of 25 reflections (24° ≤ 2θ ≤ 29°). An empirical absorption correction (ψ-scan, six reflections–216 data, at 10° increments about the diffraction vector pseudoellipsoid model) was applied to the data.

Direct methods provided the initial Sb, Co, and P atom positions; the structure was completed by difference Fourier syntheses. The P-bonded phenyl rings were constrained to rigid, planar hexagons (C–C = 1.395 Å) to conserve data. Hydrogen atoms were treated as idealized, updated contributions (C–H = 0.96 Å). All nonhydrogen atoms except for the carbon atoms of the dppm phenyl rings were refined with anisotropic thermal parameters.

SHELXTL (Version 5.1) software was used for all computations (Nicolet Corp., Madison, WI). The atomic coordinates are given in Table IV, and selected bond parameters are given in Table V.

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Supplementary Material Available: Listings of additional bond lengths (Table S2), additional bond angles (Table S3), anisotropic thermal parameters (Table S4), calculated hydrogen atom coordinates and isotropic thermal parameters (Table S5), and analytical data for [BF_4^-] salts (Table S6) (5 pages); listings of observed and calculated structure factors (Table S1) (17 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department, University of California at San Diego, La Jolla, California 92093, and Department of Chemistry, University of Delaware, Newark, Delaware 19716

Preparation and Characterization of Tris(trimethylsilyl)silyl and Tris(trimethylsilyl)germyl Derivatives of Zirconium and Hafnium. X-ray Crystal Structures of (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ and (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$

John Arnold,[†] Dean M. Roddick,[†] T. Don Tilley,*[,†] Arnold L. Rheingold,*[,‡] and Steven J. Geib[‡]

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By reaction of $(THF)_3LiSi(SiMe_3)_3$ or $(THF)_3LiGe(SiMe_3)_3$ with the appropriate metal halide, the following silyl and germyl derivatives of zirconium and hafnium have been prepared: (η^5-C_5Me_5)$Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf), (η^5-C_5H_5)$_2$Zr[Ge(SiMe$_3$)$_3$]Cl, and (η^5-C_5Me_5)$Cl_2MGe(SiMe_3)_3$ (M = Zr, Hf). In addition, the pyridine adduct (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$(py) has been isolated from reaction of (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ with pyridine. (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ and (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$ represent the first hafnium silyl and germyl complexes to be structurally characterized. Crystals of (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ are monoclinic, $C2/c$, with a = 39.62 (2) Å, b = 9.465 (5) Å, c = 17.255 (8) Å, β = 114.29 (4)°, V = 5897 (5) Å^3, Z = 8, R_F = 5.26%, and R_{wF} = 5.35%. (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$ is isomorphous, with a = 39.74 (1) Å, b = 9.504 (3) Å, c = 17.313 (6) Å, β = 114.35 (3)°, V = 5956 (4) Å^3, Z = 8, R_F = 5.04%, and R_{wF} = 5.86%. The Hf–Si bond length in (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ is 2.748 (4) Å, and the Hf–Ge bond length in (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$ is slightly shorter, at 2.740 (1) Å.

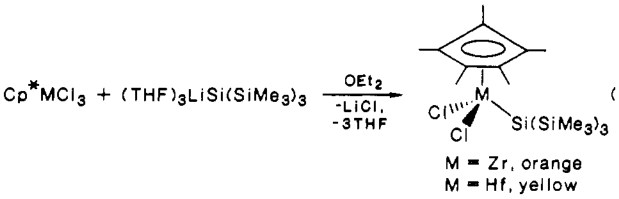
Introduction

Our investigations of early transition-metal silyl compounds have shown that the reactivity of early metal-silicon bonds can be dramatically influenced by changes of substituents at both the metal and silicon.[1] For example, whereas $Cp_2Zr(SiMe_3)Cl$[1a] (Cp = η^5-C_5H_5) and CpCp*Zr[Si(SiMe$_3$)$_3$]Cl[1b,e] (Cp* = η^5-C_5Me_5) combine rapidly with carbon monoxide to form η^2-COSiR$_3$ derivatives, $Cp_2Zr[Si(SiMe_3)_3]Cl$[1a] is unreactive toward CO under similar conditions. This implies that elucidation of structure–reactivity correlations can be very important in the development of this area. Presently studies directed toward this goal are complicated by the fact that relatively few early transition-metal silyl complexes have been described.[2] All reported zirconium and hafnium silyls are 16- or 18-electron metallocene derivatives of the type (η^5-C_5R_5)(η^5-$C_5R'_5$)M(SiR''$_3$)X (R, R' = H, Me). Clearly, thorough investigations of the chemistry of early transition-metal-silicon bonds will rely on efficient synthetic routes to a range of complexes.

We report here the synthesis and characterization of a new type of group 4 silyl derivative, the formally 12-electron species Cp*$Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf). Initial investigations indicate that these derivatives possess M–Si bonds that are exceptionally reactive toward insertion of unsaturated substrates.[1d,3] The syntheses of new germyl complexes of zirconium and hafnium, $Cp_2Zr[Ge(SiMe_3)_3]Cl$ and Cp*$Cl_2MGe(SiMe_3)_3$ (M = Zr, Hf), are also described. The only previously reported germyl derivatives of zirconium and hafnium appear to be the complexes $Cp_2M(GePh_3)Cl$ (M = Zr, Hf).[4] The X-ray structures of Cp*$Cl_2HfSi(SiMe_3)_3$ and Cp*$Cl_2HfGe(SiMe_3)_3$ are the first to be determined for silyl- and germyl-hafnium complexes.

Results and Discussion

Metal silyl complexes Cp*$Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf) are prepared by the reaction shown in eq 1. As solids, these silyl



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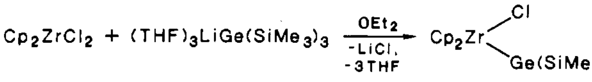
complexes are stable indefinitely under nitrogen. In moist air both decompose rapidly, and pure samples of $Cp^*Cl_2ZrSi(SiMe_3)_3$ are in fact quite pyrophoric. In the absence of light, hydrocarbon solutions of $Cp^*Cl_2ZrSi(SiMe_3)_3$ and $Cp^*Cl_2HfSi(SiMe_3)_3$ are stable for at least 1 week, but exposure to normal room lighting results in fairly rapid decomposition. As judged by ^1H NMR (benzene-d_6 solvent), these photochemical reactions are quite complex. Photolytically, $Cp^*Cl_2ZrSi(SiMe_3)_3$ is less stable than $Cp^*Cl_2HfSi(SiMe_3)_3$. On exposure to light from a high-intensity table lamp, $Cp^*Cl_2ZrSi(SiMe_3)_3$ was completely decomposed after 1 h (benzene-d_6 solution), whereas $Cp^*Cl_2HfSi(SiMe_3)_3$ required approximately 2 h of irradiation for complete decomposition. Both complexes are, however, very stable thermally in benzene-d_6. Their NMR spectra remained unchanged after 1 day at 95 °C in total darkness.

These formally 12-electron silyl complexes readily add donor ligands (PMe_3, THF, py) in solution to form adducts of the type $Cp^*Cl_2MSi(SiMe_3)_3(L)_x$. The adduct species are darker in color than their base-free precursors (zirconium adducts dark red; hafnium adducts orange). Only in the case of $Cp^*Cl_2HfSi(SiMe_3)_3(py)$ was an attempt made to isolate a pure adduct. This orange complex was characterized by ^1H NMR spectroscopy, IR spectroscopy, and elemental analysis. The THF adducts are sometimes observed in large-scale preparations of $Cp^*Cl_2ZrSi(SiMe_3)_3$ and $Cp^*Cl_2HfSi(SiMe_3)_3$, and recrystallizations from pentane are often necessary for isolation of the base-free material.

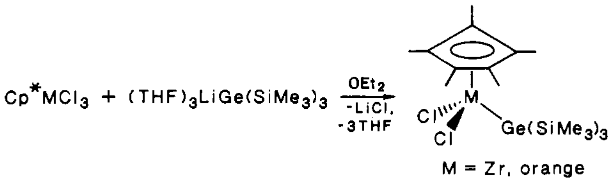
Tris(trimethylsilyl)germyl derivatives of zirconium and hafnium were obtained by reaction of the appropriate metal halide with $(THF)_3LiGe(SiMe_3)_3$,[5] which can be readily prepared from $Ge(SiMe_3)_4$ and MeLi by a procedure analogous to that for $(THF)_3LiSi(SiMe_3)_3$.[6] The orange zirconocene derivative $Cp_2Zr[Ge(SiMe_3)_3]Cl$, obtained by the reaction in eq 2, has many



$$Cp_2ZrCl_2 + (THF)_3LiGe(SiMe_3)_3 \xrightarrow[-LiCl,\ -3THF]{OEt_2} Cp_2Zr(Cl)Ge(SiMe_3)_3$$

(2)

properties in common with the previously reported silyl $Cp_2Zr[Si(SiMe_3)_3]Cl$.[1a] Like $Cp_2Zr(GePh_3)Cl$,[4] the compound is orange. The mono-ring germyl complexes $Cp^*Cl_2MGe(SiMe_3)_3$ (M = Zr, Hf) are prepared by the salt elimination route shown in eq 3. Both of the latter germyl derivatives are markedly more stable than their silyl analogues. In the solid state they decompose much more slowly in moist air (over a few hours), and are photolytically and thermally stable under ambient conditions.



(3)

M = Zr, orange
M = Hf, yellow

Description of the Structures of $Cp^*Cl_2HfSi(SiMe_3)_3$ and $Cp^*Cl_2HfGe(SiMe_3)_3$. To investigate structure and bonding in these new silyl and germyl complexes, an X-ray diffraction study was carried out with $Cp^*Cl_2HfSi(SiMe_3)_3$ and $Cp^*Cl_2HfGe(SiMe_3)_3$. To our knowledge these are the first silyl and germyl hafnium complexes to be crystallographically characterized. The structures of these two isomorphs, with the atom-labeling schemes, are shown in Figures 1 and 2. Crystal and data collection parameters are summarized in Table I. Relevant geometrical parameters are given in Tables II–IV.

In both structures the coordination environment about hafnium can be viewed as a distorted octahedron, with the Cp* ligand occupying three coordination sites. Bond angles about the hafnium atoms of the two structures are very similar, and range from ca. 100° (Cl–Hf–X; X = Si, Ge) to ca. 122° (Cp*(centroid)–Hf–X).

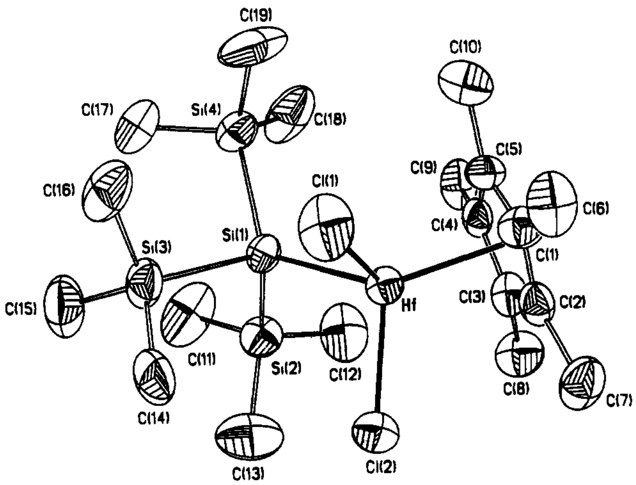


Figure 1. ORTEP view of $Cp^*Cl_2HfSi(SiMe_3)_3$ with atom-labeling scheme.

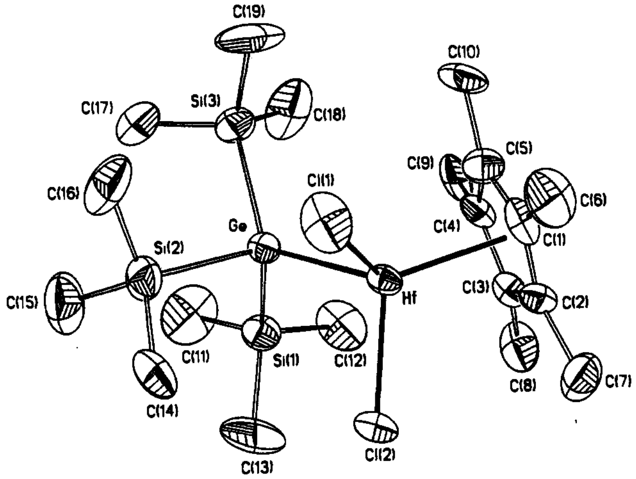


Figure 2. ORTEP view of $Cp^*Cl_2HfGe(SiMe_3)_3$ with atom-labeling scheme.

Table I. Crystallographic Data for $Cp^*Cl_2HfSi(SiMe_3)_3$ and $Cp^*Cl_2HfGe(SiMe_3)_3$

	$C_{19}H_{42}Si_4HfCl_2$	$C_{19}H_{42}GeSi_3HfCl_2$
a, Å	39.62 (2)	39.74 (1)
b, Å	9.465 (5)	9.504 (3)
c, Å	17.255 (8)	17.313 (6)
β, deg	114.29 (4)	114.35 (3)
V, Å^3	5897 (5)	5956 (4)
Z	8	8
fw	632.28	676.79
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)
T, °C	23	23
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.42	1.51
μ, cm^{-1}	40.7	50.4
T_{max}/T_{min}	0.261/0.177	1.000/0.143
R_F, %	5.26	5.04
R_{wF}, %	5.35	5.86

The Hf–C(Cp*) distances in the silyl $Cp^*Cl_2HfSi(SiMe_3)_3$ range from 2.458 (13) to 2.475 (11) Å, and the Hf–Cp*(centroid) distance is 2.151 (12) Å. These values are slightly smaller than the corresponding distances in $Cp^*Cl_2HfGe(SiMe_3)_3$, which exhibits Hf-C(Cp*) separations of 2.462 (14) to 2.508 (10) Å, and a Hf–Cp*(centroid) distance of 2.171 (12) Å. These Hf–Cp* ring distances are similar to corresponding values found in Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl[7] (Hf–Cp*(centroid) = 2.158 Å) and $Cp^*Cl_2Hf[\eta^2\text{-}COP(CMe_3)_2]$[8] (Hf–Cp*(centroid)

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Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $Cp^*Cl_2HfSi(SiMe_3)_3$

	x	*y*	*z*	*U*[a]
Hf	1839.9 (1)	1549.6 (6)	545.9 (3)	45.8 (2)
Cl(1)	1868 (1)	1293 (5)	−774 (2)	92 (2)
Cl(2)	2046 (1)	3832 (4)	1024 (3)	83 (2)
Si(1)	1089 (1)	1889 (4)	14 (2)	49 (1)
Si(2)	918 (1)	3234 (5)	943 (3)	71 (2)
Si(3)	947 (1)	3352 (5)	−1208 (2)	73 (2)
Si(4)	653 (1)	41 (5)	−518 (2)	69 (2)
C(1)	2327 (4)	−263 (15)	1060 (8)	61 (6)
C(2)	2405 (3)	676 (14)	1733 (8)	56 (5)
C(3)	2117 (3)	605 (14)	2005 (7)	52 (5)
C(4)	1850 (3)	−395 (13)	1507 (7)	48 (5)
C(5)	1998 (4)	−949 (14)	899 (8)	59 (6)
C(6)	2587 (4)	−591 (18)	641 (9)	79 (7)
C(7)	2752 (4)	1569 (16)	2126 (9)	83 (7)
C(8)	2112 (4)	1384 (16)	2755 (8)	80 (8)
C(9)	1542 (3)	−964 (16)	1670 (9)	72 (7)
C(10)	1822 (4)	−2137 (17)	313 (10)	85 (8)
C(11)	406 (4)	3486 (23)	534 (12)	140 (13)
C(12)	1063 (5)	2409 (22)	2018 (9)	118 (11)
C(13)	1136 (5)	5012 (18)	1107 (12)	122 (12)
C(14)	1311 (4)	4672 (17)	−1054 (10)	105 (9)
C(15)	510 (4)	4369 (21)	−1476 (11)	117 (10)
C(16)	882 (5)	2274 (20)	−2159 (8)	102 (9)
C(17)	191 (4)	753 (21)	−1273 (9)	97 (8)
C(18)	553 (5)	−909 (22)	309 (11)	127 (11)
C(19)	795 (5)	−1284 (19)	−1100 (13)	133 (12)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $Cp^*Cl_2HfGe(SiMe_3)_3$

	x	*y*	*z*	*U*[a]
Hf	1842.6 (1)	1541.6 (5)	545.1 (3)	36.3 (2)
Cl(1)	1875 (1)	1286 (5)	−773 (2)	78 (2)
Cl(2)	2048 (1)	3832 (4)	1028 (3)	69 (2)
Ge	1095.2 (3)	1862 (1)	15.2 (8)	39.5 (5)
Si(1)	919 (1)	3243 (4)	947 (3)	61 (2)
Si(2)	948 (1)	3343 (5)	−1227 (3)	66 (2)
Si(3)	649 (1)	14 (5)	−526 (3)	59 (2)
C(1)	2334 (4)	−277 (14)	1083 (9)	54 (6)
C(2)	2414 (3)	671 (12)	1752 (8)	45 (5)
C(3)	2122 (3)	615 (12)	2021 (7)	38 (5)
C(4)	1863 (3)	−408 (12)	1500 (8)	47 (5)
C(5)	1992 (4)	−965 (15)	912 (8)	49 (5)
C(6)	2587 (4)	−587 (19)	642 (11)	82 (9)
C(7)	2747 (4)	1580 (16)	2145 (10)	75 (7)
C(8)	2109 (5)	1367 (17)	2755 (9)	75 (8)
C(9)	1532 (4)	−970 (15)	1670 (10)	63 (6)
C(10)	1823 (4)	−2113 (15)	321 (11)	75 (8)
C(11)	411 (5)	3556 (25)	573 (16)	136 (15)
C(12)	1049 (6)	2390 (22)	1994 (10)	105 (12)
C(13)	1153 (6)	5045 (17)	1144 (16)	113 (13)
C(14)	1312 (5)	4689 (18)	−1050 (12)	89 (9)
C(15)	514 (5)	4376 (24)	−1487 (13)	113 (11)
C(16)	883 (5)	2232 (23)	−2167 (10)	100 (9)
C(17)	198 (4)	758 (21)	−1252 (10)	87 (8)
C(18)	555 (5)	−915 (25)	319 (12)	120 (11)
C(19)	789 (6)	−1343 (20)	−1131 (15)	131 (14)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

= 2.157 Å). The Hf–Cl distances for $Cp^*Cl_2HfSi(SiMe_3)_3$ (2.339 (5) and 2.337 (4) Å) and $Cp^*Cl_2HfGe(SiMe_3)_3$ (2.350 (5) and 2.354 (3) Å) are similar but slightly longer in the germyl derivative. For comparison, the Hf–Cl distances in Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl[7] (2.393 (2) Å) and $Cp^*Cl_2Hf[\eta^2\text{-}COP(CMe_3)_2]$[8] (2.393 (2), 2.383 (2) Å) are ca. 0.03–0.05 Å longer. This is consistent with the higher formal electron count (14) for the latter two complexes.

Table IV. Selected Bond Lengths and Angles for $Cp^*Cl_2HfSi(SiMe_3)_3$ and $Cp^*Cl_2HfGe(SiMe_3)_3$[a]

	$Cp^*Cl_2HfSi(SiMe_3)_3$ (X = Si)	$Cp^*Cl_2HfGe(SiMe_3)_3$ (X = Ge)
	(a) Bond Distances (Å)	
Hf–Cl(1)	2.339 (5)	2.350 (5)
Hf–Cl(2)	2.337 (4)	2.354 (3)
Hf–X	2.748 (4)	2.740 (1)
Hf–CNT	2.151 (12)	2.171 (12)
Hf–C(1)	2.459 (14)	2.483 (13)
Hf–C(2)	2.475 (11)	2.508 (10)
Hf–C(3)	2.464 (11)	2.490 (11)
Hf–C(4)	2.467 (12)	2.462 (14)
Hf–C(5)	2.458 (13)	2.474 (14)
⟨av⟩ X–Si	2.368 (5)	2.409 (5)
⟨av⟩ Si–C	1.86 (2)	1.87 (2)
	(b) Bond Angles (deg)	
Cl(1)–Hf–Cl(2)	106.9 (2)	106.9 (2)
Cl(1)–Hf–X	99.6 (1)	99.9 (1)
Cl(2)–Hf–X	100.5 (1)	100.7 (1)
Cl(1)–Hf–CNT	113.1 (3)	113.3 (3)
Cl(2)–Hf–CNT	113.2 (3)	112.9 (3)
X–Hf–CNT	121.7 (4)	121.4 (3)
⟨av⟩ Hf–X–Si	109.0 (2)	109.0 (2)
Hf–X–Si	101.1 (2) 114.3 (1) 124.1 (2)	101.1 (1) 114.4 (1) 125.1 (1)

[a] CNT = centroid of Cp ring.

The environments about Si(1) in $Cp^*Cl_2HfSi(SiMe_3)_3$ and Ge in $Cp^*Cl_2HfGe(SiMe_3)_3$ are distorted tetrahedra with bond angles ranging from 101.1 (2) to 124.1 (2)° in $Cp^*Cl_2HfSi(SiMe_3)_3$ and 101.1 (1) to 125.1 (1)° in $Cp^*Cl_2HfGe(SiMe_3)_3$. For $Cp^*Cl_2HfSi(SiMe_3)_3$, the average Si–Si–Si angle is 104.9 (2)° and the Hf–Si–Si angles are 101.1 (2), 114.3 (1), and 124.1 (2)°. The average Si–Si distance in the latter compound is 2.37 (1) Å. For comparison, in the silyls $(CO)_5MSi(SiMe_3)_3$ (M = Mn,[9] Re[10]), the mean Si–Si–Si angles are 106.1 (3) and 105.8 (6)°, respectively. The mean M–Si–Si angles for the latter complexes are 112.7 (3) and 113.0 (5)°, and the mean Si–Si distances are 2.374 (8) and 2.37 (1) Å, respectively. For $Cp^*Cl_2HfGe(SiMe_3)_3$, the average Si–Ge–Si angle is 104.4 (2)° and the Hf–Ge–Si angles are 101.1 (1), 114.4 (1), and 125.1 (1)°. The average Si–Ge distance is 2.41 (1) Å.

The Hf–Si bond length in $Cp^*Cl_2HfSi(SiMe_3)_3$, 2.748 (4) Å, is somewhat shorter than Zr–Si distances found in $Cp_2Zr(SiPh_3)Cl$ (2.183 (2) Å)[11] and $Cp_2Zr(SiMe_3)S_2CNEt_2$ (2.815 (1) Å),[12] which have been characterized as being surprisingly long. Since the effective ionic radius for Hf(IV) in six coordination is 0.13 Å smaller than that for Zr(IV) in eight coordination and 0.18 Å smaller than Zr(IV) in nine coordination,[13] the Hf–Si distance observed here also appears to be longer than expected for a single covalent bond. A Hf–Si single-bond distance for this compound can be estimated from covalent radii for Hf and Si. The covalent radius for Hf may be estimated by subtracting the radius for Cl (0.99 Å)[14] from the observed Hf–Cl separation (2.34 Å), to give 1.35 Å. The Si radius may be taken from the observed Si–Si distances (average 2.37 Å) as 1.18 Å. This results in a predicted Hf–Si bond distance of 2.53 Å, a value considerably less than what is observed.

A remarkable feature of the structure of $Cp^*Cl_2HfGe(SiMe_3)_3$ is the Hf–Ge bond length of 2.740 (1) Å, which is slightly *shorter* than the Hf–Si distance in $Cp^*Cl_2HfSi(SiMe_3)_3$. This result was

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unexpected, since the covalent radius of germanium is ca. 0.05 Å greater than that for silicon.[14] This is reflected in Co–X (X = Si or Ge) distances observed for the cobalt complexes $(CO)_4CoSiH_3$ (Co–Si = 2.38 Å)[15] and $(CO)_4CoGeH_3$ (Co–Ge = 2.42 Å).[16] A similar comparison can be made with manganese and rhenium complexes: $(CO)_5MnSiH_3$ (Mn–Si = 2.41 Å);[17] $(CO)_5MnGeH_3$ (Mn–Ge = 2.49 Å);[17] $(CO)_5ReSiH_3$ (Re–Si = 2.56 Å);[18] $(CO)_5ReGeH_3$ (Re–Ge = 2.63 Å).[18] Presently we do not have a very convincing rationalization for the observed ordering of bond distances in $Cp^*Cl_2HfSi(SiMe_3)_3$ and $Cp^*Cl_2HfGe(SiMe_3)_3$. One possible explanation is that the Hf–Ge bond is shortened relative to the corresponding Hf–Si bond by a greater degree of ionic character.[17,19] More likely, the Hf–Ge bond is simply less hindered due to the less sterically demanding $Ge(SiMe_3)_3$ group (due to the longer Ge–Si bonds). Indeed, evidence for steric interactions between Cp* rings and the $X(SiMe_3)_3$ groups is found in the Hf–X–Si angles (X = Si, Ge) mentioned above. In both compounds, one rather large Hf–X–Si angle (124.1 (2)° for $Cp^*Cl_2HfSi(SiMe_3)_3$; 125.1 (1)° for $Cp^*Cl_2HfGe(SiMe_3)_3$) results from close Cp*–$SiMe_3$ contacts. Clearly, further synthetic and structural investigations are needed to establish a more accurate bonding picture for early transition-metal silyl and germyl complexes. Finally, it is worth noting that the Hf–Ge bond length is comparable to the Ti–Ge distance of 2.710 (2) Å in $Cp_2Ti(\eta^2\text{-}COMe)GePh_3$.[20]

Experimental Section

General Data. All manipulations were conducted under an atmosphere of nitrogen or argon by using Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Galbraith or Schwarzkopf Laboratory. UV–vis spectra were recorded with an IBM 9420 instrument on pentane solutions in a 1.00-cm quartz cell equipped with a Teflon needle valve and a ground-glass joint. Infrared spectra were recorded on a Perkin-Elmer 1330 instrument. NMR spectra were obtained with a GE QE-300 instrument at 300 MHz (^1H), 75.5 MHz (^{13}C), and 59.6 MHz (^{29}Si). An INEPT sequence[21] was employed to enhance signals in the ^{29}Si spectra. The lithium silyl $(THF)_3LiSi(SiMe_3)_3$[6] and the lithium germyl $(THF)_3LiGe(SiMe_3)_3$[5] were prepared by the literature procedures, with the modification that halide-free MeLi (Aldrich) was used. The halides $ZrCl_4$ and $HfCl_4$ (Aesar) were sublimed before use. Zirconocene dichloride (Boulder Scientific) was used as received. The complexes Cp^*ZrCl_3[22] and Cp^*HfCl_3[22] were prepared according to established methods.

$Cp^*Cl_2ZrSi(SiMe_3)_3$. A solution of $(THF)_3LiSi(SiMe_3)_3$ (1.00 g, 2.1 mmol) in diethyl ether (10 mL, −78 °C) was added to a diethyl ether (30 mL) suspension of Cp^*ZrCl_3 (0.71 g, 2.1 mmol) at −78 °C. The solution was warmed to ambient temperature and stirred for an additional 30 min. Volatiles were removed by vacuum transfer, and the orange solid was extracted with pentane (2 × 30 mL). Concentration and cooling to −45 °C for 8 h afforded 0.82 g (71%) of orange crystals (mp 145–150 °C dec). Anal. Calcd for $C_{19}H_{42}Cl_2Si_4Zr$: C, 41.9; H, 7.77; Cl, 13.0. Found: C, 42.3; H, 7.89; Cl, 12.2. IR (Nujol, CsI; cm^{-1}): 2730 w, 1300 w, 1255 sh, 1241 s, 1027 m, 830 br, s, 733 m, 680 s, 620 s, 417 m, 392 s, 369 s, 345 m, 295 w. ^1H NMR (benzene-d_6, 300 MHz, 22 °C): δ 0.48 (s, 27 H, $SiMe_3$), 1.93 (s, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 22 °C): δ 4.84 ($SiMe_3$), 13.45 ($C_5\mathit{Me}_5$); C_5Me_5 resonance obscured by solvent. $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 22 °C): δ −55.65 ($\mathit{Si}(SiMe_3)_3$), −6.26 ($Si(\mathit{Si}Me_3)_3$). UV–vis (pentane; nm): 222 (ϵ = 9000 L mol^{-1} cm^{-1}), 258 (ϵ = 5000 L mol^{-1} cm^{-1}), 333 (ϵ = 2000 L mol^{-1} cm^{-1}).

$Cp^*Cl_2HfSi(SiMe_3)_3$. The method used to prepare the zirconium derivative was followed by using Cp^*HfCl_3 (1.43 g, 3.40 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (1.60 g, 3.40 mmol). After workup, the yield was 75% (1.61 g) of yellow crystals (mp 179–180 °C). Anal. Calcd for $C_{19}H_{42}Cl_2HfSi_4$: C, 36.1; H, 6.70; Cl, 11.2. Found: C, 36.3; H, 6.66; Cl, 10.9. IR (Nujol, CsI; cm^{-1}): 2730 w, 1302 w, 1255 m, sh, 1242 s, 1027 w, 830 s, br, 746 w, 735 m, 682 m, 621 s, 420 m, 341 s. ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.48 (s, 27 H, $SiMe_3$), 2.01 (s, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 5.09 ($SiMe_3$), 12.94 ($C_5\mathit{Me}_5$), 125.9 (C_5Me_5). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 22 °C): δ −49.77 ($\mathit{Si}(SiMe_3)_3$), −3.69 ($Si(\mathit{Si}Me_3)_3$). UV–vis (pentane; nm): 219 (ϵ = 1000 L mol^{-1} cm^{-1}), 292 (ϵ = 2000 L mol^{-1} cm^{-1}).

$Cp^*Cl_2HfSi(SiMe_3)_3(py)$. Pyridine (69 μL, 0.79 mmol) was added to a solution of $Cp^*Cl_2HfSi(SiMe_3)_3$ (0.50 g, 0.79 mmol) in pentane (20 mL). The orange microcrystalline product that deposited from solution was collected and crystallized from cold (−45 °C) diethyl ether to yield 0.45 g (80%) of orange crystals (mp 134–136 °C). Anal. Calcd for $C_{24}H_{47}Cl_2HfNSi_4$: C, 40.5; H, 6.66; Cl, 9.97. Found: C, 40.3; H, 6.82; Cl, 9.88. IR (Nujol, CsI; cm^{-1}): 3082 w, 2730 w, 1629 w, 1603 m, 1485 m, 1440 s, 1250 m, sh, 1230 s, 1156 w, 1068 s, 1041 m, 1022 w, 1000 s, 830 s, br, 757 s, 698 s, 677 s, 625 s, 618 sh, 425 w, 390 m, 349 m, 302 s. ^1H NMR (benzene-d_6, 90 MHz, 34 °C): δ 0.55 (s, 27 H, $SiMe_3$), 1.98 (s, 15 H, C_5Me_5), 6.40–6.80 (m, 3 H, py), 8.89 (m, 2 H, py).

$Cp_2Zr[Ge(SiMe_3)_3]Cl$. Diethyl ether was added to a mixture of Cp_2ZrCl_2 (0.30 g, 1.0 mmol) and $(THF)_3LiGe(SiMe_3)_3$ (0.50 g, 1.0 mmol). The orange solution was stirred for 1 day and the volatiles were then removed by vacuum transfer. After extraction with pentane (30 mL), concentration of the pentane extract to ca. 20 mL, and cooling to −45 °C for 8 h, large orange crystals (mp 241–245 °C) were isolated in 71% yield (0.40 g). Anal. Calcd for $C_{19}H_{37}ClGeSi_3Zr$: C, 41.6; H, 6.79; Cl; 6.46. Found: C, 41.5; H, 6.86; Cl, 6.40. IR (Nujol, CsI; cm^{-1}): 3110 w, 1292 m, 1252 sh, 1235 s, 1065 w, br, 1018 s, 830 s, br, 745 sh, 675 s, 618 s, 341 s, 290 m. ^1H NMR (benzene-d_6, 300 MHz, 22 °C): δ 0.43 (s, 27 H, $SiMe_3$), 5.99 (s, 10 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 22 °C): δ 5.44 ($SiMe_3$), 111.3 (C_5H_5).

$Cp^*Cl_2ZrGe(SiMe_3)_3$. Following the method used to prepare $Cp^*Cl_2ZrSi(SiMe_3)_3$, Cp^*ZrCl_3 (0.32 g, 0.97 mmol) and $(THF)_3LiGe(SiMe_3)_3$ (0.50 g, 0.97 mmol) were combined to produce 0.33 g (78%) of orange crystals (mp 170–173 °C, dec). Anal. Calcd for $C_{19}H_{42}Cl_2GeSi_3Zr$: C, 38.7; H, 7.18; Cl, 12.0. Found: C, 39.0; H, 7.30; Cl, 12.2. IR (Nujol, CsI; cm^{-1}): 1300 w, br, 1255 sh, 1240 s, 1028 m, 840 s, br, 732 m, 680 s, 616 s, 418 sh, 392 s, 370 s, 341 s. ^1H NMR (benzene-d_6, 300 MHz, 22 °C): δ 0.52 (s, 27 H, $SiMe_3$), 1.94 (s, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 22 °C): δ 5.25 ($SiMe_3$), 13.45 ($C_5\mathit{Me}_5$), 127.57 (C_5Me_5).

$Cp^*Cl_2HfGe(SiMe_3)_3$. The method used to prepare the silyl analogue was followed with Cp^*HfCl_3 (0.25 g, 0.58 mmol) and $(THF)_3LiGe(SiMe_3)_3$ (0.30 g, 0.58 mmol) used instead. Yellow crystals of the product were isolated in 64% yield (0.25 g, mp 180–182 °C). Anal. Calcd for $C_{19}H_{42}Cl_2GeHfSi_3$: C, 33.7; H, 6.26; Cl, 10.5. Found: C, 34.5; H, 6.23; Cl, 10.3. IR (Nujol, CsI; cm^{-1}): 2730 w, 1305 w, 1255 sh, 1244 s, 1130 w, 840 s, br, 746 sh, 736 m, 722 sh, 683 s, 618 s, 420 w, 367 s, 348 s. ^1H NMR (benzene-d_6, 300 MHz, 22 °C): δ 0.52 ($SiMe_3$), 2.01 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 22 °C): δ 5.52 ($SiMe_3$), 12.96 ($C_5\mathit{Me}_5$), 125.8 (C_5Me_5).

X-ray Structure Determinations. The parameters used during collection of diffraction data for $Cp^*Cl_2HfSi(SiMe_3)_3$ and $Cp^*Cl_2HfGe(SiMe_3)_3$ are contained in Table I. Yellow crystals of both compounds were sealed in glass capillaries. $Cp^*Cl_2HfSi(SiMe_3)_3$ and $Cp^*Cl_2HfGe(SiMe_3)_3$ are isomorphous, and systematic absences indicated that they crystallize in either of two space groups, *Cc* or *C*2/*c*. The centrosymmetric alternative *C*2/*c* was initially chosen based on *E* values and later confirmed by the successful solution and refinement of the structures. Unit cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections (20° ≤ 2θ ≤ 26°). Data were corrected for absorption by an empirical procedure that employs six refined parameters to define a pseudoellipsoid. No decay was observed in three standard reflections during the data collection.

The compound $Cp^*Cl_2HfSi(SiMe_3)_3$ was solved via heavy-atom methods, which located the Hf atom. Isomorph $Cp^*Cl_2HfGe(SiMe_3)_3$ was solved by utilizing the Hf and Si coordinates of $Cp^*Cl_2HfSi(SiMe_3)_3$. All remaining nonhydrogen atoms for both compounds were located from subsequent difference Fourier syntheses and were refined anisotropically. Hydrogen atom positions were calculated (d(C–H) = 0.96 Å, with thermal parameters equal to 1.2 times the isotropic equivalent for the carbon to which it was attached). The final difference Fourier synthesis of $Cp^*Cl_2HfSi(SiMe_3)_3$ showed only a diffuse background (maximum 0.86 e/Å^3 near Hf). An inspection of F_o vs F_c values and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic errors in the data for either structure.

Atomic coordinates are provided in Tables II and III, with selected bond distances and angles given in Table IV. Additional crystallographic

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data are available as supplementary material. All computations used the SHELXTL (Version 5.1) program library (Nicolet Corp., Madison, WI).

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Registry No. $(THF)_3LiSi(SiMe_3)_3$, 81859-95-2; $(THF)_3LiGe(SiMe_3)_3$, 116232-31-6; Cp_2ZrCl_2, 1291-32-3; Cp^*ZrCl_3, 75181-07-6; Cp^*HfCl_3, 75181-08-7; $Cp^*Cl_2ZrSi(SiMe_3)_3$, 116232-26-9; $Cp^*Cl_2HfSi(SiMe_3)_3$, 115677-43-5; $Cp^*Cl_2HfSi(SiMe_3)_3(py)$, 116232-27-0; $Cp_2Zr[Ge(SiMe_3)_3]Cl$, 116232-28-1; $Cp^*Cl_2ZrGe(SiMe_3)_3$, 116232-29-2; $Cp^*Cl_2HfGe(SiMe_3)_3$, 116232-30-5.

Supplementary Material Available: Tables of complete crystal and data collection parameters (Table 1S), bond distances (Tables 2S and 7S), bond angles (Tables 3S and 8S), anisotropic thermal parameters (Tables 4S and 9S), and hydrogen atom coordinates and their isotropic thermal parameters (Tables 5S and 10S) (10 pages); listings of calculated and observed structure factors (Tables 1S and 6S) (61 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of Potassium Aquatetrakis(nitrito)nitrosylplatinate(IV), a Blue, Mononuclear Platinum Complex with a Bent Nitrosyl Group, and of Potassium Trichlorobis(nitrito)nitrosylplatinate(IV)

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The compounds $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$ (**1**) and $K_2[Pt(NO_2)_2(NO)Cl_3]$ (**2**) have been synthesized and the structures determined by X-ray crystallography. Compound **1** is unusual because it is a mononuclear, blue platinum complex. It was isolated from the reaction that leads to binuclear platinum(III) sulfate and has been suggested to be an intermediate on the route to the sulfate. Both complexes feature a bent nitrosyl ligand and are best formulated as complexes of Pt(IV). They are the first mononuclear platinum nitrosyl complexes whose structures have been determined by X-ray crystallography. Crystallographic data are as follows: **1**, $P\bar{1}$, $a = 6.685$ (2) Å, $b = 8.712$ (2) Å, $c = 9.829$ (3) Å, $\alpha = 91.04$ (2)°, $\beta = 100.36$ (2)°, $\gamma = 92.11$ (2)°, $V = 562.6$ (3) Å^3, $Z = 2$ ($R = 0.065$, $R_w = 0.068$); **2**, $P2_1/c$, $a = 6.227$ (3) Å, $b = 11.690$ (2) Å, $c = 14.525$ (5) Å, $\alpha = 90°$, $\beta = 99.31$ (3)°, $\gamma = 90°$, $V = 1043.4$ (6) Å^3, $Z = 4$ ($R = 0.051$, $R_w = 0.050$).

Introduction

Although blue compounds are uncommon among the third-row transition metals, platinum seems to have three classes of them. Best known are the tetrameric, mixed-valence complexes.[1] A second class is less well characterized but is mononuclear and probably has a charge-transfer band in the long-wavelength part of the visible spectrum.[2,3] The third class has a single well-characterized example, a mononuclear platinum(III) species with rather bulky ligands, which may serve to prevent dimerization.[4]

Recently, it has been shown that certain simple platinum(II) complexes react with phosphoric[5] or sulfuric acid[6] to give dimeric platinum(III) complexes with platinum-platinum bonds.[7-12] The reaction conditions appear simple. All that is required is heating the platinum(II) complex with the appropriate acid. During the reaction, four color changes can be observed. The reaction mixture begins as a colorless solution. It becomes sequentially blue, green, yellow, and then red. The product is red-orange.

Several studies have been reported on the blue solutions that form when platinum(II) nitrites react with phosphoric or sulfuric acid.[13-15] The blue solutions owe their color to an absorption band near 630 nm. It has been asserted that the blue complexes are platinum nitrosyl complexes, but structural information has been unavailable owing to difficulties in handling them.[13,16] We are interested in elucidating the process by which platinum-platinum bonds form. We report the structure of the mononuclear blue platinum(IV) complex $K[Pt(NO_2)_4(NO)(H_2O)]$ (**1**), which forms in the early part of the reaction in phosphoric acid. We also report the structure of the mononuclear green platinum(IV) complex $K_2[Pt(NO_2)_2(NO)Cl_3]$ (**2**), which forms when chloride ion is added to the blue solution containing **1**.

A substantial number of mononuclear platinum nitrosyl complexes have been synthesized.[15-17] None of the compounds that were characterized were blue. Of the three platinum nitrosyl complexes for which molecular structures have been reported, two are dinuclear[18,19] and the third is tetranuclear.[20]

Experimental Section

Preparation of $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$. $K_2Pt(NO_2)_4$ was prepared as described elsewhere.[21] A 3:1 solution of H_3PO_4 in H_2O was

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