MHz under inverse-gated ^1H decoupling to avoid negative NOE. Typically 12000 points were sampled for a spectral width of 8000 Hz. A pulse width of 20 μs was used, which corresponds to a flip angle of 45°. The time intervals between the pulses typically were 4 s. The chosen relaxation delays were 5 times longer than the acquisition periods. The ^{103}Rh chemical shifts are reported in ppm versus the absolute frequency standard of $\Xi_{ref} = 3.16$ MHz[11] and are expected to be reproducible within ±1–2 ppm.

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Registry No. $(\eta^5\text{-}C_5H_4NO_2)Rh(CO)_2$, 75862-04-3; $(\eta^5\text{-}C_5H_4Cl_2)Rh(CO)_2$, 94890-74-1; $(\eta^5\text{-}C_5H_4CF_3)Rh(CO)_2$, 115406-90-1; $(\eta^5\text{-}C_5H_4N(CH_3)_2)Rh(CO)_2$, 115406-91-2; $(\eta^5\text{-}C_5H_4CH_3)Rh(CO)_2$, 63544-85-4; $(\eta^5\text{-}C_5H_4H)Rh(CO)_2$, 12192-97-1; PPh_3, 603-35-0.

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Phosphine Complexes of Zirconium and Hafnium. Synthesis, Structure, and Fluxional Behavior of the Trimethyl Derivatives $MMe_3[N(SiMe_2CH_2PR_2)_2]$ (R = Me, Pr^i, Bu^t). Evidence for a Bicapped-Tetrahedral Geometry

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Summary: The addition of 3 equiv of methyl Grignard (MeMgCl) to the amidodiphosphine derivatives $MCl_3[N(SiMe_2CH_2PR_2)_2]$ (M = Zr, Hf; R = Me, Pr^i, Bu^t) generates the corresponding trimethyl complexes $MMe_3[N(SiMe_2CH_2PR_2)_2]$. The solution structures and fluxional behavior of these molecules along with the X-ray structure of $HfMe_3[N(SiMe_2CH_2PMe_2)_2]$ are presented.

Because of the recent renewed interest in soluble models for Ziegler–Natta polymerization catalysts based on group 4 hydrocarbyl complexes,[1-9] the synthesis of such derivatives continues to be a worthy goal. The most well-studied group 4 hydrocarbyl systems utilize cyclopentadienyl or substituted cyclopentadienyl ligands as ancillary ligands.[10] Examples are $Cp'MR_3$ and Cp'_2MR_2 (where $Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$, $\eta^5\text{-}C_5H_4Me$; R = Me, Ph).[11-14] Of course many other examples are known and include simple homoleptic hydrocarbyl complexes MR_4,[15] phosphine-stabilized derivatives such as $MMe_4(dmpe)_2$[16] and $M(CH_2Ph)_4(dmpe)$ (where M = Zr or Hf),[17] and the bis- and tris(amido) derivatives $MR_2[N(SiMe_3)_2]_2$ and $MR[N(SiMe_3)_2]_3$.[18-20]

Our approach to investigating the organometallic chemistry of the early metals and the lanthanides[21-28] has been through the use of the mixed-donor tridentate ligand $^-N(SiMe_2CH_2Pr_2)_2$. In this paper we present the preparation and solution behavior of a series of trimethyl derivatives of zirconium and hafnium of the formula $MMe_3[N(SiMe_2CH_2PR_2)_2]$ (M = Zr, Hf; R = Me, Pr^i, Bu^t); in addition, the X-ray crystal structure of the hafnium derivative $HfMe_3[N(SiMe_2CH_2PMe_2)_2]$ is described. Not surprisingly, the stability of these hydrocarbyl derivatives is directly related to the steric bulk of the phosphorus substituents on the tridentate ligand.

Experimental Section

General Procedures. All manipulations were performed under prepurified nitrogen in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system or in

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standard Schlenk-type glassware on a dual vacuum/nitrogen line. Anhydrous $ZrCl_4$ and $HfCl_4$ (Aldrich) were sublimed prior to use in the literature preparation[22] of $MCl_3[N(SiMe_2CH_2PR_2)_2]$ (M = Zr, Hf; R = Bu^t, Pr^i, Me). Methylmagnesium chloride (MeMgCl) was obtained form Aldrich as a tetrahydrofuran (THF) solution (1.1 M). Hexanes and THF were initially dried over CaH_2 followed by distillation from sodium-benzophenone ketyl. Diethyl ether (Et_2O) was distilled from sodium-benzophenone ketyl. Deuterated benzene (C_6D_6) and toluene (C_7D_8) were obtained form MSD Isotopes and dried overnight with activated 4-Å molecular sieves, vacuum-transferred to an appropriate container, "freeze-pump-thawed" three times, and stored in the glovebox. Carbon, hydrogen, and nitrogen analyses were performed by P. Borda of this department. ^{1}H NMR spectra (referenced to C_6D_5H at 7.15 ppm or $C_6D_5CD_2H$ at 2.09 ppm) were performed on a Bruker WP-80 or a Bruker WH-400 spectrometer. ^{31}P NMR spectra (referenced to external $P(OMe)_3$ in C_6D_6 or $C_6D_5CD_3$ at 141.0 ppm) were run at 32.442 MHz on the WP-80 spectrometer. Coupling constants, J, are reported in hertz.

Preparation of MMe$_3$[N(SiMe$_2$CH$_2$PR$_2$)$_2$]. The same procedure was used for the preparation of all of the trimethyl derivatives. To the starting trichlorides $MCl_3[N(SiMe_2CH_2PR_2)_2]$ (approximately 1.0–1.5 g) dissolved in Et_2O (20–30 mL) was added 3 equiv of MeMgCl (1.1 M in THF) dropwise over a period of 10–20 min. The resultant mixture was stirred for either a further 3 h (M = Hf) or just 5 min (M = Zr) and then the volatiles were removed under vacuum. The residue was extracted with hexanes (10–15 mL) and filtered through a fine-porosity frit and the solvent reduced in volume to approximately 5 mL. Cooling to −30 °C overnight produced crystals in yields of 65–75%.

ZrMe$_3$[N(SiMe$_2$CH$_2$PBu$^t_2$)$_2$]. Yield: 70%. ^{1}H NMR (C_6D_6, ppm): $SiCH_3$, 0.45 (s); PCH_2Si, 0.73 (d, $^2J_P = 6$ Hz); $PC(CH_3)$, 1.03 (d, $^2J_P = 11$ Hz); $Zr(CH_3)$, 1.07 (t, $^3J_P = 1$ Hz). $^{31}P\{^1H\}$ NMR (C_7D_8, ppm): 20.35 (s). Anal. Calcd for $C_{25}H_{61}NP_2Si_2Zr$: C, 51.22; H, 10.51; N, 2.39. Found: C, 51.34; H, 10.45; N, 2.49.

ZrMe$_3$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]. Yield: 67%. ^{1}H NMR (C_6D_6, ppm): $SiCH_3$, 0.37 (s); PCH_2Si, 0.84 (d, $^2J_P = 7.5$ Hz); $Zr(CH_3)$, 0.90 (t, $^3J_P = 3.8$ Hz); $PCH(CH_3)$, 1.17 (m); $PCH(CH_3)$, 2.04 (m). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): 8.7 (s). Anal. Calcd for $C_{21}H_{53}NP_2Si_2Zr$: C, 47.68; H, 10.10; N, 2.65. Found: C, 47.63; H, 10.13; N, 2.80.

ZrMe$_3$[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]. This compound was not prepared in pure form using the above conditions. So far only mixtures have been obtained.

HfMe$_3$[N(SiMe$_2$CH$_2$PBu$^t_2$)$_2$]. Yield: 65%. ^{1}H NMR (C_6D_6, ppm): $SiCH_3$, 0.48 (s); PCH_2Si, 0.78 (d, $^2J_P = 6.1$ Hz); $PC(CH_3)$, 1.12 (d, $^2J_P = 11.2$ Hz); $Hf(CH_3)$, 0.87 (t, $^3J_P = 1.2$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): 20.88 (s). Anal. Calcd for $C_{25}H_{61}NP_2Si_2Hf$: C, 44.66; H, 9.14; N, 2.08. Found: C, 44.46; H, 9.14; N, 1.88.

HfMe$_3$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]. Yield: 75%. ^{1}H NMR (C_6D_6, ppm): $SiCH_3$, 0.41 (s); PCH_2Si, 0.89 (d, $^2J_P = 6.3$ Hz); $Hf(CH_3)$, 0.74 (t, $^3J_P = 3.5$ Hz); $PCH(CH_3)$, 1.17 (m); $PCH(CH_3)$, 1.94 (m). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): 2.4 (s). Anal. Calcd for $C_{21}H_{53}NP_2Si_2Hf$: C, 40.92; H, 8.67; N, 2.27. Found: C, 41.03; H, 8.65; N, 2.39.

HfMe$_3$[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]. Yield: 73%. ^{1}H NMR (C_6D_6, ppm): $SiCH_3$, 0.20 (s); PCH_2Si, 0.67 (d, $^2J_P = 8$ Hz); $Hf(CH_3)$, 0.47 (t, $^3J_P = 6.7$ Hz); $P(CH_3)$, 0.96 (d, $^3J_P = 4.5$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): −17.3 (s). Anal. Calcd for $C_{13}H_{37}NP_2Si_2Hf$: C, 30.98; H, 7.39; N, 2.77. Found: C, 30.78; H, 7.32; N, 2.80.

X-ray Crystallographic Analysis of HfMe$_3$[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]. Crystallographic data appear in Table I. The final unit-cell parameters were obtained by least-squares on $2(\sin\theta)/\lambda$ values for 25 reflections with $2\theta = 35–40°$. The intensities of three standard reflections, measured every 1 h of X-ray exposure time throughout the data collection, decayed linearly by 14.1%. The data were processed[29] and corrected for Lorentz and polarization effects, decay, and absorption (numerical integration, 192 sampling points). A total of 5237 independent reflections was collected on an Enraf-Nonius CAD4F diffractometer, and those 2942 having $I \geq 3\sigma(I)$ were employed in the solution and refinement of the structure.

Table I. Crystallographic Data[a]

compd	$HfMe_3[N(SiMe_2CH_2PMe_2)_2]$
formula	$C_{13}H_{37}HfNP_2Si_2$
fw	504.05
color, habit	colorless plate
cryst size, mm	0.15 × 0.50 × 0.60
cryst syst	orthorhombic
space group	*Pbcn*
a, Å	13.6237 (8)
b, Å	20.819 (2)
c, Å	16.1271 (9)
V, Å^3	4574.1 (5)
Z	8
T, °C	21
ρ_c, g/cm^3	1.464
$F(000)$	2016
radiation	Mo
wavelength, Å	0.710 73
μ, cm^{-1}	47.54
transm factors	0.096–0.500
scan type	ω–2θ
scan range, deg in ω	0.70 + 0.35 tan θ
scan speed, deg/min	0.75–10.0
data collcd	$+h,+k,+l$
$2\theta_{max}$, deg	55
cryst decay, %	14.1
no. of unique reflns	5237
no. of reflns with $I \geq 3\sigma(I)$	2942
no. of variables	172
R	0.034
R_w	0.037
gof	1.72
max Δ/σ (final cycle)	0.10
residual density, e/Å^3	2.35 (near Hf)

[a] Temperature 294 K, Enraf-Nonius CAD4-F diffractometer, Mo Kα radiation ($\lambda(K\alpha_1) = 0.709\,30$, $\lambda(K\alpha_2) = 0.713\,59$ Å), graphite monochromator, takeoff angle 3.0°, aperture 4.0 × 2.0 + 1.0 tan θ mm at a distance of 173 mm from the crystal, scan extended by 25% on each side for background measurement, $\sigma^2(I) = [C = 2B + (0.040(C - B))^2]$ with C = scan count, B = normalized total background count, function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

Table II. Final Positional (Fractional ×10^5, N and C ×10^4) and Isotropic Thermal Parameters (U × 10^3, Å^2) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq}
Hf	29629 (2)	40217 (1)	48351 (2)	43
P(1)	31602 (14)	47943 (9)	34537 (12)	64
P(2)	10242 (12)	37363 (9)	52938 (11)	53
Si(1)	27172 (12)	34547 (10)	28537 (12)	60
Si(2)	18113 (12)	36879 (8)	42016 (13)	53
N	2392 (3)	3391 (2)	3890 (3)	43
C(1)	3474 (5)	4201 (3)	2684 (4)	63
C(2)	1029 (5)	2874 (3)	5141 (4)	67
C(3)	3258 (5)	3510 (4)	6054 (5)	90
C(4)	4591 (5)	3951 (3)	4635 (5)	68
C(5)	2592 (6)	4992 (4)	5351 (5)	86
C(6)	2052 (6)	5173 (4)	3054 (7)	121
C(7)	4070 (7)	5441 (4)	3381 (6)	122
C(8)	67 (6)	4015 (4)	4578 (6)	86
C(9)	453 (5)	3862 (4)	6306 (5)	90
C(10)	1663 (6)	3521 (5)	2134 (5)	105
C(11)	3506 (6)	2772 (4)	2506 (7)	121
C(12)	2710 (6)	2052 (4)	4506 (7)	97
C(13)	961 (5)	2336 (3)	3413 (5)	78

The structure was solved by conventional heavy-atom methods, the coordinates of the Hf, P, and Si atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. The

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(29) Computer programs used include locally written programs for data processing and locally modified versions of the following: MULTAN80, multisolution program by P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson; ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson.

Table III. Bond Lengths with Estimated Standard Deviations in Parentheses

bond	length, Å	bond	length, Å
Hf-P(1)	2.761 (2)	P(2)-C(8)	1.836 (8)
Hf-P(2)	2.806 (2)	P(2)-C(9)	1.827 (8)
Hf-N	2.156 (4)	Si(1)-N	1.735 (5)
Hf-C(3)	2.272 (7)	Si(1)-C(1)	1.884 (6)
Hf-C(4)	2.246 (7)	Si(1)-C(10)	1.851 (8)
Hf-C(5)	2.243 (8)	Si(1)-C(11)	1.869 (8)
P(1)-C(1)	1.803 (7)	Si(2)-N	1.739 (5)
P(1)-C(6)	1.821 (8)	Si(2)-C(2)	1.892 (7)
P(1)-C(7)	1.835 (8)	Si(2)-C(12)	1.869 (7)
P(2)-C(2)	1.811 (7)	Si(2)-C(13)	1.870 (7)

Table IV. Bond Angles with Estimated Standard Deviations in Parentheses

bond	angle, deg	bond	angle, deg
P(1)-Hf-P(2)	115.32 (6)	Hf-P(2)-C(8)	115.8 (3)
P(1)-Hf-N	79.60 (13)	Hf-P(2)-C(9)	127.3 (2)
P(1)-Hf-C(3)	162.6 (2)	C(2)-P(2)-C(8)	103.3 (3)
P(1)-Hf-C(4)	80.0 (2)	C(2)-P(2)-C(9)	105.4 (3)
P(1)-Hf-C(5)	78.3 (2)	C(8)-P(2)-C(9)	102.3 (4)
P(2)-Hf-N	73.62 (11)	N-Si(1)-C(1)	110.0 (3)
P(2)-Hf-C(3)	80.8 (2)	N-Si(1)-C(10)	114.3 (3)
P(2)-Hf-C(4)	162.4 (2)	N-Si(1)-C(11)	112.2 (4)
P(2)-Hf-C(5)	83.2 (2)	C(1)-Si(1)-C(10)	105.8 (4)
N-Hf-C(3)	113.0 (3)	C(1)-Si(1)-C(11)	105.6 (3)
N-Hf-C(4)	102.4 (2)	C(10)-Si(1)-C(11)	108.4 (5)
N-Hf-C(5)	136.8 (3)	N-Si(2)-C(2)	108.3 (3)
C(3)-Hf-C(4)	85.3 (3)	N-Si(2)-C(12)	112.0 (3)
C(3)-Hf-C(5)	98.1 (3)	N-Si(2)-C(13)	114.5 (3)
C(4)-Hf-C(5)	109.6 (3)	C(2)-Si(2)-C(12)	107.7 (4)
Hf-P(1)-C(1)	100.3 (2)	C(2)-Si(2)-C(13)	106.0 (3)
Hf-P(1)-C(6)	117.2 (3)	C(12)-Si(2)-C(13)	107.9 (4)
Hf-P(1)-C(7)	123.0 (3)	Hf-N-Si(1)	122.9 (2)
C(1)-P(1)-C(6)	104.4 (4)	Hf-N-Si(2)	118.2 (3)
C(1)-P(1)-C(7)	107.4 (4)	Si(1)-N-Si(2)	117.3 (3)
C(6)-P(1)-C(7)	102.7 (5)	P(1)-C(1)-Si(1)	109.6 (3)
Hf-P(2)-C(2)	99.8 (2)	P(2)-C(2)-Si(2)	108.3 (3)

non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions (methyl group orientations based on observed peaks, C(sp^2)-H = 0.98, C(sp^3)-H = 0.98 Å, $U_H = \propto U_{\mathrm{bondedatom}}$). Neutral-atom scattering factors and anomalous dispersion corrections for all atoms were taken from ref 30. Final atomic coordinates and equivalent isotropic thermal parameters [$U_{eq} = {}^1/_3(\text{trace } U_{\mathrm{diag}})$], bond lengths and bond angles appear in Tables II–IV, respectively. A more detailed table of crystallographic data (Table SI), calculated hydrogen atom parameters, anisotropic thermal parameters, intraannular torsion angles, general torsion angles, and measured and calculated structure factor amplitudes are included as supplementary material.

Results and Discussion

The preparation of the trimethyl derivatives is quite straightforward; the chlorides of the starting material $MCl_3[N(SiMe_2CH_2PR_2)_2]$ can be replaced with methyl groups upon reaction with methylmagnesium chloride, as shown in eq 1. The products are isolated as colorless,

$$MCl_3[N(SiMe_2CH_2PR_2)_2] \xrightarrow[\substack{Et_2O/THF \\ (-3MgCl_2)}]{3MeMgCl} NMe_3[N(SiMe_2CH_2PR_2)_2] \quad (1)$$

$$M = Zr, Hf;\ R = Me, Pr^i, Bu^t$$

crystalline air- and moisture-sensitive, thermally labile solids with the exception of the zirconium derivative having methyl substituents at phosphorus, $ZrMe_3[N(SiMe_2CH_2PMe_2)_2]$; this particular complex apparently decomposed upon attempted isolation to give mixtures of unidentified products. The thermal stability of the hafnium complexes is qualitatively higher than the analogous zirconium derivatives with the overall stability increasing as the size of the phosphorus substituent increases.

The NMR spectroscopic parameters for these trimethyl derivatives are very simple. At room temperature, the ^1H NMR spectrum is indicative of a highly symmetric structure since only one type of environment is found for the ligand substituents (e.g., the silylmethyl protons, Si(CH_3), appear as a single sharp singlet) and the three methyls bound to the metal are equivalent since only a single sharp triplet resonance is observed; all of the $^{31}P\{^1H\}$ NMR spectra at room temperature show a singlet indicative of equivalent phosphine donors. From the ^1H NMR spectral data, it is interesting to point out that the magnitude of the coupling constant from phosphorus-31 to the metal-bound methyls (^3J_P) correlates with the size of the substituent at phosphorus: the smaller the substituent, the larger the coupling constant, and with the limited examples herein, apparently independent of whether the metal is Zr or Hf (cf., R = Bu^t, ^3J_P = 1–1.2 Hz; R = Pr^i, ^3J_P = 3.5–3.8 Hz; R = Me, ^3J_P = 6.7 Hz for M = Hf only).

A static solution structure with all three methyl substituents equivalent combined with a highly symmetric environment for the tridentate ancillary ligand is difficult to reconcile. Using an octahedral structure as a starting point, the two possibilities are the *fac* and *mer* stereoisomers, neither of which is consistent with the data given above; in particular, both geometries generate inequivalent methyl environments. A trigonal-prismatic geometry is also a viable alternative for certain six-coordinate d^0 metal complexes;[31] however, once again consideration of possible stereoisomers does not generate a reasonable structure for these trimethyl derivatives. One is left with no recourse except to suggest that these molecules are undergoing some fluxional process. Attempts to detect this process have only been successful in one of the above complexes, the hafnium derivative having the bulky *tert*-butyl substituents at phosphorus, i.e., $HfMe_3[N(SiMe_2CH_2PBu^t{}_2)_2]$. In this case, as the temperature was lowered, the singlet in the $^{31}P\{^1H\}$ NMR spectrum broadened and decoalesced into two singlets at approximately 21 and 19 ppm. As there is no coupling between these resonances and the high-field peak is observed close to the resonance of the free ligand (cf., 18.2 ppm for $LiN(SiMe_2CH_2PBu^t{}_2)_2$), we suggest that this is indicative of one of the arms of the tridenate ligand dissociated in the low-temperature limit. All of the remaining trimethyl complexes described here show only broadened NMR spectra at low temperatures.

The solid-state molecular structure of the hafnium trimethyl complex having methyl substituents at phosphorus, i.e., $HfMe_3[N(SiMe_2CH_2PMe_2)_2]$, is shown in Figure 1. The structure is distorted and at first glance could be considered as having an octahedral geometry. However, some of the distortions are immense. For example, the N-Hf-C(5) angle is 136.8 (3)°, much smaller than the expected 180° for two transoid ligands in an octahedral array. The distortion is compounded by the fact that, within the coordination sphere, there are four relatively short bonds from the hafnium to the amide nitrogen and the three carbons (Hf–N and Hf–C range from 2.156 (4) to 2.272 (7) Å) and two long Hf–P bond lengths (2.761 (2) Å and 2.806 (2) Å). A simpler geometric picture of this molecule is to consider it as a bicapped

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(30) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 99–102 and 149 (present distributor D. Reidel: Dordrecht, The Netherlands).

(31) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114.

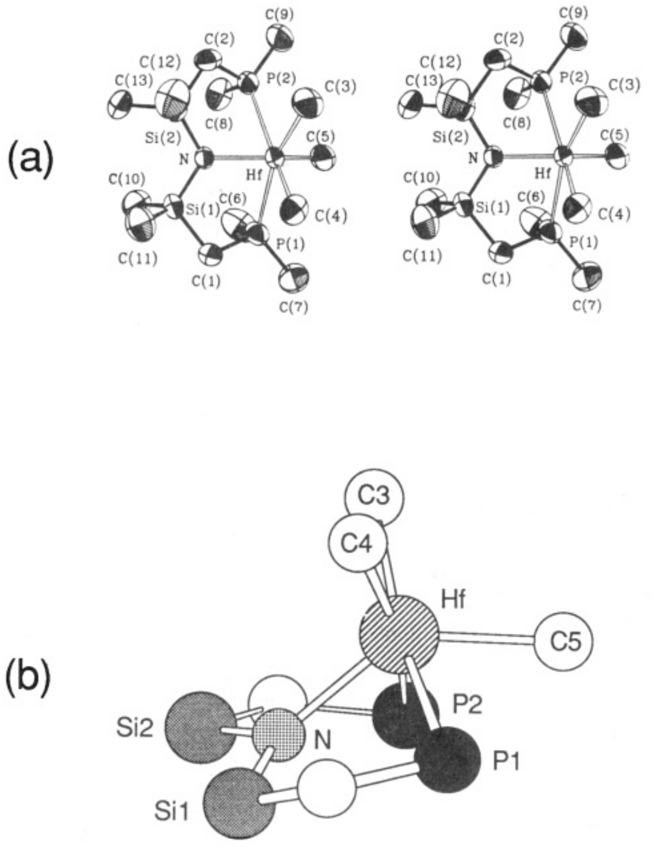
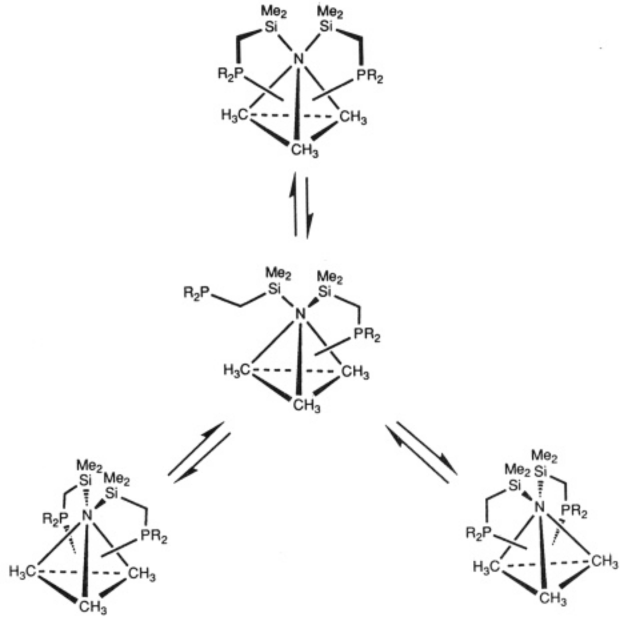


Figure 1. (a) Stereoscopic view of the molecular structure of $HfMe_3[N(SiMe_2CH_2PMe_2)_2]$ with the numbering scheme. (b) Chem 3D drawing with the methyl substituents removed from the phosphorus and silicon groups to more clearly show the bicapped-tetrahedral geometry.

tetrahedron,[32] that is, a tetrahedral array of the four formally anionic ligands, amide (NR_2^-) and three methyls (CH_3^-), capped on two faces by the neutral phosphine donors (see Figure 1b). While this proposal might initially be considered unnecessarily pedantic, it should be noted that the distortions become less pronounced for this model as compared to the octahedral one. For example, the six angles that define the tetrahedral geometry at hafnium range from a low of 85.3 (3)° (C(3)–Hf–C(4) to 136.8 (3)° (N–Hf–C(5)), with the remaining being close to that expected for a tetrahedral shape. The P(1)–Hf–P(2) angle is 115.32 (6)°, which is quite close to what one would predict for two caps on a tetrahedron (predict 109.4°). The already mentioned bond lengths are not unusual, as they are very similar to those found in $Hf(\eta^4\text{-}C_4H_6)Ph[N(SiMe_2CH_2PMe_2)_2]$.[26] Also noteworthy in this structure is the virtually planar $Hf\text{-}NSi_2$ unit; that is the disilylamido ligand is planar (sum of the bond angles is 358.4°).

Scheme I



The bicapped-tetrahedral model used above in the analysis of the solid-state structure can also be applied to rationalize the solution behavior of these complexes. A fluxional process which involves dissociation of one of the phosphine arms from a tetrahedral face and recoordination to another face will provide equivalent methyl ligands and a symmetric ligand environment in the fast-exchange limit. This is shown in Scheme I. Other mechanisms can also be discussed particularly if one of the phosphine arms dissociates to generate a five-coordinate intermediate, as this can subsequently rearrange via classical Berry pseudorotation or turnstile processes.

These simple hydrocarbyl derivatives of zirconium and hafnium may be useful precursors for Ziegler–Natta polymerization reactions. Studies on the reactivity of these species are in progress.

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Registry No. $ZrMe_3[N(SiMe_2CH_2PBu^t_2)_2]$, 137203-38-4; $ZrMe_3[N(SiMe_2CH_2PPr^i_2)_2]$, 137203-39-5; $HfMe_3[N(SiMe_2CH_2PBu^t_2)_2]$, 137203-40-8; $HfMe_3[N(SiMe_2CH_2PPr^i_2)_2]$, 137203-41-9; $HfMe_3[N(SiMe_2CH_2PMe_2)_2]$, 137203-42-0; $ZrCl_3[N(SiMe_2CH_2PBu^t_2)_2]$, 94372-19-7; $ZrCl_3[N(SiMe_2CH_2PPr^i_2)_2]$, 137328-85-9; $HfCl_3[N(SiMe_2CH_2PBu^t_2)_2]$, 94372-18-6; $HfCl_3[N(SiMe_2CH_2PPr^i_2)_2]$, 94372-16-4; $HfCl_3[N(SiMe_2CH_2PMe_2)_2]$, 98758-74-8.

Supplementary Material Available: Tables of calculated hydrogen atom parameters, anisotropic thermal parameters, and torsion angles (intraannular and general) for $HfMe_3[N(SiMe_2CH_2PMe_2)_2]$ (5 pages); a listing of measured and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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[32] Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.