Hafnium−Rhodium and Hafnium−Iridium Heterobimetallic Complexes Featuring the Bridging Germole Dianion Ligand $[GeC_4Me_4]^{2-}$

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The complex $[Cp^*(\eta^5\text{-}C_4Me_4Ge)HfMe_2Li(THF)]_2$ (**1**; $Cp^* = C_5Me_5$), prepared via treatment of Cp^*HfMe_2Cl with 2 equiv of $Li[C_4Me_4GeSiMe_3]$, reacted rapidly with 2 equiv of $(PMe_3)_4RhOTf$ ($OTf = OSO_2CF_3$) to give the novel Rh(III) zwitterionic complex *ansa*-$\{\eta^4\text{-}C_4Me_4Ge[Rh(PMe_3)_4H](\eta^5\text{-}C_5Me_4CH_2)\}HfMe_2$ (**2**), via loss of LiOTf. An intermediate in this reaction, presumed to be $Cp^*\{\eta^5\text{-}C_4Me_4Ge[Rh(PMe_3)_4]\}HfMe_2$ (**3**), was observed at low temperature by ^{31}P NMR spectroscopy. Reactions of **1** with $(dmpe)_2MOTf$ (dmpe = 1,2-bis(dimethylphosphino)ethane; M = Rh, Ir) produced the complexes $Cp^*\{\eta^5\text{-}C_4Me_4Ge[Rh(dmpe)_2]\}HfMe_2$ (**5**) and $Cp^*\{\eta^5\text{-}C_4Me_4Ge[Ir(dmpe)_2]\}HfMe_2$ (**6**), respectively. Complexes **5** and **6** possess the $[GeC_4Me_4]^{2-}$ ligand, which bridges the two metal atoms in a σ,π fashion.

Introduction

Recent interest in cyclic π-systems containing the heavier congeners of the group 14 elements[1] has motivated investigations of the chemistry of sila- and germacyclopentadienyl anions, and the corresponding silole and germole dianions.[2] These studies have included exploration of the transition-metal chemistry of these species, which has led to isolation of a η^5-germolyl complex of a transition metal, $[Cp^*Ru(\eta^5\text{-}C_4Me_4GeSi(SiMe_3)_3)]$,[3] synthesis of the η^5-silolyl complex $[Cp^*Ru(\eta^5\text{-}C_4Me_4SiSi(SiMe_3)_3)]$,[4] and the isolation and structural characterization of η^5-germolyl and η^5-silolyl d^0 metal complexes.[5] Recently we reported the synthesis and characterization of the aromatic germole dianion complex $[Cp^*(\eta^5\text{-}C_4Me_4Ge)HfMe_2Li(THF)]_2$ (**1**), which possesses a structure featuring Li ions coordinated in both an η^1 and η^5 fashion by the germole dianion unit.[6] The silylation of **1** produces the neutral germolyl complex $[Cp^*(\eta^5\text{-}C_4Me_4GeSiMe_3)HfMe_2]$, which readily loses its $-SiMe_3$ group to regenerate the germole dianion complex.[6] This reactivity, and the structure of the germole dianion complex, suggested that it might be possible to synthesize interesting heterobimetallic complexes[7] in which the germole dianion $[C_4Me_4Ge]^{2-}$ serves as a bridging ligand. More specifically, we envisioned access to early−late bimetallic complexes via reaction of **1** with an electrophilic late-transition-metal fragment. Here we report the isolation of complexes containing a germole dianion bound to both early- and

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late-transitionn-metal centers and a rare example of structural characterization of a complex containing a Rh^{I}−Ge bond.[8]

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, toluene, benzene, and diethyl ether were distilled from sodium/benzophenone, whereas benzene-d_6 and toluene-d_8 were distilled from Na/K alloy. The compounds [Cp*(η^5-C_4Me$_4$Ge)HfMe$_2$Li(THF)]$_2$,[6] (PMe$_3$)$_4$RhOTf,[9] (dmpe)$_2$RhOTf,[9] and (dmpe)$_2$IrOTf[9] were prepared according to literature procedures. Me$_3$SiOTf was purchased from Aldrich Chemical Co. and distilled prior to use. NMR spectra were recorded at 300 or 500 MHz (^{1}H) with Bruker AMX-300 and DRX-500 spectrometers and at 125 MHz (^{13}C{^{1}H}) or 202 MHz (^{31}P{^{1}H}) with the DRX-500 spectrometer, at ambient temperature unless otherwise noted. Elemental analyses were performed by the microanalytical laboratory in the College of Chemistry at the University of California, Berkeley, CA. IR samples of solid materials were prepared as KBr pellets. All IR absorptions are reported in cm^{-1} and were recorded with a Mattson Infinity 60 MI FTIR spectrometer.

***ansa*-{η^4-C$_4$Me$_4$Ge[Rh(PMe$_3$)$_3$H](η^5-C$_5$Me$_4$CH$_2$)}HfMe$_2$ (2).** A 100 mL Schlenk tube was charged with [Cp*(η^5-C$_4$Me$_4$Ge)HfMe$_2$Li(THF)]$_2$ (0.257 g, 0.213 mmol) and 25 mL of benzene to generate a deep yellow solution. This solution was then added to a 100 mL round-bottom Schlenk flask containing (PMe$_3$)$_4$RhOTf (0.237 g, 0.426 mmol) in 50 mL of benzene to immediately produce a deep green solution. This reaction mixture was stirred for 30 min before the volatile materials were removed under dynamic vacuum. The remaining green residue was extracted with pentane (3 × 20 mL), and the combined pentane extracts were evaporated to give **2** as green crystals in 95% yield (0.359 g, 0.405 mmol). ^{1}H NMR (benzene-d_6, 500 MHz, 25 °C): δ 2.36 (s, 2 H, C$_5$Me$_4$CH_2), 2.28 (s, 6 H, C$_4$*Me*$_4$Ge), 2.18 (s, 6 H, C$_4$*Me*$_4$Ge), 1.96, 1.87 (s, 12 H, C$_5$*Me*$_4$CH$_2$), 1.23 (d, $^2J_{HP}$ = 5 Hz, 18 H, P*Me*$_3$), 0.95 (d, $^2J_{HP}$ = 5 Hz, 9 H, P*Me*$_3$), −0.48 (s, 6 H, Hf*Me*$_2$), −9.70 (dm, J_{HRh} = 120 Hz, 1 H, Rh*H*). ^{13}C{^{1}H} NMR (500 MHz, benzene-d_6, 25 °C): δ 140, 110 (s, *C*$_4$Me$_4$Ge) 131, 119, 113 (s, *C*$_5$Me$_4$CH$_2$), 41.1 (s, Hf*Me*$_2$), 26.4 (s, *C*H$_2$), 22.5 (bm, 3 P*Me*$_3$), 22.5, 16.8, 13.0, 12.0 (s, C$_4$*Me*$_4$Ge and C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (202 MHz, benzene-d_6, 25 °C): δ −11.6 (dd, J_{PRh} = 152 Hz, $^2J_{PP}$ = 32 Hz, 2 P, Rh(*P*Me$_3$)$_2$), −15.3 (dt, J_{PRh} = 119 Hz, $^2J_{PP}$ = 32 Hz, 1 P, Rh(*P*Me$_3$)). Anal. Calcd for C$_{29}$H$_{60}$GeHfP$_3$Rh: C, 40.70, H, 7.01. Found: C, 40.35, H, 7.09. IR (cm^{-1}): 2974 s, 2904 s, 2868 s, 1858 m (Rh−H), 1420 m, 1294 m, 1621 w, 1140 w, 1094 w, 945 s, 850 w, 747 w, 668 w. Mp: 95 °C dec.

Cp*{η^5-C$_4$Me$_4$Ge[Rh(dmpe)$_2$]}HfMe$_2$ (5). A 100 mL Schlenk tube was charged with [Cp*(η^5-C$_4$Me$_4$Ge)HfMe$_2$Li(THF)]$_2$ (0.099 g, 0.082 mmol) and 25 mL of benzene to give a deep yellow solution. This solution was then added to a 100 mL round-bottom Schlenk flask containing (dmpe)$_2$RhOTf (0.091 g, 0.164 mmol) in 50 mL of benzene, resulting in a deep red solution. This reaction mixture was stirred for 30 min before the volatile materials were removed under dynamic vacuum. The remaining red-orange residue was extracted with toluene (3 × 20 mL). The combined extracts were concentrated to 10 mL and cooled to −35 °C to give **5** as red-orange needles in 83% yield (0.126 g, 0.136 mmol). ^{1}H NMR (benzene-d_6, 500 MHz, 25 °C): δ 2.43 (s, 6 H, C$_4$*Me*$_4$Ge), 2.39 (s, 6 H, C$_4$*Me*$_4$Ge), 2.19 (s, 15 H, C$_5$*Me*$_5$), 1.37 (bs, 8 H, Me$_2$PCH_2CH_2PMe$_2$), 1.14 (bs, 24 H, *Me*$_2$PCH$_2$CH$_2$P*Me*$_2$), −0.470 (s, 6 H, Hf*Me*$_2$). ^{13}C{^{1}H} NMR (500 MHz, benzene-d_6, 25 °C): δ 151, 127 (s, *C*$_4$Me$_4$Ge), 116 (s, *C*$_5$Me$_5$), 40.8 (s, Hf*Me*$_2$), 33.4 (m, Me$_2$P*C*H$_2$*C*H$_2$PMe$_2$), 24.1 (m, *Me*$_2$PCH$_2$CH$_2$P*Me*$_2$), 21.6, 17.3 (s, C$_4$*Me*$_4$Ge), 13.3 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (202 MHz, benzene-d_6, 25 °C): δ −33.4 (d, J_{PRh} = 123 Hz, Me$_2$*P*CH$_2$CH$_2$*P*Me$_2$). Anal. Calcd for C$_{32}$H$_{65}$GeHfP$_4$Rh: C, 41.43, H, 7.06. Found: C, 41.04, H, 7.41. IR (cm^{-1}): 2950 s, 2898 s, 1419 m, 1293 m, 1274 m, 1261 m, 1177 w, 1100 w, 1021 w, 933 m, 841 w, 807 w. Mp: 155−159 °C.

Cp*{η^5-C$_4$Me$_4$Ge[Ir(dmpe)$_2$]}HfMe$_2$ (6). A 100 mL Schlenk tube was charged with [Cp*(η^5-C$_4$Me$_4$Ge)HfMe$_2$Li(THF)]$_2$ (0.236 g, 0.196 mmol) and 25 mL of benzene to give a deep yellow solution. This solution was then added to a 100 mL round-bottom Schlenk flask containing (dmpe)$_2$IrOTf (0.251 g, 0.392 mmol) in 50 mL of benzene. The resulting light red solution was stirred for 30 min before the volatile materials were removed under dynamic vacuum. The remaining red residue was extracted with toluene (3 × 20 mL). The combined extracts were concentrated to 10 mL and cooled to −35 °C to give **6** as an orange powder in 87% yield (0.346 g, 0.340 mmol). ^{1}H NMR (benzene-d_6, 500 MHz, 25 °C): δ 2.40 (s, 6 H, C$_4$*Me*$_4$Ge), 2.35 (s, 6 H, C$_4$*Me*$_4$Ge), 2.15 (s, 15 H, C$_5$*Me*$_5$), 1.56 (bs, 8 H, Me$_2$PCH_2CH_2PMe$_2$), 1.15 (bs, 24 H, *Me*$_2$PCH$_2$CH$_2$P*Me*$_2$), −0.440 (s, 6 H, Hf*Me*$_2$). ^{13}C{^{1}H} NMR (500 MHz, benzene-d_6, 25 °C): δ 143, 124 (s, *C*$_4$Me$_4$Ge), 116 (s, *C*$_5$Me$_5$), 40.2 (s, Hf*Me*$_2$), 34.8 (m, Me$_2$P*C*H$_2$*C*H$_2$PMe$_2$), 26.1 (m, *Me*$_2$PCH$_2$CH$_2$P*Me*$_2$), 20.7, 17.0 (s, C$_4$*Me*$_4$Ge), 13.0 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (202 MHz, benzene-d_6, 25 °C): δ 0.315 (s, Me$_2$*P*CH$_2$CH$_2$*P*Me$_2$). Anal. Calcd for C$_{32}$H$_{65}$GeHfP$_4$Ir: C, 37.79, H, 6.44. Found: C, 38.10, H, 6.26. IR (cm^{-1}): 2968 s, 2909 s, 1998 w, 1420 m, 1375 w, 1293 w, 1122 w, 1078 w, 933 m, 845 w, 723 w, 651 w. Mp: 180 °C dec.

X-ray Crystallography. Red-orange, platelike crystals were obtained from a concentrated toluene solution at −35 °C. A crystal of dimensions 0.62 × 0.19 × 0.04 mm was mounted on a glass fiber using Paratone-N hydrocarbon oil. Data were collected using a Siemens SMART diffractometer with a CCD area detector. A preliminary orientation matrix and unit cell parameters were determined by collecting 60 10 s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using ω scans of 0.3°. Frame data were integrated (*xy* spot spread 1.60°; *z* spot spread 0.60°) using the program SAINT (SAX area detector integration program, version 4.024; Siemens Industrial Automation, Inc., Madison, WI, 1995). The data were corrected for Lorentz and polarization effects. An absorption correction was performed using SADABS (T_{max} = 0.9765, T_{min} = 0.3466). The 37 143 integrated reflections were averaged in point group 2/*m* to give 15 003 unique reflections (R_{int} = 0.076), but only 7136 reflections were considered observed ($I > 3.00\sigma(I)$). No decay correction was necessary. Inspection of the systematic absences uniquely defined the space group as $P2_1/n$. The structure was solved using direct methods (SIR92) and refined by full-matrix least-squares methods using teXsan software. Only one of the two independent molecules in the unit cell is displayed in Figure 1. The non-hydrogen atoms were refined anisotropically in both molecules. The number of variable parameters was 703, giving a data/parameter ratio of 10.15. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.34 and −7.33 e/Å^3. R = 0.052, R_w = 0.056, GOF = 1.38. The crystallographic data are summarized in Table 1.

Results and Discussion

Initial reactivity studies focused on attempts to coordinate a transition-metal fragment to the germole

(8) A keyword search for complexes containing Rh and Ge in the Cambridge Structural Database as well as the Web of Science returned no examples of structurally characterized compounds with a Rh^{I}−Ge bond. However, the related germylene complex *cis*-[RhCl{Ge(N(SiMe$_3$)$_2$)}(PPh$_3$)$_2$], mentioned only in review, was structurally characterized as possessing a Ge···Cl interaction (Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267).

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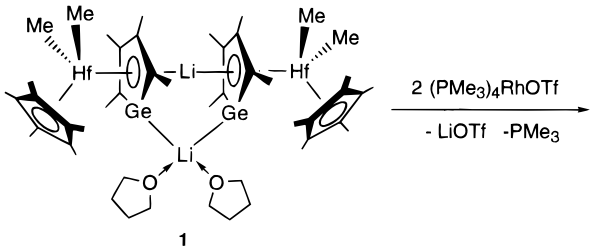
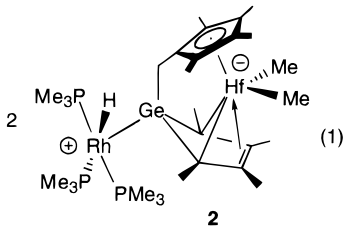
Table 1. Summary of Crystallographic Data

empirical formula	$RhHfP_4GeC_{32}H_{65}$
fw	927.75
cryst color, habit	red-orange, platelike
cryst dimens	0.62 × 0.19 × 0.04 mm
cryst syst	monoclinic
cell determn (2θ range)	8192 (4.0−45.0°)
lattice params	
a	23.7258(2) Å
b	15.0198(2) Å
c	24.2155(2) Å
β	117.0811)°
V	7683.3(1) Å^3
space group	$P2_1/n$ (No. 14)
Z	8
D_{calcd}	1.604 g/cm^3
μ(Mo Kα)	40.77 cm^{-1}
diffractometer	Siemens SMART
radiation	MoKα (λ = 0.710 69 Å), graphite monochromated
temp	−105 °C
scan type	ω (0.3° per frame)
no. of rflns measd	total, 37 143; unique, 15 003 (R_{int} = 0.076)
no. of observns ($I > 3.00\sigma(I)$)	7136
structure soln	direct methods (SIR92)
refinement	full-matrix least squares
residuals: R; R_w	0.052; 0.056
max peak in final diff map	2.34 e/Å^3
min peak in final diff map	−7.33 e/Å^3

ring of [Cp*(η^5-C_4Me_4Ge)$HfMe_2Li$(THF)]$_2$ (**1**)[6] with formation of a "sandwich" structure. This possibility is suggested by the structure of **1**, which features a lithium atom coordinated in an η^5 fashion by the germole rings of two [Cp*(η^5-C_4Me_4Ge)$HfMe_2$]$^-$ anions. However, reaction of **1** with $FeCl_2$, $FeCl_2$(THT) (THT = tetrahydrothiophene) (in benzene, toluene, or THF), or $^1/_4$ [Cp*$RuCl]_4$[10] (in THF or toluene) resulted only in complex mixtures of products. In contrast, the reaction of **1** with 2 equiv of $(PMe_3)_4RhOTf$[9] at room temperature in benzene resulted in loss of LiOTf with formation of an intensely colored green solution. The soluble product from this reaction, isolated as green crystals from pentane in 95% yield, is the unusual zwitterionic *ansa*-{η^4-C_4Me_4Ge[$Rh(PMe_3)_3H$](η^5-$C_5Me_4CH_2$)}$HfMe_2$ (**2**; eq 1).



1



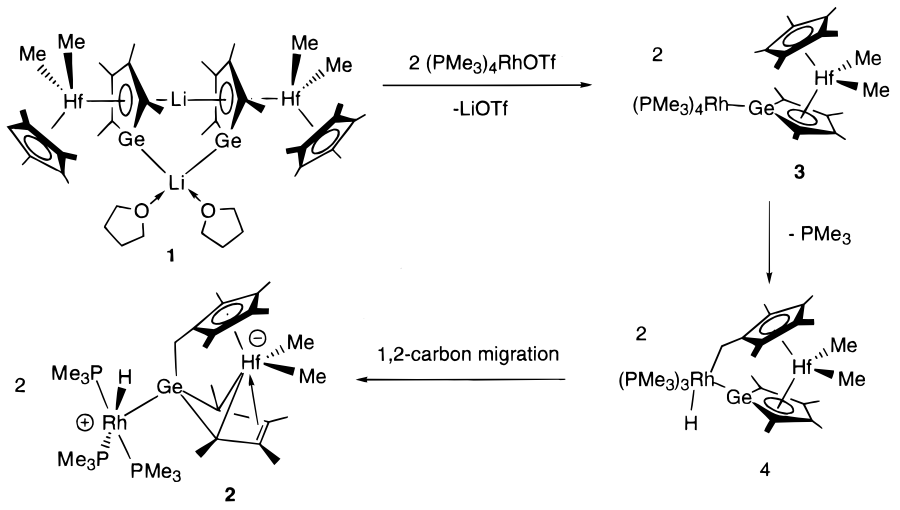
2 (1)

The ^{1}H NMR spectrum of **2** exhibits a characteristic shift for the Hf−Me protons at δ −0.48, along with resonances at δ 0.95 and 1.23 for two different types of PMe_3 ligands. The activated Cp* group gives rise to three singlets in a 6:6:2 ratio at δ 1.87, 1.96, and 2.36, respectively, while the η^4-germole group is associated with two methyl peaks at δ 2.28 and 2.36. Notably, the absence of coupling between Rh and the methylene hydrogens bound to Ge indicates that rhodium is not bonded to the $CH_2C_5Me_4$ fragment. There is a Rh−H resonance at δ −9.70 which appears as a doublet of multiplets coupled to both Rh (J_{HRh} = 120 Hz) and inequivalent phosphorus atoms (J_{HP} = 15 Hz, J_{H-2P} = 25 Hz). The ^{31}P NMR spectrum of **2** displays two separate resonances for the different kinds of phosphine ligands at δ −11.6 (dd, J_{PRh} = 152 Hz, $^2J_{PP}$ = 32 Hz, 2 P, Rh(PMe_3)$_2$) and −15.3 (dt, J_{PRh} = 119 Hz, $^2J_{PP}$ = 32 Hz, 1 P, Rh(PMe_3)). The spectroscopic data for **2** are consistent with a square-pyramidal coordination geometry for Rh, with apical coordination of the germanium atom, and this structure was confirmed by X-ray crystallography (vide infra). Also, the ^{13}C NMR spectrum of **2** exhibits two distinct shifts for the ring carbons of the germole ring at 110 and 140 ppm. X-ray-quality crystals of **2** were obtained by cooling a concentrated pentane solution to −30 °C. Although X-ray crystallography confirmed the connectivity and main structural features for **2**, including the η^4-coordination of the germole unit, the refinement of accurate metric parameters was not possible, due to a poor data set.

A possible mechanism for the formation of **2** is given in Scheme 1. Presumably, the initial step in this reaction is nucleophilic attack on the Rh center by the germole anion complex to give a new Rh−Ge-bonded species (**3**). The formation of **3** is supported by low-temperature NMR spectra of the reaction mixture. Treatment of **1** with 2 equiv of $(PMe_3)_4RhOTf$ at −78 °C in toluene-d_8 resulted in formation of a red solution (rather than a green solution as observed at room temperature). Although attempts to isolate a product from such solutions failed, the ^{31}P NMR spectrum at −70 °C revealed clean formation of an intermediate, giving rise to two complex multiplets at δ −5.2 and −32. As the solution is warmed, these two multiplets broaden and eventually coalesce at −20 °C into a doublet (δ −20, J_{PRh} = 146 Hz), which would be expected for **3** if all of the PMe_3 ligands were rendered equivalent on the NMR time scale. The ^{1}H NMR spectrum of **3** at −70 °C revealed the presence of equivalent Hf−Me groups, which resonate at δ −0.40, and additional resonances at δ 2.2 for the Cp* ligand and at δ 2.4 and 2.6 for the Me groups of the germole ring. As the solution was warmed from −70 to −20 °C, the ^{1}H NMR spectrum remained virtually unchanged, except that the PMe_3 resonances broadened and coalesced into one broad peak at ca. δ 1.3. The coalescence observed in the variable-temperature NMR spectra for compound **3** may be attributed to dynamic behavior involving rotation of a trigonal bipyramidal P_4Rh group about the Rh−Ge bond or Berry pseudorotation at the Rh center. Both of these processes would preserve the mirror plane symmetry (equivalent HfMe groups) observed in the ^{1}H NMR spectra. At 0 °C the doublet attributed to **3** at δ −20 disappeared and new resonances for **2** and free PMe_3 grew in with no evidence for intermediate **4**. Presumably, **3** loses a PMe_3 ligand from the Rh(I) center to form

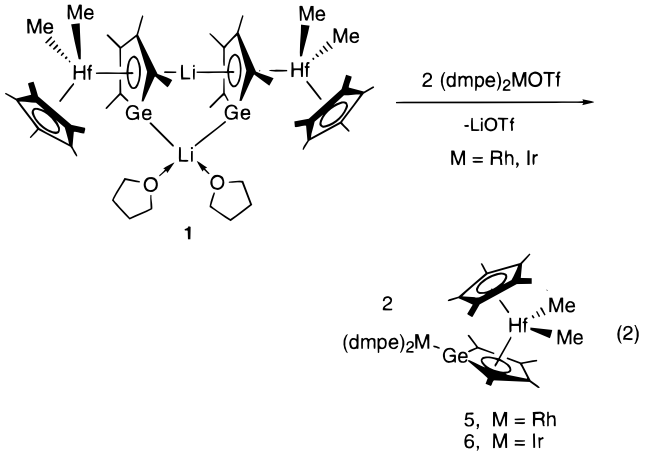
(10) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981.

Scheme 1



a coordinately unsaturated, 16-electron complex which oxidatively adds a C−H bond of the Cp* ligand to generate a new 18-electron, pseudo-octahedral Rh(III) center (**4**). A 1,2-carbon migration of the metalated CH_2 group from Rh to germanium would result in the formation of **2**, containing square-pyramidal Rh(III) and d^0 hafnium centers. This last step, the generation of a diene complex of the germole unit, has previously been observed in different reactions of **1**.[6]

To isolate a complex analogous to the proposed intermediate **3**, we employed the rhodium triflate $(dmpe)_2RhOTf$[9] possessing relatively nonlabile phosphine ligands. In fact, reaction of **1** with 2 equiv of $(dmpe)_2RhOTf$ at room temperature in benzene resulted in formation of the new (η^5-germolyl)hafnium complex $Cp^*\{\eta^5\text{-}C_4Me_4Ge[Rh(dmpe)_2]\}HfMe_2$ (**5**) in 83% yield after crystallization from toluene at −35 °C (eq 2).



(2)

Compound **5** is quite thermally stable, as heating a toluene solution to 140 °C for 24 h resulted in no detectable decomposition.

The ^1H NMR spectrum of **5** exhibits a characteristic Hf−Me peak at δ −0.47, a Cp* resonance at δ 2.20, and two peaks for the germolyl ring methyl protons at δ 2.39 and 2.43. In addition, there are two very broad resonances at δ 1.15 and 1.37 for the dmpe ligands, which resonate as a sharp doublet (J_{P-Rh} = 123 Hz) in the ^{31}P NMR spectrum. Finally, the ^{13}C NMR shifts for the ring

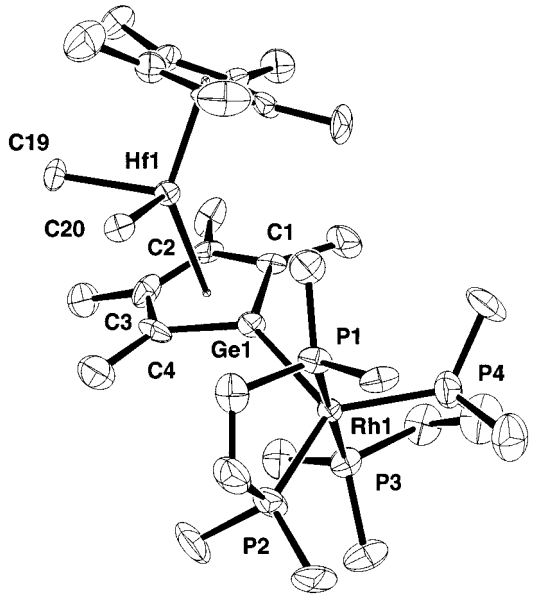


Figure 1. ORTEP diagram of $Cp^*\{\eta^5\text{-}C_4Me_4Ge\text{-}[Rh(dmpe)_2]\}HfMe_2$ (**5**).

carbons of the germole ring (δ 127 and 151) lie in a region consistent with η^5 coordination of the germolyl unit.[6]

X-ray-quality crystals of **5** were grown by slow cooling of a concentrated toluene solution to −35 °C, and the molecular structure of one of the two independent molecules in the unit cell is shown in Figure 1. The molecular structure of **5** is typical of bent metallocene derivatives of hafnium and is analogous to the previously reported structure for $Cp^*[\eta^5\text{-}C_4Me_4GeSiMe_3]\text{-}HfCl_2$.[5] The Rh-containing portion of **5** adopts a trigonal-bipyramidal geometry with the Ge atom of the germole ring, P2, and P4 occupying the equatorial positions. The Ge−C bond lengths (1.92(1) and 1.95(2) Å; Table 2) are short relative to the analogous germanium−carbon bonds in localized germole anions (1.957(7)−2.007(9) Å).[2j] The C−C bonds in the germole ring are roughly equivalent (1.48(2), 1.43(2), and 1.43(2) Å) and are comparable to those found in **1** (1.42(2), 1.40(2), and 1.43(2) Å), suggesting an aromatic η^5-germolyl ligand. Compound **5**, which represents the first structurally characterized complex possessing an unambiguous Rh^I−

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 5

(a) Bond Distances

Hf(1)−Ge(1)	2.963(2)	Ge(1)−C(1)	1.92(1)
Hf(1)−Ge*[a]	2.3000(6)	Ge(1)−C(4)	1.95(2)
Hf(1)−Cp*[a]	2.2702(6)	C(1)−C(2)	1.48(2)
Hf(1)−C(19)	2.29(1)	C(2)−C(3)	1.43(2)
Hf(1)−C(20)	2.30(1)	C(3)−C(4)	1.43(2)
Rh(1)−Ge(1)	2.488(2)	Rh(1)−P(1)	2.273(4)
Rh(1)−P(2)	2.273(4)		

(b) Bond Angles

Ge*−Hf(1)−Cp*	137.80(3)	C(19)−Hf(1)−C(20)	89.2(5)
P(1)−Rh(1)−Ge(1)	94.1(1)	P(2)−Rh(1)−Ge(1)	113.1(1)
Ge*−Ge(1)−Rh(1)	155.24	C(1)−Ge(1)−C(4)	86.9(6)

[a] Ge* and Cp* denote the centroids of the germolyl and Cp* rings, respectively.

Ge single bond, exhibits a Rh−Ge bond length of 2.488(2) Å. Finally, the Cp*(centroid)−Hf distance (2.27 Å), the germole(centroid)−Hf distance (2.30 Å), and the germole−Hf−Cp* angle (137.8°) are comparable to those found in Cp*[η^5-$C_4Me_4GeSiMe_3$]$HfCl_2$ (2.22 Å, 2.33 Å, and 136.1°, respectively).[5]

Surprisingly, the analogous reaction of **1** with 2 equiv of $(PMe_3)_4IrOTf$[9] (in benzene, toluene, or THF) was not clean, and in each case a mixture of products was observed, none of which possessed an Ir−H bond (by ^{1}H NMR spectroscopy). However, reaction of **1** with 2 equiv of $(dmpe)_2IrOTf$[9] at room temperature in benzene resulted in clean formation of Cp*{η^5-C_4Me_4Ge[Ir(dmpe)$_2$]}$HfMe_2$ (**6**) in 87% yield after crystallization from toluene. The characterization of **6** is based largely on comparisons of spectroscopic data with those for **5**. The ^{31}P NMR spectrum of **6** exhibits one sharp singlet for all four dmpe phosphorus atoms at δ 0.32. In addition, as for **5**, the ^{13}C NMR spectrum of **6** exhibits peaks for the germolyl ring carbons (δ 143 and 124) in a region consistent with η^5 coordination.

In summary, we have observed heterobimetallic complexes containing an η^5-germole dianion as a bridging ligand. In one of these systems, C−H activation and 1,2-migration generate an unusual zwitterion containing cationic Rh(III) and anionic Hf(IV) centers. In addition, early−late-transition-metal complexes containing a germole dianion bound both in an η^5 fashion to d^0 hafnium and in an η^1 fashion to either Rh(I) or Ir(I) were synthesized. Future investigations will focus on both the reaction chemistry of these complexes and the synthesis of new compounds in which the germole dianion is "sandwiched" in an η^5 manner between two transition metals.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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