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Coordination Chemistry of a Kinetically Stabilized Germabenzene: Syntheses and Properties of Stable η^6-Germabenzene Complexes Coordinated to Transition Metals

Norihiro Tokitoh,*[a] Norio Nakata,[a, b] Akihiro Shinohara,[a] Nobuhiro Takeda,[a] and Takahiro Sasamori[a]

Abstract: The first stable η^6-germabenzene complexes, that is, $[M(CO)_3(\eta^6\text{-}C_5H_5GeTbt)]$ {M = Cr (**2**), Mo (**3**), and W (**4**); Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}, have been synthesized by ligand-exchange reactions between $[M(CO)_3(CH_3CN)_3]$ (M = Cr, Mo, and W) and the kinetically stabilized germabenzene **1** and characterized by ^{1}H and ^{13}C NMR, IR, and UV/Vis spectroscopy. In the ^{1}H and ^{13}C NMR spectra of **2**–**4**, all of the signals for the germabenzene rings were shifted upfield relative to their counterparts in the free germabenzene **1**. X-ray crystallographic analysis of **2** and **4** revealed that the germabenzene ligand was nearly planar and was coordinated to the $M(CO)_3$ group (M = Cr, W) in an η^6 fashion. The formation of complexes **2**–**4** from germabenzene **1** should be noted as the application of germaaromatics as 6π-electron ligands toward complexation with Group 6 metals. On the other hand, treatment of **1** with $[\{RuCp^*Cl\}_4]$ ($Cp^* = C_5Me_5$) in THF afforded a novel η^5-germacyclohexadienido complex of ruthenium—$[RuCp^*\{\eta^5\text{-}C_5H_5GeTbt(Cl)\}]$ (**9**)—instead of the expected η^6-germabenzene-ruthenium cationic complex $[RuCp^*\{\eta^6\text{-}C_5H_5GeTbt\}]Cl$ (**10**). Crystallographic structural analysis of **9** showed that the five carbon atoms of the germacyclohexadienido ligand of **9** were coordinated to the Ru center in an η^5 fashion.

Keywords: chromium · germanium · molybdenum · ruthenium · tungsten

Introduction

As it is well known that aromatic compounds react with some transition metals to afford a variety of unique complexes such as metallocenes and arene complexes,[1] aromatic compounds containing heavier Group 14 elements might also be expected to serve as a new class of ligands for transition metal complexes, due to their π-delocalized ring structures and aromatic characters. In recent years, considerable interest has been focused on transition metal complexes incorporating η^5-coordinated silolyl and germolyl ligands,[2] in view of their coordination modes and unique structures. Tilley et al. have reported a number of complexes of delocalized silolyl and germolyl anions, stabilized by coordination to transition metal fragments. As one example, the first cationic ruthenocene complex containing an η^6-silabenzene ligand—$[RuCp^*\{\eta^6\text{-}C_5H_5Si(tBu)\}][BH(C_6F_5)_3]$—was synthesized and characterized by NMR and IR spectroscopy.[3]

Meanwhile, we have already reported the synthesis and isolation of kinetically stabilized 1-Tbt-silabenzene,[4] 1-Tbt-1-sila- and 2-Tbt-2-silanaphthalenes,[5,6] and 9-Tbt-silaanthracene,[7] with the aid of some efficient steric protection groups: 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt).[8] Furthermore, the germanium analogues, 1-Tbt-germabenzene,[9] 2-Tbt-2-germanaphthalene,[10] 9-Tbt-9-germaanthracene, and 9-Tbt-9-germaphenanthrene,[11] have been synthesized as stable compounds. These stable examples of sila- and germaaromatics made it possible to investigate the structures, properties, and aromaticities of the metallaaromatics in detail by spectroscopic analyses (NMR, UV/Vis, Raman, etc.), study of their reactivities, X-ray crystallographic analyses, and theoretical calculations.[12] We have preliminarily reported the reaction

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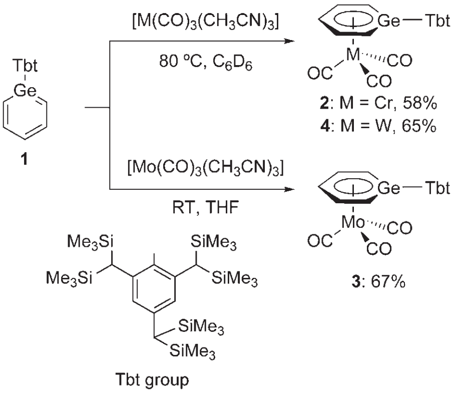
[a] Prof. Dr. N. Tokitoh, Dr. N. Nakata, Dr. A. Shinohara, Dr. N. Takeda, Dr. T. Sasamori
Institute for Chemical Research, Kyoto University
Gokasho, Uji, Kyoto 611-0011 (Japan)
Fax: (+81) 774-38-3209
E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp

[b] Dr. N. Nakata
Present address: Department of Chemistry
Faculty of Science, Saitama University
Urawa, Saitama 338-8570 (Japan)

behavior of the stable germabenzene [TbtGeC_5H_5] (**1**) with [$M(CO)_3(CH_3CN)$] (M = Cr, Mo), resulting in the formation of the first stable η^6-germabenzene–Group 6 metal complexes, [$M(CO)_3(\eta^6$-C_5H_5GeTbt)].[13] In this paper we describe the details of the synthesis and characterization of the first stable η^6-germabenzene–Group 6 metal complexes, [$M(CO)_3(\eta^6$-C_5H_5GeTbt)] [M = Cr, Mo, and W], along with a metallocene-type, η^5-germacyclohexadienido–Ru complex, [RuCp*{η^5-C_5H_5GeTbt(Cl)}] (Cp* = C_5Me_5).

Results and Discussion

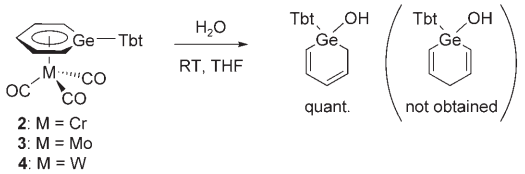
Synthesis of η^6-germabenzene complexes: There are two main known approaches for the synthesis of arene tricarbonylmetal complexes [$M(CO)_3(\eta^6$-arene)] (M = Cr, Mo, and W).[1a] The preferred method for the synthesis of [$M(CO)_3$-(η^6-arene)] is the thermal reaction between [$M(CO)_6$] and the arene in di-*tert*-butyl ether and THF, a procedure suitable for the preparation of a wide range of complexes, often in high yields and with reaction times typically in the 1–4 days range. On the other hand, milder complexation conditions and shorter reaction times can be achieved by the use of suitable precursors such as [$M(CO)_3L_3$] (L = CH_3CN, pyridine, NH_3, etc.), which offer better compatibility with arenes bearing functional groups, and so we selected [$M(CO)_3(CH_3CN)_3$] (M = Cr, Mo, and W) as starting materials for the synthesis of η^6-germabenzene–Group 6 metal tricarbonyl complexes (Scheme 1).



Scheme 1. Syntheses of η^6-germabenzene complexes **2**–**4**.

Ligand exchange between [$Cr(CO)_3(CH_3CN)_3$] and germabenzene **1** at 80 °C in C_6D_6 afforded the corresponding η^6-germabenzene complex—[$Cr(CO)_3(\eta^6$-C_5H_5GeTbt)] (**2**)—as yellow crystals in 58 % isolated yield. The corresponding Mo complex—[$Mo(CO)_3(\eta^6$-C_5H_5GeTbt)] (**3**)—was also obtained as yellow crystals in 67 % isolated yield when [$Mo(CO)_3(CH_3CN)_3$] was used as a metal source in place of [$Cr(CO)_3(CH_3CN)_3$] at ambient temperature in THF. Furthermore, the heavier congener [$W(CO)_3(\eta^6$-C_5H_5GeTbt)] (**4**) was also synthesized by treatment of **1** with [$W(CO)_3$-($CH_3CN)_3$] at 80 °C in C_6D_6 (65 % yield).

The germabenzene complexes **2**–**4** are thermally quite stable either in the solid state or in solution under argon, and no changes were observed on heating **2**–**4** in C_6D_6 at 120 °C in a sealed tube for a few days. In addition, complexes **2**–**4** were found to be somewhat more insensitive than the free **1** towards air and moisture, reflecting the thermodynamic stabilization afforded by the coordination to the tricarbonylmetal center of Group 6 metals. However, they are still moisture-sensitive and in all cases undergo 1,2-addition of water to give the corresponding hydroxygermane **5** quantitatively (Scheme 2). The high regioselectivity observed for the addition of water to **2**–**4** is in sharp contrast with the competitive 1,2- and 1,4-addition of water to the free germabenzene **1**.[9a]

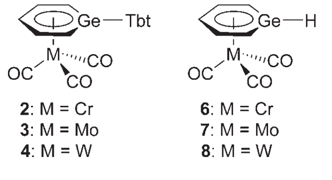


Scheme 2. Reactions of η^6-germabenzene complexes **2**–**4** with water.

Structures of η^6-germabenzene complexes: Complexes **2**–**4** were characterized by their ^{1}H and ^{13}C NMR, IR, and UV/Vis spectra. NMR measurements on **2**–**4** showed that, in solution, each germabenzene ligand—as well as free **1**—had a C_2 axis passing through the Ge and C4 atoms. The ^{1}H NMR chemical shifts of the germabenzene ring protons for **2** (δ = 3.95, 4.73, and 4.98 ppm), **3** (δ = 4.05, 4.73, and 5.17 ppm), and **4** (δ = 4.04, 4.75, and 4.86 ppm) are shifted upfield relative to those for the free **1** (δ = 6.72, 7.85, and 8.06 ppm).[9a] The ^{13}C NMR signals for the germabenzene ring carbons of **2** (δ = 83.00, 85.87, and 100.91 ppm), **3** (δ = 81.64, 83.77, and 103.11 ppm), and **4** (δ = 79.64, 80.02, and 98.51 ppm) also appeared at much higher field than those for **1** (δ = 114.23, 132.23 and 140.96 ppm).[9a] Such spectral features are similar to those observed in the case of arene tricarbonylmetal complexes, which generally show NMR signals shifted upfield relative to those of the free aromatic compounds, due to the reduction of π-electron density in the arene ring on complex formation.[14] In addition, the chemical shifts corresponding to the germabenzene rings in **2**–**4** were observed at slightly higher field than the range for the corresponding η^6-arene complexes [$M(\eta^6$-arene)$(CO)_3$] (M = Cr, Mo, and W, δ = 90.9–118.8 ppm).[14b] In addition, the ^{13}CO chemical shifts for **2**–**4** (δ = 235.05, 222.19, and 211.88 ppm) are deshielded with increasing electron richness on the metal center, and are quite similar to those seen in [$M(\eta^6$-mesitylene)$(CO)_3$] [M = Cr (δ = 235.1 ppm), Mo (δ = 223.7 ppm), and W (δ = 212.6 ppm)].[14c]

The UV/Vis spectra of **2**–**4** in hexane each showed three absorption maxima [**2**: 225 (ε 4.9×10^4), 279 (ε 1.7×10^4), and 340 nm (ε 8.0×10^3 mol^{-1}dm^{3}cm^{-1}); **3**: 228 (ε 4.1×10^4), 287 (ε 1.0×10^4), and 344 nm (ε 1.3×10^4 mol^{-1}dm^{3}cm^{-1}); **4**: 228 (ε 4.2×10^4), 283 (ε 1.2×10^4), and 339 nm (ε 1.5×10^3 mol^{-1}dm^{3}cm^{-1})]. The intense absorptions appearing at the longest wavelength for **2**–**4** can be assigned to the metal-to-ligand charge transfer (MLCT) band, in accordance with the calculated and experimentally observed electronic spectra of $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$.[15] These values are slightly red-shifted in relation to those seen for the corresponding benzene complexes: 217 (ε 23700), 263 (ε 6720), and 315 nm (ε 9450 mol^{-1}dm^{3}cm^{-1}) for $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$; 220 ($\varepsilon$ 17900), 240 (ε 10560), 282–287 (ε 3980), and 323 nm (ε 18400 mol^{-1}dm^{3}cm^{-1}) for $[\mathrm{Mo}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$; and 214–215 ($\varepsilon$ 18400), 240 (ε 8850), 272–274 (ε 4470), and 316 nm (ε 20000) for $[\mathrm{W}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$.[16]

In their IR spectra, complexes **2**–**4** each present three CO stretching modes (ν_{CO}) of almost equal intensity, in accordance with C_s symmetry (**2**: 1867, 1887, and 1954; **3**: 1865, 1883, and 1952; **4**: 1853, 1881, and 1949 cm^{-1}). These values are observed in a similar region to those of the corresponding benzene complexes $[\mathrm{M}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$ [M = Cr (ν_{CO} (KBr) = 1860, 1874 and 1971 cm^{-1}),[17] M = Mo (ν_{CO}(KBr) = 1845, 1866, and 1971 cm^{-1}),[17] and M = W (ν_{CO} = 1886 and 1968 cm^{-1}).[18] In our preliminary communication[13] we compared the ν_{CO} values (in KBr) of **2** and **3** with those of $[\mathrm{M}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$ (M = Cr, Mo) in cyclohexane and concluded that those of **2** and **3** were smaller than those of $[\mathrm{M}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$, indicating a weaker π-donating ability of **1** than benzene. However, the vibrational frequencies should be compared in the same phase, and we would like to correct our original conclusion and to assign germabenzene **1** almost the same coordination ability as benzene, due to the fact that the ν_{CO} values (in KBr) of **2** and **3** are close to those of $[\mathrm{M}(\eta^6\text{-}\mathrm{C_6H_6})(\mathrm{CO})_3]$ (M = Cr, Mo) in KBr as described above. Furthermore, three carbonyl stretching frequencies calculated by vibrational analysis for the model compounds $[\mathrm{M}(\eta^6\text{-}\mathrm{C_5H_5GeH})(\mathrm{CO})_3]$ (M = Cr, Mo, and W, **6**–**8**) were in good agreement with those of **2**–**4** if allowance is made for the overestimation of vibrational frequencies in the theoretical calculations (Scheme 3 and Table 1).[19] These results suggest that the germabenzene can act as efficiently as benzene as a 6π-electron arene ligand.



Scheme 3. Model compounds **6**–**8** for theoretical calculations.

Table 1. Observed and calculated carbonyl stretching frequencies for η^6-germabenzene complexes **2**–**4** and **6**–**8**.

$[\mathrm{M}(\mathrm{CO})_3(\eta^6\text{-}\mathrm{C_5H_5GeR})]$ M	R	ν_{CO} [cm^{-1}]
Cr	Tbt (**2**)[a]	1867, 1887, 1954
Cr	H (**6**)[b]	1876, 1894, 1937
Mo	Tbt (**3**)[a]	1865, 1883, 1952
Mo	H (**7**)[b]	1881, 1889, 1940
W	Tbt (**4**)[a]	1853, 1881, 1949
W	H (**8**)[b]	1879, 1885, 1939

[a] KBr. [b] Calculated at the B3PW91/6-31G(d) (for C, H, O), 6-311G(3d) (for Ge), and LanL2DZ (for Cr, Mo, W) levels and scaled by 0.93. See ref. [19].

Single crystals of η^6-germabenzene complexes **2** and **4** suitable for X-ray crystallographic analysis were obtained by slow evaporation of concentrated benzene solutions, so the molecular geometries of **2** and **4** were determined by X-ray crystallographic analysis. The ORTEP drawings of **2** and **4** are illustrated in Figures 1 and 2, respectively. Each features a nearly planar germabenzene ring (the Ge atoms deviate from the least-squares planes of the germabenzene rings by 3.7° in **2** and by 3.2° in **4**, while the sums of the bond angles around the central Ge atoms and the sums of the interior bond angles of the germabenzene rings are 359.9 and 719.4° for **2** and 359.9 and 719.2° for **4**), which is coordinated to the $\mathrm{M(CO)_3}$ (M = Cr and W) fragments in an η^6 fashion. The dihedral angles between the germabenzene rings and the benzene rings of the Tbt groups are about 35° in **2** and 28° in **4**. The $\mathrm{M(CO)_3}$ (M = Cr and W) fragments adopt *syn*-eclipsed conformations typical of arene complexes bearing electron-donating substituents, and, in addition, the angles between the Ge atoms in the germabenzene rings and one of the legs of the piano stools formed by the three CO ligands are about 28° in **2** and 26° in **4**. These results are probably due to steric repulsion between the Tbt group and the CO ligand. The lengths of the Ge–C [1.869(6) and

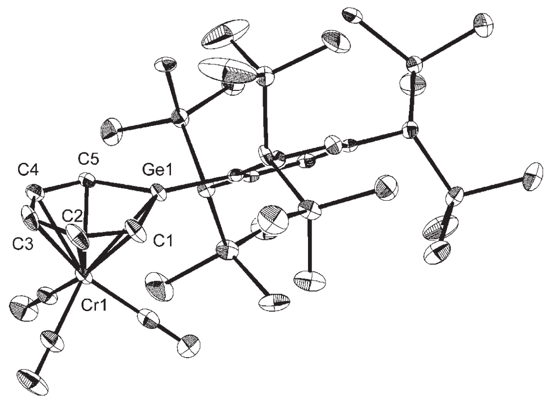


Figure 1. ORTEP drawing of $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_5H_5GeTbt})(\mathrm{CO})_3]$ (**2**, 50% probability; the benzene atom and hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1–C1 1.878(5), Ge1–C5 1.859(5), C1–C2 1.396(7), C2–C3 1.404(7), C3–C4 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).

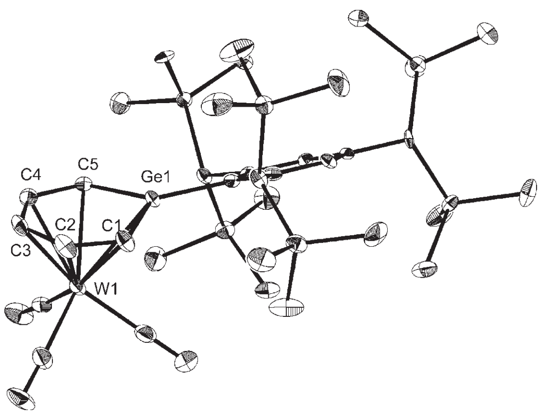


Figure 2. ORTEP drawing of $[W(\eta^6\text{-}C_5H_5GeTbt)(CO)_3]$ (**4**, 50 % probability; the benzene molecule and hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1–C1 1.893(6), Ge1–C5 1.869(6), C1–C2 1.405(9), C2–C3 1.431(9), C3–C4 1.413(9), C4–C5 1.432(8), Ge1–W1 2.7055(7), C1–W1 2.427(6), C2–W1 2.348(6), C3–W1 2.342(6), C4–W1 2.363(6), C5–W1 2.438(6), C1-Ge1-C5 100.9(3), C1-Ge1-C9 128.1(3), C5-Ge1-C9 130.9(3), Ge1-C1-C2 121.0(5), C1-C2-C3 126.2(6), C2-C3-C4 124.1(6), C3-C4-C5 125.2(6), Ge1-C5-C4 121.7(5).

1.893(6) Å] and the four C–C bonds [1.405(9)–1.432(8) Å] in the germabenzene ligand of W complex **4** are slightly longer than those in the free germabenzene **1** [Ge–C = 1.827(2) and 1.829(2) Å], C–C = 1.385(3)–1.396(3) Å][9a] and the Cr complex **2** [Ge–C = 1.859(5) and 1.878(5) Å, C–C = 1.393(7)–1.404(7) Å]. While the C–Cr bond lengths in **2** [2.186(5)–2.314(4) Å] and the C–W bond lengths [2.342(6)–2.438(6) Å] in **4** are similar to those in $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$[2.217(2)–2.240(2) Å][20] and $[W(CO)_3(\eta^6\text{-}C_6H_6)]$ [2.353(5)–2.375(5) Å],[21] the Ge–Cr [2.5849(12) Å] and Ge–W [2.7055 (7) Å] distances are somewhat longer than the bond lengths reported for Ge–Cr and Ge–W bonds in the related complexes $[\{(OC)_5Cr\}I_2Ge{-}GeI_2\{Cr(CO)_5\}]^{2-}$ [2.468(1) Å],[22] and $[Cp^{Et}W(CO)_2({=}GeMe_2)(GeMe_3)]$ (Cp^{Et} = C_5Me_4Et) [2.667(3) Å].[23]

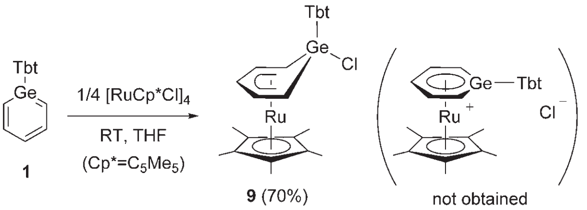
Theoretical calculations for the model compounds **6** and **8** were also performed for comparison (Table 2). The agreement between the experimentally measured and the theoretical values is excellent except in the cases of the Ge–Cr and Ge–W bond lengths, indicating that the Ge–C and C–C bond lengths in the germabenzene rings are little affected by substituents on the germanium atom. The slightly longer Ge–Cr and Ge–W bond lengths in **2** and **4**, in relation to the corresponding computed values in **6** and **8**, should be due to the steric repulsion between the Tbt and CO moieties.

Table 2. Observed and calculated bond lengths (Å) in Cr and W complexes **2**, **4**, **6** and **8**.

	$[Cr(CO)_3(\eta^6\text{-}C_5H_5GeR)]$	
	2 (R = Tbt)	**6** (R = H)[a]
Ge1–C1, Ge1–C5	1.878(5), 1.859(5)	1.862
C1–C2, C4–C5	1.396(7), 1.404(6)	1.408
C2–C3, C3–C4	1.404(6), 1.393(7)	1.419
Ge1–Cr1	2.5849(12)	2.499
	$[W(CO)_3(\eta^6\text{–}C_5H_5GeR)]$	
	4 (R = Tbt)	**8** (R = H)[a]
Ge1–C1, Ge1–C5	1.893(6), 1.869(6)	1.871
C1–C2, C4–C5	1.405(9), 1.432(8)	1.417
C2–C3, C3–C4	1.431(9), 1.413(9)	1.426
Ge1–Cr1	2.7055(7)	2.653

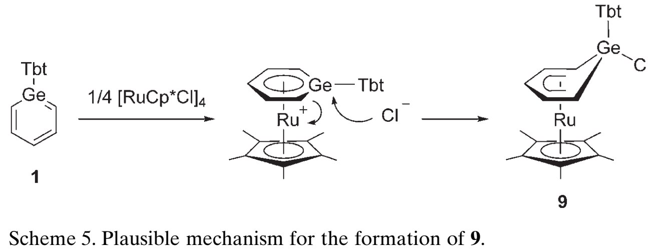
[a] Calculated at the B3PW91/6-31G(d) (for C, H, O), 6-311G(3d) (for Ge), and LanL2DZ (for Cr, Mo, W) levels.

Synthesis of an η^5-germabenzene Ru complex: As part of a program geared to exploring the synthesis of new types of germabenzene complexes, we next focused our attention on derivatives of the electron-rich $[Cp^*Ru]^+$ fragment, which has been widely employed in the coordination chemistry of arenes.[24] As starting material for the synthesis of an η^6-germabenzene sandwich-type complex we selected $[Cp^*RuCl]_4$ (Scheme 4).



Scheme 4. Synthesis of η^5-germabenzene complex **9**.

Treatment of germabenzene **1** with $[Cp^*RuCl]_4$ at ambient temperature in THF afforded the novel η^5-germabenzene complex $[Cp^*Ru\{\eta^5\text{-}C_5H_5GeTbt(Cl)\}]$ (**9**), isolated in 71 % yield as brown crystals, without any formation of the corresponding η^6-type cationic complex $[Cp^*Ru\{\eta^6\text{-}C_5H_5GeTbt\}][Cl]$ (**10**). The formation of the η^5-complex **9** can be reasonably explained in terms of the initial formation of a cationic η^6-complex **10**, followed by the nucleophilic attack of the counter-anion—chloride ion (Cl^-)—on the germanium atom, along with cleavage of the Ge–Ru bond (Scheme 5).



Scheme 5. Plausible mechanism for the formation of **9**.

Since the η^5-complex **9** is relatively stable towards air and moisture, its separation and purification was performed by gel permeation liquid chromatography (toluene as eluent). On standing in solution (benzene or toluene) for a few hours, however, **9** gradually decomposed with liberation of ruthenium to give complicated mixtures.

Structure of the η^5-germabenzene Ru complex: The formation of **9** was confirmed by NMR spectroscopy, and the molecular structure of **9** was determined by low-temperature X-ray analysis. The ^{1}H NMR spectrum of **9** exhibits resonances for the germacyclohexadienyl ring at $\delta = 2.61$ ppm (H1, H5) and $\delta = 4.48$–4.50 ppm (H2, H3, and H4). These chemical shifts are similar to those seen in the related silacyclohexadiene complexes [Fe(η^5-$C_5H_5SiMe_2)_2$] ($\delta = 2.20$, 4.85, and 4.97 ppm)[25] and [Cp*Ru{η^5-C_5H_5SiH(*t*-Bu)}] ($\delta = 1.88$ and 4.65 ppm).[3] In addition, a singlet signal at $\delta = 1.76$ ppm is attributable to the protons of the Cp* group. The ^{13}C NMR signals for the germacyclohexadienyl ring carbons of **9** [$\delta = 46.19$ (C1, C5), 83.41 (C3), and 90.56 ppm (C2, C4)] are consistent with the shifts for the pentadienyl ligand in [Cp*Ru(η^5-pentadienyl)] ($\delta = 42.5$, 82.5, and 91.5 ppm),[26] and quite different from those in the η^6-germabenzene complexes **2**–**4** (see above).

Single crystals of **9** were grown from a concentrated hexane solution: the molecular geometry of **9** is shown in Figure 3, and consists of two planar rings bound to the Ru atom in sandwich fashion. The germacyclohexadienide ligand of **9** is coordinated to Ru in an η^5 manner through the five essentially planar carbon atoms. The angle between the C1−Ge1−C5 plane and the C1-C2-C3-C4-C5 plane in **9** is 39.6°, which is roughly similar to those in the Fe complexes with sila- and stannacyclohexadienes: [Fe(η^5-$C_5H_5SiMe_2)_2$] (36.9°) and [Fe{η^5-$C_5H_5SnMe_2$}(η^6-C_6H_6)]$_2$-[Fe_2Cl_6] (37.6°).[25] The Cp* fragment adopts an *anti*-eclipsed conformation and is nearly parallel to the η^5-germacyclohexadiene fragment. Whereas the Ru–centroid bond distance for the Cp* ligand (1.808 Å) compares with that recorded in [Cp*Ru(η^6-C_6Me_6)][OTf] (1.753 Å),[27] the Ru–centroid (germacyclohexadiene) one appears to be shorter (1.631 Å), a result that indicates that the germacyclohexadiene ligand has a stronger π-accepting capability than the Cp* ligand. In the germacyclohexadiene ligand, the lengths of the two Ge−C bonds [1.916(4) and 1.914(4) Å] are found to vary within almost the same range as typical Ge−C single bonds (1.908–2.001 Å). The lengths of the four C−C bonds [1.392(8)–1.428(8) Å] are almost equal, and are also similar to the C−C bond lengths in the parent benzene (1.39–1.40 Å). The Ge···Ru distance is 3.00 Å longer than the Ge−Ru single bond in the related η^5-germolyl Ru complex [Cp*Ru{η^5-$C_4Me_4GeSi(SiMe_3)_3$}] (2.493(1) Å),[2a] suggesting non-bonding between Ge and Ru atoms.

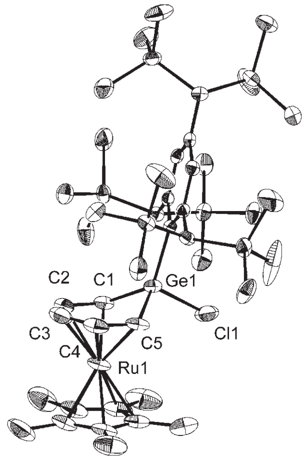


Figure 3. ORTEP drawing of [Cp*Ru{η^5-C_5H_5GeTbt(Cl)}] (**9**, major part, 50 % probability; the hydrogen atoms have omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge−Cl1 2.2175(18), Ge1−C1 1.916(4), Ge1−C5 1.914(4), C1−C2 1.422(7), C2−C3 1.428(8), C3−C4 1.415(8), C4−C5 1.392(8), C1−Ru1 2.213(7), C2−Ru1 2.189(7), C3−Ru1 2.200(7), C4−Ru1 2.181(7), C5−Ru1 2.221(8), C1-Ge1-C5 90.4(2), C1-Ge1-Cl1 104.32(19), C5-Ge1-Cl1 108.42(19), Ge1-C1-C2 119.1(4), C1-C2-C3 122.3(5), C2-C3-C4 123.1(5), C3-C4-C5 123.4(5), Ge1-C5-C4 120.0(4).

Conclusion

We have synthesized the first stable η^6-germabenzene–Group 6 metal complexes—[(η^6-C_5H_5GeTbt)M$(CO)_3$] (M = Cr, Mo, and W; **2**–**4**)—by ligand exchange between the kinetically stabilized germabenzene **1** and [M$(CO)_3$-$(CH_3CN)_3$]. Additionally, treatment of **1** with [Cp*RuCl]$_4$ resulted in the successful isolation of the novel η^5-germabenzene Ru complex [Cp*Ru{η^5-C_5H_5GeTbt(Cl)}] (**9**). Complex **9** can be regarded as a potential precursor for the synthesis of a η^6-type cationic complex [Cp*Ru{η^6-C_5H_5GeTbt}]$^+$. Their molecular structures were revealed by the spectroscopic data and by X-ray structural analysis, so these results are the first examples showing the coordination ability of the germabenzene **1**.

Experimental Section

General: All experiments were performed under argon unless otherwise noted. All solvents were dried by standard methods and freshly distilled prior to use. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in C_6D_6 or $CDCl_3$ with a JEOL JNM AL-300 spectrometer at room temperature. Infrared spectra were obtained on a JASCO FT/IR-300E spectrophotometer, electronic spectra were recorded on a JASCO Ubest-50 UV/VIS spectrometer, and high-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 instrument (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: toluene). The preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected, while elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

1-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1-germabenzene (1):[9a] [M$(CH_3CN)_3(CO)_3$] (M = Cr,[28] Mo,[29] and W[28]), and [RuCp*Cl]$_4$[30] were prepared by the reported procedures.

[Cr(η^6-C_5H_5GeTbt)$(CO)_3$] (2): In a glovebox 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 put into a 5 ϕ NMR tube, which was evacuated and sealed. Heating of the mixture at 80 °C for 48 h resulted in the disappearance of the NMR signals for **1**, and the tube was then opened and the solvent was removed. The 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, 18H), 0.19 (s, 36H), 1.49 (s, 1H), 2.45 (brs, 1H), 2.52 (brs, 1H), 3.95 (d, ^3J(H,H) = 10.5 Hz, 2H), 4.73 (t, ^3J(H,H) = 6.3 Hz, 1H), 4.98 (dd, ^3J(H,H) = 6.3, 10.5 Hz, 2H), 6.63 (brs, 1H), 6.73 ppm (brs, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 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 (4.9×10^4), 279 (1.7×10^4), 340 nm (8×10^3 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{35}H_{64}CrGeO_3Si_6$: C 50.89, H 7.81; found: C 49.96, H 7.76. Although the elemental analysis of **2** was attempted several times (more than ten times) with samples obtained from different batches, satisfactory analytical data have not yet been obtained, most probably due to its incombustibility. The measurement of high-resolution mass spectrum also failed, probably due to the instability of **2** under the FAB-MS conditions.

[Mo(η^6-C_5H_5GeTbt)(CO)$_3$] (3): In a glovebox filled with argon, [Mo(CH_3CN)$_3$(CO)$_3$] (16.3 mg, 0.054 mmol) was added at ambient temperature to a solution of **1** (40.1 mg, 0.058 mmol) in THF (1 mL), and the solution was stirred for 5 h. After the solvent had been removed, 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): δ = 0.11 (s, 18H), 0.18 (s, 36H), 1.47 (s, 1H), 2.39 (brs, 1H), 2.49 (brs, 1H), 4.05 (d, ^3J(H,H) = 9.9 Hz, 2H), 4.73 (t, ^3J(H,H) = 6.6 Hz, 1H), 5.17 (dd, ^3J(H,H) = 6.6, 9.9 Hz, 2H), 6.61 (brs, 1H), 6.70 ppm (brs, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 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 (4.1×10^4), 287 (1.0×10^4), 344 nm (1.3×10^4 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{35}H_{64}GeMoO_3Si_6$: C 48.32, H 7.42; found: C 47.91, H 7.48.

[W(η^6-C_5H_5GeTbt)(CO)$_3$] (4): In a glovebox filled with argon, **1** (53.8 mg, 0.078 mmol) and W(CH_3CN)$_3$(CO)$_3$ (33.6 mg, 0.086 mmol) were dissolved in C_6D_6 (0.5 mL) and the solution was placed in a 5ϕ NMR tube, which was evacuated and sealed. Heating of the mixture at 80 °C for 12 h resulted in the disappearance of the NMR signals for **1**, and the tube was then opened and the solvent removed. The residue was recrystallized from hexane at −40 °C to give **4** (48.3 mg, 65 %) as yellow crystals. M.p. 261–263 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.11 (s, 18H), 0.17 (s, 36H), 1.47 (s, 1H), 2.36 (brs, 1H), 2.45 (brs, 1H), 4.03 (d, ^3J(H,H) = 9.9 Hz, 2H), 4.75 (t, ^3J(H,H) = 6.6 Hz, 1H), 4.86 (dd, ^3J(H,H) = 6.6, 9.9 Hz, 2H), 6.61 (brs, 1H), 6.70 ppm (brs, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 0.60 (q), 0.76 (q), 0.85 (q), 31.47 (d), 35.04 (d), 35.39 (d), 79.64 (d), 80.02 (d), 98.51 (d), 122.34 (d), 122.80 (s), 127.23 (d), 148.47 (s), 151.72 (s×2), 211.88 ppm (s); IR (KBr): $\tilde{\nu}$ = 1853, 1881, 1949 cm^{-1} (C=O); UV/Vis (n-hexane): λ_{max} (ε) = 228 (4.2×10^4), 283 (1.2×10^4), 339 nm (1.5×10^4 mol^{-1}dm^{3}cm^{-1}); high-resolution FAB-MS: m/z: calcd for $C_{35}H_{65}{}^{74}GeO_3Si_6W$: 959.2271; found: 959.2260 [M+H]$^+$. Although the elemental analysis of **4** was attempted several times (more than ten times) with samples obtained from different batches, satisfactory analytical data have not yet been obtained, most probably due to its incombustibility.

Treatment of Cr complex 2 with water: Water (0.5 mL) was added at room temperature to a solution of **2** (31.9 mg, 0.039 mmol) in THF (2 mL), and the solution was stirred for 1 h. After the solvent had been removed, purification of the residue by PTLC (hexane/$CHCl_3$ 3:1) afforded 1-hydroxy-1-{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}-1-germacyclo-hexa-2,4-diene (**5a**; 25.9 mg, 94 %) as a colorless solid. M.p. 161–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 18H), 0.04 (s, 36H), 0.67 (s, 1H), 1.31 (s, 1H), 2.04–2.07 (m, 2H), 2.28 (brs, 2H), 5.90–5.97 (m, 1H), 6.08–6.15 (m, 1H), 6.26 (brs, 1H), 6.38 (brs, 1H), 6.47 (d, ^3J(H,H) = 12.9 Hz, 1H), 6.70 ppm (dd, ^3J(H,H) = 6.3, 12.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.50 (q), 0.69 (q), 0.85 (q), 1.03 (q), 21.20 (t), 28.17 (d), 28.47 (d), 30.31 (d), 121.99 (d), 125.33 (d), 126.91 (d), 129.27 (s), 129.83 (d), 131.27 (d), 138.52 (d), 144.85 (s), 150.15 (s), 150.49 ppm (s); elemental analysis calcd (%) for $C_{32}H_{66}GeOSi_6$: C 54.29, H 9.40; found C 53.91, H 9.46.

Treatment of Mo complex 3 with water: Water (0.5 mL) was added at room temperature to a solution of **3** (32.1 mg, 0.037 mmol) in THF (1 mL), and the solution was stirred for 1 h. After the solvent had been removed, purification of the residue by PTLC (hexane/$CHCl_3$ 3:1) afforded **5a** (24.1 mg, 92 %).

Treatment of W complex 4 with water: Water (0.5 mL) was added at room temperature to a solution of **4** (32.8 mg, 0.034 mmol) in THF (2 mL), and the solution was stirred for 1 h. After the solvent had been removed, purification of the residue by PTLC (hexane/$CHCl_3$ 3:1) afforded **5a** (23.6 mg, 97 %).

[RuCp*{η^5-C_5H_5GeTbt(Cl)}] (9): In a glovebox filled with argon, [RuCp*Cl]$_4$ (23.7 mg, 0.0871 mmol) was added to a solution of **1** (50.0 mg, 0.0725 mmol) in THF (1 mL) at ambient temperature, and the solution was stirred for 13 h. After the solvent had been removed, the residue was recrystallized from hexane at 25 °C to give **9** (49.4 mg, 71 %) as brown crystals. M.p. 244–246 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.15 (s, 18H), 0.30 (s, 36H), 1.42 (s, 1H), 1.76 (s, 15H), 2.63 (d, ^3J(H,H) = 9.9 Hz, 2H), 2.74 (brs, 2H), 4.48–4.50 (m, 3H), 6.40 (brs, 1H), 6.51 ppm (brs, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 0.89 (q), 1.23 (q), 1.37 (q), 10.92 (q), 26.02 (d), 26.56 (d), 30.62 (d), 46.18 (d), 83.41 (d), 89.62 (d), 90.55 (s), 122.46 (d), 127.11 (d), 137.39 (s), 144.87 (s), 149.28 ppm (s×2); high-resolution FAB-MS: m/z: calcd for $C_{42}H_{79}{}^{35}Cl^{74}Ge^{102}RuSi_6$: 962.2741; found: 962.2752 [M]$^+$.

X-ray data collection for complexes 2, 4, and 9: The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer. The structures were solved by direct methods (SHELXS-97)[31] and refined by full-matrix, least-squares procedures on F^2 for all reflections (SHELXL-97).[31] All the non-hydrogen atoms were refined anisotropically. All hydrogens were placed by use of AFIX instructions.

Crystal data for **2**·0.5 benzene ($C_{38}H_{67}CrGeO_3Si_6$): M = 865.05, T = 103(2) K, monoclinic, $P2_1/n$ (no. 14), a = 12.613(6), b = 32.756(13), c = 12.661(5) Å, β = 115.767(6)°, V = 4711(3) Å^3, Z = 4, ρ_{calcd} = 1.220 g cm^{-3}, μ = 1.053 mm^{-1}, λ = 0.71070 Å, $2\theta_{max}$ = 50.0°, 28628 measured reflections, 8231 independent reflections, 460 refined parameters, GOF = 1.246, R_1 = 0.0700 and wR_2 = 0.1808 ($I > 2\sigma(I)$), R_1 = 0.0820 and wR_2 = 0.1871 (for all data), largest difference peak and hole 0.497 and −0.491 e Å^3.

Crystal data for **4**·0.5 benzene ($C_{38}H_{67}GeO_3Si_6W$): M = 996.90, T = 103(2) K, monoclinic, $P2_1/n$ (no. 14), a = 12.556(2), b = 32.953(5), c = 12.585(2) Å, β = 114.366(6)°, V = 4743.2(14) Å^3, Z = 4, ρ_{calcd} = 1.396 g cm^{-3}, μ = 3.240 mm^{-1}, λ = 0.71070 Å, $2\theta_{max}$ = 50.0°, 21024 measured reflections, 8045 independent reflections, 460 refined parameters, GOF = 1.090, R_1 = 0.0394 and wR_2 = 0.1433 ($I > 2\sigma(I)$), R_1 = 0.0504 and wR_2 = 0.1492 (for all data), largest difference peak and hole 0.667 and −0.821 e Å^3.

Crystal data for **9** ($C_{42}H_{79}ClGeRuSi_6$): M = 961.70, T = 103(2) K, monoclinic, $P2_1/n$ (no. 14), a = 9.2899(6), b = 25.6748(15), c = 22.0729(16) Å, β = 93.396(4)°, V = 5255.5(6) Å^3, Z = 4, ρ_{calcd} = 1.215 g cm^{-3}, μ = 1.072 mm^{-1}, λ = 0.71070 Å, $2\theta_{max}$ = 50.0°, 31857 measured reflections, 9236 independent reflections, 662 refined parameters, GOF = 1.077, R_1 = 0.0467 and wR_2 = 0.1007 ($I > 2\sigma(I)$), R_1 = 0.0576 and wR_2 = 0.1063 (for all data), largest difference peak and hole 0.626 and −0.463 e Å^3.

CCDC-192689 (**2**), -243030 (**4**), and -243031 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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