

Synthesis of Oxo- and Sulfido-Bridged Germanium–Ruthenium Complexes and Reactions on the Chalcogenido Bridges

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A series of heterodinuclear germanium–ruthenium complexes having sulfido/oxo bridges, $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-E}^1)(\mu\text{-E}^2)\text{Ru}(\eta^6\text{-arene})$ ($\text{E}^1, \text{E}^2 = \text{S}, \text{O}$; arene = benzene, *p*-cymene; Dmp = 2,6-dimesitylphenyl, Dep = 2,6-diethylphenyl) were synthesized by the reaction of $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2]_2$ and the corresponding diarylgermanedichalcogenoles, $\text{Dmp}(\text{Dep})\text{Ge}(\text{E}^1\text{H})(\text{E}^2\text{H})$. The reaction with tertiary phosphines gave the corresponding adducts $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-E})\text{Ru}(\text{PR}_3)$ ($\text{E} = \text{S}, \text{O}$; $\text{R} = \text{Ph}, \text{Et}$), in which the arene ligand on the ruthenium was replaced by a mesityl group of Dmp. When $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})_2\text{Ru}(\text{PPh}_3)$ was treated with the Brønsted acids $\text{H}(\text{OEt})_2\text{BAR}^{\text{F}}_4$ and HOTf, a sulfido bridge was protonated to afford $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-SH})\text{Ru}(\text{PPh}_3)]\text{X}$ ($\text{X} = \text{BAR}^{\text{F}}_4, \text{OTf}$). Likewise, the methylation reaction with Me_3OBF_4 proceeded at a $\mu\text{-S}$, generating $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-SMe})\text{Ru}(\text{PPh}_3)](\text{BF}_4)$. On the other hand, protonation of $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-O})\text{Ru}(\text{PPh}_3)$ gave a $\mu\text{-OH}$ complex, $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-OH})\text{Ru}(\text{PPh}_3)]^+$, while the analogous methylation afforded the cationic $\mu\text{-SMe}$ complex $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-SMe})(\mu\text{-O})\text{Ru}(\text{PPh}_3)]^+$.

Introduction

Transition-metal thiolato complexes have been widely studied due to their structural diversity and versatile reactivities, which may be related to unique functions of sulfur-containing active sites of metalloenzymes.¹ The chemistry of alkoxido complexes of transition metals also is quite varied, and its importance has been manifested in its broad application to various organometallic reactions.² However, research that sheds light on the differences between late-transition-metal sulfides and oxides is limited. A few reports have focused on the relative stabilities of thiolates and alkoxides of late-transition-metal complexes.^{3–7} Although the reactions of thiolato sulfurs and alkoxido oxygens coordinated to late transition metals have also been investigated by alkylation, protonation, metalation, and so forth, their differences have not been understood clearly due to the lack of

closely related thiolate/alkoxide series.^{8,9} We report herein a new series of bis(chalcogenido)-bridged heterodinuclear complexes containing germanium, a main-group element, and ruthenium, a late transition metal. These complexes are of interest from the following points of view. First, heterodinuclear germanium–ruthenium complexes that have three different types of bis(chalcogenido) bridges, bis($\mu\text{-sulfido}$), $\mu\text{-sulfido}/\mu\text{-oxo}$, and bis($\mu\text{-oxo}$) complexes, allow a systematic comparison of their structures and the reactions of thiolates and alkoxides. These complexes were prepared using $\text{Dmp}(\text{Dep})\text{Ge}(\text{SH})_2$,^{10,11} $\text{Dmp}(\text{Dep})\text{Ge}(\text{SH})(\text{OH})$, and $\text{Dmp}(\text{Dep})\text{Ge}(\text{OH})_2$, respectively, which were readily prepared in a few steps by sulfurization or oxidation of $\text{Dmp}(\text{Dep})\text{GeH}_2$ (Dmp = 2,6-dimesitylphenyl, Dep = 2,6-diethylphenyl). Another interesting point with regard to the heterodinuclear Ge–Ru system arises from the possible cooperativity of Ge and Ru in reactions. The semimetallic nature of the heavy group 14 element could confer intriguing reactivities to the transition-metal chalcogenides. Metallacycles that consist of chalcogens, late transition metals, and heavy group 14 elements are scarce. In fact, there have been no reports of the metallacycles that contain an S/O mixed system. Ando et al.

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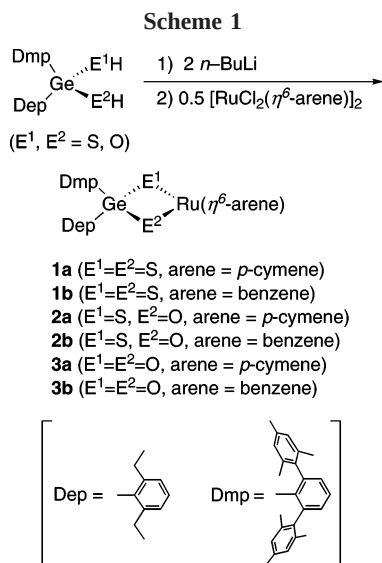
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and Steudel et al. reported independently on four- and five-membered dithiatitana- and dithiazirconacycles containing silicon, germanium, and tin.¹² Recently, Holl et al. reported the synthesis of dinuclear germanium–platinum and germanium–palladium complexes containing oxo or sulfido bridges in the course of their studies of germylene complexes.¹³ Thiolato-bridged heterodinuclear Ru–M (M = Ge, Sn, Pb) complexes were also synthesized by Goh via the reaction of the ruthenium thiolate [(η⁶-C₆Me₆)Ru(tpdt)] (tpdt = 3-thiapentane-1,5-dithiolate) with Ph₃MCl.¹⁴

Results and Discussion

Synthesis of Dmp(Dep)Ge(μ-E¹)(μ-E²)Ru(η⁶-arene) (E¹, E² = O, S). Bis(μ-sulfido) Ge–Ru complexes, Dmp(Dep)Ge(μ-S)₂Ru(η⁶-arene) (arene = *p*-cymene (**1a**), arene = benzene (**1b**)), were isolated as deep blue crystals in 87 and 84% yields, respectively, from the reactions of the corresponding [(η⁶-arene)RuCl₂]₂ complexes and Dmp(Dep)Ge(SLi)₂, which was prepared from Dmp(Dep)Ge(SH)₂ and 2 equiv of *n*-BuLi in THF (Scheme 1).¹⁰ All of the spectral data are in accord with the above formulation. In the ¹H NMR spectra, the aromatic protons of the η⁶-coordinated *p*-cymene of **1a** were observed at δ 4.71 and 4.57 as an AX pattern. The η⁶-benzene proton signal of **1b** was observed as a singlet at δ 4.74. Despite the coordinative unsaturation of the ruthenium, these complexes are quite stable in air, even in a toluene solution.

Similarly, the μ-oxo/μ-sulfido and the bis(μ-oxo) complexes Dmp(Dep)Ge(μ-S)(μ-O)Ru(η⁶-arene) (arene = *p*-cymene (**2a**), benzene (**2b**)) and Dmp(Dep)Ge(μ-O)₂Ru(η⁶-arene) (arene = *p*-cymene (**3a**), benzene (**3b**)) were synthesized from Dmp(Dep)Ge(SH)(OH) and Dmp(Dep)Ge(OH)₂, respectively, as deep purple and reddish purple crystals. Because a mixture of *R* and *S* isomers of Dmp(Dep)Ge(SH)(OH) was used for the reactions, **2a,b** were obtained as racemic mixtures. The chirality at Ge is reflected by the ¹H NMR spectra of **2a,b**. For instance, two mesityl groups of Dmp are observed independently in each

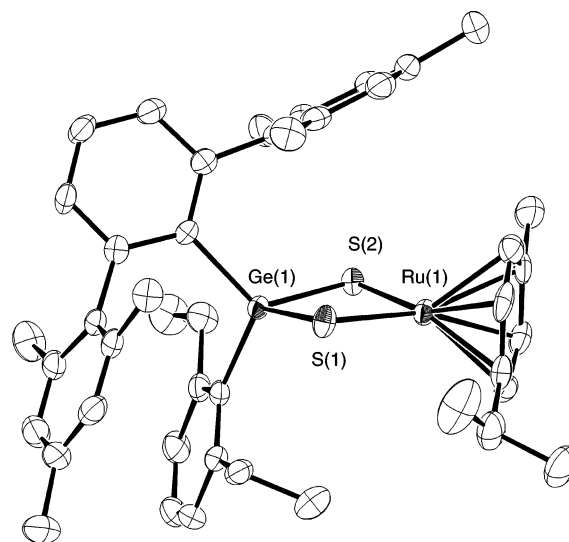


Figure 1. Molecular structure of Dmp(Dep)Ge(μ-S)₂Ru(η⁶-*p*-cymene) (**1a**) with thermal ellipsoids drawn at the 40% level.

complex, exhibiting two singlets for the four mesityl aromatic protons and two singlets for the four *o*-Me group protons. Two *m*-CH protons of the Dmp central ring are also inequivalent.

The UV–vis spectra of **1a,b–3a,b** each show an absorption band characteristic of coordinatively unsaturated half-sandwich ruthenium complexes. Complexes **1a,b** show bands at 658 and 660 nm, respectively, which are similar to those of (η⁶-arene)Ru(SR)₂ and related coordinatively unsaturated complexes.¹⁵ The bands are blue-shifted on going from the complexes with bis(sulfido) bridges to sulfido/oxo bridges and to bis(oxo) bridges, where the corresponding bands for **2a,b** and **3a,b** appear at 598, 601 nm and 475, 476 nm, respectively. As is evident from the large ε values (~10³) and from the observed blue shift, the absorptions are attributable to the LMCT transitions from the pπ orbitals of the bridging chalcogens to a vacant Ru d orbital. A similar hypsochromic shift was reported for the absorption band of (η⁶-arene)Ru(SAr)₂ relative to that of the selenolato analogue.^{15c}

Crystal Structures of 1a–3a. The monomeric nature of complexes **1a–3a** was confirmed by X-ray structural analysis. The molecular structure of **1a** is shown in Figure 1, while the structures of the other compounds are very much alike; selected bond distances and angles are given in Table 1. The bulky aryl groups on Ge and η⁶-arene on Ru prevent the molecule from being dimerized. The geometry around the ruthenium may be described as a two-legged piano stool. All of the four-membered Ge(μ-E¹)(μ-E²)Ru rings are approximately planar, and the largest deviation from planarity was found for **1a**, in which the dihedral angle between the planes S(1)–Ge(1)–S(2) and S(1)–Ru(1)–S(2) is 11.6°. The planar geometry would enhance the π overlap between S (or O) pπ orbitals and a vacant Ru d orbital to ease the electron deficiency at Ru, as was discussed for Cp*Ru-(PR₃)X by Caulton et al.¹⁶ The multiple-bonding character of

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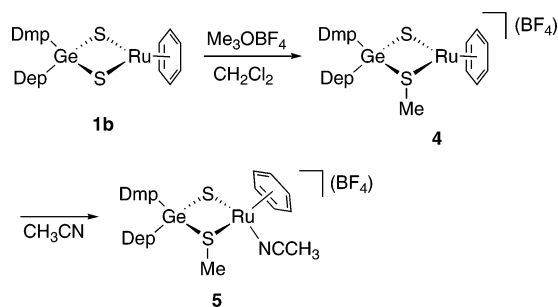
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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1a–3a** and **4**

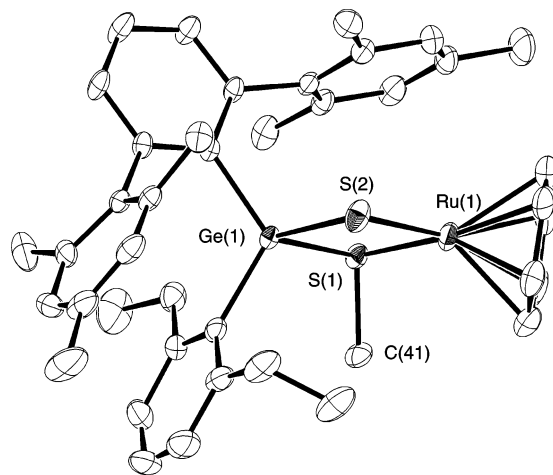
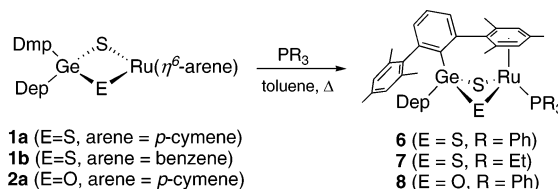
	1a (E ¹ = S(1), E ² = S(2))	2a (E ¹ = S(1), E ² = O(1))	3a (E ¹ = O(1), E ² = O(2))	4 (E ¹ = S(1), E ² = S(2))
Ru(1)–E ¹	2.3091(10)	2.295(2)	1.990(2)	2.3878(12)
Ru(1)–E ²	2.2954(8)	1.998(2)	1.991(3)	2.2466(14)
Ge(1)–E ¹	2.2201(8)	2.2424(9)	1.789(3)	2.3081(11)
Ge(1)–E ²	2.2327(9)	1.762(2)	1.787(2)	2.2307(13)
Ru(1)–(η^6 -arene)	1.669(2)	1.649(2)	1.655(3)	1.670(3)
S(1)–C(41)				1.818(4)
Ru(1)–E ¹ –Ge(1)	90.77(3)	81.39(3)	94.81(12)	89.09(3)
Ru(1)–E ² –Ge(1)	90.81(3)	103.63(11)	94.82(13)	94.76(5)
E ¹ –Ru(1)–E ²	86.74(3)	83.79(7)	79.36(11)	86.89(4)
E ¹ –Ge(1)–E ²	90.49(3)	91.00(7)	90.59(13)	89.28(5)
Ru(1)–S(1)–C(41)				102.70(16)
Ge(1)–S(1)–C(41)				104.50(17)
dihedral ^a	11.6	4.4	6.5	2.5

^a Dihedral angles between planes Ru–E¹–E² and Ge–E¹–E².**Scheme 2**

the Ru–S and the Ru–O bonds is manifested by their short bond distances in **1a** (Ru–S = 2.3091(10), 2.2954(8) Å), **2a** (Ru–S = 2.295(2) Å, Ru–O = 1.998(2) Å), and **3a** (Ru–O = 1.990(2), 1.991(3) Å), which are similar to the Ru–S and the Ru–O bond lengths of the reported electron-deficient ruthenium thiolates and alkoxides, respectively.^{15,17,18} The short distances between Ru and the η^6 -arene planes (**1a**, 1.669(2) Å; **2a**, 1.649(2) Å; **3a**, 1.655(3) Å) are also attributable to the electron deficiency of the ruthenium. On the other hand, the Ge–S bond distances of **1a** (2.2201(8), 2.2327(9) Å) and **2a** (2.2424(9) Å) and the Ge–O bond distances of **2a** (1.762(2) Å) and **3a** (1.789(3), 1.787(2) Å) are ordinary values for Ge–S and Ge–O single bonds, respectively.^{10a,19,20}

Methylation of 1b on μ -Sulfide. Treatment of **1b** with Me₃OBF₄ in CH₂Cl₂ afforded the monomethylated complex Dmp(Dep)Ge(μ -S)(μ -SMe)Ru(η^6 -benzene) (**4**) in 64% yield as purple crystals (Scheme 2). Further methylation did not take place, even in the presence of excess Me₃OBF₄.

In the UV–vis spectra, the CT band was observed at 548 nm, which is notably blue-shifted from the absorption maximum of **1b**. The ¹H NMR spectrum shows the μ -SMe signal as a sharp singlet at δ 1.83 with an integrated intensity of 3H, indicating that one of the two bridging sulfurs is methylated. According to the X-ray-derived structure of **4**, as shown in Figure 2, methylation occurred from the side opposite to Dmp, probably to avoid steric congestion. The methyl group orients

**Figure 2.** Molecular structure of Dmp(Dep)Ge(μ -S)(μ -SMe)Ru(η^6 -benzene) (**4**) with thermal ellipsoids drawn at the 40% level. Hydrogen atoms and the BF₄[−] anion are omitted for clarity.**Scheme 3**

perpendicularly to the Ru(1)–Ge(1) vector, and the four-membered metallacycle assumes a planar geometry, as was observed for **1a**. The elongation of the Ru(1)–S(1) bond (2.3878(12) Å) and concomitant shortening of the Ru(1)–S(2) bond (2.2466(14) Å), relative to those of **1a** (vide supra), are understandable, because the S(1) $p\pi$ –Ru(1) d interaction becomes weaker upon methylation at S(1). The methylation also brought about the elongation of the Ge(1)–S(1) bond (2.3081(11) Å) relative to that of **1a**, while the Ge(1)–S(2) bond distance is unchanged.

The coordinative unsaturation of **4** is manifested in its reactions. When the purple complex **4** was dissolved in acetonitrile, the solution turned brown, from which the acetonitrile adduct **5** was isolated in quantitative yield. The ¹H NMR spectrum shows singlet signals at δ 1.41 for SMe and δ 2.11 for MeCN. The facile addition of MeCN is in contrast with the robustness of **1b** even in a refluxing acetonitrile solution, indicating that the S-methylation enhances coordinative unsaturation of Ru.

Reactions of 1a,b and 2a,b with PPh₃ and PET₃. When a toluene solution of **1a** and PPh₃ was heated to 100 °C for 10 h, the solution changed from deep blue to orange. A standard workup, followed by recrystallization from toluene/hexane, gave the phosphine adduct Dmp(Dep)Ge(μ -S)₂Ru(PPh₃) (**6**) in 87% yield as orange crystals (Scheme 3). In this reaction, the *p*-cymene ligand was replaced by a mesityl group of Dmp, and the coordination of PPh₃ led to the 18-electron ruthenium complex. A similar reaction of **1b**, having the more labile η^6 -benzene instead of η^6 -*p*-cymene, proceeded more quickly and gave the same adduct, **6**, in 82% yield within 5 h at 100 °C. The PET₃ adduct **7** was also synthesized similarly in 87% yield from **1a** within 6 h at 80 °C.

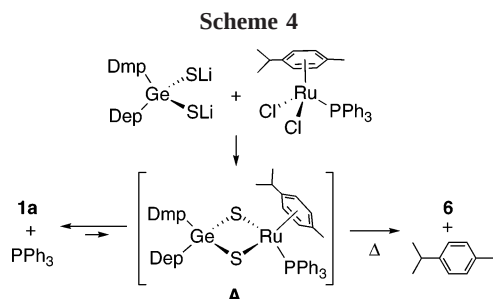
The reaction of Dmp(Dep)Ge(SLi)₂ and the triphenylphosphine-coordinated ruthenium complex (η^6 -cymene)Ru(PPh₃)Cl₂ provided information on the phosphine-addition reaction

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(18) A similar electron-deficient ruthenium alkoxide complex, Cp^{*}Ru(PCy₃)OR (R = CH₂CF₃ and SiPh₃, Cy = cyclohexyl), was reported to have values of 2.0278(17) and 2.090(3) Å for the Ru–O distances.^{16a}

(19) Baines, K. M.; Stubbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.

(20) The Ge–O bond distances of Dmp(Dep)Ge(OH)₂ are 1.761(2) and 1.789(2) Å: unpublished results.



mechanism. After addition of $(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{PPh}_3)\text{Cl}_2$ to $\text{Dmp}(\text{Dep})\text{Ge}(\text{SLi})_2$ in THF at -70°C , gradual warming of the yellow solution caused the color change to deep blue, where the generation of $1\mathbf{a}$ was detected by UV–vis spectra. When the crude blue product was heated to 100°C in toluene thereafter, the phosphine adduct 6 was obtained in 88% yield. A mechanism consistent with the observations is depicted in Scheme 4. The phosphine adduct $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})_2\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{PPh}_3)$ ($\mathbf{A}$) may be involved as an intermediate in the reaction of $1\mathbf{a}$ and PPh_3 as well as of that of $(\eta^6\text{-}p\text{-cymene})\text{-Ru}(\text{PPh}_3)\text{Cl}_2$ and $\text{Dmp}(\text{Dep})\text{Ge}(\text{SLi})_2$. The reverse reaction from $\mathbf{A}$ to $1\mathbf{a}$ would compete with an irreversible pathway to 6 , where $1\mathbf{a}$ is the kinetic product while 6 is the thermodynamic product.

In the ^1H NMR spectrum of 6 , two mesityl groups of Dmp appeared independently, exhibiting two inequivalent singlets for the four mesityl aromatic protons, two inequivalent singlets for the four *o*-Me groups, and two inequivalent singlets for the two *p*-Me groups at room temperature. Since these respective signals did not show any signs of coalescing even at 70°C in benzene- d_6 , π -coordination of the mesityl ring to Ru is strong enough to inhibit the exchange of the two mesityl groups in Dmp.

The reaction of $2\mathbf{a}$ with PPh_3 gave a similar adduct, $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-O})\text{Ru}(\text{PPh}_3)$ (8), as orange crystals in 84% yield, although $3\mathbf{a}$ and $3\mathbf{b}$ having bis(μ -oxo) bridges did not afford the corresponding adduct. Complex 8 decomposed slowly in air, which is in contrast to the extremely stable bis(μ -sulfide) complexes 6 and 7 . The ^1H NMR spectrum of 8 displays four singlets for the mesityl aromatic protons and six singlets for the mesityl methyl groups. The inequivalency is derived from the asymmetric center at Ge as well as the fixation of the η^6 -mesityl group on Ru.

Crystal Structures of Compounds 6 and 8. The molecular structures of 6 and 8 are shown in Figures 3 and 4, respectively. The geometry around Ru is an ordinary three-legged piano-stool configuration capped by a mesityl group of Dmp in each complex. The central four-membered metallacycles are extremely puckered, and the dihedral angle of 6 between the planes of $\text{S}(1)\text{—Ge}(1)\text{—S}(2)$ and $\text{S}(1)\text{—Ru}(1)\text{—S}(2)$ is 46.8° , while the corresponding dihedral angle of 8 is 40.4° . In complex 8 , the four-membered ring is rather strained, as indicated by the acute $\text{Ru}(1)\text{—S}(1)\text{—Ge}(1)$ angle ($76.25(2)^\circ$), due to the $\mu\text{-O}$ atom, which has a smaller bond radius relative to that of $\mu\text{-S}$. The Ru—S bond distances of 6 (2.4185(7) and 2.4007(8) Å) are significantly longer compared to those of $1\mathbf{a}$ and the coordinatively unsaturated ruthenium(II) thiolato complexes (Table 2).^{15,21} Similarly, the distances of $\text{Ru}(1)\text{—S}(1)$ (2.4371(9) Å) and $\text{Ru}(1)\text{—O}(1)$ (2.075(2) Å) for 8 are longer than those for $2\mathbf{a}$ (Table 3).²²

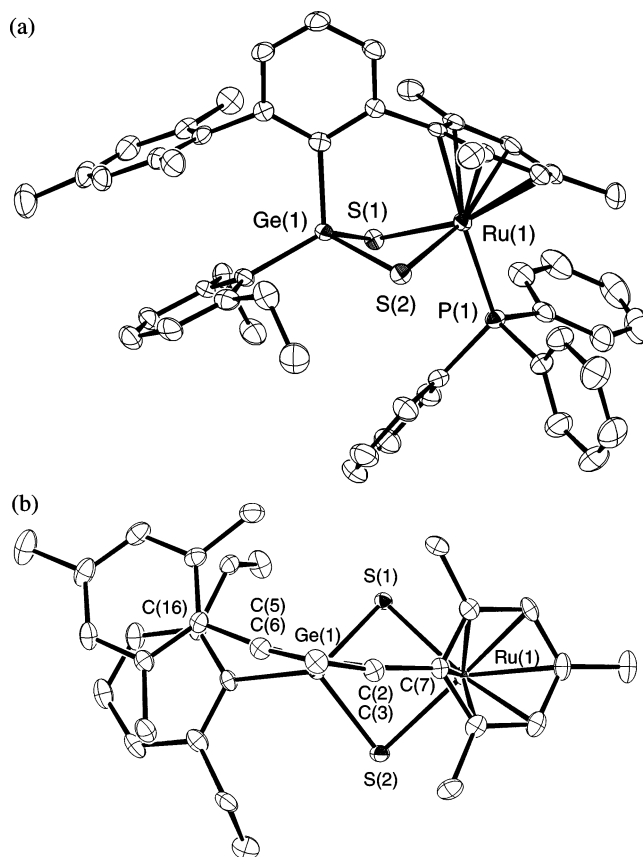


Figure 3. Molecular structures of $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})_2\text{Ru}(\text{PPh}_3)$ (6) with thermal ellipsoids drawn at the 40% level: (a) side view, with hydrogen atoms omitted for clarity; (b) top view, with hydrogen atoms and PPh_3 omitted for clarity.

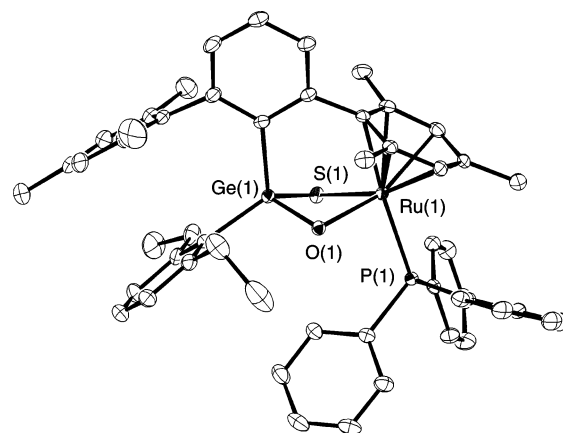


Figure 4. Molecular structure of $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-O})\text{Ru}(\text{PPh}_3)$ (8) with thermal ellipsoids drawn at the 40% level. Hydrogen atoms are omitted for clarity.

A structural feature common to 6 and 8 is the distorted *m*-terphenyl arrangement of Dmp. As is obvious from the top view of 6 (Figure 3b), the projection of the two bonds that conjunct the Dmp central aromatic ring and each mesityl group is significantly deviated from a straight line. The distortion is also obvious from the significantly large dihedral angle, 19.0° , between the planes defined by $\text{C}(5)\text{—C}(6)\text{—C}(16)$ and $\text{C}(2)\text{—C}(3)\text{—C}(7)$ for 6 . As is observed for $1\mathbf{a}$ – $3\mathbf{a}$, as well as for germanium compounds having both Dmp and Dep ligands such as $\text{Dmp}(\text{Dep})\text{GeS}_x$ ($x = 4, 6$), Dep and a mesityl group of Dmp prefer to assume an offset $\pi\text{—}\pi$ stacked configuration.^{10b} The offset $\pi\text{—}\pi$ stacking is reported to be thermodynamically preferable and is observed in various $\pi\text{—}\pi$ stacked aromatic

(21) For several examples of ruthenium(II) thiolate, see: (a) Coto, A.; Rios, I. D. I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1999**, 4309. (b) Bartucz, T. Y.; Golombek, A.; Lough, A. J.; Maltby, P. A.; Morris, R. H.; Ramachandran, R.; Schlaf, M. *Inorg. Chem.* **1998**, 37, 1555. (c) Huang, J.; Li, C.; Nolan, S. P.; Petersen, J. L. *Organometallics* **1998**, 17, 3516. (d) Burn, M. J.; Fickes, M. G.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1995**, 14, 137.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6**, **9**, and **12**

	6	9	12
Ru(1)–S(1)	2.4185(7)	2.3682(6)	2.4098(9)
Ru(1)–S(2)	2.4007(8)	2.4133(7)	2.4057(6)
Ge(1)–S(1)	2.2082(7)	2.3227(6)	2.3148(7)
Ge(1)–S(2)	2.2106(6)	2.1905(6)	2.2004(8)
Ru(1)–P(1)	2.3248(8)	2.3516(7)	2.3708(8)
Ru(1)–(η^6 -Mes)	1.742(2)	1.737(1)	1.773(2)
S(1)–R		1.23(3) (to H(66))	1.811(3) (to C(53))
Ru(1)–S(1)–Ge(1)	82.12(2)	83.61(2)	83.59(2)
Ru(1)–S(2)–Ge(1)	82.48(2)	85.43(2)	86.15(2)
S(1)–Ru(1)–S(2)	83.57(2)	83.44(2)	81.95(2)
S(1)–Ge(1)–S(2)	93.23(3)	89.62(2)	88.71(2)
S(1)–Ru(1)–P(1)	85.54(3)	92.04(2)	99.32(3)
S(2)–Ru(1)–P(1)	87.08(2)	85.46(2)	87.08(2)
dihedral ^a	46.8	45.2	46.9

^a Dihedral angles between planes Ru(1)–S(1)–S(2) and Ge(1)–S(1)–S(2).

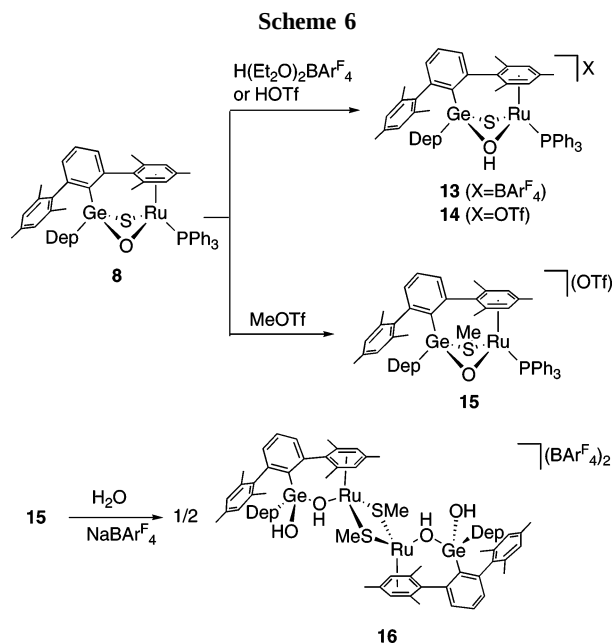
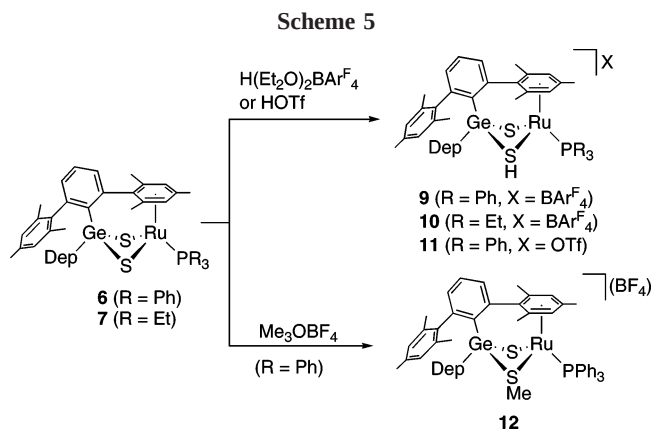
Table 3. Selected Bond Lengths (Å) and Angles (deg) for **8** and **13**

	8	13
Ru(1)–S(1)	2.4371(9)	2.4210(5)
Ru(1)–O(1)	2.075(2)	2.1371(15)
Ge(1)–S(1)	2.2220(10)	2.1886(6)
Ge(1)–O(1)	1.770(2)	1.8837(17)
Ru(1)–P(1)	2.3526(11)	2.3508(6)
Ru(1)–(η^6 -Mes)	1.714(2)	1.7047(11)
O(1)–H(66)		0.84(3)
Ru(1)–S(1)–Ge(1)	76.25(2)	79.672(18)
Ru(1)–O(1)–Ge(1)	96.73(10)	94.54(6)
S(1)–Ru(1)–O(1)	79.60(6)	79.57(4)
S(1)–Ge(1)–O(1)	92.54(8)	91.51(4)
S(1)–Ru(1)–P(1)	90.64(3)	88.86(2)
O(1)–Ru(1)–P(1)	88.90(7)	89.03(4)
dihedral ^a	40.5	40.3

^a Dihedral angles between planes Ru(1)–S(1)–O(1) and Ge(1)–S(1)–O(1).

compounds.²³ In **6** and **8**, configurations having a greater overlap of Dep and a mesityl group would be quite unfavorable, due to the large steric repulsion between their *o*-alkyl substituents. Since the Dmp group of **6** or **8** includes another mesityl group which is coordinated onto Ru fixed by two μ -sulfides, it assumes a deformed *m*-terphenyl configuration.

Protonation and Methylation Reactions of 6–8. To a dichloromethane solution of **6** and **7** was added 1 equiv of H(OEt₂)₂BARF₄ to give the protonated cationic compounds **9** (72% yield) and **10** (61% yield) as yellow crystals, respectively (Scheme 5). In either reaction, one μ -S was selectively proto-



nated. Addition of HOTf to **6** also gave the same protonated compound **11**, having a triflate as a counteranion instead of BARF₄.

The S–H stretching bands of **9** were observed in the Raman and IR spectra at 2490 and 2489 cm^{−1}, respectively. The ¹H NMR spectrum shows the μ -SH signal at δ −0.33 as a doublet with *J*_{P–H} = 6.9 Hz. The assignment was confirmed by treatment of **9** with D₂O, which caused the facile disappearance of the signal in the ¹H NMR spectra.

The reaction of **6** with Me₃OBF₄ in dichloromethane also proceeded similarly to give the monomethylated cationic complex **12** in 62% yield. The ¹H NMR spectrum exhibits a singlet for SMe at δ 0.71, which resonates at higher magnetic field compared to the normal SMe proton region. This is probably due to the anisotropic effect of the phenyl groups of PPh₃, which stay close to SMe, as is obvious from the crystal structure (vide infra).

As for the protonation of **8** having oxo/sulfido bridges, the oxo bridge was selectively protonated. Addition of H(OEt₂)₂BARF₄ or HOTf to **8** in toluene afforded **13** or **14** in 85% and 88% yield, respectively (Scheme 6). All the spectral data support their μ -OH structure. The IR spectra did not show the S–H stretching band that was clearly observed for the μ -SH complex **9**. In the ¹H NMR spectra of **13** and **14**, the signals at δ −1.01 and 0.66 assigned to the μ -OH protons were observed as a singlet, respectively, while the μ -SH signal of either **9** or **10** appeared as a doublet due to the proton–phosphorus coupling.

(22) For several examples of ruthenium(II) alkoxide, aryloxide, and siloxide, see: (a) Yip, K.-L.; Yu, W.-Y.; Chan, P.-M.; Zhu, N.-Y.; Che, C.-M. *Dalton Trans.* **2003**, 3556. (b) Hirano, T.; Oi, T.; Nagano, H.; Morokuma, K. *Inorg. Chem.* **2003**, 42, 6575. (c) Lai, Y.-H.; Chou, T.-Y.; Song, Y.-H.; Liu, C.-S.; Chi, Y.; Carty, A. J.; Peng, S.-M.; Lee, G.-H. *Chem. Mater.* **2003**, 15, 2454. (d) Hennig, M.; Puntener, K.; Scalone, M. *Tetrahedron: Asymmetry* **2000**, 11, 1849. (e) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, 123, 1090. (f) Everaere, K.; Mortreux, A.; Bulliard, M.; Brussee, J.; van der Gen, A.; Nowogrocki, G.; Carpentier, J.-F. *Eur. J. Org. Chem.* **2001**, 275. (g) Onitsuka, K.; Ajioka, Y.; Matsushima, Y.; Takahashi, S. *Organometallics* **2001**, 20, 3274. (h) Rath, R. K.; Nethaji, M.; Chakravarty, A. R. *Polyhedron* **2001**, 20, 2735. (i) Brunner, H.; Zwack, T.; Zabel, M.; Beck, W.; Böhm, A. *Organometallics* **2003**, 22, 1741. (j) Stobart, S. R.; Zhou, X.; Cea-Olivares, R.; Toscano, A. *Organometallics* **2001**, 20, 4766.

(23) (a) Janiak, C. *Dalton Trans.* **2000**, 3885. (b) Lorenzo, S.; Lewis, G. R.; Dance, I. *New J. Chem.* **2000**, 24, 295.

The absence of coupling between the phosphorus and the μ -OH proton may be attributed to the weak interaction between Ru and OH, as is shown in the X-ray-derived structure of **13** (vide infra).

In contrast to the protonation reaction, methylation of **8** occurred at the sulfido bridge selectively. Treatment with methyl trifluoromethanesulfonate in ether afforded the monomethylated product as a yellow powder in 52% yield, which was identified as [Dmp(Dep)Ge(μ -SMe)(μ -O)Ru(PPh₃)](OTf) (**15**). Although we failed to crystallize **15**, the X-ray structural analysis of **16** that formed by hydrolyzation of **15** obviously shows the S-selective methylation of **8**.²⁴ The S-methylated complex **15** was hydrolyzed at the Ge-SMe bond, and the subsequent formation of the intermolecular bis(μ -SMe) bridges at the ruthenium centers with concomitant PPh₃ dissociation would afford **16**.

The properties of μ -sulfide and μ -oxide of **8** can be summarized as follows. The μ -sulfide of **8** shows higher nucleophilicity relative to the μ -oxide. Meanwhile, the μ -oxide is more basic compared to the μ -sulfide. These characteristic properties are reasonable according to the HSAB (hard and soft acid-base) principle²⁵ and also fit the known results that alkanethiols and protonated alkyl thioethers show higher acidity relative to the corresponding alcohols and protonated alkyl ethers, respectively.²⁶

Crystal Structures of Compounds 9, 12, and 13. X-ray structures of **9**, **12**, and **13** reveal the unique properties of the cationic Ge-Ru complexes. Of interest is their characteristic geometrical changes around the chalcogen bridges. The S(1)-protonated complex **9** has a shorter Ru(1)-S(1) bond distance (2.3682(6) Å) compared to that of the Ru(1)-S(2) bond (2.4133(7) Å) and to those of the Ru-S bonds for **6** (Table 2). A similar M-S bond shortening upon S-alkylation of coordinatively saturated metal thiolato complexes has been reported.^{10,27} The bond shortening would be due to the elimination of repulsive interactions between the filled d orbitals on the metals and the sulfur lone pair, although the lower σ -donor properties of the sulfur atom could increase the M-S bond distance concurrently.²⁷

On the other hand, the corresponding Ru(1)-S(1) bond of the S(1)-methylated complex **12** does not become shorter, having a distance similar to that of the Ru(1)-S(2) bond (Figure 5, Table 2). This might be because the steric repulsion between SMe and PPh₃ hampers the Ru(1)-S(1) bond shortening, as is suggested by the X-ray structure in Figure 5. The steric congestion around the SMe group is evident in the larger bond angle of S(1)-Ru(1)-P(1) (99.32(3)°) compared to that of the protonated complex **9** (92.04(2)°). Furthermore, the S(1)-C(53) vector is directed toward the germanium side due to steric congestion.

In contrast to the Ru-S bond shortening upon protonation, the O-protonation brought about a significant Ru-O bond elongation from 2.075(2) Å for **8** to 2.1371(15) Å for **13**. This result indicates that the σ -donor ability of O greatly affects the Ru-O bond, while the decreased repulsive π -orbital interaction may be less important here.

The bond elongations between the germanium and the protonated/methylated sulfur are also notable. The Ge(1)-S(1)

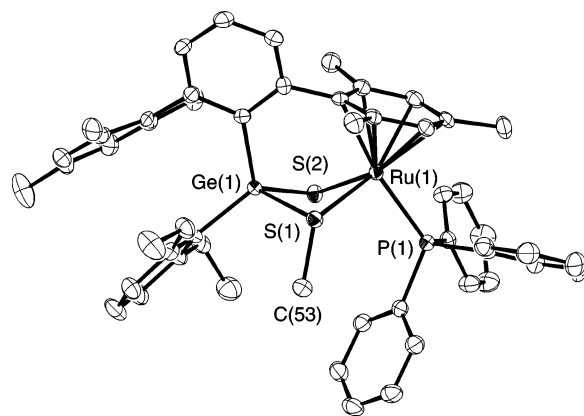


Figure 5. Molecular structure of [Dmp(Dep)Ge(μ -S)(μ -SMe)-RuPPh₃](BF₄) (**12**) with thermal ellipsoids drawn at the 40% level. Hydrogen atoms, dichloromethane, and the BF₄⁻ anion are omitted for clarity.

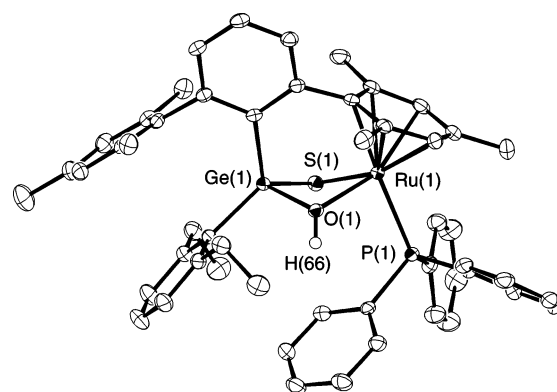
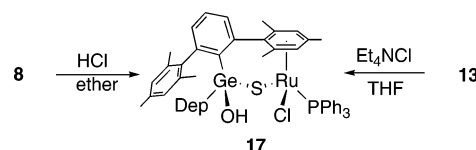


Figure 6. Molecular structure of [Dmp(Dep)Ge(μ -S)(μ -OH)-RuPPh₃](BARF₄) (**13**) with thermal ellipsoids drawn at the 40% level. Hydrogen atoms, toluene, and the BARF₄⁻ anion are omitted for clarity.

Scheme 7



bond distances of **9** and **12** (2.3227(6) and 2.3148(7) Å) are significantly longer than those of **6** as well as the reported Ge-S single bonds,¹⁹ which indicates that the Ge-S bonds become weak upon protonation/methylation of μ -S. Likewise, the Ge-O bond is elongated upon protonation of the μ -oxide of **8** (Figure 6 and Table 3).

Reactions of the Methylated/Protonated Complexes 9, 12, and 13 with NEt₄Cl. The characteristic structural changes caused by the protonation and the methylation were reflected in the reactivities of these complexes with NEt₄Cl. Reaction of the μ -OH complex **13** with NEt₄Cl in THF took place immediately at room temperature, and the Ru-O bond was cleaved by nucleophilic Cl⁻ addition at Ru to afford the ruthenium-chloride complex **17** (Scheme 7). Reaction of the μ -oxo/ μ -sulfido complex **8** with HCl in ether also afforded **17** in 83% yield. The stereochemistry of **17** was confirmed by X-ray structural analysis. Another diastereomer was not observed, probably due to its steric congestion. The Cl...O distance of **17** (3.25(1) Å) indicates the O-H...Cl hydrogen bonding, which could also facilitate the formation of **17**.^{9a}

(24) Although the structure of **16** is evident from the X-ray analysis, the other possible diastereomers could be generated by hydrolyzation reactions of **15**. The ¹H NMR spectrum of the crude product is too complicated to allow identification of all the signals.

(25) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643.

(26) Ho, T.-L. *Chem. Rev.* **1975**, *75*, 1.

(27) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L. *Inorg. Chem.* **1988**, *27*, 191.

In contrast to the facile Ru–O dissociation, the S-protonated/methylated complexes **9** and **12** either did not afford any adduct by treatment with NEt_4Cl , even at 60 °C in THF. The difference in the reactivities of the $\mu\text{-OH}$ complex **13** and the $\mu\text{-SH}$ complex **9** is due to the respective structural changes upon protonation described above.

Summary

We synthesized a series of μ -sulfido and μ -oxo heterodinuclear germanium–ruthenium complexes, $\text{Dmp(Dep)Ge}(\mu\text{-E})_2\text{Ru}(\eta^6\text{-arene})$ and $\text{Dmp(Dep)Ge}(\mu\text{-S})(\mu\text{-E})\text{Ru}(\text{PR}_3)$ ($\text{E} = \text{O}, \text{S}$), from the corresponding diarylgermanedichalcogenols, respectively. The characteristic properties of the μ -oxide and the μ -sulfide are represented by protonation and methylation reactions. X-ray structural analysis reveals their characteristic structural changes upon protonation and methylation around both the ruthenium and the germanium atoms, which is in accordance with their reactions. As is suggested from the reaction of the dinuclear $\mu\text{-OH}$ complex with Cl^- , the ruthenium and the germanium work cooperatively through the bridging chalcogen atom. The chalcogenido-bridged Ge–Ru complexes undergo various new reactions via cooperation of Ge and Ru as well as S and O.

Experimental Section

General Considerations. All reactions and manipulations of air-sensitive compounds were conducted under an inert atmosphere of dry nitrogen by employing standard Schlenk techniques. Toluene, THF, diethyl ether, and hexane were distilled from sodium/benzophenone ketyl under nitrogen. Dichloromethane, acetonitrile, and hexamethyldisiloxane (HMDSO) were distilled from CaH_2 .

^1H NMR (500 or 600 MHz) and ^{31}P NMR spectra (202 or 243 MHz) were recorded on a JEOL JNM-ECP500 or ECA600 spectrometer. ^1H NMR chemical shifts are given in ppm relative to the residual protons of deuterated solvents. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts were referenced to signals of external 85% H_3PO_4 . IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Raman spectra were measured on a Perkin-Elmer Spectrum 2000 with a Nd YAG laser. For UV–vis spectra, a JUSCO V-560 spectrometer was used. Elemental analyses were performed on LECO CHN-900 and CHNS-932 microanalyzers.

Synthesis of Dmp(Dep)Ge(SH)_2 . A THF/ethanol (20/1) solution of Dmp(Dep)GeS_x ($x = 4, 6$) prepared by sulfurization of Dmp(Dep)GeH_2 (1.0 g, 1.9 mmol)¹ was treated with NaBH_4 (150 mg, 4.0 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h. After treatment with aqueous 0.5 M HCl and extraction with CH_2Cl_2 , the organic layer was dried over MgSO_4 and evaporated to dryness. The residue was recrystallized from CH_2Cl_2 /hexane to give Dmp(Dep)Ge(SH)_2 (470 mg, 0.80 mmol, 42% yield based on Dmp(Dep)GeH_2) as a white powder. ^1H NMR (500 MHz, CDCl_3): δ 7.45 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.14 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.01 (d, $J = 7.8$ Hz, 2H, $m\text{-CH}$ of Dmp), 6.82 (d, $J = 7.8$ Hz, 2H, $m\text{-CH}$ of Dmp), 6.74 (s, 4H, $m\text{-CH}$ of Mes), 2.26 (dq, $J = 7.8$ Hz, 14.2 Hz, 4H, CH_2CH_3 of Dep), 2.26 (s, 6H, $p\text{-CH}_3$ of Mes), 1.97 (s, 12H, $o\text{-CH}_3$ of Mes), 1.01 (t, $J = 7.3$ Hz, 6H, CH_2CH_3 of Dep), 0.52 (s, 2H, GeSH). Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{GeS}_2$: C, 69.76; H, 6.89; S, 10.95. Found: C, 69.55; H, 7.30; S, 10.28.

Synthesis of $\text{Dmp(Dep)Ge(SH)(OH)}$. To a THF solution of Dmp(Dep)GeS_x ($x = 4, 6$) prepared from Dmp(Dep)GeH_2 (1.0 g, 1.9 mmol) was added H_2O (1 mL) and PPh_3 (1.5 g, 5.7 mmol) in air. After the mixture was stirred at room temperature for 12 h, the solution was evaporated to dryness and the residue was chromatographed on silica gel eluted with 5/1 hexane/ CH_2Cl_2 to give $\text{Dmp(Dep)Ge(SH)(OH)}$ (550 mg, 0.97 mmol, 51% yield based on

Dmp(Dep)GeH_2) as a white powder. ^1H NMR (500 MHz, CDCl_3): δ 7.47 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.10 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.04 (d, $J = 7.3$ Hz, 2H, $m\text{-CH}$ of Dmp), 6.79 (s, 2H, $m\text{-CH}$ of Mes), 6.64 (s, 2H, $m\text{-CH}$ of Mes), 2.49 (br q, $J = 7.8$ Hz, 4H, CH_2CH_3 of Dep), 2.25 (s, 6H, $p\text{-CH}_3$ of Mes), 2.06 (s, 6H, $o\text{-CH}_3$ of Mes), 1.93 (s, 6H, $o\text{-CH}_3$ of Mes), 1.17 (s, 1H, GeOH), 1.01 (t, $J = 7.8$ Hz, 6H, CH_2CH_3 of Dep), 0.06 (s, 1H, GeSH). Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{GeOS}$: C, 71.72; H, 7.08; S, 5.63. Found: C, 71.66; H, 7.50; S, 5.56.

Synthesis of Dmp(Dep)Ge(OH)_2 . To a CH_2Cl_2 solution of Dmp(Dep)GeH_2 (504.2 mg, 0.967 mmol) was added 3-chloroperoxybenzoic acid (500.7 mg, 2.90 mmol), and the mixture was stirred overnight at room temperature. The resulting light yellow suspension was filtered, and the solution was separated by silica gel chromatography (with 4/1 hexane/ CH_2Cl_2) and recrystallized from CH_2Cl_2 /EtOH to afford Dmp(Dep)Ge(OH)_2 as a white powder (215.2 mg, 0.389 mmol, 40% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.50 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.11 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.07 (d, $J = 7.3$ Hz, 2H, $m\text{-CH}$ of Dmp), 6.78 (d, $J = 7.8$ Hz, 2H, $m\text{-CH}$ of Dmp), 6.74 (s, 4H, $m\text{-CH}$ of Mes), 2.39 (dq, $J = 7.8$ Hz, 14.2 Hz, 4H, CH_2CH_3 of Dep), 2.25 (s, 6H, $p\text{-CH}_3$ of Mes), 2.00 (s, 12H, $o\text{-CH}_3$ of Mes), 1.14 (s, 2H, GeOH), 1.00 (t, $J = 7.3$ Hz, 6H, CH_2CH_3 of Dep). Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{GeO}_2$: C, 73.81; H, 7.29. Found: C, 73.80; H, 7.33.

Synthesis of $\text{Dmp(Dep)GeS}_2\text{Ru}(\eta^6\text{-p-cymene})$ (1a**).** To a THF solution of Dmp(Dep)Ge(SH)_2 (150 mg, 0.26 mmol) was added $n\text{-BuLi}$ (0.34 mL of a 1.6 M solution in hexane, 0.54 mmol) at -78 °C, and the mixture was stirred for 30 min. $[(\eta^6\text{-p-cymene})\text{-RuCl}_2]_2$ (79 mg, 0.13 mmol) was then added, and this mixture was stirred at 25 °C for 12 h to give a dark blue solution. The solvent was removed in vacuo, and the residue was treated with toluene (5 mL) and the solution centrifuged to remove LiCl. The toluene solution was removed and crystallized from DME to give **1a** as deep blue crystals in 87% yield. ^1H NMR (500 MHz, C_6D_6): δ 7.19 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.08 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dep), 6.93 (d, $J = 7.3$ Hz, 1H, $m\text{-CH}$ of Dmp), 6.84 (d, $J = 7.3$ Hz, 1H, $m\text{-CH}$ of Dmp), 6.89 (s, 2H, $m\text{-CH}$ of Mes), 6.81 (d, 1H, $J = 7.3$ Hz, $m\text{-CH}$ of Dep), 6.77 (s, 4H, $m\text{-CH}$ of Mes), 4.71 (d, 2H, $J = 6.0$ Hz, $p\text{-cymene}$ arom), 4.57 (d, 2H, $J = 6.0$ Hz, $p\text{-cymene}$ arom), 3.34 (dq, $J = 7.3$ Hz, 6.9 Hz, 2H, CH_2CH_3 of Dep), 2.68 (sept, $J = 6.9$ Hz, 1H, $p\text{-cymene}$), 2.34 (dq, $J = 7.3$ Hz, 6.9 Hz, 2H, CH_2CH_3 of Dep), 2.32 (s, 6H, CH_3 of Mes), 2.27 (s, 12H, CH_3 of Mes), 2.13 (s, 6H, CH_3 of Mes), 1.93 (s, 3H, $p\text{-cymene}$), 1.14 (d, $J = 6.9$ Hz, 6H, $p\text{-cymene}$), 0.89 (t, $J = 6.9$ Hz, 3H, Me of Dep). Anal. Calcd for $\text{C}_{44}\text{H}_{52}\text{GeRuS}_2$: C, 64.55; H, 6.40; S, 7.83. Found: C, 64.16; H, 6.65; S, 7.51. UV–vis (THF): λ_{max} 658 nm (ϵ 4.1×10^3).

Synthesis of $\text{Dmp(Dep)Ge}(\mu\text{-S})_2\text{Ru}(\eta^6\text{-benzene})$ (1b**).** The synthesis of **1b** was carried out as described for **1a**, but using Dmp(Dep)Ge(SH)_2 (100 mg, 0.17 mmol) and $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ (45 mg, 0.09 mmol). Compound **1b** was isolated as deep blue crystals in 84% yield. ^1H NMR (500 MHz, C_6D_6): δ 7.18 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.08 (t, $J = 7.8$ Hz, 1H, $p\text{-CH}$ of Dep), 6.94 (d, $J = 7.8$ Hz, 2H, $m\text{-CH}$ of Dmp), 6.83 (d, $J = 7.8$ Hz, 2H, $m\text{-CH}$ of Dep), 6.70 (s, 4H, $m\text{-CH}$ of Mes), 4.74 (s, 6H, benzene), 3.27 (dq, $J = 7.3$ Hz, 6.9 Hz, 2H, CH_2CH_3 of Dep), 2.34 (dq, $J = 7.3$ Hz, 6.9 Hz, 2H, CH_2CH_3 of Dep), 2.30 (s, 6H, CH_3 of Mes), 2.27 (s, 12H, CH_3 of Mes), 1.26 (t, $J = 7.4$ Hz, 6H, CH_2CH_3 of Dep). Anal. Calcd for $\text{C}_{40}\text{H}_{44}\text{GeRuS}_2$: C, 63.00; H, 5.82; S, 8.41. Found: C, 62.88; H, 5.77; S, 8.87. UV–vis (THF): λ_{max} 660 nm (ϵ 3.8×10^3).

Synthesis of $\text{Dmp(Dep)Ge}(\mu\text{-S})(\mu\text{-O})\text{Ru}(\eta^6\text{-p-cymene})$ (2a**).** The synthesis of **2a** was carried out as described for **1a**, but using $\text{Dmp(Dep)Ge(SH)(OH)}$ (100 mg, 0.18 mmol) and $[(\eta^6\text{-p-cymene})\text{-RuCl}_2]_2$ (55 mg, 0.09 mmol). Compound **2a** was isolated as purple crystals in 88% yield. ^1H NMR (500 MHz, C_6D_6): δ 7.19 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.09 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dep),

6.95 (d, $J = 7.3$ Hz, 1H, *m*-CH of Dmp), 6.94 (s, 2H, *m*-CH of Mes), 6.83 (d, $J = 7.3$ Hz, 1H, *m*-CH of Dmp), 6.82 (d, $J = 7.3$ Hz, 1H, Dep arom), 6.78 (d, $J = 7.3$ Hz, 1H, Dep arom), 6.61 (s, 2H, *m*-CH of Mes), 4.85 (d, $J = 5.0$ Hz, 1H, *p*-cymene arom), 4.77 (d, $J = 5.0$ Hz, 1H, *p*-cymene arom), 4.69 (d, $J = 5.0$ Hz, 1H, *p*-cymene arom), 4.67 (d, $J = 5.0$ Hz, 1H, *p*-cymene arom), 3.30 (dq, $J = 7.3$ Hz, 6.9 Hz, 1H, CH_2CH_3 of Dep), 3.09 (dq, $J = 7.3$ Hz, 6.9 Hz, 1H, CH_2CH_3 of Dep), 2.65 (sept, 1H, $J = 6.9$ Hz, *p*-cymene), 2.44 (s, 6H, Mes), 2.40 (dq, $J = 7.3$ Hz, 6.9 Hz, 1H, CH_2CH_3 of Dep), 2.34 (s, 6H, Mes), 2.22 (dq, $J = 7.3$ Hz, 6.9 Hz, 1H, CH_2CH_3 of Dep), 2.08 (s, 6H, Mes), 2.01 (s, 3H, *p*-cymene), 1.28 (d, $J = 6.9$ Hz, 6H, *p*-cymene), 1.26 (br t, $J = 7.3$ Hz, 3H, CH_2CH_3 of Dep), 1.24 (br t, $J = 7.3$ Hz, 3H, CH_2CH_3 of Dep). Anal. Calcd for $\text{C}_{44}\text{H}_{52}\text{GeORuS}$: C, 65.76; H, 6.65; S, 3.99. Found: C, 65.66; H, 6.64; S, 4.38. UV-vis (THF): λ_{max} 598 nm ($\epsilon \ 3.4 \times 10^3$).

Synthesis of Dmp(Dep)Ge(μ -S)(μ -O)Ru(η^6 -benzene) (2b). The synthesis of **2b** was carried out as described for **1a**, but using Dmp(Dep)Ge(SH)(OH) (100 mg, 0.18 mmol) and $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ (45 mg, 0.09 mmol). Compound **2b** was isolated as purple crystals in 81% yield. ^1H NMR (500 MHz, C_6D_6): δ 7.17 (t, $J = 7.8$ Hz, 1H, *p*-CH of Dmp), 7.08 (t, $J = 7.8$ Hz, 1H, *p*-CH of Dep), 7.04 (d, $J = 7.3$ Hz, 1H, *m*-CH of Dmp), 6.94 (d, $J = 7.3$ Hz, 1H, *m*-CH of Dmp), 6.89 (s, 2H, *m*-CH of Mes), 6.81 (d, $J = 7.8$ Hz, 1H, *m*-CH of Dep), 6.78 (d, $J = 7.8$ Hz, 1H, *m*-CH of Dep), 6.58 (s, 2H, *m*-CH of Mes), 4.86 (s, 6H, benzene), 2.40 (br m, 1H, $\text{CH}_2\text{-CH}_3$ of Dep), 3.43 (dq, 1H, $J = 7.3$ Hz, 6.9 Hz, CH_2CH_3 of Dep), 2.24 (br m, 1H, CH_2CH_3 of Dep), 3.06 (dq, $J = 7.3$ Hz, 6.9 Hz, 1H, CH_2CH_3 of Dep), 2.43 (s, 6H, CH_3 of Mes), 2.30 (s, 6H, CH_3 of Mes), 2.13 (s, 6H, CH_3 of Mes), 1.33 (t, $J = 7.3$ Hz, 3H, CH_2CH_3 of Dep), 1.26 (t, $J = 7.3$ Hz, 3H, CH_2CH_3 of Dep). Anal. Calcd for $\text{C}_{40}\text{H}_{44}\text{GeORuS}$: C, 64.36; H, 5.94; S, 4.30. Found: C, 64.00; H, 5.82; S, 4.65. UV-vis (THF): λ_{max} 601 nm ($\epsilon \ 3.0 \times 10^3$).

Synthesis of Dmp(Dep)Ge(μ -O) $_2$ Ru(η^6 -*p*-cymene) (3a). The synthesis of **3a** was carried out as described for **1a**, but using Dmp(Dep)Ge(OH) $_2$ (100 mg, 0.18 mmol) and $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ (55 mg, 0.09 mmol). Compound **3a** was isolated as purple crystals in 69% yield. ^1H NMR (500 MHz, C_6D_6): δ 7.19 (t, $J = 7.3$ Hz, 1H, *p*-CH of Dmp), 7.09 (t, $J = 7.3$ Hz, 1H, *p*-CH of Dep), 6.95 (d, $J = 7.3$ Hz, 1H, *m*-CH of Dmp), 6.88 (d, $J = 7.3$ Hz, 1H, *m*-CH of Dmp), 6.89 (s, 2H, *m*-CH of Mes), 6.81 (d, $J = 7.3$ Hz, 1H, *m*-CH of Dep), 6.75 (s, 4H, *m*-CH of Mes), 4.68 (d, $J = 6.0$ Hz, 2H, *p*-cymene arom), 4.55 (d, $J = 6.0$ Hz, 2H, *p*-cymene arom), 3.40 (dq, $J = 7.3$ Hz, 6.9 Hz, 2H, CH_2CH_3 of Dep), 2.68 (sept, $J = 6.9$ Hz, 1H, *p*-cymene), 2.34 (dq, $J = 7.3$ Hz, 6.9 Hz, 2H, $\text{CH}_2\text{-CH}_3$ of Dep), 2.32 (s, 6H, CH_3 of Mes), 2.29 (s, 12H, CH_3 of Mes), 2.13 (s, 6H, CH_3 of Mes), 1.93 (s, 3H, *p*-cymene), 1.14 (d, $J = 6.9$ Hz, 6H, *p*-cymene), 0.93 (t, $J = 6.9$ Hz, 3H, Me of Dep). Anal. Calcd for $\text{C}_{44}\text{H}_{52}\text{GeO}_2\text{Ru}$: C, 67.19; H, 6.66. Found: C, 67.05; H, 6.69. UV-vis (THF): λ_{max} 475 nm ($\epsilon \ 2.5 \times 10^3$).

Synthesis of Dmp(Dep)Ge(μ -O) $_2$ Ru(η^6 -benzene) (3b). The synthesis of **3b** was carried out as described for **1a**, but using Dmp(Dep)Ge(OH) $_2$ (107 mg, 0.19 mmol) and $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ (49 mg, 0.097 mmol). Compound **3b** was isolated as purple crystals in 63% yield. ^1H NMR (500 MHz, C_6D_6): δ 7.14 (t, $J = 7.8$ Hz, 1H, *p*-CH of Dmp), 7.11 (t, $J = 7.8$ Hz, 1H, *p*-CH of Dmp), 6.89 (d, $J = 7.3$ Hz, 2H, *m*-CH of Dmp), 6.82 (d, $J = 7.3$ Hz, 2H, *m*-CH of Dep), 6.74 (s, 4H, *m*-CH of Mes), 4.83 (s, 6H, $\eta^6\text{-C}_6\text{H}_6$), 3.30 (dq, $J = 7.8$ Hz, 14.2 Hz, 2H, CH_2CH_3 of Dep), 2.39 (dq, $J = 7.8$ Hz, 14.2 Hz, 2H, CH_2CH_3 of Dep), 2.28 (s, 6H, *p*-CH $_3$ of Mes), 2.27 (s, 12H, *o*-CH $_3$ of Mes), 1.35 (t, $J = 7.8$ Hz, 6H, CH_2CH_3 of Dep). Anal. Calcd for $\text{C}_{40}\text{H}_{44}\text{GeO}_2\text{Ru}$: C, 65.77; H, 6.07. Found: C, 66.02; H, 6.00. UV-vis (THF): λ_{max} 476 nm ($\epsilon \ 2.0 \times 10^3$).

Synthesis of [Dmp(Dep)Ge(μ -S)(μ -SCH $_3$)Ru($\eta^6\text{-C}_6\text{H}_6$)](BF $_4$) (4). Compound **1b** (53.2 mg, 0.0697 mmol) and trimethyloxonium tetrafluoroborate (11.1 mg, 0.0750 mmol) were dissolved in $\text{CH}_2\text{-Cl}_2$ (5.0 mL), and the mixture was stirred at room temperature for

2 h. To the solution was added ether (15 mL) to give a purple powder, which was washed with ether to afford **4** (38.4 mg, 0.0444 mmol, 64%). X-ray-quality crystals were grown by layering ether onto a CH_2Cl_2 solution of **4** at room temperature. ^1H NMR (500 MHz, C_6D_6): δ 7.47 (t, $J = 7.8$ Hz, 1H, *p*-CH of Dmp), 7.18 (t, $J = 7.3$ Hz, 1H, *p*-CH of Dep), 6.97 (d, $J = 7.3$ Hz, 2H, *m*-CH of Dmp), 6.90 (d, $J = 7.4$ Hz, 1H, *m*-CH of Dep), 6.77 (d, $J = 7.4$ Hz, 1H, *m*-CH of Dep), 5.96 (s, 6H, benzene), 2.48 (s, 3H, CH_3 of Mes), 2.18 (s, 3H, CH_3 of Mes), 2.10 (s, 3H, CH_3 of Mes), 1.83 (s, 3H, $\mu\text{-SCH}_3$), 1.8 (br s, 3H, CH_3 of Mes), 1.66 (s, 3H, CH_3 of Mes), 1.36 (s, 3H, CH_3 of Mes), 1.07 (t, $J = 7.8$ Hz, 3H, CH_2CH_3 of Dep), 0.74 (t, $J = 7.8$ Hz, 3H, CH_2CH_3 of Dep). UV-visible (λ_{max} , CH_2Cl_2): 548 nm. Anal. Calcd for $\text{C}_{41}\text{H}_{47}\text{BF}_4\text{GeRuS}_2$: C, 56.96; H, 5.48; S, 7.42. Found: C, 56.32; H, 5.62; S, 6.94. UV-vis (THF): λ_{max} 548 nm ($\epsilon \ 3.4 \times 10^3$).

Synthesis of [Dmp(Dep)Ge(μ -S)(μ -SCH $_3$)Ru(CH_3CN)]($\eta^6\text{-C}_6\text{H}_6$)](BF $_4$) (5). Compound **4** (35 mg, 0.040 mmol) was dissolved in CH_3CN (5.0 mL) and stirred at room temperature for 2 h. The brown solution was evaporated to dryness, and the brown residue was washed with ether to afford compound **5** as a brown powder in 86% yield. ^1H NMR (500 MHz, CD_3CN): δ 7.48 (t, $J = 7.8$ Hz, 1H, *p*-CH of Dmp), 7.28 (t, $J = 7.8$ Hz, 1H, *p*-CH of Dep), 7.00–6.90 (m, 6H), 5.56 (s, 6H, benzene), 3.15 (dq, $J = 7.4$ Hz, 14.2 Hz, 1H, CH_2CH_3 of Dep), 2.31 (dq, $J = 7.4$ Hz, 14.2 Hz, 1H, CH_2CH_3 of Dep), 2.08 (dq, $J = 7.4$ Hz, 14.2 Hz, 1H, CH_2CH_3 of Dep), 1.81 (dq, $J = 7.4$ Hz, 14.2 Hz, 1H, CH_2CH_3 of Dep), 2.36 (br s, 6H, CH_3 of Mes), 2.22 (br s, 6H, CH_3 of Mes), 2.14 (br s, 6H, CH_3 of Mes), 2.11 (s, 3H, CH_3CN), 1.41 (s, 3H, SCH_3), 0.90 (t, $J = 7.3$ Hz, 6H, CH_2CH_3 of Dep). Anal. Calcd for $\text{C}_{43}\text{H}_{50}\text{NBF}_4\text{GeRuS}_2$: C, 57.04; H, 5.57; N, 1.55; S, 7.08. Found: C, 56.82; H, 5.98; N, 1.81; S, 6.55.

Reaction of 1a with PPh $_3$. Compound **1a** (100 mg, 0.122 mmol) and PPh_3 (34 mg, 0.13 mmol) were dissolved in toluene (5 mL) and stirred at 100 °C for 16 h. All of the volatiles were removed in vacuo, and the residue was crystallized from toluene/hexane to afford compound **6** as orange crystals in 87% yield. ^1H NMR (600 MHz, C_6D_6): δ 7.82 (br m, 6H, PPh_3), 7.33 (t, $J = 7.5$ Hz, 1H, Dmp *p*-arom), 7.00 (br m, 9H, PPh_3), 6.98 (t, $J = 7.5$ Hz, 1H, Dep *p*-arom), 6.96 (dd, $J = 7.5$ Hz, 1.4 Hz, 1H, Dmp *m*-arom), 6.90 (dd, $J = 7.5$ Hz, 1.4 Hz, 1H, Dmp *m*-arom), 6.66 (d, $J = 7.5$ Hz, 2H, Dep *m*-arom), 6.35 (s, 2H, Mes arom), 4.44 (s, 2H, Mes arom), 3.61 (dq, $J = 14.4$ Hz, 7.2 Hz, 2H, CH_2CH_3 of Dep), 2.43 (dq, $J = 14.4$ Hz, 7.2 Hz, 2H, CH_2CH_3 of Dep), 2.29 (s, 6H, *o*-CH $_3$ of Mes), 2.21 (s, 6H, *o*-CH $_3$ of Mes), 2.03 (s, 3H, *p*-CH $_3$ of Mes), 1.26 (t, $J = 7.2$ Hz, 6H, CH_2CH_3 of Dep), 0.91 (s, 3H, *p*-CH $_3$ of Mes). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 Hz, C_6D_6): δ 44.38. Anal. Calcd for $\text{C}_{52}\text{H}_{53}\text{GeP}_2\text{RuS}_2$: C, 65.97; H, 5.64; S, 6.77. Found: C, 65.71; H, 5.64; S, 6.59.

Reaction of 1b with PPh $_3$. Compound **1b** (100 mg, 0.131 mmol) and PPh_3 (37 mg, 0.14 mmol) were dissolved in toluene (5 mL) and stirred at 100 °C for 5 h. All of the volatiles were removed in vacuo and crystallized from toluene/hexane to afford **6** as orange crystals in 82% yield.

Reaction of 1a with PEt $_3$. Compound **1a** (100 mg, 0.121 mmol) and PEt_3 (0.090 mL of 20% solution in toluene, 0.14 mmol) were dissolved in toluene (5 mL), and the mixture was stirred at 80 °C for 6 h. All of the volatiles were removed in vacuo and crystallized from toluene/hexane to afford **7** as orange crystals in 87% yield. ^1H NMR (600 MHz, C_6D_6): δ 7.37 (t, $J = 7.5$ Hz, 1H, Dmp *p*-arom), 7.03 (t, $J = 7.5$ Hz, 1H, Dep *p*-arom), 7.02 (dd, $J = 7.5$ Hz, 1.4 Hz, 1H, Dmp *m*-arom), 6.95 (dd, $J = 7.5$ Hz, 1.4 Hz, 1H, Dmp *m*-arom), 6.76 (d, $J = 7.5$ Hz, 2H, Dep *m*-arom), 6.43 (s, 2H, Mes arom), 4.30 (s, 2H, Mes arom), 3.88 (dq, $J = 14.4$ Hz, 7.2 Hz, 2H, CH_2CH_3 of Dep), 2.58 (dq, $J = 14.4$ Hz, 7.2 Hz, 2H, CH_2CH_3 of Dep), 2.33 (s, 6H, *o*-CH $_3$ of Mes), 2.23 (s, 6H, *o*-CH $_3$ of Mes), 2.11 (s, 3H, *p*-CH $_3$ of Mes), 1.90 (dq, $J_{\text{H-H}} = 7.5$ Hz, $J_{\text{P-H}} = 7.5$ Hz, 6H, PCH_2CH_3), 1.60 (t, $J = 7.2$ Hz, 6H, CH_2CH_3

of Dep), 0.99 (dt, $J_{\text{H-H}} = 7.5$ Hz, $J_{\text{P-H}} = 15.0$ Hz, 9H, PCH_2CH_3), 0.50 (s, 3H, $p\text{-CH}_3$ of Mes). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 Hz, C_6D_6): δ 26.82. Anal. Calcd for $\text{C}_{40}\text{H}_{53}\text{GePRuS}_2$: C, 59.86; H, 6.66; S, 7.99. Found: C, 59.67; H, 6.64; S, 7.65.

Reaction of 2a with PPh_3 . Compound **2a** (100 mg, 0.124 mmol) and PPh_3 (37 mg, 0.14 mmol) were dissolved in toluene (5 mL), and the mixture was stirred at 100 °C for 16 h. All of the volatiles were removed in vacuo and crystallized from toluene/hexane to afford compound **8** as orange crystals in 87% yield. ^1H NMR (500 MHz, C_6D_6): δ 7.86 (br m, 6H, PPh_3), 7.35 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.17 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dep), 7.05–7.00 (m, 9H, PPh_3), 6.94 (d, $J = 7.3$ Hz, 1H, $m\text{-CH}$ of Dmp), 6.92 (d, $J = 7.3$ Hz, 1H, $m\text{-CH}$ of Dmp), 6.80 (d, $J = 7.8$ Hz, 1H, $m\text{-CH}$ of Dep), 6.64 (d, $J = 7.8$ Hz, 1H, $m\text{-CH}$ of Dep), 6.62 (s, 1H, $m\text{-CH}$ of Mes), 6.17 (s, 1H, $m\text{-CH}$ of Mes), 4.37 (s, 1H, $m\text{-CH}$ of Mes), 4.32 (s, 1H, $m\text{-CH}$ of Mes), 3.42 (dq, $J = 15.0$ Hz, 7.5 Hz, 1H, CH_2CH_3 of Dep), 3.31 (dq, $J = 15.0$ Hz, 7.5 Hz, 1H, CH_2CH_3 of Dep), 2.55 (dq, $J = 15.0$ Hz, 7.5 Hz, 1H, CH_2CH_3 of Dep), 2.41 (s, 3H, CH_3 of Mes), 2.27 (s, 3H, CH_3 of Mes), 2.26 (dq, $J = 15.0$ Hz, 7.5 Hz, 1H, CH_2CH_3 of Dep), 2.14 (s, 3H, CH_3 of Mes), 2.07 (s, 3H, CH_3 of Mes), 2.01 (s, 3H, CH_3 of Mes), 1.19 (t, $J = 7.3$ Hz, 3H, CH_2CH_3 of Dep), 1.26 (t, $J = 7.3$ Hz, 3H, CH_2CH_3 of Dep), 0.98 (s, 3H, CH_3 of Mes). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): δ 39.17. Anal. Calcd for $\text{C}_{52}\text{H}_{53}\text{GeOPRuS}$: C, 67.11; H, 5.74; S, 3.45. Found: C, 66.86; H, 5.97; S, 3.24.

Protonation of Compound 6 by $\text{H}(\text{OEt}_2)_2\text{BARF}_4$. To a diethyl ether solution of compound **6** (50 mg, 0.053 mmol) was added $\text{H}(\text{OEt}_2)_2\text{BARF}_4$ (55 mg, 0.54 mmol), and the mixture was stirred for 10 h at room temperature. All of the volatiles were removed in vacuo, and the residue was washed with hexane. The orange powder was recrystallized from toluene/HMDSO to give $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-SH})\text{Ru}(\text{PPh}_3)]\text{BARF}_4$ (**9**) as orange crystals in 72% yield. ^1H NMR (600 MHz, C_6D_6): δ 8.45 (s, 8H, Ar^F), 7.70 (s, 4H, Ar^F), 7.33–7.27 (m, 6H, PPh_3), 7.28 (t, $J = 7.5$ Hz, 1H, Dmp $p\text{-arom}$), 6.97 (br m, 9H, PPh_3), 6.84 (dd, $J = 7.5$ Hz, 1.4 Hz, 1H, Dmp $m\text{-arom}$), 6.83 (t, $J = 7.5$ Hz, 1H, Dep $p\text{-arom}$), 6.81 (dd, $J = 7.5$ Hz, 1.4 Hz, 1H, Dmp $m\text{-arom}$), 6.47 (d, $J = 7.5$ Hz, 1H, Dep $m\text{-arom}$), 6.44 (d, $J = 7.5$ Hz, 1H, Dep $m\text{-arom}$), 6.23 (s, 1H, Mes arom), 6.13 (s, 1H, Mes arom), 4.70 (s, 1H, Mes arom), 4.15 (s, 1H, Mes arom), 2.90 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.30 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.20 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.16 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 1.93 (s, 3H, CH_3 of Mes), 1.88 (s, 3H, CH_3 of Mes), 1.87 (s, 3H, CH_3 of Mes), 1.85 (s, 3H, CH_3 of Mes), 1.61 (s, 3H, CH_3 of Mes), 0.59 (s, 3H, CH_3 of Mes), 1.04 (t, $J = 7.2$ Hz, 3H, CH_2CH_3 of Dep), 0.75 (t, $J = 7.2$ Hz, 3H, CH_2CH_3 of Dep), -0.33 (d, $J_{\text{P-H}} = 3.1$ Hz, 1H, $\mu\text{-SH}$). IR (KBr disk) 2490 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (243 Hz, C_6D_6): δ 44.33. Anal. Calcd for $\text{C}_{84}\text{H}_{66}\text{BF}_{24}\text{GePRuS}_2$: C, 55.71; H, 3.67; S, 3.54. Found: C, 55.59; H, 3.66; S, 3.22.

Protonation of Compound 6 by HOTf. To a dichloromethane solution of compound **6** (112 mg, 0.118 mmol) was added HOTf (0.22 mL of 0.54 M dichloromethane solution, 0.12 mmol), and the mixture was stirred for 12 h at room temperature. All of the volatiles were removed in vacuo, and the yellow residue was washed with ether to afford $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-SH})\text{Ru}(\text{PPh}_3)]\text{OTf}$ (**11**) in 96% yield. Single crystals suitable for X-ray analysis were grown by layering of ether onto the dichloromethane solution. ^1H NMR (500 MHz, CDCl_3): δ 7.70 (t, $J = 7.5$ Hz, 1H, Dmp $p\text{-arom}$), 7.48–7.32 (br m, 15H, PPh_3), 7.43 (dd, $J = 7.5$ Hz, 1.3 Hz, 1H, Dmp $m\text{-arom}$), 7.14 (dd, $J = 7.5$ Hz, 1.3 Hz, 1H, Dmp $m\text{-arom}$), 7.01 (t, $J = 7.5$ Hz, 1H, Dep $p\text{-arom}$), 6.65 (d, $J = 7.5$ Hz, 1H, Dep $m\text{-arom}$), 6.61 (d, $J = 7.5$ Hz, 1H, Dep $m\text{-arom}$), 6.36 (s, 1H, Mes arom), 6.19 (s, 1H, Mes arom), 5.58 (s, 1H, Mes arom), 5.10 (s, 1H, Mes arom), 2.88 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.31 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.26 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.22 (dq, $J =$

14.4 Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.24 (s, 3H, CH_3 of Mes), 2.20 (s, 3H, CH_3 of Mes), 1.95 (s, 3H, CH_3 of Mes), 1.91 (s, 3H, CH_3 of Mes), 1.89 (s, 3H, CH_3 of Mes), 1.16 (s, 3H, CH_3 of Mes), 1.12 (t, $J = 7.2$ Hz, 3H, CH_2CH_3 of Dep), 0.78 (t, $J = 7.2$ Hz, 3H, CH_2CH_3 of Dep), -0.45 (d, $J_{\text{P-H}} = 6.4$ Hz, 1H, $\mu\text{-SH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3): δ 45.15. IR (KBr disk): 2490 cm^{-1} . Raman (solid, excitation; Nd:YAG laser 1064 nm): 2489 cm^{-1} . Anal. Calcd for $\text{C}_{53}\text{H}_{54}\text{F}_3\text{GeO}_3\text{PRuS}_3$: C, 58.04; H, 4.96; S, 8.77. Found: C, 58.46; H, 4.68; S, 8.29.

Protonation of 7 by $\text{H}(\text{OEt}_2)_2\text{BARF}_4$. To a diethyl ether solution of **7** (45 mg, 0.048 mmol) was added $\text{H}(\text{OEt}_2)_2\text{BARF}_4$ (51 mg, 0.50 mmol), and the mixture was stirred for 10 h at room temperature. All the volatiles were removed in vacuo, and the residue was washed with hexane. The orange powder was recrystallized from toluene/HMDSO to give $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-SH})\text{Ru}(\text{PEt}_3)]\text{BARF}_4$ (**10**) as orange crystals in 61% yield. ^1H NMR (600 MHz, C_6D_6): δ 8.44 (s, 8H, Ar^F), 7.73 (s, 4H, Ar^F), 7.25 (t, $J = 7.5$ Hz, 1H, Dmp $p\text{-arom}$), 6.91 (t, $J = 7.5$ Hz, 1H, Dep $p\text{-arom}$), 6.87 (d, $J = 7.5$ Hz, 1H, Dmp $m\text{-arom}$), 6.74 (d, $J = 7.5$ Hz, 1H, Dmp $m\text{-arom}$), 6.63 (d, $J = 7.5$ Hz, 1H, Dep $m\text{-arom}$), 6.57 (d, $J = 7.5$ Hz, 1H, Dep $m\text{-arom}$), 6.29 (s, 1H, Mes arom), 6.15 (s, 1H, Mes arom), 4.28 (s, 1H, Mes arom), 3.87 (s, 1H, Mes arom), 3.11 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.57 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.36 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.26 (dq, $J = 14.4$ Hz, 7.2 Hz, 1H, CH_2CH_3 of Dep), 2.00 (s, 3H, CH_3 of Mes), 1.93 (s, 3H, CH_3 of Mes), 1.89 (s, 3H, CH_3 of Mes), 1.65 (s, 3H, CH_3 of Mes), 1.51 (s, 3H, CH_3 of Mes), 1.43 (s, 3H, CH_3 of Mes), 1.28–1.12 (m, 6H, PCH_2CH_3), 1.22 (t, $J = 7.2$ Hz, 3H, CH_2CH_3 of Dep), 1.18 (t, $J = 7.2$ Hz, 3H, CH_2CH_3 of Dep), 0.52 (dt, $J_{\text{H-H}} = 7.5$ Hz, $J_{\text{P-H}} = 15.0$ Hz, 9H, PCH_2CH_3), -0.47 (d, $J_{\text{P-H}} = 4.9$ Hz, 1H, $\mu\text{-SH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 Hz, C_6D_6): δ 27.31. IR (KBr disk): 2482 cm^{-1} . Anal. Calcd for $\text{C}_{72}\text{H}_{66}\text{BF}_{24}\text{GePRuS}_2$: C, 51.88; H, 3.99; S, 3.85. Found: C, 51.24; H, 4.28; S, 3.45.

Synthesis of $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-SCH}_3)\text{RuPPh}_3][\text{BF}_4]$ (12**).** Compound **6** (70 mg, 0.067 mmol) and trimethyloxonium tetrafluoroborate (12 mg, 0.081 mmol) were dissolved in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 10 h. All of the volatiles were removed in vacuo, and the residue was washed with diethyl ether to afford $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-SCH}_3)\text{RuPPh}_3][\text{BF}_4]$ (**12**) as a yellow powder in 62% yield. X-ray-quality crystals were grown by layering of diethyl ether onto the CH_2Cl_2 solution at room temperature. ^1H NMR (500 MHz, CDCl_3): δ 7.68 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dmp), 7.62 (br m, 6H, PPh_3), 7.42 (br m, 9H, PPh_3), 7.33 (dd, $J = 6.9$ Hz, 0.9 Hz, 1H, $m\text{-CH}$ of Dmp), 7.18 (dd, $J = 6.9$ Hz, 0.9 Hz, 1H, $m\text{-CH}$ of Dmp), 6.97 (t, $J = 7.3$ Hz, 1H, $p\text{-CH}$ of Dep), 6.70 (d, $J = 7.3$ Hz, 1H, $m\text{-CH}$ of Dep), 6.55 (d, $J = 7.3$ Hz, 1H, $m\text{-CH}$ of Dep), 6.47 (s, 1H, $m\text{-CH}$ of Mes), 6.11 (s, 1H, $m\text{-CH}$ of Mes), 5.67 (s, 1H, $m\text{-CH}$ of Mes), 4.44 (s, 1H, $m\text{-CH}$ of Mes), 2.80 (dq, $J = 7.4$ Hz, 14.8 Hz, 1H, CH_2CH_3 of Dep), 2.31 (dq, $J = 7.4$ Hz, 14.8 Hz, 1H, CH_2CH_3 of Dep), 2.31 (dq, $J = 7.4$ Hz, 14.8 Hz, 1H, CH_2CH_3 of Dep), 2.20 (s, 3H, CH_3 of Mes), 2.18 (s, 3H, CH_3 of Mes), 2.13 (s, 3H, CH_3 of Mes), 1.94 (s, 3H, CH_3 of Mes), 1.91 (s, 3H, CH_3 of Mes), 1.18 (s, 3H, CH_3 of Mes), 1.12 (t, $J = 7.8$ Hz, 3H, CH_2CH_3 of Dep), 0.74 (t, $J = 7.8$ Hz, 3H, CH_2CH_3 of Dep), 0.71 (br s, 3H, SCH_3). Anal. Calcd for $\text{C}_{53}\text{H}_{56}\text{BF}_4\text{GeRuS}_2\cdot\text{CH}_2\text{Cl}_2$: C, 57.21; H, 5.16; S, 5.60. Found: C, 56.82; H, 5.29; S, 5.40.

Synthesis of $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-OH})\text{RuPPh}_3][\text{BARF}_4]$ (13**).** Compound **8** (31.3 mg, 0.0336 mmol) and $\text{H}(\text{Et}_2\text{O})_2\text{BARF}_4$ (70 mg, 0.0692 mmol) were dissolved in diethyl ether (5.0 mL), and the mixture was stirred at room temperature for 12 h. The orange solution was evaporated to dryness, and the orange residue was washed with hexane to afford **13** as a yellow-orange powder (51.4 mg, 0.0286 mmol, 85%). X-ray-quality crystals were grown by layering of HMDSO onto the toluene solution. ^1H NMR (500 MHz, C_6D_6): δ 8.44 (s, 8H, $o\text{-CH}$ of Ar^F), 7.71 (s, 4H, $p\text{-CH}$ of Ar^F),

Table 4. Crystal Data for Compounds **1a–3a**, **4**, **6**, **8**, **10**, **12**, **13**, **16**, and **17**

	1a	2a	3a ·0.5Et ₂ O	4	6	8
formula	C ₄₄ H ₅₂ GeRuS ₂	C ₄₄ H ₅₂ GeORuS	C ₄₆ H ₅₇ GeO _{1.5} RuS	C ₄₁ H ₄₇ BF ₄ GeRuS ₂	C ₅₂ H ₅₃ GePRuS ₂	C ₅₂ H ₅₃ GeOPRuS
formula wt	818.67	802.61	823.62	864.41	946.74	930.68
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> ₂ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>C</i> ₂ / <i>c</i> (No. 15)	<i>P</i> ₂ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	11.5964(16)	12.082(11)	11.5964(16)	15.576(7)	22.292(2)	11.5964(16)
<i>b</i> , Å	11.817(3)	15.324(14)	11.964(8)	14.378(8)	10.6693(12)	12.8083(16)
<i>c</i> , Å	15.5409(18)	20.528(19)	16.076(13)	34.35(2)	22.1440(4)	16.8593(9)
α , deg	78.9528(13)		89.86(3)			82.603(3)
β , deg	79.8165(13)	93.843(13)	88.00(3)	90.87(2)	117.2224(4)	78.7029(10)
γ , deg	69.499(4)		65.82(2)			79.7565(12)
<i>V</i> , Å ³	1943.8(6)	3792.0(60)	2013.9(25)	7691(7)	4683.5(7)	2177.1(5)
<i>Z</i>	2	4	2	8	4	2
<i>D</i> _{calcd} , g cm ^{−3}	1.399	1.406	1.358	1.493	1.343	1.420
μ , cm ^{−1}	12.984	12.785	11.583	13.308	11.207	11.595
<i>F</i> ₀₀₀	848	1664	848	3536	1952	960
2 θ _{max} , deg	55.1	55.0	55.0	55.0	55.4	55.0
no. of rflns collected	28 241	30 219	16 320	38 280	65 104	25 616
indep (<i>R</i> _{int})	8895 (0.031)	8608 (0.043)	8487 (0.032)	8743 (0.044)	10 809 (0.040)	9829 (0.024)
no. of params	485	485	530	525	567	571
<i>R</i> ₁ ^a	0.0468	0.0407	0.0577	0.0545	0.0417	0.0420
<i>wR</i> ₂ ^b	0.0943	0.1104	0.1369	0.1349	0.0837	0.0957
GOF on <i>F</i> ² ^c	1.406	0.962	1.294	1.137	1.022	1.155

	10	12 ·CH ₂ Cl ₂	13 ·0.5Tol	16 ·4THF	17 ·0.5CHCl ₃
formula	C ₈₄ H ₆₆ BF ₂₄ Ge-PRuS ₂	C ₅₄ H ₅₈ BCl ₂ F ₄ Ge-PRuS ₂	C _{87.5} H ₇₀ BF ₂₄ Ge-OPRuS	C ₇₅ H ₇₁ BF ₂₄ Ge-O ₄ RuS	C _{52.5} H ₅₄ Cl _{2.5} Ge-OPRuS
formula wt	1810.97	1133.52	1840.98	1708.9	1026.33
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> ₂ / <i>n</i> (No. 14)	<i>P</i> ₂ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> ₂ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	20.770(4)	15.802(2)	12.5318(15)	14.703(5)	15.088(9)
<i>b</i> , Å	12.102(2)	20.691(4)	17.246(2)	28.665(8)	17.308(12)
<i>c</i> , Å	31.916(6)	16.6500(6)	19.560(3)	19.456(6)	19.953(19)
α , deg			84.988(4)		104.69(3)
β , deg	95.255(3)	113.8913(10)	84.367(4)	113.351(3)	90.14(3)
γ , deg			75.790(3)		91.929(16)
<i>V</i> , Å ³	7989(3)	4977.4(11)	4069.5(9)	7529(4)	5037(7)
<i>Z</i>	4	4	2	4	4
<i>D</i> _{calcd} , g cm ^{−3}	1.506	1.513	1.502	1.508	1.353
μ , cm ^{−1}	7.379	11.825	7.019	7.346	11.373
<i>F</i> ₀₀₀	3656	2320	1862	3436	2106
2 θ _{max} , deg	55.0	55.2	55.0	55.0	55.0
no. of rflns collected	80 156	54 460	33 230	59 133	72 080
indep (<i>R</i> _{int})	18 296 (0.049)	11 428 (0.043)	17 870 (0.024)	17 221 (0.057)	22 918 (0.035)
no. of params	1204	653	1165	1091	1207
<i>R</i> ₁ ^a	0.0409	0.0364	0.0414	0.0874	0.0633
<i>wR</i> ₂ ^b	0.1133	0.0689	0.1080	0.1757	0.1591
GOF on <i>F</i> ² ^c	0.922	0.930	1.043	0.906	1.123

^a *R*₁ = $\sum||F_o| - |F_c|| / \sum|F_o|$ (*I* > 2 σ (*I*)). ^b *wR*₂ = $[(\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)]^{1/2}$ (all data). ^c GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ (*N*_o = number of observations, *N*_v = number of variables).

7.35 (br m, 6H, PPh₃), 7.33 (t, *J* = 7.8 Hz, 1H, *p*-CH of Dmp), 7.01–6.92 (br m, 9H, PPh₃), 6.97 (d, *J* = 6.9 Hz, 1H, *m*-CH of Dep), 6.89 (d, *J* = 6.9 Hz, 1H, *m*-CH of Dmp), 6.85 (t, *J* = 7.8 Hz, 1H, *p*-CH of Dep), 6.48 (d, *J* = 6.9 Hz, 2H, *m*-CH of Dmp), 6.39 (s, 1H, *m*-CH of Mes), 6.02 (s, 1H, *m*-CH of Mes), 4.54 (s, 1H, *m*-CH of Mes), 3.93 (s, 1H, *m*-CH of Mes), 2.75 (dq, *J* = 7.4 Hz, 14.8 Hz, 1H, CH₂CH₃ of Dep), 2.12 (dq, *J* = 7.4 Hz, 14.8 Hz, 1H, CH₂CH₃ of Dep), 2.06 (s, 3H, CH₃ of Mes), 2.03 (dq, *J* = 7.4 Hz, 14.8 Hz, 1H, CH₂CH₃ of Dep), 1.88 (s, 3H, CH₃ of Mes), 1.86 (s, 3H, CH₃ of Mes), 1.79 (s, 3H, CH₃ of Mes), 1.56 (s, 3H, CH₃ of Mes), 1.18 (dq, *J* = 7.4 Hz, 14.8 Hz, 1H, CH₂CH₃ of Dep), 0.95 (t, *J* = 7.4 Hz, 3H, CH₂CH₃ of Dep), 0.60 (s, 3H, CH₃ of Mes), 0.32 (t, *J* = 7.4 Hz, 3H, CH₂CH₃ of Dep), −1.01 (s, 1H, μ -OH). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 45.70. Anal. Calcd for C₈₄H₆₆BF₂₄GeOPRuS: C, 56.21; H, 3.71; S, 1.79. Found: C, 55.86; H, 3.99; S, 1.92.

Synthesis of [Dmp(Dep)Ge(μ -S)(μ -OH)RuPPh₃][OTf] (14**).** To a diethyl ether solution of **8** (97.9 mg, 0.105 mmol) was added TfOH (0.23 mL of 0.54 M ether solution, 0.123 mmol), and the mixture was stirred at room temperature for 12 h. The yellow

solution was evaporated to dryness, and the yellow residue was washed with diethyl ether to afford **14** as a yellow-orange powder (99.5 mg, 0.0921 mmol, 88%). X-ray-quality crystals were grown by layering of ether onto a THF solution at room temperature. ¹H NMR (500 MHz, C₆D₆): δ 7.72 (br m, 6H, PPh₃), 7.32 (t, *J* = 7.8 Hz, 1H, *p*-CH of Dmp), 7.00 (br m, 9H, PPh₃), 6.79 (d, *J* = 7.8 Hz, 2H, *m*-CH of Dmp), 6.74 (d, *J* = 7.8 Hz, 1H, *m*-CH of Dep), 6.69 (d, *J* = 7.8 Hz, 1H, *m*-CH of Dep), 6.77 (s, 1H, *m*-CH of Mes), 6.16 (s, 1H, *m*-CH of Mes), 3.82 (s, 1H, *m*-CH of Mes), 3.44 (dq, *J* = 7.4 Hz, 14.8 Hz, 1H, CH₂CH₃ of Dep), 3.15 (dq, *J* = 7.4 Hz, 14.8 Hz, 1H, CH₂CH₃ of Dep), 2.36 (s, 3H, CH₃ of Mes), 2.32 (s, 3H, CH₃ of Mes), 2.14 (s, 3H, CH₃ of Mes), 1.86 (s, 3H, CH₃ of Mes), 1.77 (s, 3H, CH₃ of Mes), 1.46 (s, 3H, CH₃ of Mes), 1.25 (t, *J* = 7.8 Hz, 3H, CH₂CH₃ of Dep), 1.05 (t, *J* = 7.8 Hz, 3H, CH₂CH₃ of Dep), 0.66 (s, 1H, μ -OH). Anal. Calcd for C₅₃H₅₄F₃GeO₄PRuS₂: C, 58.90; H, 5.04; S, 5.93. Found: C, 58.25; H, 4.73; S, 6.11.

Reaction of **8 with MeOTf.** To a diethyl ether solution of **8** (65.4 mg, 0.0703 mmol) was added MeOTf (0.18 mL of 0.42 M diethyl ether solution, 0.075 mmol), and the mixture was stirred

for 12 h at room temperature. All of the volatiles were removed in vacuo, and the yellow residue was washed with ether to afford [Dmp(Dep)Ge(μ -SMe)(μ -O)Ru(PPh₃)](OTf) (**15**) in 52% yield. ¹H NMR (500 MHz, C₆D₆): δ 7.67 (6H, m, PPh₃), 7.31 (t, J = 7.8 Hz, 1H, p -CH of Dmp), 7.16 (br m, 6H, PPh₃), 7.00 (br m, 3H, PPh₃), 6.89 (t, J = 7.8 Hz, 1H, p -CH of Dep), 6.77 (dd, J = 1.4 Hz, 7.8 Hz, 1H, m -CH of Dep), 6.68 (d, J = 7.8 Hz, 1H, m -CH of Dmp), 6.56 (s, 1H, m -CH of Mes), 6.46 (s, 1H, m -CH of Mes), 6.38 (d, J = 7.4 Hz, 1H, m -CH of Dmp), 5.95 (s, 1H, m -CH of Mes), 3.94 (s, 1H, m -CH of Mes), 3.02 (dq, J = 7.4 Hz, 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.47 (s, 3H, CH₃ of Mes), 2.29 (br s, 3H, CH₃), 1.95 (s, 3H, CH₃ of Mes), 1.80 (s, 3H, CH₃ of Mes), 1.78 (s, 3H, CH₃ of Mes), 1.70 (s, 3H, CH₃ of Mes), 1.62 (dq, J = 7.4 Hz, 14.2 Hz, 1H, CH₂CH₃ of Dep), 1.40 (s, 3H, CH₃ of Mes), 1.17 (t, J = 7.4 Hz, 3H, CH₂CH₃ of Dep), 0.71 (t, J = 7.4 Hz, 3H, CH₂CH₃ of Dep). Anal. Calcd for C₅₄H₅₆F₃GeO₄PRuS₂: C, 59.24; H, 5.16; S, 5.86. Found: C, 58.89; H, 4.92; S, 5.48.

{[Dmp(Dep)(OH)Ge(μ -OH)Ru]₂(μ -SMe)₂}[BAr^F₄]₂ (**16**). Anal. Calcd for C₁₃₄H₁₁₀B₂F₄₈Ge₂O₄Ru₂S₂: C, 51.43; H, 3.54; S, 2.05. Found: C, 51.80; H, 3.68; S, 1.87.

Reaction of 13 and NEt₄Cl. To a THF solution of **13** (28 mg, 0.016 mmol) was added NEt₄Cl (5.0 mg, 0.03 mmol), and the mixture was stirred for 1 h at room temperature. The solvent was evaporated, and the residue was chromatographed on silica gel (eluted by ether) to afford Dmp(Dep)(OH)Ge(μ -S)RuCl(PPh₃) (**17**) quantitatively as a yellow powder. ¹H NMR (500 MHz, CDCl₃): δ 7.75 (br m, 6H, Ph), 7.41 (t, J = 7.3 Hz, 1H, p -CH of Dmp), 7.30 (br m, 9H, Ph), 7.08 (dd, J = 7.3 Hz, 1.4 Hz, 1H, m -CH of Dmp), 6.96 (t, J = 7.3 Hz, 1H, p -CH of Dep), 6.93 (dd, J = 7.3 Hz, 1.4 Hz, 1H, m -CH of Dmp), 6.75 (d, J = 7.3 Hz, 1H, m -CH of Dep), 6.67 (s, 1H, m -CH of Mes), 6.57 (d, J = 7.3 Hz, 1H, m -CH of Dep), 5.99 (s, 1H, m -CH of Mes), 5.45 (s, 1H, m -CH of Mes), 4.03 (s, 1H, GeOH), 3.33 (dq, J = 7.4 Hz, 14.2 Hz, 1H, CH₂CH₃ of Dep), 3.24 (d, $J_{\text{P-H}}$ = 2.8 Hz, 1H, m -CH of Mes), 2.34 (dq, J = 7.4 Hz, 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.14 (s, 3H, CH₃ of Mes), 2.08 (s, 3H, CH₃ of Mes), 2.00 (d, $J_{\text{P-H}}$ = 2.3 Hz, 3H, CH₃ of Mes), 1.90 (dq, J = 7.4 Hz, 14.2 Hz, 1H, CH₂CH₃ of Dep), 1.84 (s, 3H, CH₃ of Mes), 1.75 (s, 3H, CH₃ of Mes), 1.66 (s, 3H, CH₃ of Mes), 1.10 (t, J = 7.4 Hz, CH₂CH₃ of Dep), 0.98 (t, J = 7.4 Hz, CH₂CH₃ of Dep). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 33.62. Anal. Calcd for C₅₂H₅₄ClGeOPRuS: C, 64.58; H, 5.63; S, 3.32. Found: C, 64.67; H, 5.84; S, 3.01.

Reaction of 8 and HCl. To a toluene solution of **8** (200 mg, 0.215 mmol) was added HCl (1 M ether solution, 0.5 mmol), and the mixture was stirred at room temperature. The solution was treated as described above to afford **17** in 83% yield.

X-ray Structural Analysis. Crystallographic data are summarized in Table 4. Crystals of **1a–3a**, **4**, **6**, **8**, **9**, **12**, **13**, **16**, and **17** were mounted on a loop using oil (CryoLoop, Immersion Oil, Type B or Paratone, Hampton Research Corp.) and set on a Rigaku AFC-8 instrument equipped with a ADSC Quantum 1 CCD detector (for **1a**, **4**, **6**, **8**, **12**, and **17**), with a Mercury CCD detector (for **2a** and **3a**), or with a Saturn CCD detector (for **16**) or on a Rigaku RA-Micro007 with a Saturn CCD detector (for **9** and **13**). The measurements were made by using graphite-monochromated Mo K α radiation (λ = 0.710 690 Å) under a cold nitrogen stream. The frame data were integrated and corrected for absorption with the MSC d*TREK program package for **1a**, **6**, **8**, and **12** or with the Rigaku/MSD CrystalClear package for **2a**, **3a**, **4**, **9**, **13**, **16**, and **17**. The structures were solved with use of direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 by a Rigaku/MSD CrystalStructure package. Anisotropic refinement was applied to all non-hydrogen atoms, but the disordered crystalline solvent molecules for **3a**, **13**, and **17** (see Table 4) were refined isotropically. For **10**, **13**, and **16**, some CF₃ groups of BAr^F₄ disordered over several positions were also refined isotropically, in which the ratio was refined freely, while the total occupancy of the components was constrained to unity. The disordered hydrogen atoms of SH(66) in **9**, OH(66) in **13**, and OH(54,108) in **17** were assigned from the Fourier map and refined isotropically. All of the other hydrogen atoms were placed at calculated positions. Additional crystallographic data are given in the Supporting Information.

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Supporting Information Available: X-ray crystallographic data for **1a–3a**, **4**, **6**, **8**, **9**, **12**, **13**, **16**, and **17** as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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