The first hafnium methandiide complexes: the assembly of an entire triad of group 4 metal 'pincer' bis(phosphinimine) complexes possessing the M=C carbene–ylide structure

Ruppa P. Kamalesh Babu,[a] Robert McDonald[b] and Ronald G. Cavell*[a]

[a] *Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2. E-mail:Ron.Cavell@Ualberta.ca*
[b] *Structure Determination Laboratory, University of Alberta, Edmonton, AB, Canada T6G 2G2*

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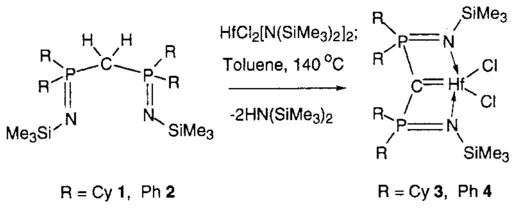
Dichlorobis[bis(trimethylsilylamido)]hafnium(IV) reacts with $(R_2P{=}NSiMe_3)_2CH_2$ (R = Cy, Ph) cleaving the C–H bonds of the P–C–P backbone methylene group and eliminating 2 mol of hexamethyldisilazane to yield the hafnium methandiide (carbene) complexes 3 and 4, thus completing the triad of group 4 metal complexes containing the M=C moiety.

Although extensive systems of group 5, 6 and 7 carbene complexes are known,[1] similar group 4 carbene complexes are rare[2] being limited to a few titanium,[3] and zirconium alkylidene complexes[4] and some zirconium Fischer carbene complexes.[5] In particular, carbene complexes of hafnium have long eluded isolation. Whereas hafnium alkylidene species have been implicated as intermediates in stoichiometric reactions, attempted isolation gave orthometallated[6] or dimeric products.[7] We now report a novel, high yield synthesis of the first examples of hafnium bis(iminophosphorano)methandiide complexes which have a hafnium–carbon bond with multiple (hence carbene) character supported by phosphinimine substituents in a "pincer" structure. With these hafnium complexes we now complete the triad of group 4 metal complexes with similar structural features.[8]

The reaction of $[HfCl_2\{N(SiMe_3)_2\}_2]$[9] with $CH_2(R_2P{=}NSiMe_3)_2$ [R = Cy **1** (prepared by heating $(Cy_2P)_2CH_2$[10] with N_3SiMe_3), or Ph **2**[11]] in refluxing toluene (Scheme 1) gave the electron deficient methandiide complexes, $[HfCl_2\{C(R_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]$ (R = Cy **3** or Ph **4**), as the result of a facile C–H bond cleavage process whereby the protons of the methylene group in the backbone of the ligand are removed;† 2 mol of hexamethyldisilazane were eliminated. This hafnium precursor reacts much more rapidly with the phenyl substituted bis(iminophosphorano)methane ligand, **2**, compared to the cyclohexyl analog, **1**, which we attribute to the higher acidity of the methylene protons in the former. Under similar conditions $[ZrCl_2\{N(SiMe_3)_2\}_2]$[9] reacts with **1** and **2** to yield the zirconium methandiide analogs, $[ZrCl_2\{C(R_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}$, prepared previously[8] by a different route. The hafnium methandiide complexes have a relatively high thermal stability, as do the Ti and Zr complexes,[8] which can be attributed to the steric protection of the carbene center by the formation of the tridentate chelate "pincer" structure.

The ^{31}P NMR spectra of complexes **3** and **4** consist of one sharp singlet showing that the two phosphorus nuclei are equivalent. The carbene resonances (δ 66.6 for **3**, 84.6 for **4**) appear as triplet signals because of coupling to two equivalent phosphorus atoms. The unusual upfield carbon chemical shift values for these carbene complexes relative to the general range exhibited by group 4 carbene complexes[2] may arise from the electronic influence of the phosphorus substituents, the presence of conjugated phosphinimine structures or because of the constrained geometry of the encapsulated carbene center.[12] We note that these shift values are similar to those of the previously reported carbodiphosphorane complexes of W[13] and Re[14] which show definitive M=C character. These latter complexes have neither the pincer nor the cyclic ring structure, thus the NMR properties probably devolve from the nature of the phosphorus–carbon interaction.

The molecular structure of $[HfCl_2\{C(Cy_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]$ **3**,‡ shown in Fig. 1,[15] is similar to that of the zirconium analog.[8] The key structural feature of the complex is the relatively short Hf–C(1) bond length [2.162(6) Å] which is shorter than the Hf–C bonds in other hafnium hydrocarbyl complexes (mean Hf–CH_2C 2.300 Å, Hf–CHC_2 2.387 Å[16,17]). The two four-membered ring systems defined by the common Hf=C bond are nearly coplanar with a dihedral angle of 5.4(4)°. The C(1) atom lies above the least square plane defined by P(1), P(2), N(1), N(2) and Hf by 0.108(7) Å. The structure is consistent with a considerable degree of multiple bond character between the metal and the carbene center. A closer look at the bond lengths within the six-membered frame shows that the Hf–N bonds [mean 2.167(5) Å] are slightly shorter than values typical of neutral amine complexes but longer than values typical of amide complexes.[18] If we compare the P–C and P–N bond lengths in the complex to those of the free ligand,[19] we see that the endocyclic P–C bonds [mean 1.665(7) Å] of the P–C–P backbone are shorter and the P–N [mean 1.637(5) Å] bonds are



Scheme 1

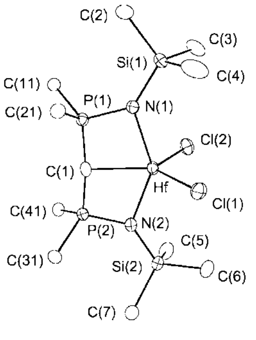


Fig. 1 An ORTEP[15] view of $[HfCl_2\{C(Cy_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]$ **3** showing the atom labeling scheme. All cyclohexyl (except the *ipso*) carbon atoms and all hydrogen atoms have been removed for clarity. The remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic lengths (Å) and angles (°) Hf–Cl(1) 2.377(2), Hf–Cl(2) 2.389(2), Hf–C(1) 2.162(6), Hf–N(1) 2.164(5), Hf–N(2) 2.170(5), P(1)–N(1) 1.639(5), P(2)–N(2) 1.635(5), P(1)–C(1) 1.662(7), P(2)–C(1) 1.668(7), P(1)–C(11) 1.834(6), P(2)–C(31) 1.825(6), P(1)–C(1)–P(2) 169.9(4), Hf–C(1)–P(1) 93.5(3), Hf–C(1)–P(2) 93.6(3), N(1)–Hf–N(2) 143.3(2), N(1)–P(1)–C(1) 100.5(3), N(2)–P(2)–C(1) 100.3(3).

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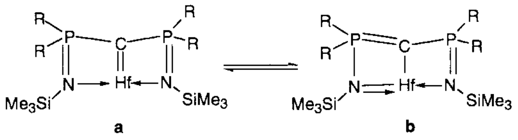
longer which implies delocalization of π-electron density in the four-membered planes which would arise from the conjugation of the P=N and the M=C bonds,[20] as delineated in Scheme 2. The central carbon NMR shifts in complexes **3** and **4** suggest that a tautomeric ylide–carbene formulation may be an appropriate description.



Scheme 2

Having assembled a complete triad of Ti, Zr and Hf complexes with the same chemical structures we are now in a position to conduct a comparison of the similarities and differences in reaction behaviour which derive from the metal alone. Such comparative reactivity studies are now in progress.

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Notes and references

† *Preparation* of **3**: all experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox. The complex, $[HfCl_2\{N(SiMe_3)_2\}_2]$ (0.2 g, 0.35 mmol) was dissolved in 10 mL of toluene. Solid $CH_2(Cy_2P{=}NSiMe_3)_2$ **1** (0.204 g, 0.35 mmol) was added to this solution with stirring and the colorless solution was heated at 140 °C for seven days. The resultant pale yellow solution was concentrated and cooled to −15 °C for 24 h to obtain colorless crystals which were isolated by filtration (yield: 0.21 g, 72.1%). IR (Nujol mull): 1447s, 1404w, 1377w, 1356w, 1320s, 1297w, 1260s, 1246s, 1202w, 1192w, 1176w, 1168w, 1112m, 1024s br, 915w, 887m, 836s br, 783m, 771s, 754s, 747s, 707w, 679m, 654s, 635m, 615s, 552s, 542m, 495m, 485m, 464w. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 2.1–1.1 (br m, 40 H, methylene-Cy and 4 H, methine-Cy), 0.47 (s, 18 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 66.6 (t, $^1J_{PC}$ 158.0 Hz, 1 C, quaternary C-PCP), 40.7 (m, 4 C, methine-Cy), 26.8 (m, 8 C, *ortho* methylene-Cy), 26.6 (s, 4 C, *para* methylene-Cy), 26.4 (s, 4 C, *meta* methylene-Cy), 26.3 (s, 4 C, *meta* methylene-Cy), 3.5 (s, 6 C, $SiMe_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 32.6 (2 P). Anal. Calc. for $C_{31}H_{62}Cl_2HfN_2P_2Si_2$: C, 44.84; H, 7.53; N, 3.37. Found: C, 45.04; H, 7.98; N, 3.29%.

Preparation of **4:** in a similar fashion, $[HfCl_2\{N(SiMe_3)_2\}_2]$ (0.104 g, 0.18 mmol) in toluene solution was treated with solid $CH_2(Ph_2P{=}NSiMe_3)_2$ **2** (0.102 g, 0.18 mmol) and heated at 140 °C for 3 d. The solution was reduced to a small volume and layered with hexane. After 2 days at ambient temperature, colorless crystals were deposited which were isolated by filtration (yield: 0.11 g, 74.8%). IR (Nujol mull): 1589w, 1574w, 1480w, 1463m, 1436s, 1378m, 1311s, 1251s, 1181w, 1156w, 1111s, 1070m, 1057s, 1037s, 999m, 843s, 787s, 772m, 754m, 738m, 716s, 696s, 654s, 631m, 622s, 615m, 576m, 524s. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.63 (m, Ph), 6.97 (m, Ph), 6.91 (m, Ph), 0.22 (s, 18 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 134.7 (m, 4 C, *ipso* Ph), 131.5 (t, $^2J_{PC}$ 6.0 Hz, 8 C, *ortho* Ph), 131.0 (s, 4 C, *para* Ph), 128.5 (t, $^3J_{PC}$ 5.6 Hz, 8 C, *meta* Ph), 84.6 (t, $^1J_{PC}$ 145.0 Hz, 1 C, quaternary C-PCP), 2.6 (s, 6 C, $SiMe_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 12.2 (2 P). Anal. Calc. for $HfCl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]\cdot 0.5C_6H_5Me$, $C_{34.5}H_{42}Cl_2HfN_2P_2Si_2$: C, 48.62; H, 4.97; N, 3.29. Found: C, 48.24; H, 5.21; N, 3.34%.

‡ *Crystal data* for $[HfCl_2\{C(Cy_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]$ **3**: monoclinic, space group, $P2_1/c$ (no. 14), a = 10.3572(7), b = 20.8156(10), c = 17.8865(10) Å, β = 93.226(5)°, V = 3850.1(4) Å^3, Z = 4, D_c = 1.433 g cm^{-3}, μ = 7.829 mm^{-1} (Cu-Kα, λ = 1.54178 Å), T = 213 K; the structure was solved by direct methods and refined by full matrix least squares procedures: R_1 = 0.0432 and 0.0495, (wR_2 = 0.1100 and 0.1148) for 4864 reflections with $F_o^2 > 2\sigma(F_o^2)$ and all data respectively.

CCDC 182/1543. See http://www.rsc.org/suppdata/cc/a9/a909771f/ for crystallographic files in .cif format.

1 For some recent review articles, see: K. H. Dötz and P. Tomuschat, *Chem. Soc. Rev.*, 1999, **28**, 187; M. P. Doyle and D. C. Forbes, *Chem. Rev.*, 1998, **98**, 911; R. R. Schrock, *Acc. Chem. Res.*, 1990, **23**, 158; D. M. Hoffman, ch 10, *High-valent Organorhenium Compounds*, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 6, pp. 231–255; W. D. Wulff, *Organometallics*, 1998, **17**, 3116.
2 R. Beckhaus, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 686.
3 J. D. Meinhart, E. V. Anslyn and R. H. Grubbs, *Organometallics*, 1989, **8**, 583; P. Binger, P. Müller, P. Philipps, B. Gabor, R. Mynott, A. T. Herrmann, F. Langhauser and C. Krüger, *Chem. Ber.*, 1992, **125**, 2209; J. A. van Doorn, H. van der Heijden and A. G. Orpen, *Organometallics*, 1995, **14**, 1278; H. van der Heijden and B. Hessen, *J. Chem. Soc., Chem. Commun.*, 1995, 145; P. Sinnema, L. v. Veen, A. L. Spek, N. Veldman and J. H. Teuben, *Organometallics*, 1997, **16**, 4245; S. Kahlert, H. Görls and J. Scholz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1857; R. Baumann, R. Stumpf, W. M. Davis, L.-C. Liang and R. R. Schrock, *J. Am. Chem. Soc.*, 1999, **121**, 7822.
4 M. S. Clift and J. Schwartz, *J. Am. Chem. Soc.*, 1984, **106**, 8300 and references therein; M. D. Fryzuk, P. B. Duval, S. S. S. H. Mao, M. J. Zaworotko and L. R. MacGillivray, *J. Am. Chem. Soc.*, 1999, **121**, 2478.
5 P. T. Barger, B. D. Santarsiero, J. Armantrout and J. E. Bercaw, *J. Am. Chem. Soc.*, 1984, **106**, 5178.
6 A. R. Bulls, W. P. Schaefer, M. Serfas and J. E. Bercaw, *Organometallics*, 1987, **6**, 1219.
7 B. Hessen, F. v. Bolhuis and J. H. Teuben, *Organometallics*, 1987, **6**, 1352; R. P. Planalp, R. A. Andersen and A. Zalkin, *Organometallics*, 1983, **2**, 16.
8 R. G. Cavell, R. P. Kamalesh Babu, A. Kasani and R. McDonald, *J. Am. Chem. Soc.*, 1999, **121**, 5805.
9 R. A. Andersen, *Inorg. Chem.*, 1979, **18**, 2928.
10 M. D. Fryzuk, D. H. McConville and S. J. Rettig, *J. Organomet. Chem.*, 1993, **445**, 245.
11 R. Appel and I. Ruppert, *Z. Anorg. Allg. Chem.*, 1974, **406**, 131.
12 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, John Wiley & Sons, Inc., New York, 1988, p. 260.
13 A. E. Bruce, A. S. Gamble, T. L. Tonker and J. L. Templeton, *Organometallics*, 1987, **6**, 1350.
14 J. Sundermeyer, K. Weber, K. Peters and H. G. v. Schnering, *Organometallics*, 1994, **13**, 2560.
15 C. K. Johnson, ORTEP, Report ORNL No. 5138, Oak Ridge Nat. Lab., Oak Ridge, TN, 1976.
16 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187. The values were calculated from the data retrieved from the Cambridge Crystallographic Data Base.
17 R. D. Rogers, R. V. Bynum and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 692.
18 See, for example: $HfCl\{N(SiMe_3)_2\}_3$, Hf–$N(SiMe_3)_2$ 2.04(1) Å (C. Airoldi, D. C. Bradley, H. Chudzynska, M. B. Hursthouse, K. M. Abdul Malik and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1980, 2010); $Hf(NPh_2)_4$, Hf–NPh_2 2.047–2.085 Å (M. Polamo, I. Mutikainen and M. Leskelä, *Acta Crystallogr., Sect. C*, 1996, **52**, 1348); $Me_2NHf\{(Me_3SiNCH_2CH_2)_3N\}$, Hf–$NMe_2$ 2.048(6) Å (Z. Duan, A. A. Naiini, J.-H. Lee and J. G. Verkade, *Inorg. Chem.*, 1995, **34**, 5477); $(C_5Me_5)_2Hf(H)(NHMe)$; Hf–NHMe 2.027(8) Å (G. L. Hillhouse, A. R. Bulls, B. D. Santarsiero and J. E. Bercaw, *Organometallics*, 1988, **7**, 1309).
19 Unpublished results, R. P. Kamalesh Babu, R. McDonald and R. G. Cavell, The X-ray structure of $CH_2\{Cy_2P{=}NSiMe_3\}_2$, University of Alberta Structure Determination Laboratory, Report RGC 9802. The important bond parameters are: mean P–C (P–C–P frame) length, 1.819(2), P–C (Cy bonds) length, 1.837(2), P–N length, 1.547(2) Å and the P–C–P angle, 117.4(1)°.
20 R. P. Kamalesh Babu, R. McDonald, S. A. Decker, M. Klobukowski and R. G. Cavell, *Organometallics*, 1999, **18**, 4226.

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