Communications to the Editor

η^5-Silolyl and η^5-Germolyl Complexes of d^0 Hafnium. Structural Characterization of an η^5-Silolyl Complex

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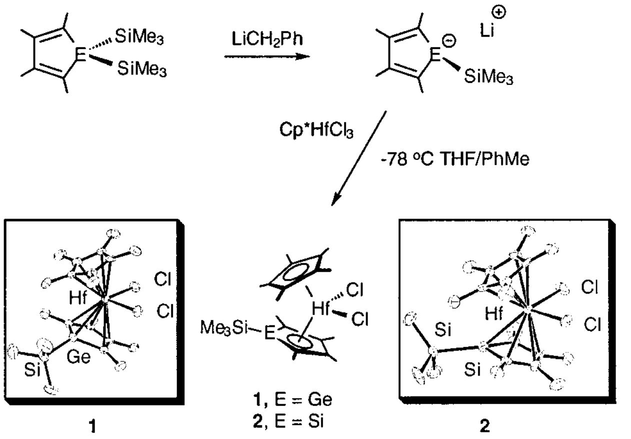
In recent years, there has been considerable interest in the aromatic properties of cyclic π-systems containing silicon and germanium.[1] Part of this interest has inspired efforts toward the isolation and characterization of transition metal complexes containing sila- and germaaromatic compounds as ligands.[2−4] Our work in this area produced the first η^5-germolyl complex, Cp*Ru[η^5-$Me_4C_4GeSi(SiMe_3)_3$] (Cp* = C_5Me_5), prepared via reaction of [Cp*Ru(μ-Cl)]$_4$ with the germolyl anion.[3] In addition, we have reported generation of the η^5-silolyl complex Cp*Ru[η^5-$Me_4C_4SiSi(SiMe_3)_3$], and its characterization in solution, but unfortunately this species could not be isolated in pure form.[4] In related work, we have characterized free silolyl and germolyl anions of the type $[Me_4C_4E{-}R]^-$ (E = Si, Ge) as possessing pyramidal E centers and bond-localized structures.[5] Thus, coordination to ruthenium has a dramatic effect on the delocalization in these rings.

To assess the importance of π-donation from the metal in supporting electronically delocalized silolyl and germolyl rings, we sought to form coordination complexes of these anions with d^0 transition metal centers. An additional motivation for examining complexes of this type stems from the possibility that silolyl and germolyl groups might represent novel ancillary ligands in early transition metal chemistry, since electrochemical studies on the ruthenium derivatives suggested that they might be significantly more electron-donating than Cp*.[3] Here we report the first examples of d^0 silolyl and germolyl complexes and the isolation and structural characterization of an η^5-silolyl complex.

Scheme 1



Our initial synthetic strategy, involving reactions of silolyl and germolyl anions with early metal halides, has met with limited success. Among the anions employed in this approach were the lithium derivatives Li[$Me_4C_4ESiMe_3$] (E = Ge, Si),[5] generated quantitatively in tetrahydrofuran solution by reactions of the silole and germole starting materials $Me_4C_4E(SiMe_3)_2$[5,6] with $LiCH_2Ph$. Although reactions of these lithium derivatives with $ZrCl_4$, $HfCl_4$, $CpTiCl_3$, and Cp^*TiCl_3 did not afford isolable products, reactions with Cp^*HfCl_3 in a mixture of THF and toluene at −78 °C produced the bent metallocene complexes shown in Scheme 1, as orange crystals in low and variable yields (5−30%). The intensely colored, green reaction solutions suggest the participation of competing redox processes involving Hf.

Coordination of the heterocyclic rings to hafnium results in only moderate ^{13}C NMR shifts for the ring carbon atoms in **1** (δ 146.0 and 135.8) and **2** (δ 136.1 and 122.3) with respect to corresponding values for the free anions [K(18-crown-6)][$Me_4C_4GeSiMe_3$] (δ 158.6 and 136.7) and [Li(12-crown-4)$_2$][$Me_4C_4SiSiMe_3$] (δ 148.6 and 135.8).[5] Notably, the ^{29}Si NMR resonance for the ring Si atom in **2** (δ 49.7) lies significantly downfield from the analogous resonance in [Li(12-crown-4)$_2$][$Me_4C_4SiSiMe_3$] (δ −44.0), strongly suggesting the participation of Si in π-delocalization.

The molecular structure of **1** consists of two planar five-membered rings coordinated in a bent fashion to the metal atom. The germolyl ring is planar, with the Ge atom deviating by only 0.001 Å from the C_4Ge least-squares plane. As expected, the $SiMe_3$ group is bent out of the C_4Ge least-squares plane and away from the Cp* group (by 26.2°). This structural feature, which presumably results from steric interactions between the Cp* and germolyl ring, appears to account for the somewhat nonplanar coordination about Ge (the sum of the bond angles about Ge = 346.6°). The C−C bond length alternation in the germolyl ring (1.387(9) − 1.452(8) − 1.406(8) Å) is slight (0.04−0.06 Å), and significantly less than in the germole $Me_4C_4Ge(H)Si(SiMe_3)_3$ (0.16 Å).[7] The hafnium atom in **1** lies 2.33 Å from the germolyl ring centroid and 2.22 Å from the Cp* ring centroid, and the centroid−hafnium−centroid angle is 136.1°. Finally, the Hf−Ge distance (2.7978(7) Å) is clearly bonding, given that the corresponding bond distance in $Cp^*HfCl_2Ge(SiMe_3)_3$ is 2.740 Å.[8]

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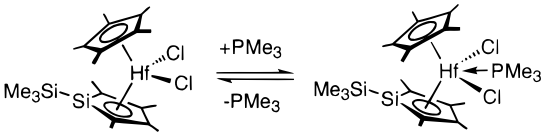
The molecular structure of **2** in the crystal differs from that of **1** in the position of the heteroatom ring substituent (Scheme 1). In contrast to **1**, the silicon atom in **2** lies close to the approximate mirror plane bisecting the molecule. At this point, it is unclear whether this reflects differences in packing forces or rotational barriers. The hafnium atom in **2** lies 2.29 Å from the C_4Si centroid and 2.15 Å from the C_5(Cp*) centroid, with a centroid−hafnium−centroid angle of 135.2°. Silicon adopts a nearly planar geometry in the silolyl ring, as evidenced by the summation of bond angles about Si (354.7°). In addition, the Si−C bond distances in the ring (1.798(7) and 1.780(1) Å) are relatively short compared to the analogous distances in the anion [K(18-crown-6)][$C_4Me_4SiSiMe_3$] (1.880(3) and 1.890(4) Å),[5] which possesses a pyramidal silicon center in the ring. The silicon atom deviates by only 0.004(2) Å from the least-squares plane of the five-membered ring in **2**. Surprisingly, the C−C bond lengths in the C_4Si ring of **2** vary according to a pattern (1.42(1), 1.37(2), and 1.46(2) Å) that is contrary to what has been seen for previous silole and silolyl anion structures[3−7] and suggests σ^2,π-coordination of the C_4 fragment to hafnium. This σ^2,π-metallacyclopentene structural motif is common for diene complexes of the early metals.[9] For comparison, the diene complex [Hf(η^4-$CH_2{=}CMeCMe{=}CH_2$)$(PMe_3)_2Cl_2$] possesses C−C(diene) bond lengths of 1.452(3), 1.401(3), and 1.475(4) Å.[10]

Complexes **1** and **2** are stable for weeks in refluxing toluene, but solutions of both are highly air- and moisture-sensitive. To investigate the stablitity of the η^5-bonding mode in these compounds, **2** was exposed to a slight excess of PMe_3 at room temperature in toluene-d_8. This produced a new, labile, PMe_3 adduct (**3**) that was characterized in solution by NMR spectroscopy. Removal of solvent from solutions of **3** led to quantitative conversion back to **2**, and cooling of a toluene solution of **3** to −78 °C resulted only in the crystallization of **2**. The $^{31}P\{^1H\}$ NMR spectrum of **3** at room temperature contains a broad resonance at δ −60.2 corresponding to free PMe_3 involved in an exchange process. Upon cooling to 0 °C a new resonance appears at δ −16.1, in addition to a broad peak at δ −60.3. Further reduction in temperature to −90 °C resulted in full resolution of these peaks into two sharp singlets, at δ −13.8 (**3**) and −61.5 (free phosphine). At −20 °C, the ^1H NMR spectrum consists of two distinct sets of resonances for the metallocene complexes **2** and **3**. Upon further cooling, the equilibrium is shifted toward **3** and the resonances for **2** decrease substantially. At −90 °C, the spectrum for **3** is completely resolved with resonances at δ 0.52 ($SiMe_3$), 0.66 (PMe_3), 1.78 (Cp*), and 2.24, 2.44 (ring CH_3 groups). The $^{29}Si\{^1H\}$ NMR spectrum of **3** at −90 °C revealed a doublet at $\delta = 34.9$ ($J_{Si-P} = 34.2$ Hz) for the ring silicon atom, further confirming the formation of a 1:1 adduct. The proximity of this shift to that for **2**, and the significant downfield shift relative to those for the $[Me_4C_4Si(SiMe_3)]^-$ anion (−44.0) and the silole $Me_4C_4Si(SiMe_3)_2$ (−34.3), suggest that the silolyl ligand in **3** is planar, as shown in eq 1. However, we cannot at this time completely rule out a structure involving the η^1-silolyl ligand.



2 **3**

(1)

In conclusion, we have obtained the first examples of d^0 transition metal complexes containing η^5-germolyl and η^5-silolyl ligands. Compound **2** represents the first isolated example of a transition metal η^5-silolyl complex. Thus, d^0 metal centers promote the planarization of germolyl and silolyl anions upon coordination (as does d^6 ruthenium), and apparently π-back-bonding from filled metal d orbitals into empty $\pi^* =$ levels of the ligand does not play a major role in this process. Our future efforts will concentrate on the exploration of germolyls and silolyls as new ancillary ligands in early transition metal chemistry. Along these lines, we are attempting to develop more convenient synthetic routes to complexes of this type.

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Supporting Information Available: Characterization data for compounds **1**−**3**, tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **1** and **2** (16 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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