, do not indicate that the isobutylene cannot be displaced under the appropriate conditions. It should be noted that a similar C–H activation is not seen with zirconocene olefin complexes; heating **1a** results only in the loss of the olefin, with formation of I as the major product.[10b]

Work is ongoing in our laboratory to further delineate the structure of **6**[11] and to probe the reactivity of **5** and other related hafnocene complexes.

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Supplementary Material Available: Experimental section containing the preparation and spectroscopic and analytical characterization of compounds **3–5**, **7**, and **9–11** along with crystallographic data and procedures, an ORTEP diagram of **5**, tables of bond distances and angles for **5**, and table of final positional and thermal parameters for **5** (19 pages); table of structure factors for **5** (22 pages). Ordering information is given on any current masthead page.

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[11] We believe that **6** may be an unstable allyl hydride complex. ^1H NMR (500 MHz, C_6D_6, 60 °C): δ 5.12 (s, 10 H), 3.56 (br, 1 H), 2.32 (d, J = 2.0 Hz, 4 H), 1.43 (d, J = 1.5 Hz, 3 H), free PMe_3 is observed at δ 0.87 (d, J = 2.4 Hz). ^{13}C NMR (125 MHz, C_6D_6, 60 °C): δ 99.79, 50.59. No other ^{13}C signals that were not attributed to either **5**, **11**, or PMe_3 were observed in the sample. Allyl hydride complexes have been observed and studied in the bis(pentamethylcyclopentadienyl) zirconocene system.[12]

(12) (a) Roddick, D. M. Ph.D. Thesis, California Institute of Technology, 1984. (b) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

(13) Sabade, M. B.; Farona, M. F. *J. Organomet. Chem.* **1986**, *310*, 311.

(14) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(15) For examples of C–H activation by Zr(IV) complexes, cf.: Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731 and ref 13.

(16) For a description of the generation and trapping of the analogous hydridophenylzirconocene, cf.: Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

Cationic TBP Silicon: A Stable Intermediate in the Proton-Assisted Departure of an Equatorial Substituent

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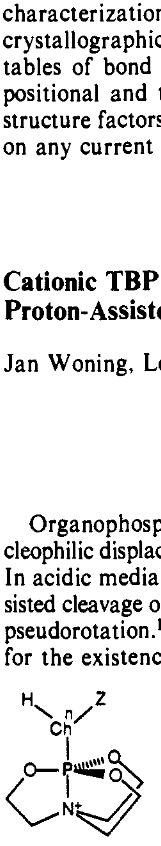
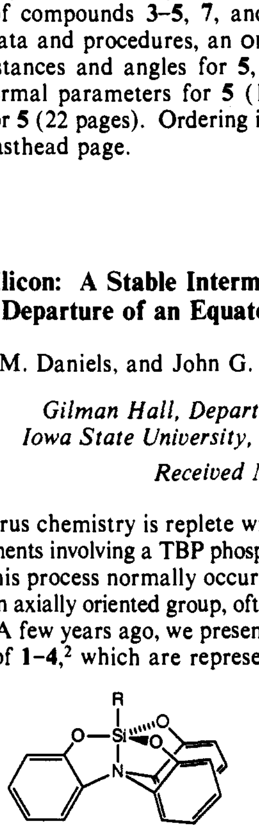
Organophosphorus chemistry is replete with examples of nucleophilic displacements involving a TBP phosphorus intermediate. In acidic media, this process normally occurs via the proton-assisted cleavage of an axially oriented group, often following a Berry pseudorotation.[1] A few years ago, we presented NMR evidence for the existence of **1–4**,[2] which are representatives of five-coordinate intermediates wherein protonation of the chalcogen (Ch) weakens the binding of this axial substituent to the central atom as departure of the axial ChH substituent begins to occur. Nucleophilic displacements at silicon can proceed by a similar process,[3] although equatorial departure of the leaving group cannot be ruled out. Indeed **5** has been postulated to form in a rapid equilibrium with its unprotonated parent, prior to the rate-determining cleavage of the $Si–O_{eq}$ bond in an acid-catalyzed hydrolysis reaction.[4] Here we report the synthesis of **6**, the first stable representative of incipient proton-assisted equatorial bond cleavage of a five-coordinate intermediate to be isolated, and its structure determination.

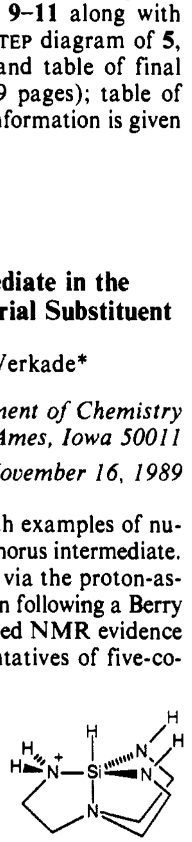


	Ch	Z	n
1	O	lp	0
2	O	H	+1
3	S	lp	0
4	S	lp	+1



5

R = Me, Ph, *p*-tolyl



6

When weakly electrophilic Me_3SiN_3 is added to a solution of azasilatrane **7**, the novel, mixed crystalline compound **8** is obtained

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(1) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: London, 1976.

(2) (a) Carpenter, L. E., II; De Ruiter, B.; Van Aken, D.; Buck, H. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 4918. (b) Carpenter, L. E., II; Verkade, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 7084.

(3) (a) Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallics* **1988**, *7*, 237. (b) Corriu, R. J. P. *Pure Appl. Chem.* **1988**, *60*, 99 and references cited therein.

(4) Timms, R. E. *J. Chem. Soc. A* **1971**, 1969.

0002-7863/90/1512-4601$02.50/0