

# Thermal reactions of an overcrowded germacyclopropabenzene with group 6 metal hexacarbonyl complexes $[M(CO)_6]$ ( $M = Cr, Mo,$ and $W$ ): a novel mode of CO insertion leading to the formation of cyclic germoxycarbene metal complexes†

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Thermal reactions of an overcrowded germacyclopropabenzene with hexacarbonyl complexes of group 6 metals resulted in the formation of the corresponding cyclic germoxycarbene complexes, *i.e.*, 1,2-oxagermolane-5-ylidene pentacarbonyl metal complexes, *via* a novel mode of CO insertion reaction toward cyclopropabenzene derivatives.

The chemical reactivity of cyclopropabenzene upon thermolysis, photolysis, and cycloadditions has attracted much attention from the standpoint of their high strain energy.<sup>1</sup> As another interesting feature of cyclopropaarenes, it has been reported that cyclopropaarenes react with some carbonyl complexes of group 6 metals to give the corresponding cyclobutanone derivatives, *i.e.*, the products of C=O insertion towards the cyclopropene ring as a carbonyl unit, or the arene-metal tricarbonyl complexes, depending on the kinds of substituents on the three-membered ring. For example, cyclopropabenzene itself reacts with  $Cr(CO)_3(CH_3CN)_3$  to give benzocyclobutanone,<sup>2</sup> and *1H*-cyclopropa[*b*]naphthalene reacts with  $Cr(CO)_6$  or  $Cr(CO)_3(CH_3CN)_3$  to give naphthocyclobutanone. By contrast, a bis-silylated derivative reacts with the carbonyl complexes of Cr to give the corresponding tricarbonylchromium complex of cyclopropa[*b*]naphthalene (Scheme 1).<sup>3</sup>

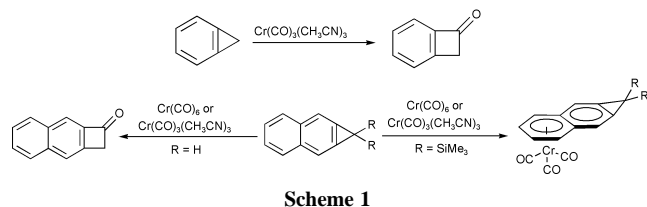
On the other hand, we have recently succeeded in the synthesis and isolation of the first stable sila-<sup>4</sup> and germacyclopropabenzene<sup>5</sup> bearing two bulky aromatic substituents, Tbt and Dip {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl}, *via* the reactions of the corresponding overcrowded dilithiosilane<sup>6</sup> and dilithiogermane<sup>5,7</sup> with *o*-dibromobenzene, respectively. As a part of the elucidation of the reactivity of these novel heteracyclopropabenzene, we examined the reactions of germacyclopropabenzene **1** with hexacarbonyl complexes of group 6 metals in expectation of obtaining germabenzocyclobutanone derivatives *via* C=O insertion reactions. Contrary to our initial expectation, germacyclopropabenzene **1** was found to undergo a novel type of insertion reaction of a C=O group into the Ge–C bond. Thus, we present here the thermal reactions of **1** with  $M(CO)_6$  ( $M = Cr, Mo,$  and  $W$ ) leading to the formation of novel Ge-containing Fischer-type carbene complexes<sup>8</sup> together with the X-ray crystallographic analyses of the newly obtained 1,2-oxagermolane-5-ylidene complexes of group 6 metals.

When a mixture of germacyclopropabenzene **1** and  $Cr(CO)_6$  (3 equiv) in *n*-Bu<sub>2</sub>O–THF (10 : 1) was heated in a sealed tube at 135 °C for 3 days, the colorless solution became wine red as the reaction proceeded. After exchange of the solvent for hexane, the uncon-

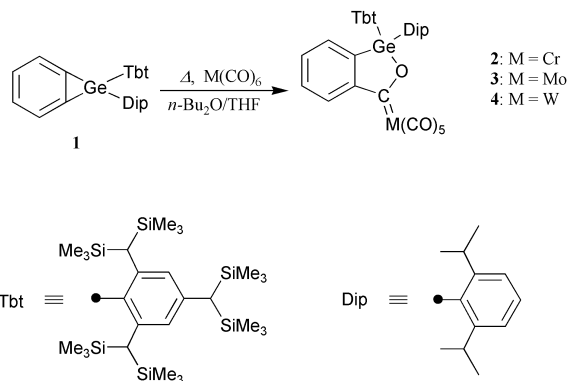
sumed  $Cr(CO)_6$  was removed by filtration. The filtrate was separated by subsequent preparative thin-layer chromatography (eluent: hexane) to afford carbene complex **2** bearing a 1,2-oxagermolane-5-ylidene ligand as red crystals in 44% yield. The thermal reactions of **1** with  $Mo(CO)_6$  and  $W(CO)_6$  under the same conditions also afforded the corresponding Ge-containing Fischer-type carbene complexes **3** (36%) and **4** (26%), respectively (Scheme 2). Interestingly, the reactions of **1** with  $M(CO)_3(CH_3CN)_3$  ( $M = Cr, Mo,$  and  $W$ ) did not occur under the same reaction conditions.

The carbene complexes **2–4** are very stable towards air and moisture, and their molecular structures were satisfactorily confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, UV/vis, and IR spectroscopy, high-resolution MS, and elemental analysis.† The spectra of **2–4** closely resemble to each other. The <sup>13</sup>C NMR signals for the carbene carbons of all complexes were observed around 310–340 ppm, which are consistent with those of typical Fischer-type carbene complexes reported so far.<sup>9</sup> The <sup>13</sup>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**, the signal at 198 ppm was observed with a couple of satellite peaks due to the coupling between the *cis*-carbonyl <sup>13</sup>C atoms and <sup>183</sup>W atom, the coupling constant of which (<sup>1</sup>*J*<sub>C–W</sub> = 127.2 Hz) is comparable with those of typical carbene-tungsten complexes.<sup>10</sup> The IR spectra of **2–4** all showed three absorptions assignable to the stretching bands of their carbonyl groups in the region of 1925–2062 cm<sup>–1</sup>. The UV/vis spectra of **3** and **4** in hexane exhibited absorptions at about 350 and 465 nm, while those of **2** in hexane were observed at 351 and 480 nm.

Molecular structures of **2**, **3**, and **4** were definitely determined by X-ray crystallographic analysis at –180 °C.‡ In Fig. 1 is shown the ORTEP drawing of **4** as a representative. The Ge-containing five-membered rings of **2–4** were found to have a completely planar geometry. The sums of interior bond angles for their 1,2-oxagermolane rings are almost 540° (**2**: 539.9°, **3**: 539.93°, and **4**: 539.87°, respectively). In all cases, the benzene rings annelated to the heterocyclic five-membered rings have an almost planar geometry, to which the group 6 metal atoms in octahedral environment linked by C(1) atom. The C(1)–O(1) bond lengths [1.293(4) Å (**2**), 1.298(6) Å (**3**), and 1.297(6) Å (**4**)] are very close to or slightly shorter than those of typical alkoxycarbene complexes



Scheme 1



Scheme 2

**2**:  $M = Cr$   
**3**:  $M = Mo$   
**4**:  $M = W$

† Electronic supplementary information (ESI) available: spectral data for **2–4**. See <http://www.rsc.org/suppdata/cc/b3/b314010e/>

(1.30–1.35 Å).<sup>10</sup> The M=C(1) bond distances [2.050(3) Å (2), 2.194(5) Å (3), and 2.190(5) Å (4)] are also comparable with those of the reported carbene complexes of group 6 metals. In addition, C(1)–C(2) bond lengths of 2–4 are within the range of carbon–carbon single bonds. Although the M(1)–C(1)–C(2)–C(3) moieties of 2–4 were found to have a completely planar geometry, 2–4 might have little delocalization of  $\pi$ -electrons in these parts in view of their total structural features. Usually, stronger  $\pi$ -electron donation to the carbene carbon from the neighboring oxygen and/or carbon atom leads to the elongation of the M–C(1) and C–O<sub>trans</sub> bond lengths together with the shortening of the M–CO<sub>trans</sub> bond distance. Thus, the distinct  $\pi$ -electron donation of the carbene carbon is not observed for the newly obtained Ge-containing Fischer-type carbene complexes 2–4.

The formation of carbene complexes 2–4 here observed is in sharp contrast to the previously reported reactions of cyclopropabenzene with transition metal hexacarbonyl complexes, which afforded no Fischer-type carbene complexes but a different type of carbonyl insertion products. These reactions resemble the reactions of titanocene–ethylene complex<sup>11</sup> or intermediary  $\eta^2$ -benzyne complexes of Zr, Cp<sub>2</sub>Zr( $\eta^2$ -C<sub>6</sub>H<sub>4</sub>) or Cp<sub>2</sub>Zr( $\eta^2$ -C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>),<sup>12</sup> with group 6 metal hexacarbonyls, which are known to give the corresponding five-membered metallacyclic carbene complexes similar to 2–4. It has been postulated that the reaction of Zr– $\eta^2$ -benzyne complexes probably proceeded via the formation of bimetallic Cp<sub>2</sub>Zr( $\eta^2$ -benzyne)( $\mu$ - $\eta^1$ - $\eta^2$ -carbonyl)M(CO)<sub>5</sub> type intermediates, followed by the cyclization with carbon–carbon bond formation to give the cyclic metalloxycarbene complexes (Scheme 3).

Although it has already been revealed that 1 has intrinsically a normal germacyclopropane ring annulated with a benzene ring as well as parent cyclopropabenzene,<sup>5</sup> the reactivity of 1 towards group 6 metal hexacarbonyl complexes is similar to that of a Zr– $\eta^2$ -benzyne complex. The detailed formation mechanism of 2–4 remains unclear at present, however, it is most likely interpreted in terms of the high reactivity of strained germacyclopropene skeleton.

In summary, we have revealed that novel germoxycarbene complexes are formed by the thermal reactions of germacyclopropabenzene 1 with hexacarbonyl complexes of group 6 metals (Cr, Mo, and W). In view of the wide utility of Fischer-type carbene complexes in organic synthesis,<sup>13</sup> further investigation on the reactivity of newly obtained germoxycarbene complexes 2–4 is currently in progress.

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## Notes and references

‡ Crystallographic data for 2: C<sub>51</sub>H<sub>80</sub>Si<sub>6</sub>GeO<sub>6</sub>Cr, MW = 1082.28, triclinic, space group P $\bar{1}$  (no. 2),  $a$  = 11.8841(16) Å,  $b$  = 13.7144(8) Å,  $c$  = 19.8020(9) Å,  $\alpha$  = 77.335(4)°,  $\beta$  = 71.540(3)°,  $\gamma$  = 84.6841(17)°,  $V$  = 2985.9(5) Å<sup>3</sup>,  $Z$  = 2,  $D_{\text{calc}}$  = 1.204 g cm<sup>-3</sup>,  $R_1(I > 2\sigma(I))$  = 0.0457,  $wR_2(\text{all data})$  = 0.1220,  $T$  = 103(2) K, GOF = 1.053; 3: C<sub>51</sub>H<sub>80</sub>Si<sub>6</sub>GeO<sub>6</sub>Mo, MW = 1126.22, triclinic, space group P $\bar{1}$  (no. 2),  $a$  = 11.911(5) Å,  $b$  = 13.826(6) Å,  $c$  = 19.818(8) Å,  $\alpha$  = 77.247(12)°,  $\beta$  = 71.363(11)°,  $\gamma$  = 84.446(14)°,  $V$  = 3015(2) Å<sup>3</sup>,  $Z$  = 2,  $D_{\text{calc}}$  = 1.241 g cm<sup>-3</sup>,  $R_1(I > 2\sigma(I))$  = 0.0688,  $wR_2(\text{all data})$  = 0.1783,  $T$  = 103(2) K, GOF = 1.075; 4: C<sub>51</sub>H<sub>80</sub>Si<sub>6</sub>GeO<sub>6</sub>W, MW = 1214.13, triclinic, space group P $\bar{1}$  (no. 2),  $a$  = 11.907(3) Å,  $b$  = 13.800(4) Å,  $c$  = 19.771(5) Å,  $\alpha$  = 77.242(8)°,  $\beta$  = 71.489(7)°,  $\gamma$  = 84.456(9)°,  $V$  = 3003.4(13) Å<sup>3</sup>,  $Z$  = 2,  $D_{\text{calc}}$  = 1.343 g cm<sup>-3</sup>,  $R_1(I > 2\sigma(I))$  = 0.0405,  $wR_2(\text{all data})$  = 0.0884,  $T$  = 93(2) K, GOF = 1.075. In the case of 2, the structures were solved by Patterson method (DIRDIF)<sup>14</sup> and refined by full-matrix least-squares procedures on F<sup>2</sup> for all reflections (SHELXL-97).<sup>15</sup> In the case of 3 and 4, the structures were solved by direct method (SIR97).<sup>16</sup> CCDC 224028–224030. See <http://www.rsc.org/suppdata/cc/b3/b314010e/> for crystallographic data in .cif or other electronic format.

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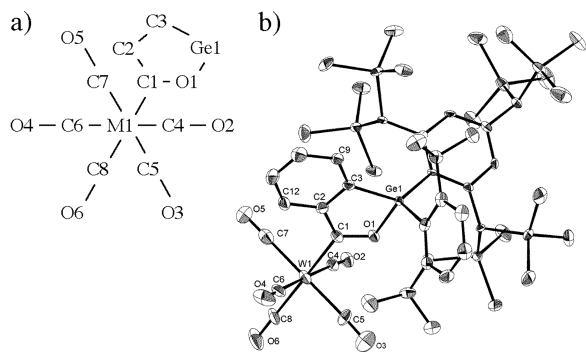
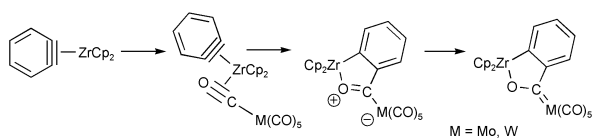


Fig. 1 ORTEP Drawing of 4 (50% probability).



Scheme 3 Reactivity of Cp<sub>2</sub>Zr( $\eta^2$ -C<sub>6</sub>H<sub>4</sub>).