J. Am. Chem. Soc. **2000,** *122,* 3097−3105

Synthesis and Reactivity of η^5-Silolyl, η^5-Germolyl, and η^5-Germole Dianion Complexes of Zirconium and Hafnium

Jeffrey M. Dysard and T. Don Tilley*

Contribution from the Department of Chemistry, University of California at Berkeley, Berkeley, California 94720-1460

Received October 4, 1999

Abstract: Reaction of 2 equiv of Li[$C_4Me_4GeSiMe_3$] with Cp*$HfMe_2Cl$ produced the first transition metal complex of a germole dianion, [Cp*(η^5-C_4Me_4Ge)$HfMe_2$Li(THF)]$_2$ (**1**), via the apparent elimination of Me_3SiCl, along with $C_4Me_4Ge(SiMe_3)_2$ as the final Me_3Si-containing product. Compound **1** adopts a dimeric structure in which one Li atom is sandwiched in an η^5-fashion between two germole rings, while the other Li atom is coordinated by both germanium atoms. Reaction of **1** with an excess of Me_3SiCl resulted in loss of the germole ligand as $C_4Me_4Ge(SiMe_3)_2$, while 2 equiv of $Me_3SiOSO_2CF_3$ reacted with **1** to give the new germolyl complex Cp*[η^5-$C_4Me_4GeSiMe_3$]$HfMe_2$ (**2**). Yet a different process results from treatment of **1** with $CH_3CH_2OSO_2CF_3$, involving migration of a methyl group from hafnium to germanium to produce Cp*(η^4-$C_4Me_4GeMeEt$)HfMe (**3**). Reaction of **2** with H_2 gave CH_4 and Me_3SiH as the result of σ-bond metathesis involving the germole-bound trimethylsilyl group and (presumably) an intermediate hafnium hydride species. Similarly, the reaction of **2** with $PhSiH_3$ gave $PhMeSiH_2$ and Me_3SiH. Compound **2** also reacted with MeI to produce $C_4Me_4Ge(Me)SiMe_3$, while the reaction with (Et_2O)$LiCH_2Ph$ gave **1** and Me_3SiCH_2Ph. Compound **2** did not react cleanly with various small molecules (CO, CN(2,6-$Me_2C_6H_3$), trimethylsilylacetylene, and benzophenone), nor with the methide abstraction reagents $B(C_6F_5)_3$ and [Ph_3C][$B(C_6F_5)_4$]. In addition, reaction of **2** with these abstraction reagents in the presence of 1-hexene or cyclohexene did not result in the formation of a polymer. The germole $C_4Me_4Ge(H)CMe_3$ was prepared via reaction of $C_4Me_4GeCl_2$ with 1.5 equiv of Me_3CLi, followed by treatment with $LiAlH_4$. This germole was cleanly deprotonated by ^{n}BuLi in THF to give the new germole anion Li[$C_4Me_4GeCMe_3$] as a THF solvate. This anion reacted with Cp*$HfMe_2Cl$ to give the product of methyl migration from hafnium to germanium, Cp*[η^4-$C_4Me_4Ge(Me)CMe_3$]HfMe (**4**). Analogously, Li[C_4Me_4GePh] reacted with Cp*$HfMe_2Cl$ to give Cp*[η^4-$C_4Me_4Ge(Me)Ph$]HfMe (**5**). Treatment of $MgBr_2(Et_2O)$ with 2 equiv of K[$C_4Me_4SiSiMe_3$] in THF resulted in formation of Mg[η^1-$C_4Me_4SiSiMe_3$]$_2$(THF) (**6**). Reaction of **6** with Cp*$ZrCl_3$ gave quantitative formation of Cp*[η^5-$C_4Me_4SiSiMe_3$]$ZrCl_2$ (**7**), while the reaction of **6** with Cp*$HfCl_3$ provided the previously reported complex Cp*[η^5-$C_4Me_4SiSiMe_3$]$HfCl_2$ (**8**) in quantitative yield.

Recent interest in cyclic π-systems containing silicon and germanium has led to an enhanced understanding of the electronic properties of these species.[1,2] For example, we have characterized free silolyl and germolyl anions of the type [$C_4Me_4E{-}R$]$^-$ (E = Si or Ge) as possessing pyramidal E centers and bond-localized structures.[2] Interestingly, however, coordination of these π-systems to electron-rich or electron-poor d^0 transition metal fragments promotes delocalization of electron density in the five-membered heterole ring and planarization of the E center.[3] Thus, silolyl and germolyl anions represent interesting new ligands in transition metal chemistry which are expected to possess novel electronic properties. In fact, electrochemical studies on Cp*Ru[η^5-$C_4Me_4GeSi(SiMe_3)_3$] (Cp* = η^5-C_5Me_5) suggest that the germolyl ligand might be significantly more electron donating than Cp*.[3a] Furthermore, it has been shown that free silole and germole dianions [C_4R_4E]$^{2-}$ possess a high degree of aromatic character.[4] Such species

---

(1) (a) Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 295. (b) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Halland, A.; Bagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (c) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (d) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039. (e) Blakeman, P.; Gehrhus, B.; Green, J. C.; Heinicke, J.; Lappert, M. F.; Kindermann, M.; Veszprémi, T. *J. Chem. Soc., Dalton Trans.* **1996**, 1275. (f) Heinemann, C.; Herrmann, W. A.; Thiel, W. *J. Organomet. Chem.* **1994**, *475*, 73. (g) Barton, T. J.; Banasiak, D. *J. Am. Chem. Soc.* **1977**, *99*, 5199. (h) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246. (i) Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51. (j) Märkl, G.; Schlosser, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 963. (k) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 52. (l) Nakadaira, Y.; Sato, R.; Sakurai, H. *Organometallics* **1991**, *10*, 435. (m) Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1982**, *104*, 6884. (n) Jutzi, P.; Meyer, M.; Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 4841. (o) Boudjouk, P.; Castellino, S.; Hong, J.-H. *Organometallics* **1994**, *13*, 3387. (p) Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig Y.; Müller, T.; West, R. *J. Am. Chem. Soc.* **1995**, *117*, 11608. (q) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1997,** *16*, 1543. (r) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951.

(2) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457.

(3) (a) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L.; Ostrander, R. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1744. (b) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8428. (c) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120,* 8245.

(4) (a) Joo, W. C.; Hong, J. H.; Choi, S. B.; Son, H. E.; Kim, C. H. *J. Organomet. Chem.* **1990**, *391*, 27. (b) Hong, J. H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387. (c) Hong, J. H.; Boudjouk P. *Bull. Soc. Chim. Fr.* **1995**, *132*, 495. (d) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *449*, C7. (e) West, R.; Sohn, H.; Powell, D. R.; Müller, T.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1002. (f) Freeman, W. P.; Tilley, T. D.; Yap, G. A. P.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882. (g) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755. (h) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608.

10.1021/ja993563n CCC: $19.00

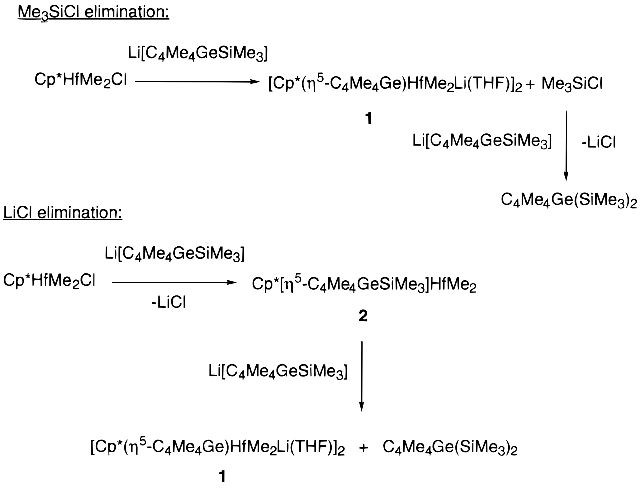
represent an additional class of novel, 6-electron π-systems that could function as ligands for transition metals. These considerations have compelled us to investigate silolyl and germolyl anions, and the corresponding silole and germole dianions, as ancillary ligands in early transition metal chemistry.

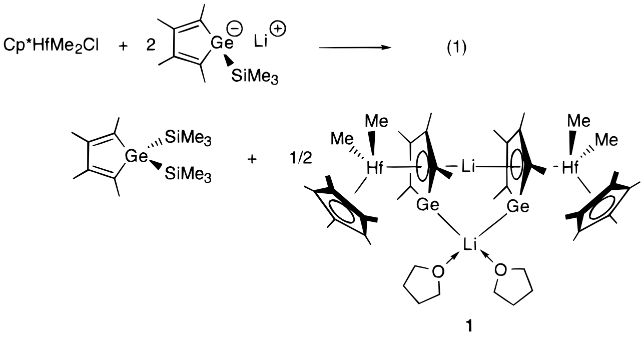
Group 4, d^0 transition metal complexes have attracted much attention in recent years, particularly as alkene polymerization catalysts, dehydropolymerization catalysts, and reagents for organic synthesis.[5] Because of this, considerable effort has been devoted to controlling the chemical properties of the metallocenes by manipulation of the electronic and steric properties of the cyclopentadienyl ligands. Part of this effort has focused on metallocenes featuring main group-containing heterocycles as ancillary ligands.[6] Given the novel electronic properties for π-systems containing silicon and germanium, we became interested in examining d^0 metallocene complexes that incorporate silolyl and germolyl ligands. A related issue concerns the degree to which d^0 metal centers might induce delocalization of charge in such rings and stabilize η^5-bonding, in the absence of $d_\pi-\pi^*$ back-bonding. Here we report investigations into the synthesis, characterization, and reactivity of germolyl and silolyl complexes of d^0 group 4 metals, including the remarkable formation and isolation of a complex containing the germole dianion $[C_4Me_4Ge]^{2-}$.

Results and Discussion

Synthesis and Reactivity of a Germole Dianion Complex. We have previously described a method for preparing the d^0 hafnium germolyl complex Cp*$[\eta^5$-$C_4Me_4GeSiMe_3]HfCl_2$, involving reaction of the salt $Li[C_4Me_4GeSiMe_3]$ with Cp*$HfCl_3$ at low temperatures.[3c] Unfortunately, this reaction produced the desired η^5-germolyl complex in low and variable yields. We postulated that complications with this reaction may arise from the presence of more than one reactive site on the hafnium metal center, which could allow the germolyl nucleophile to react with more than one chloride of Cp*$HfCl_3$. However, the monochloride Cp*$HfMe_2Cl$[7] does not give the anticipated metallocene derivative Cp*$[\eta^5$-$C_4Me_4GeSiMe_3]HfMe_2$ (**2**) upon reaction with $Li[C_4Me_4GeSiMe_3]$. Rather than proceed via LiCl elimination to give **2**, the reaction of $Li[C_4Me_4GeSiMe_3]$ and Cp*$HfMe_2Cl$ in a 2:1 molar ratio gave the germole dianion complex **1** in 86% isolated yield (eq 1). In tetrahydrofuran-d_8, this reaction produced **1** and $C_4Me_4Ge(SiMe_3)_2$ as the only identifiable products. We believe that the reaction of eq 1 proceeds via loss of Me_3SiCl (Scheme 1), which is not observed as a product because of its rapid reaction with the germolyl anion (and/or **1**, see below) to afford $C_4Me_4Ge(SiMe_3)_2$.

Scheme 1





On the basis of thermodynamic considerations, the elimination of Me_3SiCl, rather than LiCl, in the reaction of eq 1 initially seemed unlikely. We therefore considered an alternative mechanism involving the initial formation of **2**, which would be converted to **1** via nucleophilic cleavage of the Ge$-$Si bond with another equivalent of $Li[C_4Me_4GeSiMe_3]$ (Scheme 1). Indeed, the reaction of **2** (the synthesis of which is described below) with $Li[C_4Me_4GeSiMe_3]$ in tetrahydrofuran-d_8 quantitatively forms **1** and $C_4Me_4Ge(SiMe_3)_2$ (in a 1:1 molar ratio, by ^1H NMR spectroscopy). However, the reaction of Cp*$HfMe_2Cl$ with $Li[C_4Me_4GeSiMe_3]$ in a 1:1 ratio (in tetrahydrofuran-d_8, with the germolyl anion as limiting reagent) did not produce **2**, and the only products that could be identified were **1** and $C_4Me_4Ge(SiMe_3)_2$ (in 39 and 41% yields, respectively, by ^1H NMR spectroscopy). Note that according to the mechanism proceeding via LiCl elimination and intermediate **2** (Scheme 1), the 1:1 reaction of Cp*$HfMe_2Cl$ with $Li[C_4Me_4GeSiMe_3]$ should produce an equimolar mixture of **1**, $C_4Me_4Ge(SiMe_3)_2$, and unreacted Cp*$HfMe_2Cl$ (which was not observed in the

---

(5) (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (c) Kaminsky, W. *Catal. Today* **1994**, *20*, 257. (d) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13. (e) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262. (f) Ivin, K. J. *Olefin Metathesis Polymerization*; Academic Press: San Diego, 1997. (g) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (h) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (i) Schrock R. R. *Tetrahedron* **1999**, *55*, 8141. (j) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036. (k) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979. (l) Lee, N. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5985. (m) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (n) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347. (o) Molander, G. A.; Dowdy, E. D.; Noll, B. C. *Organometallics* **1998**, *17*, 3754. (p) Carter, M. B.; Schiott, B.; Gutierrez, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11667. (q) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363. (r) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (s) Corey, J. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, p 327.

(6) (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993. (c) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4459. (d) Bazan, G. C.; Donnelly, S. J.; Rodriguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671. (e) Kowal, C. M.; Bazan, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 10317. (f) Herberich, G. E.; Holger, O. *Adv. Organomet. Chem.* **1986**, *25*, 199. (g) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmand, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (h) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492. (i) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (j) Barnhart, R. W.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 1082. (k) Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 6037. (l) Ashe, A. J.; Fang, X. G.; Kampf, J. W. *Organometallics* **1999**, *18*, 2288. (m) Ashe, A. J.; Fang, X. G.; Kampf, J. W. *Organometallics* **1999**, *18*, 1363.

(7) Roddick, D. M. Ph.D. Thesis, California Institute of Technology, 1984

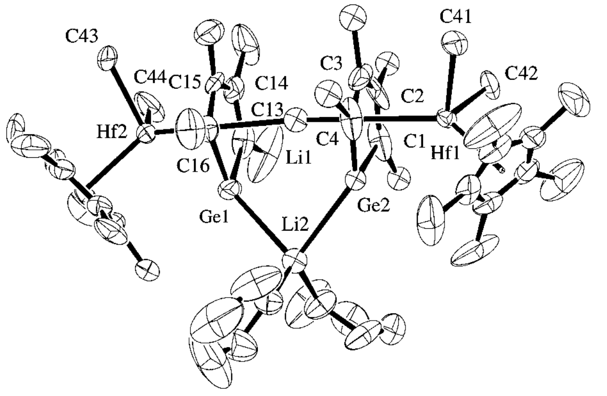


Figure 1. ORTEP diagram of $[Cp^*(\eta^5\text{-}C_4Me_4Ge)HfMe_2Li(THF)]_2$ (**1**).

product mixture). However, since **1** and Cp^*HfMe_2Cl react quantitatively (to give a mixture of uncharacterized products, by ^1H NMR spectroscopy), the 1:1 reaction of Cp^*HfMe_2Cl and $Li[C_4Me_4GeSiMe_3]$ would not have produced **1** via the LiCl-elimination process of Scheme 1.

Based on the experiments described above, we favor the mechanism involving Me_3SiCl elimination. Trimethylsilyl chloride is not observed as a product in this process, since it reacts rapidly with either the germolyl anion or the product **1**. The latter possibility was demonstrated by the observed reaction of **1** with Me_3SiCl (excess) in tetrahydrofuran-d_8 solution, which gave only $C_4Me_4Ge(SiMe_3)_2$ and unidentified Cp*Hf-containing species.

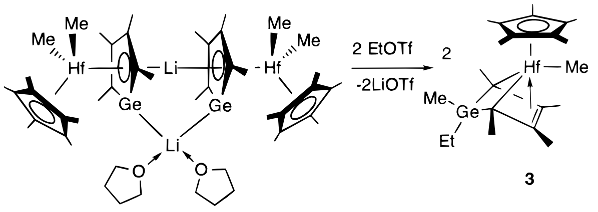
Highly air- and moisture-sensitive **1** was purified by washing with pentane, in which it is completely insoluble, and then crystallization from a toluene/THF mixture. X-ray quality crystals of **1** as a THF solvate were isolated after slow cooling of a toluene solution to −35 °C for several days. The germole ring containing Ge(2) is conformationally disordered about the Hf(1)−Li(1) axis, and Hf(2) was also disordered (see Experimental Section for details). The molecular structure of **1** (Figure 1) may be described as a dimer of $Li[Cp^*(\eta^5\text{-}C_4Me_4Ge)HfMe_2]$ in which the germole dianion rings are bridged by two lithium atoms. One lithium atom is "sandwiched" in an η^5-fashion between the two germole rings, while the other lithium atom is coordinated in an η^1 mode by both germanium atoms. This coordination geometry for the germole dianions of **1** is reminiscent of that seen in Boudjouk's germole dianion $[Li(THF)(TMEDA)][2,3,4,5\text{-}Et_4\text{-}Ge,Ge\text{-}\{Li(2,3,4,5\text{-}Et_4C_4Ge)_2\}C_4Ge]$, in which one lithium atom is sandwiched between two germole rings while the (THF)(TMEDA)Li group is bound in an η^1-fashion by one Ge atom.[8]

The C−C bond lengths within the nondisordered germole ring are equal within experimental error (1.42(2), 1.40(2), and 1.43(2) Å), and the Ge−C bond lengths are also equivalent (1.96(1) Å) and similar to those in the free germolyl dianion $[K_4(18\text{-crown-}6)_3][C_4Me_4Ge]_2(THF)$ (1.846(9) and 1.959(8) Å).[2] The Hf(2) atom lies 2.27 Å from the centroid of the planar germole ring and 2.25 Å from the Cp* centroid, and the centroid−hafnium−centroid angle is 136.4°. These values are comparable to the corresponding ones in $Cp^*(C_4Me_4GeSiMe_3)HfCl_2$ (2.33 Å, 2.22 Å, 136.1°).[3c] The $C_4Ge_{centroid}$−Li(1) distance of 1.98 Å is somewhat longer than the corresponding distance in $[Li(THF)(TMEDA)][2,3,4,5\text{-}Et_4\text{-}Ge,Ge\text{-}\{Li(2,3,4,5\text{-}Et_4C_4Ge)_2\}C_4Ge]$ (1.918 Å),[8] but is fully consistent with the Li−C_5 centroid distance of 2.008 Å in the lithocene anion $[Cp_2Li]^-$.[9]

At room temperature, the ^7Li NMR spectrum of **1** contains a single broad resonance, which splits into two resonances at 1.70 and −4.60 ppm upon cooling to −40 °C. These values are comparable to corresponding shifts for the σ- and π-bound lithium atoms in $[Li(THF)(TMEDA)][2,3,4,5\text{-}Et_4\text{-}Ge,Ge\text{-}\{Li(2,3,4,5\text{-}Et_4C_4Ge)_2\}C_4Ge]$ (−0.93 and −4.98 ppm, respectively), which are decoalesced at −50 °C.[8] Thus, the dimeric structure of **1** appears to be preserved at low temperature, but in solution at room temperature the Li ions undergo exchange on the NMR time scale.

Initial reactivity studies with **1** focused on its possible conversion to the neutral species $Cp^*[\eta^5\text{-}C_4Me_4Ge]HfMe$ upon abstraction of a Me group. Unfortunately, reaction of **1** with $B(C_6F_5)_3$ produced only complex mixtures in both benzene-d_6 and tetrahydrofuran-d_8, and use of the methide abstraction reagent $[Ph_3C][B(C_6F_5)_4]$ also yielded numerous unidentified products. These attempted abstraction reactions were not cleaner in the presence of the Li-atom sequestering reagents TMEDA and 12-crown-4. Finally, **1** did not react with $PhSiH_3$ or H_2 in benzene solution at room temperature over 1 week.

Reaction of a tetrahydrofuran solution of **1** with 2 equiv of MeI immediately produced a deep red solution, which gave a deep red powder after removal of solvent. Inspection of the ^1H NMR spectrum (benzene-d_6) of this solid revealed the quantitative formation of $Li[C_4Me_4GeMe]^2$ along with unidentified Cp*Hf-containing materials. In contrast, **1** reacted cleanly with ethyl triflate in benzene to produce the η^4-germole complex **3**, the product of methyl group migration from hafnium to germanium (eq 2). Complex **3** is formed in 90% yield by ^1H NMR spectroscopy, but its isolation was prohibited by its oily nature and high solubility in all solvents employed (toluene, pentane, ether, and hexamethyldisiloxane). The characterization of **3** follows from the interpretation of its ^1H and ^{13}C NMR spectra, which was aided by comparisons to reported spectra for analogous hafnium diene complexes of the type Cp′HfMe(diene) [Cp′ = Cp or substituted Cp].[10] Compounds of the latter type display solubility properties similar to those of **3**. The single methyl group bound to hafnium exhibits a resonance at δ −0.83, whereas the migrated methyl group exhibits a resonance consistent with a Ge−Me group, at δ 0.26.[2] In addition, the two ring carbons of the germole unit resonate at δ 130.0 and 97.16, which corresponds to a separation consistent with η^4-coordination of the germole ring to hafnium in a σ^2,π-metallacyclopentene fashion.[10] Finally, resonances for the two methyl groups (δ 49.27 for HfMe and δ 1.40 for GeMe) are consistent with analogous chemical shifts for $Cp^*[\eta^4\text{-}C_4Me_4Ge(Me)CMe_3]HfMe$ (vide infra).



1 3 (2)

Synthesis and Reactivity of Neutral Hafnium η^5-Germolyl Complex 2.

Recently, much attention has been devoted to the

---

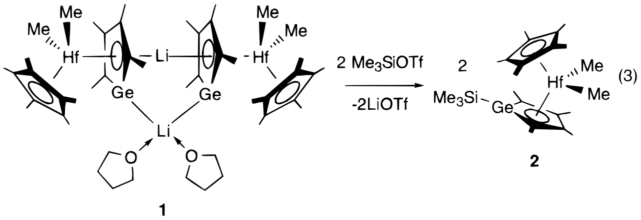
(8) Hong, J. H.; Pan, Y.; Boudjouk, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 186.

(9) (a) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744.

(10) (a) Blenkers, J.; Hessen, B.; van Bolhuis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459. (b) Pindada, G. J.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115. (c) Note that complexes of the type Cp*(diene)MR (M = Zr, Hf) polymerize ethylene without the assistance of a co-activator: Hessen, B.; van der Heijden, H. *J. Am. Chem. Soc.* **1996**, *118*, 11670.

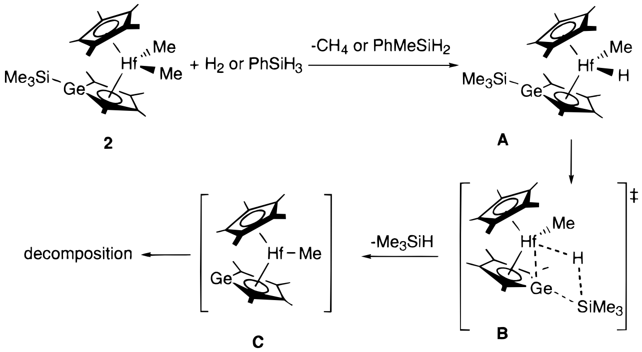
use of cationic group 4 bent metallocene complexes for the polymerization of olefins.[5a−d,11] These complexes are formed upon abstraction of a methyl anion from the group 4 metal center, usually by a Lewis acid (e.g., $B(C_6F_5)_3$). Therefore, we targeted dialkyl complexes of the type Cp*[η^5-C_4Me_4GeR]-$HfMe_2$ to study the effects of incorporation of an η^5-germolyl ligand on this chemistry. Unfortunately, alkylation of Cp*[η^5-$C_4Me_4GeSiMe_3$]$HfCl_2$ is not a viable route to these complexes due to the low and variable yields of this compound. In addition, the direct reaction of Cp*$HfMe_2Cl$ with Li[$C_4Me_4GeSiMe_3$] did not lead to a neutral species, but instead gave the dianion complex **1** as described above. Furthermore, the reaction of **1** with an alkyl triflate did not lead to a neutral η^5-ligand but rather to an η^4-germole complex (eq 2).

Reaction of **1** with 2 equiv of Me_3SiOTf in benzene produced the desired neutral η^5-germolyl complex **2** as yellow crystals in 87% isolated yield (eq 3). Assignment of the structure of **2** as an η^5-germolyl complex is based on NMR spectroscopic data. The hafnium methyl protons in **2** resonate at δ −0.58, a shift typical for hafnium methyl protons in a bent metallocene complex,[12] and the ^{13}C NMR shifts for the germole ring carbon atoms (δ 139.4 and 129.4) are similar to those found for Cp*-[η^5-$C_4Me_4GeSiMe_3$]$HfCl_2$ (δ 146.0 and 135.8).[3c]

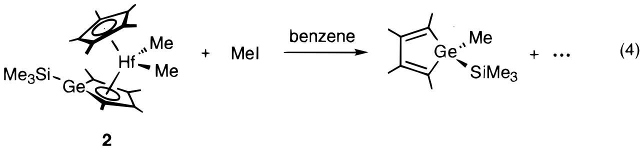


The hafnium−methyl bonds in **2** are active toward σ-bond metathesis. Exposure of **2** to an excess of H_2 at 25 °C in benzene-d_6 resulted in formation of CH_4 (1.0 equiv) and Me_3SiH (0.4 equiv) after several hours as the only characterizable products by ^1H NMR spectroscopy. Likewise, the reaction of **2** with $PhSiH_3$ at room temperature in benzene-d_6 proceeded over 24 h to $PhMeSiH_2$ (1.0 equiv) and Me_3SiH (0.63 equiv), along with unidentified organometallic species. It is interesting to note that the complex CpCp*$HfMe_2$ does not react with $PhSiH_3$ at room temperature over several weeks, or after 12 h at 90 °C.[13] Also for comparison, Cp_2ZrMe_2 requires greater than 86 h at room temperature to completely react with hydrogen at 1 atm,[14a] and $Cp^*_2ZrMe_2$ reacts with H_2 (1 atm) to give the corresponding dihydride only after heating to 70 °C for 1 week.[14b] These comparisons imply that the germolyl ring imparts significant enhancement of reactivity to the hafnium−methyl bonds, despite the greater steric demands for this ligand as compared to those for unsubstituted Cp. Presumably, the first step in both reactions is formation of a hafnium hydride (**A**) via σ-bond metathesis with H_2 or $PhSiH_3$ (Scheme 2). The Me_3SiH formed in both reactions appears to result from abstraction of the hydride ligand by the germole-bound $-SiMe_3$ group. This is also suggested by the reaction of **2** with D_2, which resulted only in formation of Me_3SiD (by ^1H NMR spectroscopy; no evidence for the formation of Me_3SiH). The germole dianion complex thus formed is apparently not stable and decomposes to unidentified products. This transformation is analogous to that seen in the reaction of (2,6-$^iPr_2C_6H_3N$)$_2$Mo[Si(SiMe$_3$)$_3$](CH$_2$CMe$_3$) with H_2, which also transiently forms a silyl hydride complex that decomposes via the elimination of Me_3SiH.[15] Unfortunately, attempts to trap the neutral germole dianion complex (**C**) with various reagents (PPh_3, PMe_3, 2,2′-bipyridine, diphenylacetylene) were unsuccessful.

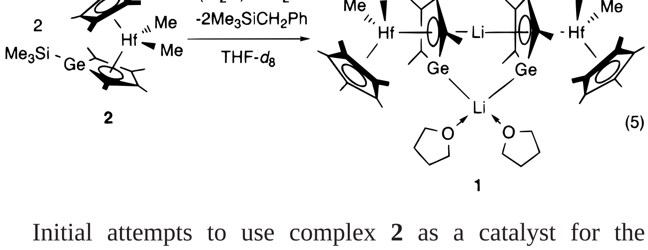
Scheme 2



Initial reactivity studies therefore suggest that the germolyl ligand in **2** is quite reactive. This is perhaps also reflected in the observed thermal decomposition of **2** in toluene solution at 100 °C, which occurred over several hours to give an array of unidentified products. It is worth noting that **2** did not decompose via a σ-bond metathesis pathway analogous to that in Scheme 2, as Me_4Si is not a decomposition product. For comparison, the dichloride Cp*[η^5-$C_4Me_4GeSiMe_3$]$HfCl_2$ is stable in toluene solution at 100 °C for several weeks.[3c] Reactions involving the germolyl ligand may also account for the complex mixtures observed when **2** was exposed to various small molecules (CO, CN(2,6-$Me_2C_6H_3$), trimethylsilylacetylene, and benzophenone). In addition, reaction of **2** with MeI in tetrahydrofuran-d_8 resulted in quantitative loss of the germolyl ligand as $C_4Me_4Ge(Me)SiMe_3$ (characterized by comparison of its NMR spectra with those for an independently synthesized sample), with generation of unidentified hafnium-containing species (eq 4). Compound **2** did not react at room temperature in benzene-d_6 with an excess of either Me_3SiCl or Me_3SiOTf.



The reaction of **2** with $(Et_2O)LiCH_2Ph$ in tetrahydrofuran-d_8 rapidly produced Me_3SiCH_2Ph and **1** quantitatively (eq 5). This result seems to reflect favorable bonding between hafnium and the aromatic germole dianion, as Li[$C_4Me_4GeSiMe_3$] did not react with $(Et_2O)LiCH_2Ph$ in THF solution under the same conditions.



Initial attempts to use complex **2** as a catalyst for the polymerization of olefins focused on generation of a cationic

---

(11) (a) Jia, L.; Yang, X. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 225. (c) Mohring, R. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (d) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57.

(12) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood Limited: West Sussex, England, 1986; p 126.

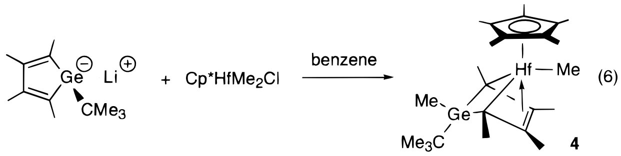
(13) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732.

species of the type [Cp*(η^5-$C_4Me_4GeSiMe_3$)HfMe][BR_4] by abstraction of a methyl group. Reaction of **2** with the neutral borane $B(C_6F_5)_3$ or [Ph_3C][$B(C_6F_5)_4$] did not result in the clean generation of a characterizable cationic complex (by ^{1}H NMR spectroscopy). Furthermore, reaction of **2** with either of these abstraction reagents in the presence of 1-hexene or cyclohexene did not result in the formation of a polymer. These results, coupled with the observed reactivity of the Ge−$SiMe_3$ bond in **2**, prompted us to focus attention on the synthesis of η^5-germolyl complexes containing a more robust germanium−alkyl linkage, which were expected to produce more stable metallocene derivatives exhibiting cleaner reaction chemistry.

Reactions of Germolyl Anions with Cp*$HfMe_2Cl$. In an effort to simplify the ligand-substitution chemistry for introduction of a germolyl ligand, we focused on the hafnium starting material Cp*$HfMe_2Cl$, which possesses only one chloride leaving group. For this strategy, we also preferred germolyl anion reagents possessing an alkyl substituent at germanium, in the hope of avoiding elimination processes of the type described in Scheme 2. Initial attempts focused on generation of Li[$C_4Me_4GeCMe_3$], via deprotonation of $C_4Me_4Ge(H)CMe_3$. This approach required synthesis of the latter germole compound, which was unknown.

Reaction of $C_4Me_4GeCl_2$ with Me_3CLi in Et_2O at −78 °C, followed by warming to room temperature and addition of $LiAlH_4$ at 0 °C, produced a 2:1 mixture containing $C_4Me_4Ge(H)CMe_3$ and $C_4Me_4Ge(CMe_3)_2$ (by ^{1}H NMR spectroscopy). Unfortunately, the desired monoalkylated species could not be separated from this mixture by distillation. In addition, the germole dichloride did not react with Me_3CMgCl in refluxing diethyl ether, and addition of tetrahydrofuran to the reaction mixture, followed by further heating to 65 °C, produced only an unidentified mixture of products. However, reaction of $C_4Me_4GeCl_2$ with 1.5 equiv of Me_3CLi in benzene at room temperature resulted in clean monoalkylation of the starting germole, which, upon treatment with $LiAlH_4$ in Et_2O at 0 °C, gave the desired product $C_4Me_4Ge(H)CMe_3$ as a clear, colorless liquid in 70% yield after distillation. Interestingly, the 1.5 molar excess of the alkyllithium species is required to drive this reaction to completion, and inspection of the reaction mixture by ^{1}H NMR spectroscopy (benzene-d_6) revealed clean formation of $C_4Me_4Ge(Cl)CMe_3$ along with isobutane (0.25 equiv) and isobutylene (0.25 equiv), suggesting that this reaction proceeds at least in part via a radical pathway. The germole $C_4Me_4Ge(H)CMe_3$ was cleanly deprotonated in tetrahydrofuran to give solutions of Li[$C_4Me_4GeCMe_3$], from which Li(THF)[$C_4Me_4GeCMe_3$] was isolated as a yellow solid in 72% yield.

Reaction of Li(THF)[$C_4Me_4GeCMe_3$] with 1 equiv of Cp*$HfMe_2Cl$ in benzene did not produce the desired η^5-germolyl species, but rather the migrated species Cp*[η^4-$C_4Me_4Ge(Me)CMe_3$]HfMe (**4**) in 40% isolated yield. This reaction (eq 6) is quantitative by ^{1}H NMR spectroscopy, and the low isolated yield of **4** is due to its high solubility in all solvents employed (pentane, hexamethyldisiloxane, ether, and toluene).



The ^{1}H NMR spectrum of deep red **4** contains separate resonances for the Hf-Me (δ −0.72) and Ge-Me protons (δ 0.30), suggesting its formulation as the η^4-germole complex. The ^{13}C NMR spectrum contains two separate resonances for the Ge-Me and Hf-Me groups, at -1.69 and 49.8 ppm, respectively. In addition, two distinct resonances for the germole ring carbons (at δ 96.0 and 131.1) are characteristic for early transition metal complexes in which a diene is bound in a σ^2,π-metallocyclopentene fashion to the metal center.[10] In contrast, the analogous separation of resonances in the η^5-germolyl complex Cp*[η^5-$C_4Me_4GeSiMe_3$]$HfMe_2$ (δ 129.4 and 139.4) is only 10 ppm. X-ray quality crystals of **4** were grown by slow cooling of a concentrated pentane solution to −35 °C over several days, and the molecular structure is shown in Figure 2. Due to a poor data set, only the two heavy atoms were refined anisotropically. Thus, a detailed analysis of bond lengths and angles is not possible.

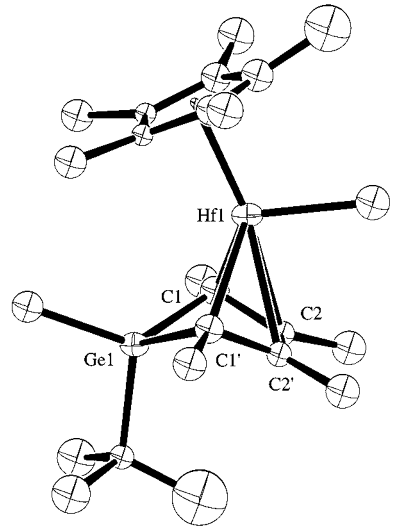


Figure 2. ORTEP diagram of Cp*[η^4-$C_4Me_4Ge(Me)CMe_3$]HfMe (**4**).

A reaction analogous to that in eq 6, of Cp*$HfMe_2Cl$ with Li[C_4Me_4GePh], also resulted in migration of a methyl group from hafnium to germanium to give Cp*[η^4-$C_4Me_4Ge(Me)Ph$]HfMe (**5**). Although complex **5** formed in high yield (90% based on ^{1}H NMR spectroscopy) it could not be isolated in pure form. The characterization of **5** as an η^4-germole complex is therefore based on its ^{1}H NMR spectrum, which contains a characteristic Hf-Me resonance at δ −0.71 and a peak for the Ge-Me group at δ 0.54. In addition, the ^{13}C NMR spectrum of **5** exhibits resonances at δ 131.4 and 95.18 for the germole ring carbons, and at δ 50.25 (HfMe) and 2.87 (GeMe) for the methyl groups.

Convenient Syntheses of η^5-Silolyl Complexes of d^0 Hafnium and Zirconium. We have recently reported the first synthesis and structural characterization of a transition metal silolyl complex, Cp*[η^5-$C_4Me_4SiSiMe_3$]$HfCl_2$, obtained from the reaction of Li[$C_4Me_4SiSiMe_3$] with Cp*$HfCl_3$.[3c] However, because the yield of this reaction is rather low, we have sought a more reliable and general route to complexes of this type.

Recent results suggest that magnesium silyl derivatives may be useful in preparing early transition metal silyl derivatives, especially in circumstances where the corresponding lithium reagents fail.[16] To employ this strategy in the preparation of silolyl complexes, we prepared the magnesium bis(silolyl) compound Mg[η^1-$C_4Me_4SiSiMe_3$]$_2$(THF) (**6**) via reaction of 2 equiv of K[$C_4Me_4SiSiMe_3$] with $MgBr_2(Et_2O)$ in THF at −80 °C. Compound **6** was isolated in 70% yield as a crystalline white

---

(14) (a) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

(15) Casty, G. L.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4746.

(16) Marschner, C.; Tilley, T. D. Unpublished results.

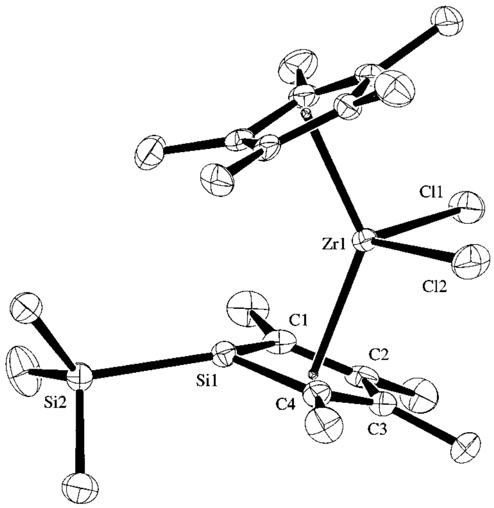
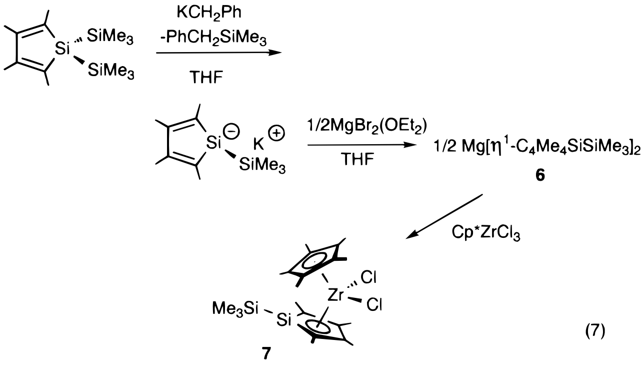


Figure 3. ORTEP diagram of Cp*[η^5-$C_4Me_4SiSiMe_3$]$ZrCl_2$ (**7**).

powder. The characterization of this compound as an η^1-silolyl derivative is based on the ^{29}Si NMR shift (δ −40.9), which is consistent with a pyramidal silicon center σ-bound to an electropositive metal.[2]

Reaction of **6** with 0.5 equiv of Cp*$ZrCl_3$ in benzene produced Cp*[η^5-$C_4Me_4SiSiMe_3$]$ZrCl_2$ (**7**) in quantitative yield (by ^{1}H NMR spectroscopy). A more convenient synthesis of **7** is illustrated in eq 7, which describes the generation of K[$C_4Me_4SiSiMe_3$] in tetrahydrofuran solution, followed by its in situ reaction with $MgBr_2(Et_2O)$ to give **6**, which was then treated with Cp*$ZrCl_3$ to provide the η^5-silolyl complex **7** in an overall yield of 65%. The ^{29}Si NMR shift of the ring silicon in this complex is δ 48.9, which is comparable to that in the previously reported hafnium analogue (δ 49.7).[3c] The molecular structure of **7** (Figure 3) is analogous to that for previously reported Cp*[η^5-$C_4Me_4SiSiMe_3$]$HfCl_2$ (**8**).[3c] The zirconium atom in **7** lies 2.30 Å from the C_4Si centroid and 2.24 Å from the Cp* centroid, and the centroid−zirconium−centroid angle is 136.6°. As in the case of the hafnium analogue, the ring silicon atom adopts a nearly planar geometry as evidenced by the summation of bond angles about Si (353.9°). Furthermore, this silicon atom deviates by only 0.002(1) Å from the C_4Si least-squares plane. The Si−C bond distances in the ring (1.816(4) and 1.794(4) Å) are short relative to those for the sp^3 silicon−carbon bonds in the free anion [K(18-crown-6)][$C_4Me_4SiSiMe_3$] (1.890(4) and 1.880(3) Å) and are comparable to the corresponding values for Cp*[η^5-$C_4Me_4SiSiMe_3$]$HfCl_2$ (1.798(7) and 1.780(1) Å).[3c] However, the C−C bond lengths in the silolyl ring of **7** are roughly equivalent (1.418(6), 1.419(5), and 1.400(6) Å), in contrast to the situation for the hafnium analogue in which these distances vary according to a pattern (1.42(1), 1.37(2), and 1.46 Å) suggesting σ^2,π-coordination of the C_4 fragment to hafnium.



(7)

The magnesium reagent **6** also reacted with 0.5 equiv of Cp*$HfCl_3$ in benzene to give the previously reported complex **8** in 68% overall yield, in a one-pot synthesis starting from $C_4Me_4Si(SiMe_3)_2$. However, the corresponding reaction of **6** with 0.5 equiv of Cp*$HfMe_2Cl$ did not produce the desired η^5-silolyl complex, but instead gave an array of products which could not be identified. In addition, reactions of **8** with MeMgBr or MeLi did not produce the desired dimethyl species, and attempts to alkylate **7** and **8** (with various reagents including MeMgBr, MeLi, $PhCH_2Li(Et_2O)$, Me_3CCH_2MgCl, $(Me_3CCH_2)_2Mg$, Me_3Al, and Me_2Zn) produced highly colored solutions (purple or green) and no isolable metal-containing products.

Conclusions

Here we have described synthetic routes to neutral η^5-silolyl and η^5-germolyl complexes of zirconium and hafnium, and to an anionic hafnium complex of the germole dianion $C_4Me_4Ge^{2-}$. In particular, the magnesium compound Mg[η^1-$C_4Me_4SiSiMe_3$]$_2$(THF) (**6**) has proven to be a useful silolyl-transfer reagent for the synthesis of η^5-silolyl complexes of hafnium and zirconium. The germole dianion complex, [Cp*(η^5-C_4Me_4Ge)$HfMe_2Li$(THF)]$_2$ (**1**), has been observed to form in various reactions, for which the driving force would seem to be formation of the delocalized germole dianion ligand. Compound **1** is reactive, and loses the germole ligand upon reaction with trimethylsilyl chloride. Attempts to alkylate at the germanium center result in hafnium-to-germanium migration of the methyl group. However, **1** provides an excellent route to the neutral η^5-germolyl complex Cp*[η^5-$C_4Me_4GeSiMe_3$]$HfMe_2$ (**2**), via a silylation reaction that converts the germole dianion ring to a germolyl ligand.

Reactivity studies with d^0 complexes of silolyl and germolyl groups have so far characterized these ligands as being non-innocent, in that they are readily lost under fairly mild reaction conditions. In some cases, germolyl complexes have been seen to participate in metal-to-germanium migration reactions which produce η^4-germole complexes (eqs 2 and 6). This process appears to be promoted by alkyl substituents at the germanium of the germolyl ligand, as the analogous silyl derivatives do not undergo such reactions. The fact that silyl substitution at the germanium atom stabilizes η^5-coordination of the germolyl ligand and guards against methyl anion migration may be related to the well-known ability of silyl groups to stabilize anions via π-bonding. Alternatively, the greater σ-donating ability of the silyl (vs alkyl) group may render the germanium center less susceptible to nucleophilic attack by a migrating carbanion.[17]

For **2**, we have also observed participation of the germolyl ligand in Me_3SiH-elimination reactions. While these reactions are not yet understood in detail, it seems clear that the germolyl ligand activates the Hf-Me bonds toward σ-bond metathesis reactions with H_2 and $PhSiH_3$ (compared to Cp and Cp* ligands in analogous complexes). This result would seem to have important implications for the development of new σ-bond metathesis chemistry, and we are therefore continuing to explore this area in search of novel chemical transformations.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk techniques or a nitrogen-filled glovebox. Dry, oxygen-free solvents were employed throughout. Pentane, THF, toluene, and

---

(17) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; p 893.

diethyl ether were distilled from sodium/benzophenone, whereas benzene-d_6 and toluene-d_8 were distilled from Na/K alloy. The compounds KCH_2Ph,[18] $(Et_2O)LiCH_2Ph$,[18] Cp^*HfMe_2Cl,[7] Cp^*ZrCl_3,[19] Cp^*HfCl_3,[20] $C_4Me_4GeCl_2$,[21] $C_4Me_4Ge(SiMe_3)_2$,[2] $C_4Me_4SiCl_2$,[4d] $C_4Me_4Si(SiMe_3)_2$,[4d] $C_4Me_4Ge(H)Ph$,[22] $Li[C_4Me_4GePh]$,[22] and $[C_4Me_4GeSiMe_3]_2$[2] were prepared according to literature procedures. Me_3SiCl, Me_3SiOTf, EtOTf, and MeI were purchased from Aldrich chemical company and distilled prior to use. $MgBr_2(Et_2O)$ was purchased from Aldrich chemical company and used as received. NMR spectra were recorded at 300 or 500 MHz (^1H) with Bruker AMX-300 and DRX-500 spectrometers, at 125 MHz ($^{13}C\{^1H\}$) with a DRX-500 spectrometer, or at 99 MHz ($^{29}Si\{^1H\}$), at ambient temperature unless otherwise noted. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. IR samples of solid materials were prepared as KBr pellets, while IR spectra of oils were obtained with neat samples between CsI plates. All IR absorptions are reported in cm^{-1} and were recorded with a Mattson Infinity 60 MI FTIR spectrometer.

$[Cp^*(\eta^5\text{-}C_4Me_4Ge)HfMe_2Li(OC_4H_8)]_2$ (1). A 100 mL Schlenk tube was charged with $C_4Me_4Ge(SiMe_3)_2$ (0.207 g, 0.633 mmol), $(Et_2O)LiCH_2Ph$ (0.109 g, 0.633 mmol), and 50 mL of THF, and the contents were stirred for 30 min. The resulting orange solution was then added to a 250 mL round-bottom Schlenk flask containing Cp^*HfMe_2Cl (0.120 g, 0.317 mmol) in 100 mL of THF. This reaction mixture was stirred for 30 min before the volatile materials were removed under dynamic vacuum. The remaining orange residue was washed with pentane (3 × 30 mL) leaving a yellow solid. This solid was extracted with toluene (3 × 20 mL) and the toluene was removed via dynamic vacuum to give **1** as yellow-orange crystals in 86% yield (0.330 g, 0.274 mmol). ^1H NMR (benzene-d_6, 500 MHz, 25 °C) δ 3.61 (m, 4 H, $OC_4\mathit{H}_8$), 2.40 (s, 6 H, $C_4\mathit{Me}_4Ge$), 2.13 (s, 6 H, $C_4\mathit{Me}_4Ge$), 2.08 (s, 15 H, $C_5\mathit{Me}_5$), 1.40 (m, 4 H, $OC_4\mathit{H}_8$), −0.660 (s, 6 H, $Hf\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR (500 MHz, benzene-d_6, 25 °C) δ 129.6 (s, C_4Me_4Ge),116.6 (s, C_5Me_5), 69.54 (s, $O\mathit{C}_4H_8$), 42.95 (s, $Hf\mathit{Me}_2$), 25.95 (s, $O\mathit{C}_4H_8$), 20.32, 16.73 (s, $C_4\mathit{Me}_4Ge$), 13.58 (s, $C_5\mathit{Me}_5$). ^7Li (194.4 MHz, toluene-d_8, −40 °C) δ 1.70 (m, η^1-Li), −4.60 (m, η^5-Li). Anal. Calcd for $C_{24}H_{41}GeHfLiO$: C, 47.76; H, 6.85. Found: C, 47.76; H, 6.52. IR (cm^{-1}) 2907 s, 2361 w, 1448 m, 1376 m, 1136 w, 1041 m, 446 m. Mp 155−158 °C dec.

$Cp^*(\eta^5\text{-}C_4Me_4GeSiMe_3)HfMe_2$ (2). To a solution of **1** (0.21 g, 0.17 mmol) in benzene (50 mL) was added Me_3SiOTf (0.07 g, 0.34 mmol, in 30 mL of benzene). The resulting solution was stirred at room temperature for 30 min, after which time the volatile materials were removed under dynamic vacuum. The remaining orange residue was extracted with pentane (3 × 10 mL). The combined extracts were concentrated to 10 mL and cooled to −80 °C to give **3** as orange crystals in 87% yield (0.18 g, 0.30 mmol). ^1H NMR (benzene-d_6, 500 MHz, 25 °C) δ 2.17 (s, 6 H, $C_4\mathit{Me}_4Ge$), 2.16 (s, 6 H, $C_4\mathit{Me}_4Ge$), 1.99 (s, 15 H, $C_5\mathit{Me}_5$), 0.440 (s, 9 H, $Si\mathit{Me}_3$), −0.580 (s, 6 H, $Hf\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 25 °C) δ 139.4, 129.4 (s, C_4Me_4Ge), 117.2 (s, C_5Me_5), 43.32 (s, $Hf\mathit{Me}_2$), 19.18, 15.96 (s, $C_4\mathit{Me}_4Ge$), 13.23 (s, $C_5\mathit{Me}_5$), 3.130 (s, $Si\mathit{Me}_3$). Anal. Calcd for $C_{23}H_{42}GeHfSi$: C, 46.22; H, 7.08. Found: C, 46.30; H, 7.08. IR (cm^{-1}) 2948 s, 2905 s br, 1436 m, 1375 m, 1246 m, 1129 w, 1020 w, 841 s, 753 w, 701 w, 628 w, 464 w. Mp 125−128 °C.

$Cp^*(\eta^4\text{-}C_4Me_4GeMeEt)HfMe$ (3). In the glovebox, a vial was charged with **1** (0.025 g, 0.040 mmol) and 0.5 mL of benzene-d_6 was added, generating a deep yellow solution. To this was added CH_3CH_2OTf (0.007 g, 0.040 mmol) generating a deep orange solution of **2**. ^1H NMR (500 MHz, benzene-d_6, 25 °C) δ 2.05 (s, 6 H, $C_4\mathit{Me}_4Ge$), 2.00 (s, 15 H, $C_5\mathit{Me}_5$), 1.86 (s, 6 H, $C_4\mathit{Me}_4Ge$), 1.28 (m, 3 H, $C\mathit{H}_3CH_2Ge$), 1.26 (m, 2 H, $CH_3C\mathit{H}_2Ge$), 0.257 (s, 3 H, $Ge\mathit{Me}$), −0.833 (s, $Hf\mathit{Me}$). $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 25 °C) δ 130.0, 97.16 (s, C_4Me_4Ge), 117.9 (s, C_5Me_5), 49.27 (s, $Hf\mathit{Me}$), 15.58, 15.08 (s, $C_4\mathit{Me}_4Ge$), 12.08 ($C_5\mathit{Me}_5$), 11.91 (s, $CH_2\mathit{C}H_3$), 8.170 (s, $\mathit{C}H_2CH_3$), 1.398 (s, $Ge\mathit{Me}$).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**

Hf(1)−Ge(2)	2.903(2)	Hf(2)−Ge(1)	2.878(1)
Hf(1)−$C_4Ge(2)_{plane}$	2.256	Hf(2)−$C_4Ge(1)_{plane}$	2.274
Hf(1)−$Cp^*_{centroid}$	2.2408(4)	Hf(2)−$Cp^*_{centroid}$	2.2492(5)
Hf(1)−C(41)	2.29(1)	Hf(2)−C(43)	2.30(1)
Hf(1)−C(42)	2.26(1)	Hf(2)−C(44)	2.27(1)
Li(1)−$C_4Ge(2)_{plane}$	1.953	Li(1)−$C_4Ge(1)_{plane}$	1.984
Ge(2)−Li(2)	2.80(2)	Ge(1)−Li(2)	2.69(2)
Ge(2)−C(1)	2.10(2)	Ge(1)−C(13)	1.96(1)
Ge(2)−C(4)	1.72(2)	Ge(1)−C(16)	1.96(1)
C(1)−C(2)	1.34(2)	C(13)−C(14)	1.42(2)
C(2)−C(3)	1.39(2)	C(14)−C(15)	1.40(2)
C(3)−C(4)	1.41(2)	C(15)−C(16)	1.43(2)
C(41)−Hf(1)−C(42)	90.1(5)	C(43)−Hf(2)−C(44)	87.5(6)
Cp*−Hf(1)−$C_4Ge(2)$	136.4	Cp*−Hf(2)−$C_4Ge(1)$	136.5
Ge(2)−Li(2)−Ge(1)	86.3(6)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **7**

Zr(1)−Si(1)	2.844(1)	Zr(1)−$Cp^*_{centroid}$	2.24
Zr(1)−$C_4Si(1)$	2.301	Si(1)−C(1)	1.816(4)
Si(1)−C(4)	1.794(4)	C(1)−C(2)	1.418(6)
C(2)−C(3)	1.419(5)	C(3)−C(4)	1.400(6)
Si(1)−Si(2)	2.352(1)	Cl(1)−Zr(1)−Cl(1)	96.51(4)
Cp*−Zr(1)−$C_4Si(1)$	134.6	C(1)−Si(1)−C(4)	92.5(2)
C(1)−Si(1)−Si(2)	131.9(1)	C(4)−Si(1)−Si(2)	129.5(2)

$C_4Me_4Ge(Me)SiMe_3$. A 200 mL Schlenk tube was charged with $[C_4Me_4GeSiMe_3]_2$ (2.00 g, 3.94 mmol) and K metal (0.320 g, 8.18 mmol), and 100 mL of THF was added to generate a light orange solution. This solution was stirred for 1 week, after which time all of the potassium had been consumed and the solution had turned to a deep red color. The flask was placed in an ice bath and the solution was cooled to 0 °C. MeI (0.520 mL, 8.27 mmol) was then added to the flask resulting in formation of a white cloudy suspension. This suspension was allowed to warm to room temperature and was then stirred for 1 h. The volatile materials were removed under dynamic vacuum, and the resulting residue was extracted with pentane (3 × 30 mL). Pentane was removed from the extracts to give the product as a colorless oil in 80% yield (1.69 g, 6.30 mmol). This oil was purified by a short-path distillation (bp 48 °C, 1 × 10^{-3} Torr). ^1H NMR (benzene-d_6, 300 MHz, 25 °C) δ 2.03 (s, 6 H, $C_4\mathit{Me}_4Ge$), 1.82 (s, 6 H, $C_4\mathit{Me}_4Ge$), 0.427 (s, 3 H, $Ge\mathit{Me}$), 0.161 (s, 9 H, $GeSi\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 25 °C) δ 146, 135 (s, C_4Me_4Ge), 16.7, 14.9 (s, $C_4\mathit{Me}_4Ge$), −0.300 (s, $GeSi\mathit{Me}_3$), −7.30 (s, $Ge\mathit{Me}$). Anal. Calcd for $C_{12}H_{24}GeSi$: C, 53.58; H, 8.99. Found: C, 52.66; H, 9.26. IR (cm^{-1}) 2951 s br, 2905 s br, 2851 s br, 1551 w, 1441 m, 1399 sh, 1245 s, 1058 m, 839 s, 785 s, 741 m, 693 m, 622 m, 578 m, 484 m.

$C_4Me_4Ge(H)CMe_3$. To a solution of $C_4Me_4GeCl_2$ (1.00 g, 3.97 mmol) in 100 mL of benzene was added a benzene (100 mL) solution of $LiCMe_3$ (0.381 g, 5.96 mmol) to generate a cloudy yellow solution that was allowed to stir at room temperature for 60 min. This solution was then added to $LiAlH_4$ (0.181 g, 4.77 mmol) in 100 mL of diethyl ether. The resulting yellowish suspension was allowed to stir at room temperature for 60 min after which time the volatile materials were removed under dynamic vacuum. The resulting yellow residue was extracted with pentane (3 × 25 mL). The combined pentane extracts were removed in vacuo to leave a yellow oil. This yellow oil was distilled (37 °C; 1 × 10^{-3} Torr) to give the pure colorless product in 70% yield (0.664 g, 2.78 mmol). ^1H NMR (benzene-d_6, 300 MHz, 25 °C) δ 4.88 (s, 1 H, $Ge\mathit{H}$), 1.97 (s, 6 H, $C_4\mathit{Me}_4Ge$), 1.73 (s, 6 H, $C_4\mathit{Me}_4Ge$), 1.15 (s, 9 H, $C\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 25 °C) δ 148.2, 129.2 (s, C_4Me_4Ge), 29.56 (s, $C\mathit{Me}_3$), 24.41 (s, $\mathit{C}Me_3$), 17.15, 14.71 (s, $C_4\mathit{Me}_4Ge$). Anal. Calcd for $C_{12}H_{22}Ge$: C, 60.33; H, 9.28. Found: C, 60.57; H, 9.86. IR (cm^{-1}) 2950 s, 2923 s, 2853 s, 2009 s (GeH), 1458 m, 1363 m, 1059 w, 1017 w, 800 w, 702 m, 665 w.

---

(18) Hartmann, J.; Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

(19) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

(20) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

(21) (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. (b) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(22) Dufour, P.; Dubac, J.; Dartiguenave, M.; Dartiguenave, Y. *Organometallics* **1990**, *9*, 3001.

Table 3. Crystallographic Data for Compounds **1**, **4**, and **7**

	1	**4**	**7**
	(a) Crystal Parameters		
formula	$Hf_2Li_2O_2C_{48}H_{82}Ge_2$	$HfGeC_{24}H_{42}$	$ZrC_{25}Cl_2Si_2H_{36}$
formula weight	1207.22	581.68	554.86
size mm	0.2 × 0.18 × 0.05	0.045 × 0.05 × 0.01	0.35 × 0.18 × 0.04
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$(No. 14)	$P2_1/m$(No. 11)	Cc(No. 9)
a (Å)	15.0143(1)	9.2701(5)	18.6163(4)
b (Å)	20.1799(2)	13.3564(7)	9.0536(2)
c (Å)	17.1168(1)	10.5768(5)	17.2578(4)
α, β, γ (deg)	90, 97.408, 90	90, 112.399, 90	90, 122.47, 90
V (Å^3)	5142.88(6)	1236.80(1)	2454.00(1)
Z	4	2	2
D_{calc} (g cm^{-3})	1.559	1.562	3.003
F_{000}	2400.00	580.00	2304.00
	(b) Data Collection		
temp (°C)	−158.0	−127.0	−104.0
unique/total	9367/24375	1858/5047	3867/5912
R_{int}	0.056	0.131	0.028
empirical absorption corr	0.07	0.10	none
T_{max}/T_{min}	0.992/0.593	0.953/0.639	
	(c) Refinement		
observations [$I > 3\sigma(I)$]	5706	888	3657
no. of variables	496	67	233
reflection/parameter ratio	11.50	13.25	15.70
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.043	0.065	0.033
$R_w = [\sum\omega(\|F_o\| - \|F_c\|)^2/\sum\omega F_o{}^2)]^{1/2}$	0.054	0.072	0.051
goodness of fit ($[\sum\omega(\|F_o\| - \|F_c\|)^2/(N_o - N_v)]^{1/2}$)	1.71	1.19	2.33
max and min peaks in final diff map (e$^-$/Å^3)	1.12/−1.04	1.62/−2.81	0.67/−0.60

Li(THF)[$C_4Me_4GeCMe_3$]. ^{n}BuLi (1.57 mL, 2.51 mmol, 1.6 M in hexanes) was added via syringe to $C_4Me_4Ge(H)CMe_3$ (0.600 g, 2.51 mmol) in 50 mL of THF. The resulting reaction solution was stirred for 30 min after which time the volatile materials were removed under dynamic vacuum. The resulting oily yellow/orange residue was extracted into 30 mL of pentane, and the resulting pentane solution was concentrated to 10 mL. Cooling to −80 °C gave the product as yellow crystals, which contained 1.2 THF molecules per lithium atom, in 72% yield (0.599 g, 1.81 mmol). ^{1}H NMR (benzene-d_6, 500 MHz, 25 °C) δ 3.66 (m, 4.6 H, OC_4H_8), 2.20 (s, 6 H, C_4Me_4Ge), 1.95 (s, 6 H, C_4Me_4Ge), 1.41 (m, 4.6 H, OC_4H_8), 1.35 (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 25 °C) δ 157.7, 128.8 (s, C_4Me_4Ge), 69.51 (s, OC_4H_8), 32.68 (s, CMe_3), 29.01 (s, CMe_3), 26.04 (s, OC_4H_8), 19.16, 15.35 (s, C_4Me_4Ge). Anal. Calcd for $C_{16.8}H_{30.8}GeO_{1.2}Li$: C, 60.90; H, 9.31. Found: C, 61.34; H, 9.52. IR (cm^{-1}) 2950 s, 2947 s, 2912 s, 2842 s, 1457 m, 1352 w, 1158 w, 1050 m, 893 w, 811 w, 665 w, 452 w. Mp 251 °C dec.

Cp*[η^4-$C_4Me_4Ge(Me)CMe_3$]HfMe (4). To a solution of Cp*$HfMe_2Cl$ (0.500 g, 1.32 mmol) in 100 mL of THF was added a THF (50 mL) solution of Li(THF)[$C_4Me_4GeCMe_3$] (0.437 g, 1.32 mmol) to give a deep orange solution. The reaction solution was allowed to stir for 60 min, and then the volatile materials were removed by vacuum transfer. The resulting oily orange residue was extracted with pentane (3 × 25 mL). The combined extracts were concentrated to 5 mL and cooled to −80 °C to give **4** as red needles in 40% yield (0.308 g, 0.530 mmol). ^{1}H NMR (benzene-d_6, 300 MHz, 25 °C) δ 2.07 (s, 6 H, C_4Me_4Ge), 1.99 (s, 15 H, CMe_5), 1.85 (s, 6 H, C_4Me_4Ge), 1.28 (s, 9 H, CMe_3), 0.300 (s, 3 H, GeMe), −0.730 (s, 3 H, HfMe). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 25 °C) δ 131.1, 96.02 (s, C_4Me_4Ge), 118.2 (s, CMe_5), 49.82 (s, HfMe), 35.42 (s, CMe_3), 31.69 (s, CMe_3), 15.47, 14.94 (s, C_4Me_4Ge), 12.19 (s, C_5Me_5), −1.686 (s, GeMe). Anal. Calcd for $C_{24}H_{42}HfGe$: C, 49.56; H, 7.28. Found: C, 49.61; H, 7.31. IR (cm^{-1}) 2914 s br, 2839 s br, 1456 m, 1377 w, 1141 w, 1018 w, 769 m, 702 w, 416 w. Mp 115−117 °C.

Cp*[η^4-$C_4Me_4Ge(Me)Ph$]HfMe (5). In the glovebox, a vial was charged with Cp*$HfMe_2Cl$ (0.020 g, 0.053 mmol), and 0.5 mL of benzene-d_6 was added to generate a colorless solution. Li[C_4Me_4GePh] (0.014 g, 0.053 mmol) was weighed into a separate vial and dissolved in 0.5 mL of benzene-d_6 to give a yellow solution. This solution was added to the vial containing Cp*$HfMe_2Cl$ to immediately generate a deep orange solution of **5**. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C) δ 7.65−7.20 (m, 5 H, GePh), 2.08 (s, 6 H, C_4Me_4Ge), 2.01 (s, 15 H, C_5Me_5), 1.86 (s, 6 H, C_4Me_4Ge), 0.540 (s, 3 H, GeMe), −0.710 (s, HfMe). δ 131.4, 95.18 (s, C_4Me_4Ge), 144.0, 135.9, 135.6, 129.2 (s, GePh), 118.3 (s, C_5Me_5), 50.25 (s, HfMe), 15.77, 14.49 (s, C_4Me_4Ge), 12.10 (C_5Me_5), 2.870 (s, GeMe).

Mg[$C_4Me_4SiSiMe_3$]$_2$(THF) (6). A 250 mL round-bottom Schlenk flask was charged with $C_4Me_4Si(SiMe_3)_2$ (2.30 g, 8.14 mmol), KCH_2Ph (1.13 g, 8.14 mmol), and 50 mL of THF. The resulting solution was cooled to −80 °C, and then $MgBr_2(Et_2O)$ (1.05 g, 4.07 mmol) in 100 mL of THF was added to give a bright red solution. The solution was allowed to stir at −80 °C for 15 min, and then the cooling bath was removed and the solution was allowed to warm to room temperature. After this time the solution turned blue-green in color. The volatile materials were removed under dynamic vacuum leaving a tan oily residue. This oily residue was extracted with pentane (3 × 30 mL). The pentane was removed from the combined extracts leaving an oily tan residue. $Me_3SiOSiMe_3$ (25 mL) was added to the flask to wash the residue. After filtration, a white powder remained which was recrystallized from pentane (−35 °C) to give **6** in 70% yield (1.47 g, 2.85 mmol) as colorless, blocklike crystals. ^{1}H NMR (benzene-d_6, 500 MHz, 25 °C) δ 3.39 (m, 4 H, OC_4H_8), 2.30 (s, 6 H, C_4Me_4Si), 2.09 (s, 6 H, C_4Me_4Si), 1.22 (m, 4 H, OC_4H_8), 0.351 (s, $SiSiMe_3$). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 25 °C) δ 143.7, 139.9 (s, C_4Me_4Si), 69.49 (s, OC_4H_8), 25.17 (s, OC_4H_8), 17.00, 15.01 (s, C_4Me_4Ge), 0.9100 (s, $SiMe_3$). ^{29}Si{^{1}H} (99.4 MHz, benzene-d_6, 25 °C) δ −40.9 (s, C_4Me_4Si), −12.0 (s, $SiMe_3$). Anal. Calcd For $C_{26}H_{50}MgOSi_4$: C, 60.60; H, 9.78. Found: C, 59.93; H, 9.77. IR (cm^{-1}) 2954 s br, 2913 s br, 1444 m, 1246 m, 1057 m br, 839 s, 757 w, 701 w, 509 w. Mp 180−185 °C dec.

Cp*(η^5-$C_4Me_4SiSiMe_3$)$ZrCl_2$ (7). A 100 mL Schlenk tube was charged with $C_4Me_4Si(SiMe_3)_2$ (1.10 g, 3.90 mmol), KCH_2Ph (0.508 g, 3.90 mmol), and 50 mL of THF. The resulting solution was cooled to −80 °C, and then $MgBr_2(Et_2O)$ (0.503 g, 1.95 mmol) in THF (100 mL) was added via cannula. This solution was allowed to stir at −80 °C for 15 min after which time the cooling bath was removed and the solution was allowed to warm to room temperature. After this time the solution turned blue-green in color. The volatile materials were removed under dynamic vacuum leaving a tan oily residue of the magnesium reagent, which was dissolved in 50 mL of benzene. The latter solution was then added to Cp*$ZrCl_3$ (1.30 g, 3.90 mmol) in 100 mL of benzene to give a light orange solution. This solution was stirred at room temperature for 30 min, and then the volatile components were removed by vacuum transfer. The remaining orange residue was extracted into pentane (3 × 50 mL). The combined extracts were concentrated to 40 mL and cooled to −80 °C to give **7** as orange crystals in 65% yield (1.29 g, 2.54 mmol). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) δ 2.36 (s, 6 H, $C_4\mathit{Me}_4Si$), 2.02 (s, 15 H, $C_5\mathit{Me}_5$), 1.96 (s, 6 H, $C_4\mathit{Me}_4Si$), 0.262 (s, 9 H, $Si\mathit{Me}_3$). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 25 °C) δ 138.2, 131.9 (s, C_4Me_4Si), 123.2 (s, C_5Me_5), 16.67, 16.01 (s, $C_4\mathit{Me}_4Si$), 13.59 (s, $C_5\mathit{Me}_5$), 1.490 (s, $Si\mathit{Me}_3$). ^{29}Si{^{1}H} (99.4 MHz, benzene-d_6, 25 °C) δ 48.9 (s, $C_4Me_4\mathit{Si}$), −9.42 (s, $\mathit{Si}Me_3$). Anal. Calcd for $C_{21}H_{36}Cl_2ZrSi_2$: C, 49.77; H, 7.16. Found: C, 49.43; H, 7.19. IR (cm^{-1}) 2950 br s, 2901 br s, 1601 w, 1454 m, 1375 m, 1248 m, 1075 w, 1016 m, 843 s, 801 sh, 698 w. Mp 199−202 °C dec.

Cp*(η^5-$C_4Me_4SiSiMe_3$)$HfCl_2$ (8). A procedure analogous to that used to prepare **7** was employed using $C_4Me_4Si(SiMe_3)_2$ (0.675 g, 2.39 mmol), KCH_2Ph (0.311 g, 2.39 mmol), $MgBr_2(Et_2O)$ (0.309 g, 1.20 mmol), and Cp*$HfCl_3$ (1.00 g, 2.39 mmol). The product was isolated after crystallization from Et_2O to provide **8** as orange blocks in 68% yield (0.965 g, 1.63 mmol). **8** was characterized by comparison of ^{1}H NMR data with that previously reported.[3c] ^{1}H NMR (benzene-d_6, 300 MHz, 25 °C) δ 2.25 (s, 12 H, $C_4\mathit{Me}_4Ge$), 2.05 (s, 15 H, $C_5\mathit{Me}_5$), 0.33 (s, 9 H, $SiMe_3$).

X-ray Structure Determinations. X-ray diffraction measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation. The crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $4 < 2\Theta < 45°$. The frame data were integrated using the program SAINT (SAX Area-Detector Integration Program; V4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1995). An empirical absorption correction based on measurements of multiply redundant data was performed using the programs XPREP (part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc.: Madison, WI, 1995) or SADABS. Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. A secondary extinction correction was applied if appropriate. The structures were solved using the teXsan crystallographic software package of the Molecular Structure Corporation, using direct methods, and expanded with Fourier techniques. All non-hydrogen atoms were refined anisotropically unless otherwise noted and the hydrogen atoms were included in calculated positions but not refined. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a p-factor to downweight the intense reflections. Crystallographic data are summarized in Table 3.

For 1: Crystals were grown from a 50:1 toluene/THF solution at −35 °C. The non-hydrogen atoms that displayed no disorder were refined anisotropically except for Li(1) and Li(2), which were refined isotropically. Hydrogen atoms were included but not refined. The two THF molecules displayed large “thermal parameters” indicative of probable disorder. This disorder was modeled with the anisotropic displacement parameters. Hf(2) and Hf(3) showed disorder and were refined anisotropically and isotropically with occupancies of 92 and 8%, respectively. In addition the germole ring containing Ge(2) showed disorder in which the ring appeared to have two orientations, twisted about the Li(1) to Hf(1) vector. The ring carbons were modeled with anisotropic displacement parameters but the Ge atoms and methyl carbons were modeled with partial occupancy isotropic atoms. The occupancy of Ge(3) was constrained to be equal to the difference of one and the occupancy of Ge(2), as were carbons 6, 8, 10, and 12. Carbons 5, 7, 9, and 11 were constrained to have the same occupancy as Ge(2). The occupancy factor was refined to 55% for Ge(2) and carbons 5, 7, 9, and 11 and occupancies of 45% for Ge(3) and carbons 6, 8, 10, and 12. See the Supporting Information for a full ORTEP view of **1**, including all of the disordered atoms.

For 4: Crystals were grown from a concentrated pentane solution at −35 °C. Due to poor data only the heavy atoms Hf(1) and Ge(1) were refined anisotropically. All of the carbon atoms were refined isotropically. Hydrogen atoms were calculated but not refined.

For 7: Crystals were grown from a concentrated ether solution at −35 °C.

Acknowledgment is made to the National Science Foundation of their generous support of this work. We thank Dr. Fred Hollander for assistance with the X-ray structure determinations.

Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **1**, **4**, and **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA993563N