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Room-Temperature Reaction of Carbon Monoxide with a Stable Diarylgermylene

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Reactions of transition organometallic compounds with carbon monoxide have been investigated extensively. Although the insertion of CO into transition metal−carbon bonds is well-known,[1] parallel studies on the insertion into main group element−carbon bonds are confined to the electropositive metals of groups 1,[2] 2,[3] and 13.[4,5] Investigations of the reactions of CO with stable group 14 compounds are much scarcer.[6−8] Carbenes are known to combine with CO to give ketenes.[7] The reaction of CO with silylenes affords silaketenes, which are stable only at low temperature and dissociate CO upon warming.[8] Reactions of CO with other heavier group 14 element carbene analogues have not been reported.[9] We now describe reactions of four diarylgermylenes :GeAr$^\#$Ar′ (**1**), :GeAr$^\#$(Ar*-3,5-Pr$^i_2$) (**2**), :GeAr′$_2$ (**3**),[10] or :GeAr$^\#_2$ (**4**)[11] (Ar$^\#$ = C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$, Ar′ = C_6H_3-2,6-(C_6H_3-2,6-Pr$^i_2$)$_2$, Ar*-3,5-Pr$^i_2$ = C_6H-2,6-(C_6H_2-2,4,6-Pr$^i_3$)$_2$-3,5-Pr$^i_2$) with CO at room temperature, which led to formation of α-germyloxy ketones via C−C bond cleavage and formation.

Exposure of blue solution of **1** in toluene to CO at 1 atm pressure yielded a dark brown solution (Scheme 1). Concentration under reduced pressure to *ca.* 5 mL and storage at ca. −18 °C overnight afforded yellow, X-ray-quality crystals of **5** in *ca.* 55% yield. The reaction of **2** with CO was carried out by a similar procedure and afforded compound **6** (Scheme 1). Similar color changes were observed for reaction of **3** or **4** with CO, but no X-ray quality crystals could be isolated. A solution of **3** became yellow within 30 min under a CO atmosphere, while the reaction of **4** with CO occurred only upon heating to ca. 70 °C overnight. The reaction rates are thus in the order **4** < **1** ≈ **2** < **3**. The products **5** and **6** were characterized by NMR spectroscopy, IR spectroscopy, and X-ray crystallography. IR bands at 1679 cm^{-1} (for **5**) and 1710 cm^{-1} (for **6**) were assigned to the C═O bond stretches.[12] The ^{13}C{^{1}H} NMR spectra display resonances (**5**: 209.18, 91.17 ppm; **6**: 206.07, 85.52 ppm) corresponding to the −*C*(O)−*C*R$_2$−O− carbons.[12] Similar IR bands and ^{13}C{^{1}H} NMR resonances were observed for the products from the reactions of CO with **3** (1706 cm^{-1}; 211.3, 90.1 ppm) or **4** (1719 cm^{-1}; 222.3, 100.7 ppm), showing their similarity to **5** and **6**.

Single crystal X-ray diffraction studies of **5** and **6** show that both are racemates (50% *R* and 50% *S*). Figure 1 shows the structure of **5**-*S* with the C25 atom as a stereocenter. A coupled (CO)$_2$ unit is incorporated into the bond between Ge and the bulkier Ar′ ligand (rather than Ar$^\#$) with a Pr^i migration from one flanking ring to one C atom of the unit, to form a puckered six-membered α-germyloxy ketone. The C29−O2 (1.222(3) Å), C25−O1 (1.400(3) Å), and C25−C29 (1.538(3) Å) distances are comparable to values reported for α-oxy ketones.[12] Alternatively, **5** can be viewed as an aryl aryloxy heterogermylene, a V-shaped monomer, whose Ge1−O1 (1.825(1) Å) and Ge1−C1 (2.022(2) Å) distances are close to (and O1−Ge1−C1 angle (93.7(1)°) is between) those in the reported diaryls **3**, **4**[10,11] and diaryloxy or dialkyloxy germylenes :Ge(OAr′)$_2$, and :Ge(OCBu$^t_3$)$_2$[13]. In contrast, the crystal structure of **6** (see Figure 2 for **6**-*R*) shows that a coupled (CO)$_2$ unit is inserted into the bond between Ge and the less bulky terphenyl ligand (Ar$^\#$) with methyl group migration. The bond distances and angles are similar to those observed in **5**.

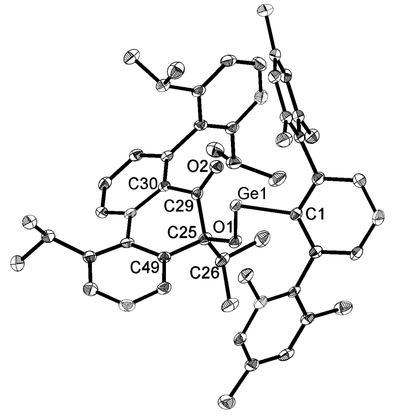
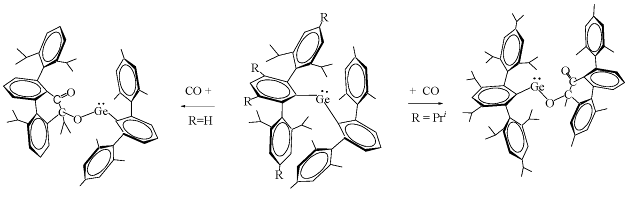


Figure 1. Thermal ellipsoid (50%) drawing of **5**-*S*. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): C1−Ge1 2.022(2), Ge1−O1 1.825(1), O1−C25 1.400(3), C25−C26 1.559(3), C25−C29 1.538(3), C29−O2 1.222(3), C29−C30 1.488(3), C25−C49 1.524(3), C25−O1−Ge1 119.8(1), O1−Ge1−C1 93.7(1).

Scheme 1



5 **1**, R = H; **2**, R = Pr^i **6**

Most probably, the initial step in the reaction sequence is the interaction between the frontier orbitals of the germylene (e.g., **1**) and CO to afford a germaketene (**7**) as illustrated in Scheme 2. Our DFT calculations (see the Supporting Information for details)[14] show that, like their silicon analogues, germaketenes feature a pyramidal germanium with a weak Ge−CO interaction through the carbon atom of CO approximately perpendicular to the GeC$_2$ plane, rather than a "normal" structure containing trigonal-planar germanium and a strong Ge═C double bond.[15] This is in agreement with the observed reaction rates, which is greatest for **3** where the HOMO−LOMO separation (λ_{max} = 608 nm) is lowest.[10] This unstable species may then rearrange to an acyl germylene (**8**), which can add another equivalent of CO via a very similar reaction sequence to that of the first to afford a germa substituted analogue of a benzyl (**10**) which then can activate a flanking ring of a terphenyl to give a racemic product **5** (50% **5**-*R* and 50% **5**-*S*).[16] The insertion sequence results in the formation a six-membered

10.1021/ja9017286 CCC: $40.75 © 2009 American Chemical Society

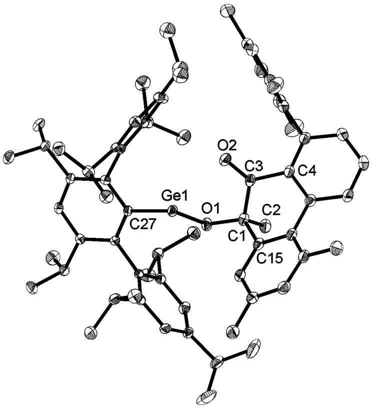
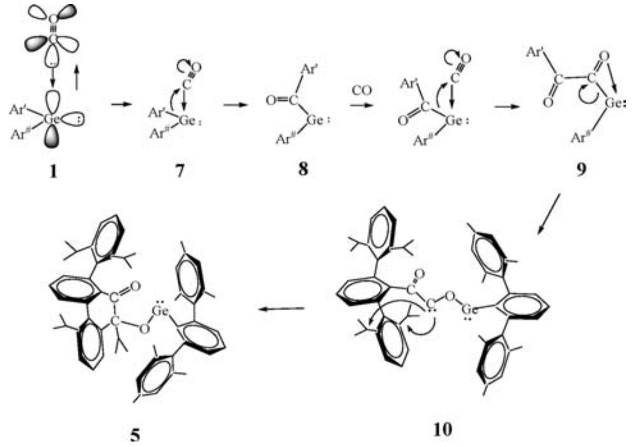


Figure 2. Thermal ellipsoid (50%) drawing of **6**-*R*. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): C27−Ge1 2.030(2), Ge1−O1 1.821(1), O1−C1 1.403(3), C1−C2 1.536(3), C1−C15 1.542(3), C1−C3 1.536(3), C3−O2 1.214(3), C3−C4 1.492(3), C1−O1−Ge1 119.5(1), O1−Ge1−C27 99.6(1).

Scheme 2



ring which may favor the double insertion reaction. For the reaction of **2** with CO, the 3,5-Pr^i groups at the central ring of the 3,5-Pr$^i_2$-Ar* ligand prevent flanking ring orientation to form such a ring. Thus CO preferentially inserts into the arene−Me bond in the Ar$^\#$ ligand instead of the arene−Pr^i bond of 3,5-Pr$^i_2$-Ar* although the anticipated C−C bond dissociation energy (BDE) of the former is higher than that of the latter (BDE: C_6H_5-Me 426 kJ/mol, C_6H_5−Pr^i 401 kJ/mol).[17]

In conclusion, we have reported the first example of the room-temperature reaction of CO with a heavier main group 14 carbene analogue and demonstrated an unusual C−C bond cleavage and formation sequence. CO insertion has not been observed for either carbenes or silylenes,[7,8] and the double insertion and resulting coupling differ from other CO insertions into main group metal−carbon bonds,[2−5] which usually afford metal acyl compounds. It may offer a route to make α-hydroxy ketones, e.g., by treatment of **5** or **6** with H_2O or HCl, useful materials in photochemistry which are normally made by catalyzed aldehyde−ketone cyclizations.[18]

Acknowledgment. We thank the National Science Foundation (CHE-0641020) for support of this research.

Supporting Information Available: Crystallographic data in CIF format for **5** and **6**, experimental section for **1**, **2**, **5**, and **6**, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA9017286