The Reaction of Thermally Generated (Ethylene)hafnocene with Methylenetriphenylphosphorane: Competing Reaction Paths Leading to $Cp_2HfC_2H_5(CH{=}PPh_3)$ and a Hafnacyclobutane

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Summary: Two competing reactions were observed upon treatment of bis(η-cyclopentadienyl)hafnacyclopentane (**3**) with methylenetriphenylphosphorane (**4**) at 90 °C in toluene solution. The major reaction path (60%) is characterized by loss of 1 equiv of ethylene and formation of the ethylhafnocene-substituted ylide **5**. **5** was characterized by an X-ray crystal structure analysis (orthorhombic space group *Pbca* with $Z = 8$, $a = 10.785$ (1), $b = 16.431$ (2), $c = 29.245$ (3) Å). The hafnium–C(ylide) bond is rather short (2.149 (6) Å). In a competing reaction sequence (40%) triphenylphosphine is set free in addition to ethylene. Methylene transfer from phosphorus to hafnium leads to the formation of the bis(η-cyclopentadienyl)hafnacyclobutane (**2**). Compound **2** was characterized spectroscopically and by chemical reactions. (η^2-Ethylene)(methylenetriphenylphosphorane)hafnocene (**7**) was proposed as a common intermediate to account for the observed competition between hydrogen migration and methylene transfer in the reaction of **3** with **4**.

Titanacyclobutanes serve as important organometallic substrates due to their interesting stoichiometric and catalytic chemistry.[1] They can easily be prepared by [2 + 2] cycloaddition reactions from olefins and Tebbe's reagent ($Cp_2Ti{=}CH_2{\cdot}ClAlMe_2$, **1**) in the presence of a base.[2] Unfortunately, methylenemetallocene sources analogous to **1** seem not to be available for the heavier group 4[14] elements.[3] Therefore, the preparation of the few known examples of, e.g., substituted hafnacyclobutanes had to rely on "classical" nucleophilic routes using 1,3-propanediyl dianion equivalents.[4] We here describe a new synthetic route to the parent compound bis(η-cyclopentadienyl)hafnacyclobutane (**2**). We have observed that **2** is available by a methylene transfer reaction from a phosphorous ylide to a reactive (η^2-olefin)metallocene complex. The starting material of the new reaction sequence is bis(cyclopentadienyl)hafnacyclopentane (**3**). This metallacycle is readily available from the reaction of Cp_2HfCl_2 with 1,4-dilithiobutane.[5] At elevated temperatures (>70 °C) **3** rapidly equilibrates with a bis(ethylene)hafnocene intermediate which can lose 1 equiv of ethylene in the presence of a variety of added reagents.[5a] Treatment of **3** with 1 equiv of the Wittig reagent methylenetriphenylphosphorane (**4**) at 90 °C for 5–6 h in toluene results in the observation of two competitive reaction pathways. The major reaction (60%) leads to the formation of the ethylhafnocene-substituted phosphorous ylide **5**.[6] The identity of this reaction product has been established by an X-ray structure analysis. Typical structural features have been found for the $Cp_2Hf{-}CH_2CH_3$ unit (Figure 1).[7] However, the C1–Hf bond length and the preferred conformation indicate a substantial metal–carbon π-interaction in the $Cp_2Hf(CHPPh_3)$ moiety. In solution, broadening of the ^{13}C NMR Cp resonances below −110 °C can be regarded as an indication for this interaction causing hindered rotation of the Hf–C(ylide) linkage.

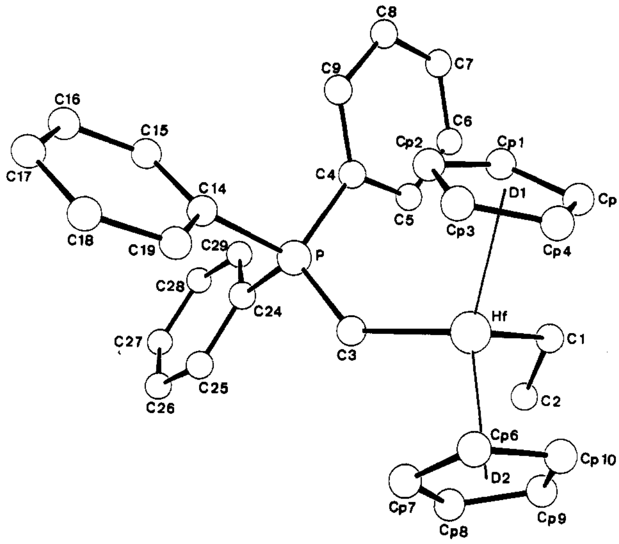

Figure 1. X-ray crystal structure of the ethylhafnocene ylide **5**: molecular geometry and atom numbering scheme.

Metallocene ylides $Cp_2MCl(CHPPh_3)$ (M = Zr, Hf) showing a pronounced metal–carbon π-interaction have previously been obtained by reacting the metallocene di-

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(1) Titanacyclobutanes have been used as olefin metathesis catalysts and stoichiometric methylene transfer reagents in Wittig-type olefinations, respectively: Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733 and references cited therein.

(2) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658. Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491.

(3) Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979.

(4) (a) Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Angew. Chem.* **1983**, *95*, 242; *Angew. Chem. Suppl.* **1983** 234–242. (b) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 825.

(5) (a) Dorf, U.; Engel, K.; Erker, G. *Angew. Chem.* **1982**, *94*, 916; *Angew. Chem. Suppl.* **1982**, 1984. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(6) (a) **5** was obtained by heating a toluene solution of 6.17 g (16.9 mmol) of **3** and 5.44 g (19.7 mmol) of ylide **4** for 5–6 h at 90 °C. After removal of the solvent in vacuo and subsequent extraction of the residue with pentane (50 mL) 4.5 g (73%) of **5** remained as an insoluble yellow solid: mp 180 °C dec; ^1H NMR (80 MHz, +34 °C, C_6D_6) δ 5.67 (s, 10 H, Cp), 3.72 (d, $^2J_{HP} = 14.6$ Hz, 1 H, CH=P), 1.90 (t, $^3J_{HH} = 7.7$ Hz, 3 H, CH_3), 0.68 (q, 2 H, CH_2), 6.9–7.3 and 7.5–7.9 (m, 15 H, PPh_3); $^{31}P\{^1H\}$-NMR (32 MHz, C_6D_6) δ 21.5; ^{13}C NMR (75.5 MHz, +40 °C, C_7D_8) δ 107.3 (d, $^1J_{CH} = 170$ Hz, Cp), 91.6 (dd, $^1J_{CH} = 120$ Hz, $^1J_{CP} = 33$ Hz, CH=P), 34.9 (t, $^1J_{CH} = 144$ Hz, CH_2), 19.7 (q, $^1J_{CH} = 125$ Hz, CH_3); PPh_3, δ 136.2 (d, $^1J_{CP} = 79$ Hz, C (quart)), 133.3 (dd, $^1J_{CH} = 162$ Hz, $^2J_{CP} = 9$ Hz, ortho-C), 128.3 (dd, $^1J_{CH} = 162$ Hz, $^3J_{CP} = 11$ Hz, meta-C), 130.5 (dd, $^1J_{CH} = 162$ Hz, $^4J_{CP} = 2$ Hz, para-C); MS, *m/e* 614 (M^+), 585 ($M^+ - C_2H_5$); IR (KBr) ν 940 cm^{-1} (P–C). Anal. Calcd for $C_{31}H_{31}PHf$: C, 60.74; 74; H, 5.09. Found: C, 60.30; H, 4.78. (b) **5** crystallizes in the orthorhombic space group *Pbca* (no. 61) with $Z = 8$. Cell dimensions are $a = 10.785$ (1) Å, $b = 16.431$ (2) Å, and $c = 29.245$ (3) Å; $R = 0.040$ ($R_w = 0.044$) for 298 refined parameters and 6512 reflections, of which 3883 were considered observed. Important bond distances (Å) and angles (deg): Hf–C3 = 2.149 (6), Hf–C1 = 2.285 (8), C1–C2 = 1.53 (1), C3–P = 1.682 (6), Hf–D1 = 2.24 (2), Hf–D2 = 2.24 (1); D1–Hf–D2 = 127.4, Hf–C1–C2 = 118.5 (5), C1–Hf–C3 = 97.3 (3), Hf–C3–P = 136.4 (4); angle between planes Hf–C1–C3 and Hf–C3–P = 93.9; torsional angles P–C3–Hf–C1 = 86.1, C2–C1–Hf–C3 = 46.3.

(7) Cp_2Hf–carbon bond distances seem to be a little shorter than their Zr counterparts: 2.18–2.29 Å appear to be typical values for unstrained Hf–C σ-bonds; for examples, see: Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1981**, *204*, 67. Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750. Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *3*, 215.

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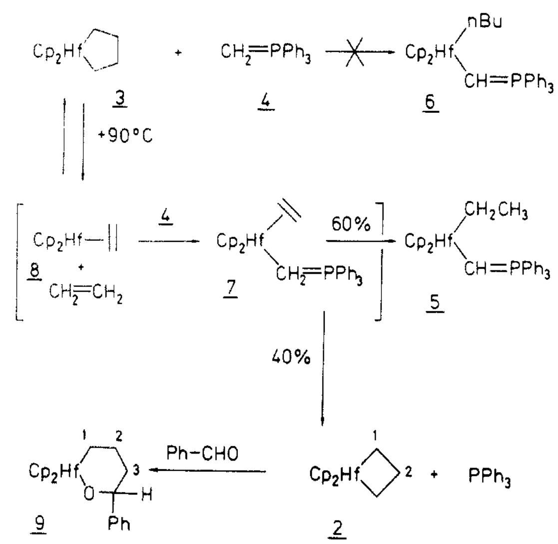
Scheme I



halides with a large excess of $CH_2{=}PPh_3$. In this reaction the ylide serves as both a nucleophile and a base in subsequent second-order reaction steps.[8] The complete absence of the *n*-butylhafnocene ylide **6** shows that the metallocene ylide formation from **3** and $CH_2{=}PPh_3$ represents a fundamentally different reaction type. Intramolecular hydrogen transfer from the ylide carbon to a coordinated olefinic ligand in the intermediate $Cp_2Hf(CH_2{=}CH_2)(CH_2{=}PPh_3)$ (**7**) accounts for the formation of the ethylhafnocene ylide **5**.[9]

A competing reaction path (40%), probably through the same intermediate **7**, leads to the formation of a 1:1 mixture of triphenylphosphine and bis(cyclopentadienyl)hafnacyclobutane (**2**), the product of a methylene transfer reaction from methylene triphenylphosphorane to the 16-electron d^2 species ethylenehafnocene (**8**). Like **5**, the metallacyclobutane **2** has been isolated from the reaction mixture by fractional crystallization. It has been characterized spectroscopically, by elemental analysis, and chemical reactions.[10] **2** exhibits NMR spectra consistent with a planar metallacyclic ring system.[11] Observed coupling constants (Hz) are as follows: $^2J(H, H) = -10.8$ (H1, H1′), -10.7 (H2, H2′); $^3J(H, H) = 5.2$ (H1, H2, "cis"), 12.4 (H1, H2′, "trans"); $^1J(C, H) = 134$ (C1, H1), 138 (C2, H2).

2 turns out to be completely stable at room temperature in the absence of air and moisture. It has even remained unaffected by thermolyzing it in the presence of diphenylacetylene to 150 °C for a period of 4 h. Treatment with bromine (stoichiometric) yields Cp_2HfBr_2 and 1,3-dibromopropane. With equimolar amounts of benzaldehyde **2** reacts at ambient temperature to give a single organometallic product **9**,[12] which is formed by a formal insertion of the organic carbonyl compound into the hafnium-carbon σ-bond of **2**. We have not obtained any experimental evidence for a retro [2 + 2] cleavage of the hafnacyclobutane.[13]

Finally, let us speculate about the scope of this new metallacyclobutane formation. It is clear that an increasing metal-alkylidene character in the metal ylide linkage in the intermediate **7** should favor the formation of the four-membered ring system at the expense of the hydrogen transfer reaction leading to the metal ylide **5**. Therefore, we expect metallacyclobutane formation according to Scheme I to become increasingly important on going from hafnium to titanium.[11] Equally, sufficiently reactive mono(olefin) complexes of the later transition elements, which tend to form more stable carbene complexes than the group 4[14] metals, should be good candidates to undergo four-membered ring formation upon treatment with an alkylidene ylide.

Acknowledgment. Financial aid from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Max-Planck-Gesellschaft is gratefully acknowledged. We thank Drs. R. Benn and R. Mynott and their co-workers for the NMR spectra.

Registry No. **2**, 98395-20-1; **3**, 83719-75-9; **4**, 3487-44-3; **5**, 98395-19-8; **9**, 98395-21-2; Cp_2HFBr_2, 37260-83-6; Ph—CHO, 100-52-7; 1,3-dibromopropane, 109-64-8.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters and a table of selected interatomic distances and angles, as well as a list of observed and calculated structure factors for **5** (20 pages). Ordering information is given on any current masthead page.

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[8] Baldwin, J. C.; Keder, N. L.; Strouse, C. F.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289.

[9] The reactions of $CH_2{=}PPh_3$ with (didehydrobenzene)$ZrCp_2$ or (butadiene)$ZrCp_2$, respectively, may represent further examples of this reaction type: Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310.

[10] After separation of **5** from the reaction mixture (see ref 6a) hafnacyclobutane **2** was obtained free of PPh_3 by a second extraction with pentane. After removal of the solvent, 10–15 mL of pentane was added and a colorless precipitate of pure **2** was obtained (510 mg, 20%; mp 105 °C dec). As this procedure turned out to be diffcult to reproduce, mixtures of **2** with PPh_3 were used for chemical reactions: ^1H NMR (400 MHz, C_7D_8) δ 5.34 (s, 10 H Cp), 1.89 (m, 4 H, α-CH_2), -0.05 (m, 2 H, β-CH_2); ^{13}C NMR (75.5 MHz, C_6D_6) δ 107.4 (Cp), 56.0 (α-CH_2), -10.3 (β-CH_2); MS, *m/e* 352 (M^+), 325 ($M^+ - C_2H_4$), 324 ($M^+ - C_2H_5$), 310 ($M^+ - C_3H_6$). Anal. Calcd for $C_{13}H_{16}Hf$: C, 44.52; H, 4.60. Found: C, 44.84; H, 4.14.

[11] Planar structures seem to be favored for the group 4 metallacyclobutanes; for experimental evidence, see: Lee, J. B.; Gajda, G. L.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358. Tikkanen, W. R.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646. See also ref. 4b); for a theoretical treatment see: Rappê, A. K.; Goddard III, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 297.

[12] ^1H NMR of **9** (400 MHz, C_6D_6): δ 5.71, 5.80 (s, each 5 H, Cp), 4.81 (dd, $^3J_{aa} = 11.1$ Hz, $^3J_{ae} = 2.6$ Hz, 1 H, H4), 0.96 (m, $^2J_{H3,H3'} = -13.7$ Hz, $^3J_{aa} = 12.8$ Hz, $^3J_{ae} = 2.3$ Hz, 1 H, H3′), 1.90 (m, $^3J_{ee} = 4.7$ Hz, $^3J_{ae} = 1.9$ Hz, 1 H, H3), 2.80 (m, $^2J_{H2,H2'} = -14.0$ Hz, $^3J_{ae} = 3.9$ Hz, $^3J_{ee} = 6.1$ Hz, 1 H, H2′), 1.52 (m, $^3J_{aa} = 13.5$ Hz, $^3J_{ae} = 2.3$ Hz, 1 H, H2), 1.39 (m, $^2J_{H1,H1'} = -13.3$ Hz, 1 H, H1′), 0.83 (m, H1); Ph, δ 7.37 (ortho-CH), 7.30 (meta-CH), 7.05 (para-CH) (a = axial; e = equatorial).

[13] For an analogous behavior of a four-membered metallacyclic zirconium complex, see: Tikkanen, W. R.; Petersen, J. L. *Organometallics* **1984**, *3*, 1651.

[14] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

The Kinetics of Some Gas-Phase Reactions of Dimethylsilanone

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Summary: The first results of a study of the reactions of dimethylsilanone with various substrates are reported, including some kinetic measurements. Comparisons are drawn with analogous reactions of dimethylsilene, and it is suggested that some reactions of both intermediates proceed stepwise, by addition followed by 1,3-silyl shifts.