Aromaticity of Germabenzenes

η^6-Germabenzene Complexes of Chromium and Molybdenum**

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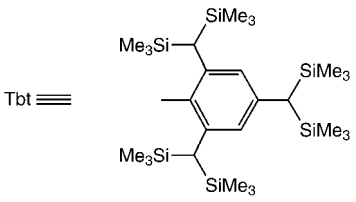
Although germabenzenes are the most fundamental germaaromatic compounds having a simple 6π-electron ring system, very little is known about their synthesis and characterization because of their extremely high reactivity. In the 1980s, Märkl et al. reported the pioneering synthesis of 1,4-di-*tert*-butylgermabenzene,[1] however, its generation was only supported by the formation of its [2+2] dimer and the trapping reaction with 2,3-dimethyl-1,3-butadiene. In addition, they described the spectroscopic detection of 1,4-dialkylgermabenzenes in the gas phase by variable temperature photoelectron spectroscopy (VTPES) experiments.[2] Kiprof and Brown have recently reported the theoretical studies of germabenzene and its valence isomers.[3] More recently, we have revealed the details of the synthesis, structure, reactivity, and aromaticity of the first stable germabenzene **1** bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, the size of which provides efficient steric protection.[4]

The coordination of cyclic π-hydrocarbon ligands to transition metals has been an attractive research field since the 1960s.[5] Recently, there has been a considerable interest in transition-metal complexes that contain sila- and germaaromatic compounds as ligands, from the viewpoint of their method of coordination and their unique structures.[6] Sila- and germabenzenes are expected to be suitable ligands for transition-metal complexes because of their delocalized ring structure and aromatic character. Recently, Tilley et al. reported the characterization of the first Ru complex containing an η^6-silabenzene ligand ($[C_5Me_5Ru\{\eta^6\text{-}C_5H_5Si(t\text{-}Bu)\}][BH(C_6F_5)_3]$) by NMR and IR spectroscopy.[7] However, the molecular structures and reactivities of η^6-sila- and germabenzene complexes have not been fully reported to date. Here, we report the synthesis and characterization of the first stable η^6-germabenzene complexes, $[\{\eta^6\text{-}C_5H_5Ge(Tbt)\}M(CO)_3]$ (M = Cr (**2**), Mo (**3**)).



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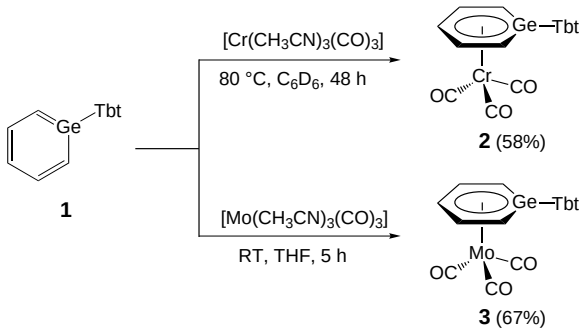


Scheme 1. Syntheses of η^6-germabenzene complexes **2** and **3**.

The ligand exchange reaction of $[Cr(CH_3CN)_3(CO)_3]$[8] with **1** at 80 °C in C_6D_6 resulted in the formation of the η^6-germabenzene–chromium complex, $[\{\eta^6\text{-}C_5H_5Ge(Tbt)\}Cr(CO)_3]$ (**2**), as yellow crystals in 58% yield (Scheme 1). The novel Mo complex, $[\{\eta^6\text{-}C_5H_5Ge(Tbt)\}Mo(CO)_3]$ (**3**), was also obtained as yellow crystals in 67% yield when $[Mo(CH_3CN)_3(CO)_3]$[9] was used as the metal source at room temperature in THF. Germabenzene complexes **2** and **3** possess reasonable thermal stability in both the solid state and in solution under argon atmosphere, and no detectable change was observed after the thermolysis of **2** and **3** in C_6D_6 at 120 °C in a sealed tube for a few days. In addition, **2** and **3** are more stable towards air and moisture than the free germabenzene **1**. These results reflect that coordination to the transition metal (Cr, Mo) leads to the thermodynamic stabilization of the reactive species **1**.

Complexes **2** and **3** were fully characterized by ^1H and ^{13}C NMR, IR, and UV/Vis spectroscopy. As expected, the ^1H NMR chemical shifts of the germabenzene ring protons for **2** ($\delta = 3.95$, 4.73, and 4.98 ppm) and **3** ($\delta = 4.05$, 4.73, and 5.17 ppm) are shifted upfield relative to those for the free germabenzene **1** ($\delta = 6.72$, 7.85 and 8.06 ppm).[4] The ^{13}C NMR signals for the germabenzene ring carbons of **2** ($\delta = 83.00$, 85.87, and 100.91 ppm) and **3** ($\delta = 81.64$, 83.77, and 103.11 ppm) also appear at much higher field than the equivalent signals for **1** ($\delta = 114.23$, 132.23, and 140.96 ppm),[4] and were observed at slightly higher field than the resonances for the corresponding η^6-arene complexes, $[(\eta^6\text{-arene})M(CO)_3]$ (M = Cr, Mo)($\delta = 92.4$–118.8 ppm).[10] Additionally, the $^{13}C{=}O$ chemical shifts for **2** and **3** ($\delta =$ 235.05 and 222.19 ppm, respectively) are quite similar to those for $[(\eta^6\text{-mesitylene})M(CO)_3]$ (M = Cr ($\delta = 235.1$ ppm), Mo ($\delta = 223.7$ ppm)).[10a] In the IR spectra, the stretching frequencies ($\tilde{\nu}_{CO}$) of **2** (1867, 1887, and 1954 cm^{-1}) and **3** (1865, 1883, and 1952 cm^{-1}) were observed at lower energy than those of the corresponding benzene complexes, $[(\eta^6\text{-}C_6H_6)M(CO)_3]$ (M = Cr ($\tilde{\nu}_{CO} = 1915$ and 1982 cm^{-1}),[11] M = Mo ($\tilde{\nu}_{CO} = 1913$ and 1983 cm^{-1})[12]). These results suggest that the benzene ligands in $[(\eta^6\text{-}C_6H_6)M(CO)_3]$ (M = Cr, Mo) are stronger electron donors than the germabenzene ligands of **2** and **3**. Furthermore, three carbonyl stretching frequencies that were calculated by vibrational analysis for the model

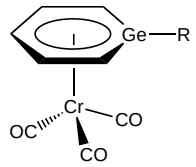
Table 1: Observed and calculated carbonyl stretching frequencies of [{η^6-$C_5H_5Ge(Tbt)$}$Cr(CO)_3$] (**2**) and [{η^6-C_5H_5GeH}$Cr(CO)_3$] (**4**).

2 (observed)[a]	**4** (calculated)[b]	Relative value (obsd/calcd)
1867	1994	0.94
1887	2011	0.94
1954	2059	0.95

[a] KBr. [b] Calculated at the B3LYP/6-311G(d,p)(LANL2DZ for Cr) level.

compound [{η^6-C_5H_5GeH}$Cr(CO)_3$] (**4**) were in good agreement with those of **2** considering the overestimation of the vibrational frequencies in the theoretical calculation (Table 1).[13]

The UV/Vis spectra of **2** and **3** in hexane showed three absorption maxima (**2**: 225 ($\varepsilon = 49000$), 279 ($\varepsilon = 17000$), and 340 ($\varepsilon = 8000$); **3**: 228 ($\varepsilon = 41000$), 287 ($\varepsilon = 10000$), and 344 nm ($\varepsilon = 13000$)). These values are slightly red-shifted compared to those for the corresponding benzene complexes (217 ($\varepsilon = 23700$), 263 ($\varepsilon = 6720$), and 315 nm ($\varepsilon = 9450$) for [(η^6-C_6H_6)$Cr(CO)_3$]; 220 (sh), 282–287 ($\varepsilon = 3980$), and 323 nm ($\varepsilon = 18400$) for [(η^6-C_6H_6)$Mo(CO)_3$], respectively).[14]



4 (R = H)
5 ($R = CH_3$)

The molecular geometry of **2** was determined by X-ray crystallographic analysis; the ORTEP diagram is given in Figure 1.[15] Complex **2** features a nearly planar germabenzene ligand (the sum of the bond angles around the central Ge atom and the sum of the interior bond angles of the germabenzene ring are 359.9 and 719.4°, respectively), which is η^6-coordinated to the {$Cr(CO)_3$} unit. The dihedral angle between the germabenzene ring and the benzene ring of the Tbt group is about 35°. In addition, the Ge atom does not reside directly above the C6 carbon atom, which is a constituent of one of the legs of the "piano stool" formed by the three CO ligands; when viewed from above the germabenzene ring, the angle formed by the Ge, Cr, and C6 atoms is 28°. These results may be attributed to the steric and electronic repulsion between the Tbt group and the CO ligand. The lengths of the two Ge–C bonds (1.859(5) and 1.878(5) Å) and the four C–C bonds (1.393(7)–1.404(7) Å) in the germabenzene ligand are slightly longer than those of the free germabenzene **1** (Ge–C: 1.827(2) and 1.829(2), C–C: 1.385(3)–1.396(3) Å).[4] While the five C–Cr bond lengths (2.186(5)–2.314(4) Å) are similar to those of [(η^6-C_6H_6)$Cr(CO)_3$] (2.217(2)–2.240(2) Å),[16] the Ge–Cr bond length of 2.5849(12) Å is somewhat longer than that which was reported for the Ge–Cr bond of the related complex, $[\{(OC)_5Cr\}I_2Ge{-}GeI_2\{Cr(CO)_5\}]^{2-}$ (2.468(1) Å).[17] In addition, theoretical calculations for the model compounds [{η^6-C_5H_5GeR}$Cr(CO)_3$] (R = H (**4**), CH_3 (**5**)) were performed for a comparison (Table 2).[18] The agreement between the experimental and theoretical values is excellent, which suggests that the Ge–C and C–C bond lengths of the germabenzene rings, in addition to the length of the Ge–Cr bonds, are little affected by substituents on the germanium atom.

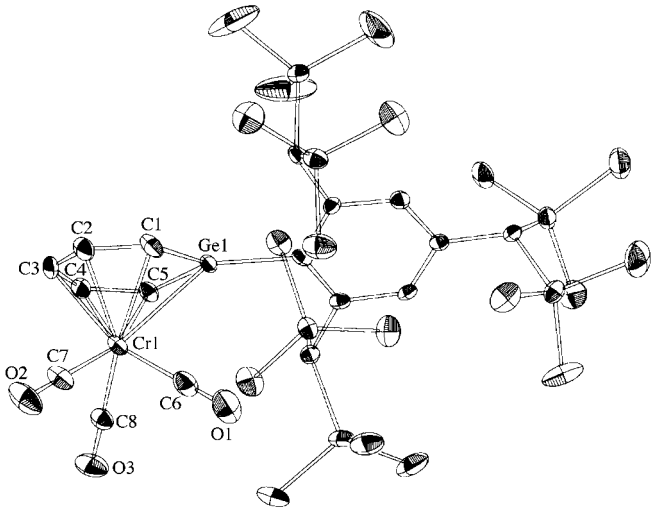


Figure 1. ORTEP diagram of [{(η^6-$C_5H_5Ge(Tbt)$}$Cr(CO)_3$] (**2,** 50% thermal ellipsoids; the fragment of solvated benzene is omitted for clarity). Selected bond lengths (Å) and angles (°): Ge1-C1 1.878(5), Ge1-C5 1.859(5), C1-C2 1.396(7), C2-C3 1.404(7), C3-C4 1.393(7), C4-C5 1.404(6), Ge1-Cr1 2.5849(12), C1-Cr1 2.300(5), C2-Cr1 2.199(5), C3-Cr1 2.186(5), C4-Cr1 2.220(5), C5-Cr1 2.314(4); C1-Ge1-C5 100.7(2), C1-Ge1-C9 128.1(2), C5-Ge1-C9 131.14(19), Ge1-C1-C2 121.0(4), C1-C2-C3 125.9(5), C2-C3-C4 124.6(4), C3-C4-C5 125.8(5), Ge1-C5-C4 121.4(4).

In conclusion, we successfully synthesized the novel η^6-germabenzene complexes **2** and **3** by the reactions of germabenzene **1** with $[M(CH_3CN)_3(CO)_3]$ (M = Cr, Mo), and their molecular structures were determined from their spectroscopic data and from X-ray structural analysis. Thus, these results convey the first description of the aromatic character of germabenzenes, from the standpoint of their chemical reactivity. Further investigations on the reactivity of **2** and **3** and the synthesis of new germabenzene complexes are currently in progress.

Experimental Section

2: In a glove-box filled with argon, **1** (50.2 mg, 0.073 mmol) and $[Cr(CH_3CN)_3(CO)_3]$ (22.6 mg, 0.087 mmol) were dissolved in C_6D_6 (0.5 mL) and the solution was placed into an NMR tube, which was then placed under vacuum and sealed. Heating the mixture at 80 °C for 48 h resulted in the disappearance of the NMR signals for **1**. The tube was then opened and the solvent was removed in vacuo. The

Table 2: Observed and calculated bond lengths [Å] of the Cr complexes **2**, **4**, and **5**.

	2 (observed)	**4** (calculated)[a]	**5** (calculated)[a]
Ge1-C1, Ge1-C5	1.878(5), 1.859(5)	1.862	1.864, 1.867
C1-C2, C4-C5	1.396(7), 1.404(6)	1.406	1.407, 1.405
C2-C3, C3-C4	1.404(6), 1.393(7)	1.417	1.415, 1.418
Ge1-Cr1	2.5849(12)	2.556	2.572

[a] Calculated at the B3LYP/6-311G(d,p) (LANL2DZ for Cr) level.

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residue was recrystallized from pentane at −40 °C to give **2** (34.7 mg, 58 %) as yellow crystals. m.p. 274–276 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.12$ (s, 18 H), 0.19 (s, 36 H), 1.49 (s, 1 H), 2.45 (br s, 1 H), 2.52 (br s, 1 H), 3.95 (d, ^3J(H,H) = 10.5 Hz, 2 H), 4.73 (t, ^3J(H,H) = 6.3 Hz, 1 H), 4.98 (dd, ^3J(H,H) = 6.3, 10.5 Hz, 2 H), 6.63 (br s, 1 H), 6.73 ppm (br s, 1 H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 0.61$ (q), 0.78 (q), 0.91 (q), 31.50 (d), 34.37 (d), 34.79 (d), 83.00 (d), 85.87 (d), 100.91 (d), 122.44 (d), 123.55 (s), 127.26 (d), 148.32 (s), 151.92 (s × 2), 235.05 ppm (s); IR (KBr): $\tilde{\nu} = 1867$, 1887, 1954 cm^{-1} (C≡O); UV/Vis (*n*-hexane): λ_{max} (ε) = 225 (49 000), 279 (17 000), 340 nm (8000); LRMS (FAB): *m*/*z* (%) = 826 (8) [M^+], 691 (75) [{C_5H_5Ge(Tbt)}$^+$], 521 (100) [{(Tbt)−2 CH_3}$^+$]. Although we have tried to obtain the elemental analysis of **2** on several occasions, the results have not been commensurate with the calculated values for **2** because of its highly moisture-sensitive properties (elemental analysis calcd for $C_{35}H_{64}CrGeO_3Si_6$: C 50.89, H 7.81; found: C 49.16, H 7.87).

3: In a glove-box filled with argon, [Mo(CH_3CN)$_3$(CO)$_3$] (16.3 mg, 0.054 mmol) was added to a solution of **1** (40.1 mg, 0.058 mmol) in THF (1 mL) at room temperature, and the mixture was stirred for 5 h. After the solvent was removed in vacuo, the residue was recrystallized from hexane at −40 °C to give **3** (31.4 mg, 67 %) as yellow crystals. M.p. 248–250 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.11$ (s, 18 H), 0.18 (s, 36 H), 1.47 (s, 1 H), 2.39 (br s, 1 H), 2.49 (br s, 1 H), 4.05 (d, ^3J(H,H) = 9.9 Hz, 2 H), 4.73 (t, ^3J(H,H) = 6.6 Hz, 1 H), 5.17 (dd, ^3J(H,H) = 6.6, 9.9 Hz, 2 H), 6.61 (br s, 1 H), 6.70 ppm (br s, 1 H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 0.57$ (q), 0.77 (q), 0.88 (q), 31.43 (d), 34.66 (d), 34.99 (d), 81.64 (d), 83.77 (d), 103.11 (d), 122.40 (d), 123.72 (s), 127.23 (d), 148.28 (s), 151.66 (s × 2), 222.19 ppm (s); IR (KBr): $\tilde{\nu} = 1865$, 1883, 1952 cm^{-1} (C≡O); UV/Vis (*n*-hexane): λ_{max} (ε) = 228 (41 000), 287 (10 000), 344 nm (13 000); elemental analysis calcd for $C_{35}H_{64}GeMoO_3Si_6$: C 48.32, H 7.42; found: C 47.91, H 7.48.

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Synthesis of Amino Acid Derivatives

A Diversity-Oriented Synthesis of α-Amino Acid Derivatives by a Silyltelluride-Mediated Radical Coupling Reaction of Imines and Isonitriles**

Shigeru Yamago, Hiroshi Miyazoe, Takeyoshi Nakayama, Masaki Miyoshi, and Junichi Yoshida**

Development of new and practical methods for the synthesis of α-amino acids and their derivatives is of considerable interest to researchers, because the importance of these compounds in biological systems and their exceptional utility as building blocks in organic synthesis is well known.[1,2]

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