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Reactivities of germacyclopropabenzene toward some transition metal carbonyl complexes†

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The thermal reactions of an overcrowded germacyclopropabenzene with group 6 metal hexacarbonyl complexes [M(CO)$_6$] (M = Cr, Mo and W) resulted in the formation of novel Fischer-type carbene complexes via the insertion reaction of a C=O group to the Ge–C bond. By contrast, the germacyclopropabenzene reacts with [Co$_2$(CO)$_8$] to give a germanium analog of benzocyclobutanone via the insertion reaction of a CO unit into the germacyclopropane ring. The reaction of the germacyclopropabenzene with [Mn$_2$(CO)$_{10}$] resulted in the formation of the intramolecular cyclization product accompanying the migration of a trimethylsilyl group, i.e. a cyclobutabenzene derivative. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: main group element; germanium; three-membered ring; germacyclopropabenzene; insertion reaction; germoxycarbene complexes; metal carbonyls of groups 6, 7, and 9; germacyclobutanone; germacyclobutabenzene

INTRODUCTION

The chemistry of cyclopropabenzenes has attracted much interest because of their unique structures and reactivities.[1–3] In particular, cycloproparenes react with hexacarbonyl complexes of group 6 metals to give various types of products depending on the kind of the substituents on the three-membered ring.[4–6] For example, cyclopropabenzene itself reacts with [Cr(CH$_3$CN)$_3$(CO)$_3$] to give benzocyclobutanone, and *1H*-cyclopropa[*b*]naphthalene reacts with [Cr(CO)$_6$] or [Cr(CH$_3$CN)$_3$(CO)$_3$] to give naphthocyclobutanone.[4,5] By contrast, a bis-silylated derivative reacts with the carbonyl complexes of Cr to afford the corresponding arene complex of tricarbonyl chromium with cyclopropa[*b*]naphthalene (Scheme 1).[6]

In recent years, there has been much attention to the three-membered metallacyclic compounds of heavier group 14 elements, i.e. heavier congeners of cyclopropane and cyclopropene.[7–9] However, the chemistry of heteroatom analogs of cyclopropabenzene has been unexplored because of their low thermal stability except for some examples of heteracyclopropabenzenes such as aza-,[10] thia-,[11,12] selena-,[13] bora-,[14] and silacyclopropabenzenes[15] postulated as reactive intermediates. On the other hand, we have recently succeeded in the synthesis of the first stable sila-[16,17] and germacyclopropabenzenes,[18] by taking advantage of a combination of efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-diisopropylphenyl (Dip), via the reactions of the corresponding overcrowded dilithiosilane[19] and dilithiogermane[18] with *o*-dibromobenzene, respectively. Furthermore, we have preliminarily reported the reactions of the germacyclopropabenzene with carbonyl complexes of groups 6 metals (Cr, Mo and W) leading to the formation of novel Ge-containing Fischer-type carbene complexes, i.e. 1,2-oxagermolan-5-ylidene pentacarbonyl metal complexes.[20]

In this paper, we present the details of the reactions of the overcrowded germacyclopropabenzene with group 6 metal hexacarbonyls [M(CO)$_6$] (M = Cr, Mo and W) together with its unique reactivities towards other transition metal carbonyl complexes, [Co$_2$(CO)$_8$] and [Mn$_2$(CO)$_{10}$].

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†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

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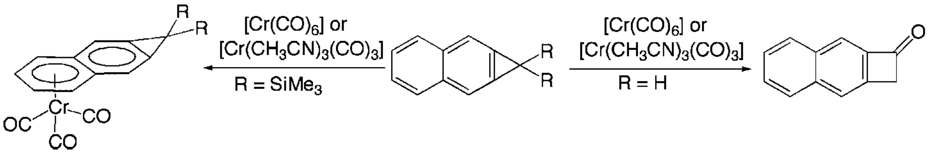
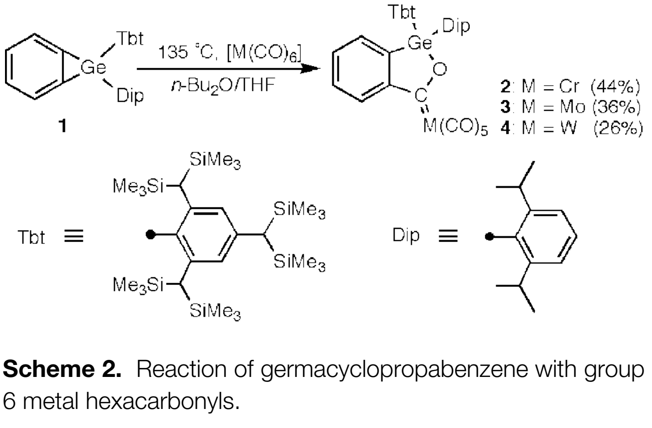


Scheme 1. Reactions of *1H*-cyclopropa[*b*]naphthalene with group 6 metal carbonyls.

RESULTS AND DISCUSSION

Thermal reactions of 1 with group 6 metal hexacarbonyls

Germacyclopropabenzene **1** was prepared by the reaction of the corresponding dilithiogermane bearing bulky substituents with *o*-dibromobenzene, according to the reported procedure.[18] Thermal reactions of **1** with [M(CO)$_6$] (M = Cr, Mo and W) resulted in the formation of the corresponding 1,2-oxagermolan-5-ylidene pentacarbonyl metal complexes **2**–**4**, which were obtained as deep red crystals (Scheme 2). The carbene complexes **2**–**4** are fairly stable towards air and moisture, and they showed satisfactory spectral and analytical data. The ^{13}C NMR spectra of **2**–**4** in C$_6$D$_6$ showed signals at 336.7, 327.7 and 311.0 ppm, respectively, which are consistent with the characteristic chemical shifts of typical Fischer-type carbene complexes reported.[21–23] The ^{13}C NMR chemical shifts for the carbonyl carbons of **2**–**4** were observed at the field of 197–225 ppm. In the case of **4**, a couple of satellite peaks due to the coupling between the *cis*-carbonyl ^{13}C atoms and ^{183}W atom were observed, and the coupling constant (198 ppm, $^1J_{\text{C–W}} = 127.2$ Hz) was comparable with those of typical carbene–tungsten complexes.[24,25] Each of **2**–**4** shows three CO stretching vibrations in the IR spectrum in the range 1925–2062 cm^{-1}. The UV/vis spectra of **2, 3** and **4** in hexane showed two absorption maxima around 340–355 and 460–480 nm.



Scheme 2. Reaction of germacyclopropabenzene with group 6 metal hexacarbonyls.

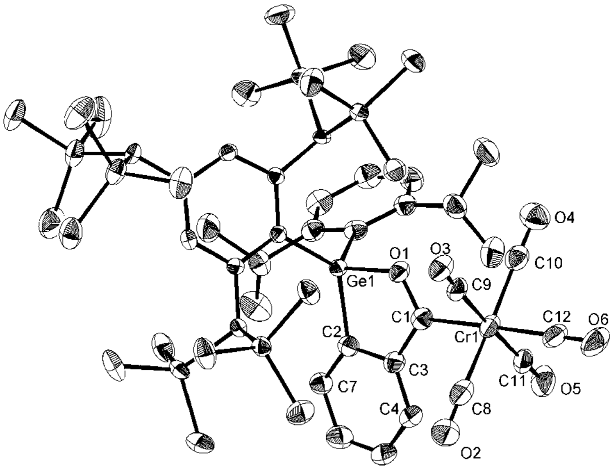


Figure 1. ORTEP drawing (50% probability) showing the solid-state structure for **2**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–O1 1.904(2), Ge1–C2 1.947(3), C1–O1 1.292(4), C1–C3 1.510(5), C1–Cr1 2.050(3), C2–C3 1.403(5), Cr1–C12 1.883(4), Cr1–C10 1.888(4), Cr1–C11 1.893(4), C1–C8 1.903(4), Cr1–C9 1.911(4), O1–Ge1–C2 85.39(12), O1–C1–C3 111.1(3), C1–O1–Ge1 117.9(2), C7–C2–C3 120.7(3), C3–C2–Ge1 108.6(2), C4–C3–C2 118.7(3), C2–C3–C1 116.9(3), O1–C1–Cr1 120.6(2), C3–C1–Cr1 128.2(2).

Molecular structures of **2, 3** and **4** were definitively determined by X-ray crystallographic analysis at −180 °C. The ORTEP diagrams and crystallographic data of **2**–**4** are shown in Figs 1– 3 and Tables 1 and 2, respectively. In each case, the 1,2-oxagermolane ring was nearly planar. The sums of interior bond angles for their 1,2-oxagermolane rings were *ca* 540°, and the group 6 metal atoms were in an octahedral environment and linked by C(carbene) atom (C1 atom for **2** and C7 atom for **3** and **4**). The C(carbene)–O1 bond lengths [1.292(4) Å (**2**), 1.298(6) Å (**3**) and 1.292(5) Å (**4**)] were very close to or slightly shorter than those of typical alkoxycarbene complexes (1.30–1.35 Å).[24,25] The M=C(carbene) bond distances [2.050(3) Å (**2**), 2.194(5) Å (**3**) and 2.194(4) Å (**4**)] were also comparable with those of the reported carbene complexes of group 6 metals. Bond lengths and angles of **2** and **3** were similar to each other due to lanthanide contraction. Usually, stronger π-electron donation to the carbene carbon from the neighboring oxygen and/or carbon atom leads to the elongation of the M–C(carbene) and C–O$_{\text{trans}}$ bond lengths together with the shortening of the M–CO$_{\text{trans}}$ bond distance. Thus, the distinct π-electron donation of the carbene carbon is not observed for the newly obtained Ge-containing Fischer-type carbene complexes **2**– **4**.

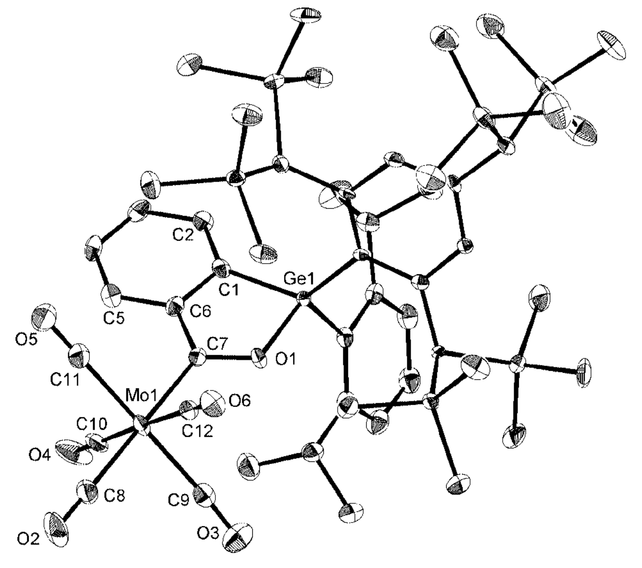


Figure 2. ORTEP drawing (50% probability) showing the solid-state structure for **3**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–O1 1.898(4), Ge1–C1 1.930(5), C1–C6 1.407(8), C6–C7 1.494(7), C7–O1 1.298(6), C7–Mo1 2.194(5), Mo1–C9 2.026(7), Mo1–C8 2.036(6), Mo1–C10 2.041(7), Mo1–C11 2.045(7), Mo1–C12 2.061(7), O1–Ge1–C1 85.33(19), C2–C1–C6 119.6(5), C6–C1–Ge1 108.9(4), C5–C6–C1 119.6(5), C1–C6–C7 116.9(5), O1–C7–C6 110.9(5), O1–C7–Mo1 120.7(4), C6–C7–Mo1 128.3(4), C7–O1–Ge1 117.9(3).

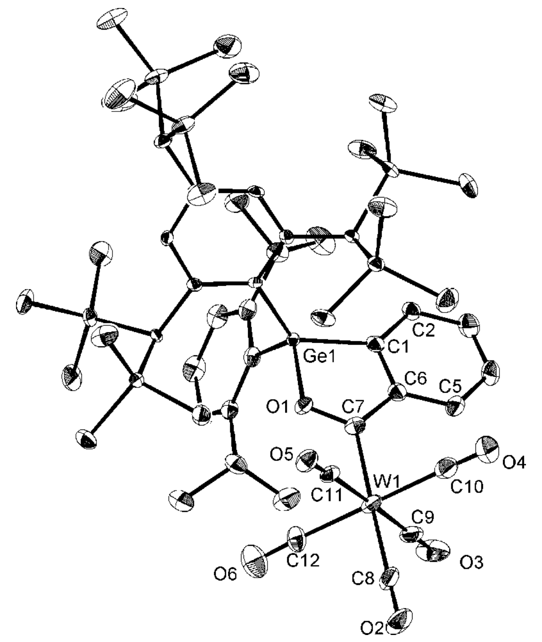


Figure 3. ORTEP drawing (50% probability) showing the solid-state structure for **4**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–O1 1.895(3), Ge1–C1 1.941(4), C1–C6 1.409(6), C6–C7 1.503(6), C7–O1 1.292(5), C7–W1 2.194(4), W1–C12 2.015(5), W1–C8 2.027(5), W1–C9 2.035(5), W1–C11 2.049(5), W1–C10 2.052(6), O1–Ge1–C1 85.81(16), C2–C1–C6 120.0(4), C6–C1–Ge1 108.5(3), C5–C6–C1 119.3(4), C1–C6–C7 116.5(4), O1–C7–C6 111.8(4), O1–C7–W1 120.4(3), C6–C7–W1 127.7(3).

Thermal reaction of 1 with [$Mn_2(CO)_{10}$]

When **1** was treated with an excess amount of [$Mn_2(CO)_{10}$] in *n*-Bu_2O at 80 °C for 11 days, an unexpected cyclic compound **5** was obtained as stable colorless crystals (Scheme 3). Germacyclobutabenzene **5** showed satisfactory spectral and analytical data, and the molecular structure of **5** was determined by X-ray crystallographic analysis. The ORTEP diagram and crystallographic data of **5** are shown in Fig. 4 and Tables 1 and 2, respectively. The germacyclobutene ring was slightly twisted, the torsion angle of Ge1–C1–C6–C7 being not 0° but 9.3°. Although all C–C bond lengths in the central benzene ring of **5** were almost the same as those in the usual benzene rings (typical C–C distances are 1.39–1.40 Å), within experimental error, the deviation of the bond angles from 120° was observed in the aromatic ring due to the strain resulting from the condensation with the four-membered ring.

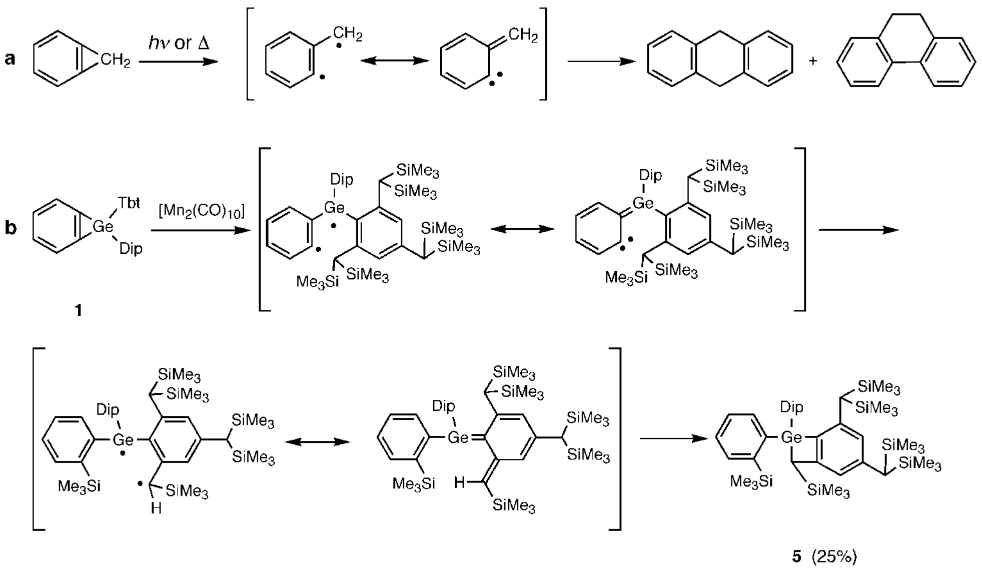
It is generally accepted that [$Mn(CO)_5$]· radicals are generated by the photolysis or thermolysis of [$Mn_2(CO)_{10}$].[26,27] In addition, cyclopropabenzenes reportedly decompose by the thermolysis[1–3,28,29] and photolysis[30] to generate the corresponding biradical via the C–C bond cleavage in the cyclopropene ring. For example, thermolysis of cyclopropabenzene results in the formation of 9,10-dihydrophenanthrene and 9,10-dihydroanthracene via the dimerization of the biradical intermediate [Scheme 3(a)].[1–3] Although the formation mechanism of cyclobutabenzene **5** is not clear at present, one might be able to postulate the formation of the corresponding ring-opened biradical as an extremely reactive intermediate and the subsequent silicon-rearrangement reaction followed by the ring-closure reaction, giving **5**. In these biradical intermediates, carbene and orthoquinodimethane structures can be depicted as resonance structures, respectively [Scheme 3(b)], although they have an unstable germanium–carbon double bond. The formation of **5** can be explained in terms of a non-radical pathway as well, i.e. the nucleophilic attack of the carbene on the silicon atom and subsequent [2 + 2] cyclization of the resulting orthoquinodimethane. As for migration of a trimethylsilyl group of the Tbt group, we have already reported that the trimethylsilyl group at the *o*-position of TbtLi easily migrated to give a 1,3-silicon rearrangement compound via the anion or radical pathway.[31] In addition, the starting material, germacyclopropabenzene **1**, did not decompose thermally under the reaction conditions (even under extremely high-temperature conditions: in *n*-Bu_2O solution at 150 °C for 1 week in a sealed tube). Therefore, it is considered that the generation of biradical from **1** requires the participation of [$Mn_2(CO)_{10}$].

Table 1. Crystallographic data for **2**–**6**

	2	**3**	**4**	**5**	**6**
Molecular formula	$C_{51}H_{80}CrGeO_6Si_6$	$C_{51}H_{80}GeMoO_6Si_6$	$C_{51}H_{80}GeO_6Si_6W$	$C_{45}H_{80}GeSi_6$	$C_{46}H_{80}GeOSi_6\cdot CHCl_3$
Formula weight	1082.28	1126.22	1214.13	862.22	1009.60
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
a (Å)	11.8841(16)	11.911(5)	11.907(3)	12.317(8)	10.1468(9)
b (Å)	13.7144(8)	13.826(6)	13.800(4)	13.898(8)	20.3429(18)
c (Å)	19.8020(9)	19.818(8)	19.771(5)	15.677(10)	27.6215(17)
α (°)	77.335(4)	77.247(12)	77.242(8)	74.899(15)	90
β (°)	71.540(3)	71.363(11)	71.489(7)	89.77(2)	90
γ (°)	84.6841(17)	84.446(14)	84.456(9)	88.78(3)	90
V(Å^{-3})	2985.9(5)	3015(2)	3003.4(13)	2591(3)	5701.5(8)
Z	2	2	2	2	4
D_{calc}(g cm^{-3})	1.204	1.241	1.343	1.105	1.176
Independent reflections	10 463	10 414	10 352	8880	10 022
Parameters	608	586	586	491	546
R_1 [$I > 2\sigma(I)$]	0.045	0.069	0.041	0.062	0.039
$I > 2\sigma(I)$	7940	8307	9542	5749	9534
wR_2 (all data)	0.119	0.178	0.088	0.134	0.091
Goodness of fit	1.02	1.08	1.08	1.05	1.10
Largest diff. Peak and hole (e Å^{-3})	1.05 and −0.63[a]	0.72 and −0.65	3.24 and −1.74[b]	0.50 and −0.47	0.53 and −0.66
CCDC deposition no.	224 028	224 029	224 030	242 413	242 412

[a] The locations of the residual electron density peaks in **2** (1.05 and 1.03 e Å^{-3}) are 1.558 Å away from Ge1 and 1.003 Å away from Cr1, respectively.

[b] The location of the residual electron density peak in **4** (3.24 e Å^{-3}) is 0.897 Å away from W1.



Scheme 3. (a) Photolysis or thermolysis of cyclopropabenzene. (b) Reaction of germacyclopropabenzene with $[Mn_2(CO)_{10}]$.

Thermal reaction of 1 with $[Co_2(CO)_8]$

Heating a solution of **1** and $[Co_2(CO)_8]$ in n-Bu_2O led to the formation of the corresponding germacyclobutanone **6**, which is probably obtained via the insertion of a carbon monoxide into the C–Ge bond of the germacyclopropene ring (Scheme 4). Germacyclobutanone **6** was fairly stable towards air and moisture, and the molecular structure of this novel germacyclic compound was satisfactorily confirmed by ^{1}H and ^{13}C NMR, and IR spectroscopy and FAB-MS. The ^{13}C NMR spectrum of **6** in C_6D_6 showed a singlet signal at

Table 2. Selected bond lengths (Å) and angles (°) for **5** and **6**

	5	6
	Bond lengths	
Ge1–C1	1.988(4)	1.985(3)
Ge1–C7	2.034(4)	2.063(3)
C1–C2	1.403(6)	1.400(5)
C2–C3	1.404(6)	1.383(5)
C3–C4	1.396(6)	1.392(5)
C4–C5	1.404(6)	1.376(5)
C5–C6	1.393(6)	1.396(5)
C6–C7	1.536(6)	1.504(5)
C1–C6	1.402(6)	1.393(5)
C7–O1	—	1.200(4)
	Bond angles	
C1–Ge1–C7	72.94(18)	69.12(14)
Ge1–C7–C6	85.8(3)	89.6 (2)
C1–C6–C7	108.8(4)	104.8 (3)
C6–C1–Ge1	91.3(3)	96.2(2)
C1–C6–C5	121.5(4)	123.4(3)
C6–C5–C4	119.4(4)	117.1(3)
C5–C4–C3	117.9(4)	120.6(3)
C4–C3–C2	124.2(4)	122.0(3)
C3–C2–C1	116.4(4)	118.6(3)
C2–C1–C6	120.5(4)	118.2(3)
O1–C7–C6	—	129.7(3)
O1–C7–Ge1	—	140.6(3)

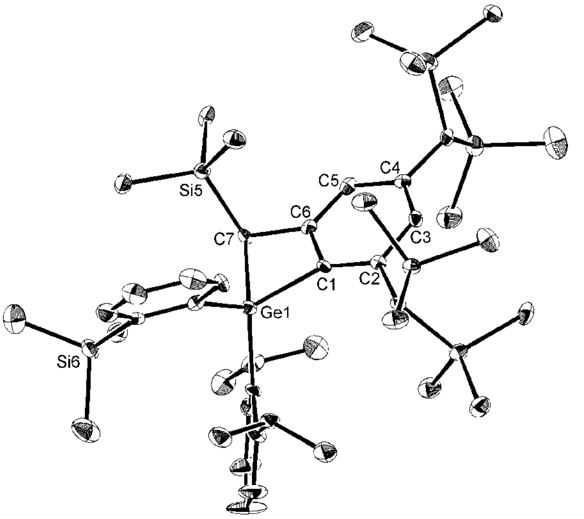
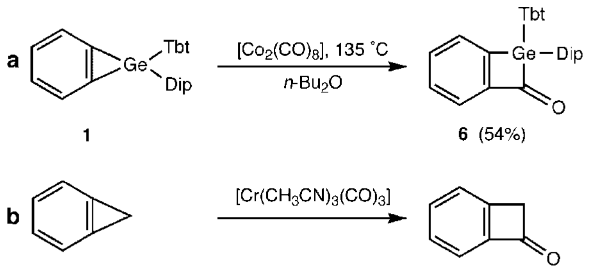


Figure 4. ORTEP drawing (50% probability) showing the solid-state structure for **5**. Hydrogen atoms were omitted for clarity.

225.0 ppm, which was assigned to that of the carbonyl carbon neighboring the Ge atom. The IR spectrum of **6** showed an absorption assignable to the stretching band of the carbonyl group at 1721 cm^{-1}.



Scheme 4. (a) Reaction of germacyclopropabenzene **1** with [Co$_2$(CO)$_8$]. (b) Reaction of cyclopropabenzene with [Cr(CH$_3$CN)$_3$(CO)$_3$].

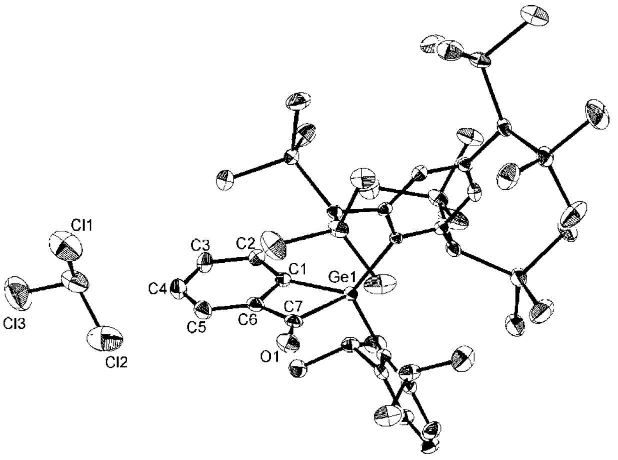
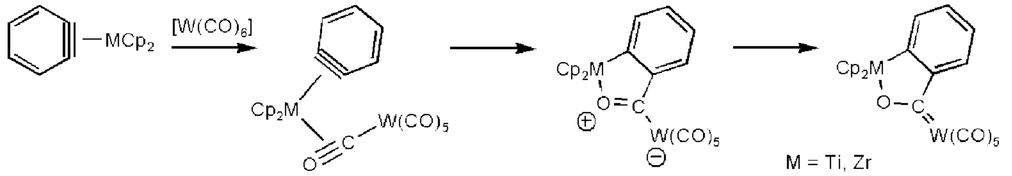


Figure 5. ORTEP drawing (50% probability) showing the solid-state structure for **6**·CHCl$_3$. Hydrogen atoms were omitted for clarity.

The molecular structure of **6** was finally determined by X-ray crystallographic analysis at −170 °C (Tables 1 and 2 and Fig. 5), which led to the first structural analysis of a germacyclobutanone ring skeleton. The deformation from the normal sp^2 configuration was larger on the C1 atom than the C6 atom judging from the bond angles of C6–C1–Ge1 [96.2°(2)] and C1–C6–C7 [104.8°(3)]. The four-membered ring was slightly twisted, the torsion angle of Ge1–C1–C6–C7 being not 0° but 4.3°. Although all C–C bond lengths the central benzene ring of **6** were almost the same, the deviation of the bond angles from 120° was observed in the aromatic ring due to the strain resulting from the condensation with the four-membered ring. In addition, we attempted simple CO insertion reaction of **1** using carbon monoxide instead of [Co$_2$(CO)$_8$]. A toluene solution of **1** was heated at 150 °C for 3 days under carbon monoxide atmosphere in an autoclave; however, **6** was not formed and the starting material **1** was recovered quantitatively. Thus, the formation of **6** requires the use of [Co$_2$(CO)$_8$].



Scheme 5. Reactivity of [$Cp_2M(\eta^2$-$C_6H_4)$] (M = Ti, Zr).

CONCLUSIONS

We have found that an overcrowded, diaryl-substituted germacyclopropabenzene **1** undergoes unique reactions with transition metal carbonyl complexes to give a variety of novel Ge-containing cyclic compounds, such as Fischer-type carbene complexes **2**–**4**, germacyclobutabenzene **5**, and germacyclobutanone **6**, depending on the kinds of reactants (metals). Thus, the insertion of a CO unit into the germacyclopropene ring of **1** giving germacyclobutanone **6** resembles the previously reported reactions of cycloproparenes with [$Cr(CO)_6$] and [$Cr(CH_3CN)_3(CO)_3$], leading to the formation of the corresponding cyclobutanones (Schemes 1 and 4). On the other hand, the reactivity of **1** towards [$M(CO)_6$] (M = Cr, Mo and W) leading to the formations of Fischer-type carbene complexes **2**–**4** is analogous not to the reactivity of cyclopropabenzenes towards metal carbonyls but to that of the intermediary η^2-benzyne complexes of group 4 metals, [$Cp_2M(\eta^2$-$C_6H_4)$] or [$Cp_2M(\eta^2$-$C_6H_3CH_3)$] (M = Ti and Zr), towards [$M'(CO)_6$] (M′ = Mo and W) (Scheme 5).[32–34] It should be noted that the reactivity of a germacyclopropabenzene toward transition metal complexes is quite different from that of the parent cyclopropabenzene. Although the detailed mechanism for the formation of **2**–**6** from **1** remains unclear at present, the unique ring-expansion reactions of **1** described here are most likely interpreted in terms of the high reactivity of Ge-containing three-membered ring in **1** due to its inherent ring strain and the susceptibility of a C–Ge bond to heterolytic bond scission compared with a C–C bond.

Further studies on the structure and reactivity of metallacyclopropabenzenes of heavier group 14 elements are currently in progress.

EXPERIMENTAL

General considerations

All experiments were performed under an argon atmosphere unless otherwise noted. Dibutylether was 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 $CDCl_3$, $C_2D_2Cl_4$, or C_6D_6 with a JEOL JNM AL-300 spectrometer. High-resolution mass spectral data were obtained on a Jeol JMS-700 spectrometer. Preparative gel permeation liquid chromatography (GPLC) was performed on LC-908 apparatus (Japan Analytical Industry Co. Ltd) equipped with JAIGEL 1H and 2H columns (eluent: toluene). 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. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

Reaction of 1 with [$Cr(CO)_6$]

A THF (0.2 ml)–*n*-Bu_2O (1.5 ml) solution of germacyclopropabenzene **1** (63.0 mg, 73.1 μmol) and [$Cr(CO)_6$] (80.0 mg, 365 μmol) was degassed and sealed in a Pyrex 10 ϕ glass tube, and then the suspension was heated at 135 °C for 3 days. After removal of the solvents, the residue was extracted with hexane several times. The unconsumed [$Cr(CO)_6$] was removed by filtration through Celite®, and the residue was evaporated. The filtrate was separated by subsequent preparative thin-layer chromatography (eluent: hexane) to afford the carbene complex **2** (34.7 mg, 32.0 μmol, 44% yield) as deep red crystals.

2: red crystals; mp 160–161 °C; ^{1}H NMR ($CDCl_3$, 323 K): δ−0.32 (s, 9H), −0.19 (s, 9H), 0.11 (s, 18H), 0.24 (s, 18H), 0.66 (brs, 3H), 0.98 (brs, 3H), 1.39 (s, 6H), 1.45 (s, 1H), 2.04 (s, 1H), 2.23 (s, 1H), 2.86 (brs, 1H), 3.69 (sept, J = 6.6 Hz, 1H), 6.38 (brs, 1H), 6.50 (brs, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.29 (t, 7.5 Hz, 1H), 7.59–7.71 (m, 2H), 7.90 (d, J = 7.2 Hz, 1H), 8.88 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 323 K) δ 1.07 (q), 1.50 (q), 2.50 (q), 22.0 (q), 26.1 (q), 26.3 (q), 26.7 (q), 28.9 (d), 30.3 (d), 31.6 (d), 33.8 (d), 37.1 (d), 123.7 (d), 125.0 (d), 127.4 (d), 128.6 (d), 130.3 (d), 130.7 (d), 131.6 (d), 133.5 (d), 137.7 (d), 138.0 (s), 140.4 (s), 144.2 (s), 146.5 (s), 147.4 (s), 148.0 (s), 151.0 (s), 152.0 (s), 154.2 (s), 217.7 (s), 223.9 (s), 336.7 (s); LRMS (FAB) *m/z*: found 1082 [M^+], calcd for $C_{51}H_{80}Cr^{74}GeO_6Si_6$ [M^+] 1082; IR (KBr) 1930.9, 1979.1, 2054.0 cm^{-1}; UV/vis (hexane) 480.0 nm ($\varepsilon = 1.0 \times 10^4$), 341.5 nm ($\varepsilon = 3.0 \times 10^3$); anal. calcd for $C_{51}H_{80}CrGeO_6Si_6$: C, 56.60, H, 7.45; found: C, 56.38; H, 7.57.

Reaction of 1 with [$Mo(CO)_6$]

A THF (0.2 ml)–*n*-Bu_2O (1.8 ml) solution of **1** (49.6 mg, 57.5 μmol) and [$Mo(CO)_6$] (75.9 mg, 287 μmol) was heated at 135 °C for 3 days in a sealed Pyrex 10 ϕ glass tube, and purified in a manner similar to the above-mentioned experiment for complex **2** to afford the product **3** (23.6 mg, 21.0 μmol, 36% yield) as deep red crystals.

3: red crystals; mp 162.5 °C (decomp); ^{1}H NMR ($CDCl_3$, 323 K): δ−0.21 (s, 9H), −0.08 (s, 9H), 0.12 (s, 18H), 0.17 (s, 9H), 0.43 (s, 9H), 0.75 (brs, 3H), 1.05 (s, 3H), 1.39 (s, 3H), 1.46 (s, 3H), 1.48 (s, 1H), 2.23 (s, 1H), 2.38 (s, 1H), 2.90 (brs, 1H), 3.88 (brs, 1H), 6.65 (brs, 2H), 6.95 (d, $J = 6.3$ Hz, 1H), 7.09 (d, $J = 6.3$ Hz, 1H), 7.10–7.19 (m, 3H), 7.78 (d, $J = 7.2$ Hz, 1H), 9.03 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 323 K) δ 1.14 (q), 1.71(q), 2.57 (q), 21.9 (q), 22.0 (q), 26.3 (q), 26.9 (q), 29.2 (d), 30.7 (d), 31.4 (d), 33.7 (d), 37.4 (d), 123.0 (d), 124.8 (d), 126.9 (d), 128.9 (d), 130.3 (d), 130.5 (d), 131.5 (d), 133.6 (d), 135.9(s), 138.6 (s), 138.9 (d), 143.7 (s), 146.4 (s), 147.1 (s), 147.8 (s), 151.9 (s), 152.1 (s), 154.0 (s), 206.6 (s), 213.2 (s), 327.7 (s); LRMS (FAB) m/z: found 1126 [M$^+$], calcd for $C_{51}H_{80}{}^{74}Ge^{96}MoO_6Si_6$ [M$^+$] 1126; HRMS (FAB) m/z: calcd for $C_{51}H_{80}{}^{74}Ge^{96}MoO_6Si_6$ 1126.2403, found 1126.2858; IR (KBr) 1930.9, 1979.1, 2062.1 cm^{-1}; UV/vis (hexane) 466.5 nm ($\varepsilon = 8.4 \times 10^3$), 349.0 ($\epsilon = 4.7 \times 10^3$); anal. calcd for $C_{51}H_{80}GeMoO_6Si_6$: C, 54.34; H, 7.24; found: C, 54.50; H, 7.12.

Reaction of 1 with [W(CO)$_6$]

A THF (0.3 ml)–n-Bu$_2$O (3.0 ml) solution of **1** (55.4 mg, 64.2 μmol) and [W(CO)$_6$] (113.0 mg, 321 μmol) was heated at 135 °C for 3 days in a sealed Pyrex 10 ϕ glass tube, and purified in a manner similar to the above-mentioned experiments to afford the product **4** (20.0 mg, 12.8 μmol, 26% yield) as deep red crystals.

4: red crystals; mp 169.2–170.8 °C; ^{1}H NMR ($CDCl_3$, 323 K): δ−0.34 (s, 9H), −0.21 (s, 9H), 0.08 (s, 18H), 0.14 (s, 9H), 0.25 (s, 9H), 0.67 (brs, 3H), 1.00 (brs, 3H), 1.28 (s, 3H), 1.40 (s, 3H), 1.46 (s, 1H), 2.02 (s, 1H), 2.15 (s, 1H), 2.84 (sept, $J = 6.6$ Hz, 1H), 3.68 (sept, $J = 6.6$ Hz, 1H), 6.30–6.65 (m, 2H), 7.14 (d, $J = 7.8$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.27–7.48 (m, 1H), 7.64–7.71 (m, 2H), 7.85–7.88 (m, 1H), 8.70–8.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 343 K) δ 1.18 (q), 1.29 (q), 1.33 (q), 1.61 (q), 2.56 (q), 22.8 (q), 26.1(q), 26.3 (q), 26.9 (q), 29.3 (d), 30.7 (d), 31.3 (d), 36.7 (d), 37.4 (d), 123.8 (d), 124.9 (d), 127.1 (d), 128.6. (d), 130.4 (d), 130.6 (d), 131.6 (d), 133.6 (d), 139.3 (d), 139.8 (s),144.0 (s), 146.5 (s), 147.1 (s), 147.8 (s), 150.8 (s), 151.9 (s), 152.2 (s), 153.9 (s), 198.5 (s, $J_{CW} = 127.2$ Hz), 209.5 (s), 311.0 (s); LRMS (FAB) m/z: found 1214 [M$^+$], calcd for $C_{51}H_{80}{}^{74}GeO_6Si_6{}^{184}W$ [M$^+$] 1214; HRMS (FAB) m/z: calcd for $C_{51}H_{80}{}^{74}GeO_6Si_6{}^{184}W$ 1214.3292, found 1214.3291; IR (KBr) 1925.1, 1975.3, 2062.1 cm^{-1}; UV/vis (hexane) 463.0 nm ($\varepsilon = 1.4 \times 10^4$), 352.0 nm ($\varepsilon = 5.6 \times 10^3$).

Reaction of 1 with [Mn$_2$(CO)$_{10}$]

An n-Bu$_2$O (1.5 ml) solution of **1** (74.9 mg, 86.8 μmol) and [Mn$_2$(CO)$_{10}$] (75.0 mg, 224 μmol) was heated at 80 °C for 11 days in a Pyrex 10 ϕ glass tube. After removal of the solvent, the mixture was subjected to GPLC (toluene) followed by PTLC (hexane) to afford **5** (18.8 mg, 21.7 μmol, 25% yield) as colorless crystals.

5: colorless crystals; mp 163.2–164.7 °C; ^{1}H NMR ($CDCl_3$): δ−0.26 (s, 9H), −0.21 (s, 9H), 0.01 (s, 18H), 0.05 (s, 9H), 0.17 (s, 9H), 0.39 (d, $J = 6.6$ Hz, 3H), 0.83 (d, $J = 6.6$ Hz, 3H), 1.08 (d, $J = 6.6$ Hz, 3H), 1.35 (d, $J = 6.6$ Hz, 3H), 1.58 (br s, 1H), 1.70 (br s, 1H), 2.93 (br s, 1H), 3.12 (sept, $J = 6.6$ Hz, 1H), 3.78 (sept, $J = 6.6$ Hz, 1H), 6.38 (brs, 1H), 6.43 (brs, 1H), 7.01 (d, $J = 6.9$ Hz, 1H), 7.08 (d, $J = 6.9$ Hz, 1H), 7.20–7.30 (m, 3H), 7.54 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.4$ Hz, 1H), 7.98 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.4$ Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 0.8 (q), 0.9 (q), 1.4 (q), 1.6 (q), 1.9 (q), 23.1 (q), 23.6 (q), 26.7 (d), 27.6 (q), 28.0 (q), 30.8 (d), 34.1 (d), 35.7 (d), 38.3 (d) 119.7 (d × 2), 123.3 (d), 124.4 (d), 127.9 (d), 128.1 (d), 129.7 (d), 135.7 (d), 136.9 (d), 139.1 (s), 141.0 (s), 145.0 (s), 146.2 (s), 147.3 (s), 151.7 (s), 154.8 (s), 155.1 (s), 155.3 (s); LRMS (FAB) m/z: found 862 [M$^+$], calcd for $C_{45}H_{80}{}^{74}GeSi_6$ [M$^+$] 862; anal. calcd for $C_{45}H_{80}GeSi_6$: C, 62.68; H, 9.35; found: C, 62.53; H, 9.25.

Reaction of 1 with [Co$_2$(CO)$_8$]

An n-Bu$_2$O (1.5 ml) solution of **1** (57.0 mg, 66.1 μmol) and [Co$_2$(CO)$_8$] (88.0 mg, 258 μmol) was heated at 135 °C for 3 days in a Pyrex 10 ϕ glass tube. After removal of the solvent, the mixture was subjected to GPLC (toluene) followed by PTLC (hexane) to afford **6** (31.8 mg, 35.7 μmol, 54% yield) as yellow crystals.

6: yellow crystals; mp 197.5–199.2 °C; ^{1}H NMR ($C_2D_2Cl_4$, 413 K): δ−0.06 (s, 18H), 0.01 (s, 18H), 0.10 (s, 18H), 1.03 (d, $J = 6.6$ Hz, 6H), 1.25 (d, $J = 6{,}6$ Hz, 6H), 1.31 (s, 1H), 2.04 (s, 2H), 3.31 (sept, $J = 6.6$ Hz, 2H), 6.41 (s, 2H), 7.12 (d, $J = 7.8$ Hz, 2H), 7.27 (t, $J = 7.8$ Hz, 1H), 7.38–7.51 (m, 3H), 8.08–8.18 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 0.4 (q), 0.5 (q), 0.9 (q), 1.0 (q), 23.3 (q), 23.6 (q), 27.1 (q), 27.5 (q), 28.2 (d), 28.6 (d), 30.0 (d), 35.0 (d), 35.5 (d), 118.7 (d), 122.6 (d), 123.4 (d), 123.5 (d), 127.9 (d), 129.4 (d), 131.8 (s), 132.5 (d), 133.2 (d), 138.9 (s), 138.9 (s), 144.1 (s), 149.6 (s), 150.5 (s), 156.2 (s), 169.3 (s), 226.5 (s); LRMS (FAB) m/z: found 890 [M$^+$], calcd for $C_{46}H_{80}{}^{74}GeOSi_6$ [M$^+$] 890; HRMS (FAB) m/z: calcd for $C_{46}H_{80}{}^{74}GeOSi_6$ 890.4037, found 890.4043; IR (KBr) 1720.6 cm^{-1}.

X-ray crystallographic analysis

Single crystals of **2**–**4** were grown by the slow evaporation of their saturated hexane solutions at room temperature. Single crystals of **5** were grown by the slow evaporation of its saturated solution in acetone at room temperature. Single crystals of **6** were grown by the slow evaporation of its saturated solution in $CHCl_3$/EtOH at room temperature. All sample preparations consisted of coating the crystal with hydrocarbon oil, mounting it on a glass fiber, and placing it under a cold stream of N_2 on the diffractometer. The intensity data of **2**–**6** were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71071$ Å) to $2\theta_{max} = 50°$ at 93 K. The structure of **2** was solved by Patterson methods (DIRDIF),[35] and the structures of **3**–**6** were solved by direct method (SIR97).[36] All crystallographic data were refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[37] All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of **4**–**6** and **2** were placed using AFIX instructions. In the structure analysis of **3**, hydrogen atoms of all methyl groups were placed using AFIX instructions, and the other hydrogen atoms were refined isotoropically. The structure of **6** was refined as a racemic twin, the absolute structure could not be determined.

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