The Chemistry of Transition Metal–Germanium Compounds. Part 2.[1] Synthesis, Characterization, Structure and Reactivity of Transition-metal Carbonyl-substituted Germacyclopent-3-enes†

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A number of transition-metal carbonyl-substituted germacyclopent-3-ene compounds have been prepared by metathesis between 1,1-dibromogermacyclopent-3-enes and sodium salts of transition-metal carbonyl anions. These species have been characterized by a variety of spectroscopic techniques and in the case of 3,4-dimethyl-1,1-bis(tetracarbonylcobaltio)-1-germacyclopent-3-ene **5**, 1-bromo-3,4-dimethyl-1-(pentacarbonylmanganio)-1-germacyclopent-3-ene **7** and 1-bromo-3,4-dimethyl-1-(tetracarbonylcobaltio)-1-germacyclopent-3-ene **11** by low-temperature single-crystal X-ray diffraction. Compound **5** crystallizes in the space group $P2_1/n$ with the cell parameters a = 15.556(3), b = 6.691(1), c = 17.726(2) Å, β = 104.23(1)° and Z = 4, **7** in the space group $P2_1/c$ with a = 14.825(2), b = 6.781(1), c = 14.765(2) Å, β = 103.43(0)° and Z = 4, and **11** in the space group $P2_1/c$ with a = 6.441(1), b = 30.040(7), c = 7.472(1) Å, β = 106.38(1)° and Z = 4. All three compounds exhibit a puckered germacyclopent-3-ene ground-state conformation, the origin of which is discussed. In solution the symmetrically substituted compounds exhibit a degenerate equilibrium which involves a planar germacyclopent-3-ene transition state. Reaction of 1-halogeno-1-(transition metal carbonyl)-substituted germacyclopent-3-enes with different transition metal carbonylate anions results in formation of mixed-metal carbonyl derivatives and reduction with $LiAlH_4$ results in formation of a germanium hydride. Thermolysis of **5** results in loss of a carbonyl ligand and formation of a compound which possesses an intramolecular carbonyl-bridged Co–Co bond. Kinetic data for this decarbonylation reaction, measured by variable-temperature ^1H NMR spectroscopy, reveal activation parameters at an average temperature of 70 °C of $\Delta G^\ddagger$ = +25.9 kcal mol^{-1}, $\Delta H^\ddagger$ = +27.6 kcal mol^{-1} and $\Delta S^\ddagger$ = +5 cal K^{-1} mol^{-1}.

The chemistry of compounds containing bonds between transition metal and Group 14 elements has recently been reviewed.[2] Relative to other compounds containing these bonds, transition metal-substituted organogermanes have received little attention. Approximately 85 organometallic compounds containing germanium–transition metal bonds have been characterized by single-crystal X-ray diffraction according to the Cambridge Crystallographic Data Base. More recently, the chemistry of transition metal–germanium species has been of wider interest due to the ability of ML_n fragments, such as $[Mo(CO)_5]$,[3,4] to act as Lewis acids and render labile germylenes, GeR_2 where R = organic group or a main-group organometallic substituent, kinetically inert with respect to oligomerization. As part of our investigation of synthetic routes to transition metal-substituted germanium(II) species, we have recently demonstrated that 1,1-transition metal-substituted germacyclopent-3-enes act as precursors.[5] Thermolysis of 3-methyl-1,1-bis(pentacarbonylmanganio)-1-germacyclopent-3-ene in the presence of a tenfold excess of 2,3-dimethylbutadiene resulted in formation of the $:Ge[Mn(CO)_5]_2$ trapping product, 3,4-dimethyl-1,1-bis(pentacarbonylmanganio)-1-germacyclopent-3-ene, in reasonable yields. A solid-state structural investigation of two prototypical transition metal-substituted germacyclopent-3-ene derivatives revealed an unexpected, intriguing aspect of this chemistry. For the first time, a puckered germacyclopent-3-ene ring conformation was preferred in the ground state over a planar one. In related studies, Marietti-Migrani and West[6] have previously shown that transition metal-substituted 7-silanorbornadienes act as sources of transition metal-substituted silylenes.

Here we report in detail the synthesis, characterization, and some reactivity studies on a range of transition metal-substituted germacyclopent-3-enes, including further structural studies to investigate the ground-state ring conformation in these species.

Experimental

(*a*) *Syntheses.*—(*i*) *General procedures.* All manipulations were carried out under an atmosphere of dry (4 Å molecular sieves), deoxygenated (MnO) nitrogen.[7] Hydrocarbon solvents were dried and distilled from sodium diphenylketyl and stored under nitrogen over molecular sieves. Deuteriated NMR solvents were dried over 4 Å molecular sieves and stored under nitrogen. The compounds $[\{Fe(CO)_2(cp)\}_2]$ (cp = η^5-C_5H_5), $[Mn_2(CO)_{10}]$, $[\{M(CO)_3(cp)\}_2]$ (M = Mo or W) and $[Co_2(CO)_8]$ were purchased from Aldrich Chemical Company and used as received. These species were reduced with sodium–mercury amalgam to form $Na[Fe(CO)_2(cp)]$, $Na[Mn(CO)_5]$, $Na[M(CO)_3(cp)]$ (M = Mo or W) and $Na[Co(CO)_4]$, respectively, according to the literature procedure.[8] Germanium dibromide was prepared by two-step bromination of powdered germanium metal (Johnson Matthey) at 400 °C in a modified version of the literature procedure.[9] 1,1-Dibromo-1-germa-

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† *Supplementary data available* (No. SUP 56833, 15 pp.): primary kinetic data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-S.I. unit employed: cal = 4.184 J.

cyclopent-3-enes were prepared by reaction of $GeBr_2$ with butadienes in diethyl ether by a method analogous to that reported previously.[9]

The NMR spectra were recorded on Bruker AC-250 or Nicolet NT-360 spectrometers. Proton chemical shifts were referenced to the protio impurity of the deuteriated solvent, ^{13}C chemical shifts to the central ^{13}C resonance of the deuteriated solvent. Where necessary, two-dimensional NMR experiments were carried out to confirm assignments by using Bruker programs COSY.AU, HETCOR.AU and 2DJRES.AU. Infrared spectra were recorded on a Perkin-Elmer 1620 FTIR spectrometer. Elemental analyses were performed by Oneida Research Services.

(*ii*) 1,1-*Di*(*transition metal*)-*substituted germacyclopent*-3-*enes*. A series of 1,1-di(transition metal)-substituted germacyclopent-3-enes were prepared by similar experimental procedures. A typical experiment describing the synthesis of 3,4-dimethyl-1,1-bis(pentacarbonylmanganio)-1-germacyclopent-3-ene is described in detail, followed by the analytical and spectroscopic data for all the derivatives.

To a suspension of an excess of $Na[Mn(CO)_5]$ in pentane (50 cm^3) was slowly added a solution of 1,1-diiodo-3,4-dimethyl-1-germacyclopent-3-ene (1.50 g, 0.0037 mol) dissolved in pentane (40 cm^3). The colourless solution became yellow during the addition. After stirring for 3 h an additional fine, white precipitate had been produced. The mixture was stirred for a total of 18 h at room temperature. The stirrer was stopped, the solution allowed to settle, and the supernatant filtered under nitrogen. The residue was washed with two portions (10 cm^3) of pentane. The washings were combined with the original filtrate, and the volatile components were removed *in vacuo* to yield a pale yellow crystalline solid. Proton NMR data of a sample of this crude product showed no sign of the monosubstituted intermediate. The crude material was then taken up in the minimum amount of pentane at room temperature and cooled to −30 °C for 12 h. During this time, 1.50 g of transparent, yellow needles were formed which analysed correctly as 3,4-dimethyl-1,1-bis(pentacarbonylmanganio)-1-germacyclopent-3-ene, a yield of 75% based on the germanium starting material.

Spectroscopic and analytical data. 3,4-*Dimethyl*-1,1-*bis*(*pentacarbonylmanganio*)-1-*germacyclopent*-3-*ene* **1**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 2.44 (s, 4 H, CH_2) and 1.82 (s, 6 H, CH_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 214.9 (CO), 211.7 (CO), 133.1 (*C*Me), 38.7 (CH_2) and 18.8 (CH_3). IR (KBr disc): ν(CO) 2100m, 2067m, 2032s(br) and 1950(sh) cm^{-1} (Found: C, 35.0; H, 2.05. Calc. for $C_{16}H_{10}GeMn_2O_{10}$: C, 35.3; H, 1.85%). Yield = 75%.

3-*Methyl*-1,1-*bis*(*pentacarbonylmanganio*)-1-*germacyclopent*-3-*ene* **2**. ^1H NMR (20 °C, 360 MHz, C_6D_6): δ 5.88 (br s, 1 H, CH), 2.46 (br s, 2 H, CH_2), 2.30 (s, 2 H, CH_2) and 1.88 (s, 3 H, CH_3). IR (KBr disc): ν(CO) 2075m, 2010s, 2001s(br) and 1986s(br) cm^{-1} (Found: C, 33.8; H, 1.60. Calc. for $C_{15}H_8GeMn_2O_{10}$: C, 34.0; H, 1.50%). Yield = 74%.

1,1-*Bis*(*pentacarbonylmanganio*)-1-*germacyclopent*-3-*ene* **3**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 6.10 (t, 1.3 Hz, 2 H, CH) and 2.28 (d, 4 H, CH_2); $^{13}C-\{^1H\}$ (62.9 MHz), δ 133.08 (CH) and 31.03 (CH_2). IR (KBr disc): 1987vs, 2048w and 2079w cm^{-1} (Found: C, 32.5; H, 0.75. Calc. for $C_{14}H_6GeMn_2O_{10}$ C, 32.5; H, 1.15%). Yield = 72%.

1,1-*Bis*[*dicarbonyl*(*cyclopentadienyl*)*ferrio*]-3,4-*dimethyl*-1-*germacyclopent*-3-*ene* **4**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 4.40 (s, 5 H, C_5H_5), 2.48 (s, 4 H, CH_2) and 2.06 (s, 6 H, CH_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 216.7 (CO), 131.8 (*C*Me), 83.8 (C_5H_5), 41.9 (CH_2) and 19.48 (CH_3). IR (KBr disc): ν(CO) 1983s, 1933(sh), 1917s and 1900(sh) cm^{-1} (Found: C, 47.6; H, 3.65. Calc. for $C_{20}H_{20}Fe_2GeO_4$: C, 47.2; H, 3.95%). Yield = 69%.

3,4-*Dimethyl*-1,1-*bis*(*tetracarbonylcobaltio*)-1-*germacyclopent*-3-*ene* **5**. NMR (20 °C): ^1H (250 MHz, C_6D_6), δ 2.47 (s, 4 H, CH_2) and 1.66 (s, 6 H, CH_3); $^{13}C-\{^1H\}$ (62.9 MHz, C_7D_8), δ 198.5 (CO), 131.1 (*C*Me), 44.9 (CH_2) and 20.6 (CH_3). IR (KBr disc): ν(CO) 2100s, 2081s, 2032s and 1944s(br) cm^{-1} (Found: C, 33.7; H, 2.10. Calc. for $C_{14}H_{10}Co_2GeO_8$: C, 33.9; H, 2.05%).

(*iii*) 1-*Bromo*-1-*transition metal*-1-*germacyclopent*-3-*enes*. These species were prepared by similar methods. The synthesis of 1-bromo-1-[dicarbonyl(cyclopentadienyl)ferrio]-3,4-dimethyl-1-germacyclopent-3-ene is described in detail as a typical example.

A suspension of $Na[Fe(CO)_2(\eta^5-C_5H_5)]$ (1.50 g, 7.5 mmol) in pentane (150 cm^3) was added very slowly to a rapidly stirred solution of 1,1-dibromo-3,4-dimethyl-1-germacyclopent-3-ene (2.56 g, 8.2 mmol) in pentane (50 cm^3). The mixture was stirred at room temperature for 16 h whereupon the initial bright red solution became dark red. The stirrer was stopped, the solution filtered, and the residue washed with two portions (20 cm^3) of pentane. The washings were combined and the volatile components were removed *in vacuo*. After confirming the presence of the monosubstituted derivative in the crude product by ^1H NMR spectroscopy, the solid was redissolved in the minimum amount of pentane at room temperature and crystallized at −30 °C. The red-brown crystalline product isolated analysed correctly as 1-bromo-1-[dicarbonyl(cyclopentadienyl)ferrio]-3,4-dimethyl-1-germacyclopent-3-ene (2.57 g, 6.3 mmol), a yield of 83.2% based on the iron starting material used.

Spectroscopic and analytical data. 1-*Bromo*-1-(*pentacarbonylmanganio*)-1-*germacyclopent*-3-*ene* **6**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 5.91 (br s, 2 H, CH), 2.41 (d, 16.3 Hz, 2 H, CH_aH_b) and 2.10 (d, 2 H, CH_aH_b); $^{13}C-\{^1H\}$ (62.9 MHz), δ 214.5 (CO), 210.5 (CO), 130.7 (CH) and 30.8 (CH_2) (Found: C, 27.0; H, 1.35; Br, 19.7. Calc. for $C_9H_6BrGeMnO_5$: C, 26.9; H, 1.50; Br, 19.9%).

1-*Bromo*-3,4-*dimethyl*-1-(*pentacarbonylmanganio*)-1-*germacyclopent*-3-*ene* **7**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 2.50 (d of m, 15.6 Hz, 2 H, CH_aH_b), 2.22 (d of m, 16.5 Hz, 2 H, CH_aH_b) and 1.59 (m, 6 H, CH_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 130.4 (*C*Me), 38.0 (CH_2) and 18.7 (CH_3). IR (KBr disc): ν(CO) 1996s, 1944s and 2010m cm^{-1} (Found: C, 30.7; H, 2.70; Br, 19.1. Calc. for $C_{11}H_{10}BrGeMnO_5$: C, 30.8; H, 2.35; Br, 18.6%).

1-*Bromo*-3-*methyl*-1-(*pentacarbonylmanganio*)-1-*germacyclopent*-3-*ene* **8**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 5.58 (m, 1 H, CH), 2.50 d of m, 17.5 Hz, 1 H, CH_aH_b), 2.32 (d of m, 17.0 Hz, 1 H, CH_aH_b), 2.25 (d of m, 1 H, CH_aH_b), 2.05 (d of m, 1 H, CH_aH_b) and 1.65 (m, 3 H, CH_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 140.0 (*C*Me), 124.8 (CH), 35.0 (CH_2), 32.2 (CH_2) and 22.0 (CH_3) (Found: C, 29.0; H, 2.10. Calc. for $C_{10}H_8BrGeMnO_5$: C, 28.8; H, 1.90%).

1-*Bromo*-1-[*dicarbonyl*(*cyclopentadienyl*)*ferrio*]-3,4-*dimethyl*-1-*germacyclopent*-3-*ene* **9**. ^1H NMR (20 °C, 250 MHz, C_6D_6): δ 4.08 (s, 5 H, C_5H_5), 2.59 (d, 16.6 Hz, 2 H, CH_aH_b), 2.16 (d, 2 H, CH_aH_b) and 1.71 (s, 6 H, CH_3). IR (KBr disc): 2042 m, 2003s, 1957s and 1927m cm^{-1} (Found: C, 37.8; H, 3.50; Br, 19.0. Calc. for $C_{13}H_{15}Br_2FeGeO_2$: C, 37.9; H, 3.70; Br, 19.4%).

1-*Bromo*-1-[*dicarbonyl*(*cyclopentadienyl*)*ferrio*]-1-*germacyclopent*-3-*ene* **10**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 6.09 (s, 2 H, CH), 3.99 (s, 5 H, C_5H_5), 2.54 (d, 16.1 Hz, CH_aH_b) and 2.02 (d, 2 H, CH_aH_b); $^{13}C-\{^1H\}$ (62.9 MHz), δ 213.1 (CO), 131.1 (CH), 84.3 (C_5H_5) and 31.8 (CH_2). IR (KBr disc): ν(CO) 2119vw, 2067vw, 2009vs and 1958vs cm^{-1}.

1-*Bromo*-3,4-*dimethyl*-1-(*tetracarbonylcobaltio*)-1-*germacyclopent*-3-*ene* **11**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 2.41 (d of m, 17.0 Hz, 2 H, CH_aH_b), 2.15 (d of m, 2 H, CH_aH_b) and 1.50 (s, 6 H, CH_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 195.6 (CO), 130.0 (*C*Me), 39.2 (CH_2) and 18.3 (CH_3). IR (KBr disc): 2101m, 2044m, 2011s(br) and 2002s(br) cm^{-1}.

(*iv*) 1,1-*Disubstituted mixed-metal germacyclopent*-3-*enes*. These derivatives were prepared by similar methods, and a typical example is described in detail.

To a suspension of $Na[Mn(CO)_5]$ (0.60 g, 2.7 mmol) in diethyl ether (70 cm^3) was added a solution of 1-bromo-3,4-dimethyl-1-(tetracarbonylcobaltio)-1-germacyclopent-3-ene in diethyl ether (20 cm^3). The reaction mixture was stirred at room temperature for 4 h, and the initial pale yellow solution became bright yellow. The solvent was removed *in vacuo*, and the residue was extracted with pentane (150 cm^3). The volatile components were removed until the product began to crystallize, whereupon nitrogen was readmitted to the flask. The flask was warmed until all the solid dissolved at room temperature, then the solution was cooled to −30 °C for 16 h. The pale yellow crystalline product was separated by filtration to yield 0.78 g (1.50 mmol) of 3,4-dimethyl-1-(pentacarbonylmanganio)-1-(tetracarbonylcobaltio)-1-germacyclopent-3-ene, a yield of 83.2%.

Spectroscopic data. 3,4-*Dimethyl*-1-(*pentacarbonylmanganio*)-1-(*tetracarbonylcobaltio*)-1-*germacyclopent*-3-*ene* **12**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 2.42 (m, 4 H, CH_2) and 1.68 (m, 6 H, CH_3); ^{13}C-{^1H} (62.9 MHz), δ 131.9 (*C*Me), 41.9 (CH_2) and 18.8 (CH_3). IR (KBr disc): 2107 (sh)w, 2077s and 2001vs cm^{-1}. Yield = 83%.

1-[*Dicarbonyl*(*cyclopentadienyl*)*ferrio*]-3,4-*dimethyl*-1-(*tetracarbonylcobaltio*)-1-*germacyclopent*-3-*ene* **13**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 4.17 (s, 5 H, C_5H_5), 2.56 (d, 16.1 Hz, 2 H, $C\mathit{H}_a\mathrm{H}_b$), 2.31 (d, 2 H, $\mathrm{CH}_a\mathit{H}_b$) and 1.77 (s, 6 H, CH_3); ^{13}C-{^1H} (62.9 MHz), δ 214.2 (CO), 200.5 (CO), 131.5 (*C*Me), 84.1 (C_5H_5), 43.6 (CH_2) and 19.0 (CH_3). IR (KBr disc): ν(CO) 2073m, 1991s (br), 1962s and 1944s cm^{-1}. Yield = 78%.

1-(*Pentacarbonylmanganio*)-1-(*tetracarbonylcobaltio*)-1-*germacyclopent*-3-*ene* **14**. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 6.01 (s, 2 H, CH), 2.35 (d, 16.6 Hz, 2 H, $C\mathit{H}_a\mathrm{H}_b$) and 2.24 (d, 2 H, $\mathrm{CH}_a\mathit{H}_b$); ^{13}C-{^1H} (62.9 MHz), δ 210.4 (br, CO), 219.3 (br, CO), 199.3 (br, CO), 131.8 (CH) and 34.3 (CH_2). IR (KBr disc): 2104m, 2079m and 1991s cm^{-1}.

(*v*) 1-*Hydrido*-1-[*dicarbonyl*(*cyclopentadienyl*)*ferrio*]-3,4-*dimethyl*-1-*germacyclopent*-3-*ene* **15a**. 1-bromo-1-[dicarbonyl-(cyclopentadienyl)ferrio]-3,4-dimethyl-1-germacyclopent-3-ene (0.35 g, 0.85 mmol) was dissolved in a mixture of diethyl ether (20 cm^3) and pentane (20 cm^3) and added to a suspension containing an excess of $LiAlH_4$ in pentane (30 cm^3) at 0 °C. The mixture was stirred for 30 min at 0 °C to give a brown suspension. The suspension was filtered and the volatile components removed *in vacuo* to give a brown residue. The residue was extracted at room temperature with toluene to give an orange oil, which exhibited NMR data consistent with the expected product. This crude product (0.265 g) was spectroscopically pure and isolated in a yield of 94%. Repeated attempts to crystallize it at −30 °C from pentane, toluene and diethyl ether were unsuccessful. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 4.72 (m, 1 H, GeH), 4.04 (s, 5 H, C_5H_5), 2.30 (d of m, 2 H, 16.8 Hz, $C\mathit{H}_a\mathrm{H}_b$), 1.76 (d of m, 2 H, $\mathrm{CH}_a\mathit{H}_b$) and 1.80 (6 H, CH_3); ^{13}C-{^1H} (62.9 MHz), δ 215.2 (CO), 131.7 (*C*Me), 82.8 (C_5H_5), 29.4 (CH_2) and 19.4 (CH_3). IR (KBr disc): 1996m, 1940s(br) and 1757m cm^{-1}.

The deuterium-labelled analogue, 1-deuterio-1-[dicarbonyl-(cyclopentadienyl)ferrio]-3,4-dimethyl-1-germacyclopent-3-ene **15b** was prepared by an analogous method using $LiAlD_4$. The ^1H NMR data for **15b** were analogous to those for **15a** except the multiplet at δ 4.72 was missing. A ^2H NMR resonance was observed at δ 4.71. A new band at 1415 cm^{-1} was observed in the IR spectrum when compared to **15a**.

(*b*) *Photolysis Experiments.*—These experiments were generally carried out in 5 mm NMR tubes by dissolving about 30 mg of sample in 800 μl of C_6D_6 and exposing to 366 nm irradiation from a Black-Ray model UVL-21 long-wavelength ultra-violet lamp.

3,4-*Dimethyl*-1-[*tricarbonyldi*(*cyclopentadienyl*)*diferrio*]-1-*germacyclopent*-3-*ene* **16**. *cis* Isomer **16a**. NMR (20 °C, C_6D_6): ^1H (360 MHz), δ 4.02 (s, 10 H, C_5H_5), 2.80 (s, 2 H, CH_2), 2.54 (s, 2 H, CH_2), 2.05 (s, 3 H, CH_3) and 1.90 (s, 3 H, CH_3); ^{13}C-{^1H} (62.9 MHz), δ 212.3 (CO), 133.8 (*C*Me), 130.8 (*C*Me), 83.8 (C_5H_5), 39.7 (CH_2), 38.6 (CH_2), 19.6 (CH_3) and 19.4 (CH_3). IR (KBr disc): 1937s, 1914m(sh) and 1741m cm^{-1}.

trans Isomer **16b**. NMR (20 °C, C_6D_6): ^1H (360 MHz), δ 4.23 (s, 10 H, C_5H_5), 2.72 (d, 15 Hz, 2 H, $C\mathit{H}_a\mathrm{H}_b$), 2.50 (s, 2 H, $\mathrm{CH}_a\mathit{H}_b$) and 1.98 (s, 6 H, CH_3); ^{13}C-{^1H} (62.9 MHz), δ 218.0 (CO), 132.2 (*C*Me), 84.7 (C_5H_5), 39.0 (CH_2) and 19.5 (CH_3).

1-(*Heptacarbonyldicobaltio*)-3,4-*dimethyl*-1-*germacyclopent*-3-*ene* **17**. NMR (20 °C): ^1H (360 MHz, C_6D_6), δ 2.46 (s, 4 H, CH_2) and 1.46 (s, 6 H, (CH_3); ^{13}C-{^1H} (62.9 MHz, C_7D_8), δ 204.7 (CO), 137.5 (*C*Me), 33.7 (CH_2) and 18.4 (CH_3). IR (KBr disc): 1999s (br), 2041s, 2088s and 1836s cm^{-1}.

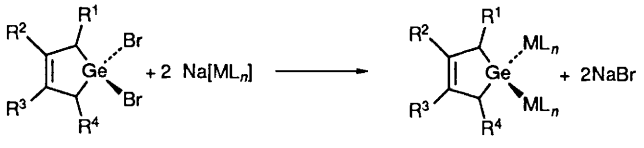
(*c*) *Kinetic Measurements of the Thermal Decarbonylation of Compound* **5**.—A dilute stock solution of compound **5** in [$^2H_8$]toluene was prepared with a concentration of 0.0025 mol dm^{-3} and stored at −30 °C in the dark under nitrogen. Small aliquots (0.5 cm^3) were removed and placed in a 5 mm NMR tube. A kinetics program was loaded on the NMR instrument and the temperature adjusted and equilibrated. The sample tube was quickly placed in the probe and the kinetics experiment started. Compound **5** does not undergo thermal decarbonylation at room temperature, and light was excluded during sample preparation to the maximum extent possible. The rate of loss of starting material was determined by integration of the methyl and methylene protons of **5**. Similar experiments performed on samples of different concentration gave the same rate constant, consistent with a first-order rate law. Rate constants were measured over a temperature range 40–90 °C, and the data obtained are presented in Table 8 with an Eyring plot in Fig. 5. The primary rate data are available as SUP 56833.

(*d*) X-*Ray Crystallographic Analyses of Compounds* **5**, **7** *and* **11**.—Suitable crystals were located and transferred to the goniostat by using the standard inert-atmosphere handling techniques employed by the Indiana University Molecular Structure Center (IUMSC), as previously described,[1] and cooled to −155 °C for **5** and **7**, 131 °C for **11**, for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima, with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$ for **5** and $P2_1/c$ for **7**. A similar search yielded a set of reflections that exhibited monoclinic (2/*m*) symmetry for **11**. The systematic extinctions of $0k0$ for $k = 2n + 1$ and of $h0l$ for $l = 2n + 1$ uniquely identified the space group as $P2_1/c$. Subsequent solution and refinement of the structure confirmed these choices.

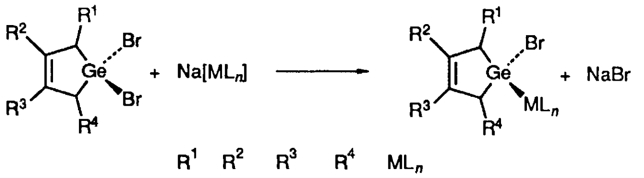
Data were collected in the usual manner for compounds **5** and **7** by using a continuous θ–2θ scan with fixed backgrounds, and reduced to unique sets of intensities and associated sigmas. The structures were solved by a combination of direct methods (MULTAN 78[1]) and Fourier techniques. All hydrogen atoms were clearly visible in a Fourier difference synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically, and non-hydrogen atoms anisotropically, in the final cycles. For **11**, the upper limit of 2θ was extended to 55° rather than the usual value of 45°. Owing to the long *b* axis, the scan width was set to 1.4°. A total of 4018 reflections (including extinctions and standard reflections) were collected in the given range. The four standard reflections measured periodically during the data collection showed no systematic trends. Following the usual data reduction and averaging of equivalent reflections, a unique set of 3197 reflections was obtained. 2621 Reflections were considered observed by the criterion $F > 3.0\sigma(F)$. No correction for absorption was performed. The crystal faces were difficult to identify since the crystal was immersed in silicone grease.

The structure was solved by the usual combination of direct methods and Fourier techniques. The three heavy atoms were located in the initial best electron-density map, and the remaining non-hydrogen atoms in the next difference map. All hydrogen atoms were located in a later difference Fourier. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters for all non-hydrogen atoms and individual isotropic thermal parameters for the hydrogen atoms. The final $R(F)$ was 0.048; $R'(F)$ was 0.046. A total of 195 parameters were varied during the least-squares refinement, giving a ratio of observations to parameters of 13.44:1.



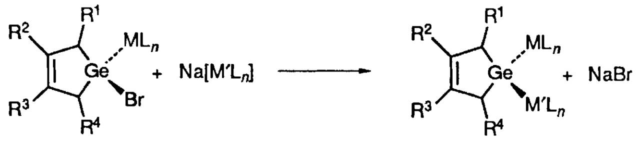
	R^1	R^2	R^3	R^4	ML_n
1	H	Me	Me	H	$Mn(CO)_5$
2	H	Me	H	H	$Mn(CO)_5$
3	H	H	H	H	$Mn(CO)_5$
4	H	Me	Me	H	$Fe(CO)_2(\eta^5\text{-}C_5H_5)$
5	H	Me	Me	H	$Co(CO)_4$

Scheme 1



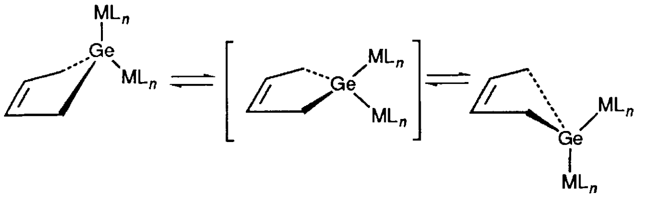
	R^1	R^2	R^3	R^4	ML_n
6	H	H	H	H	$Mn(CO)_5$
7	H	Me	Me	H	$Mn(CO)_5$
8	H	Me	H	H	$Mn(CO)_5$
9	H	Me	Me	H	$Fe(CO)_2(\eta^5\text{-}C_5H_5)$
10	H	H	H	H	$Fe(CO)_2(\eta^5\text{-}C_5H_5)$
11	H	Me	Me	H	$Co(CO)_4$

Scheme 2



	R^1	R^2	R^3	R^4	ML_n	$M'L_n$
12	H	Me	Me	H	$Co(CO)_4$	$Mn(CO)_5$
13	H	Me	Me	H	$Co(CO)_4$	$Fe(CO)_2(\eta^5\text{-}C_5H_5)$
14	H	H	H	H	$Co(CO)_4$	$Mn(CO)_5$

Scheme 3



Scheme 4

For compounds **5** and **7** final Fourier difference syntheses were featureless, with the largest peak being 0.264 e Å^{-3} for **5** and 0.94 e Å^{-3} for **7**. No absorption corrections were performed for either compound. Fractional coordinates for **5** are given in Table 1, relevant bond distances and angles in Tables 5 and 6. For **7** fractional coordinates are given in Table 2 and relevant bond lengths and angles in Tables 5 and 6. For **11** the final difference map was essentially featureless, the largest peak being 0.77 e Å^{-3} in the immediate vicinity of the Ge atom. Fractional coordinates are given in Table 3, relevant bond lengths and angles in Tables 5 and 6. Crystal data for **5**, **7** and **11** are summarized in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

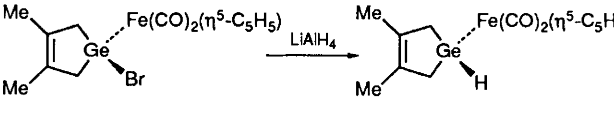
Results and Discussion

Syntheses.—A series of transition metal-substituted germacyclopent-3-enes have been prepared according to Scheme 1 and 2 by metathesis of germanium–halide bonds with transition-metal carbonylate anions.

Samples from reactions depicted in Scheme 1 taken at short reaction times indicated that the monosubstituted compounds of type **B** are intermediates in the formation of the disubstituted compounds of type **A**. The products **1**–**11** were isolated in high yields and were characterized by NMR, IR and mass spectroscopies, and by elemental analyses of representative examples (see Experimental section).

Mixed-metal carbonyl-substituted germacyclopent-3-enes were prepared by metathesis reactions of monosubstituted germacyclopent-3-enes of type **B** with different transition-metal carbonylate anions, according to Scheme 3.

Reduction of **9** with $LiAlH_4$ resulted in the formation of the corresponding germanium hydride according to equation (1).



(1)

9 **15a**

The presence of the hydride was identified by ^{1}H NMR spectroscopy as a multiplet at δ 4.72 and was confirmed by preparing the analogous germanium deuteride, which gave a ^{2}H NMR resonance at δ 4.71. The position of ν(Ge–H) for **15a** was not unambiguously identifiable, but ν(Ge–D) was identified by comparison to the IR spectrum of the protio derivative as 1415 cm^{-1}. The calculated stretching frequency of ν(Ge–H) of 1988 cm^{-1} is in a region obscured by the carbonyl bands, which is consistent with the observed data.

Solid-state and Solution Structures.—There are relatively little structural data available for germacyclopent-3-enes. Liquid-phase vibrational analysis of 1,1-dichloro, -dimethyl and -dimethoxy derivatives have been interpreted in terms of planar, C_{2v}, ring structures rather than a puckered, C_s, ground-state ring conformation.[10] We have recently demonstrated, however, that, in the ground state, the conformation of the germacyclopent-3-ene ring in certain 1,1-di(transition metal)-substituted germacyclopent-3-enes is significantly puckered.[1] Solution NMR data for compounds **1**–**5** indicate that, at room temperature, the methylenic protons are non-diastereotopic, which is consistent with the presence of a molecular mirror plane lying in the plane of the five-membered germacyclopenta-3-ene ring on the NMR time-scale. Variable-temperature ^{1}H NMR data indicate that, over the temperature range of +40 to −90 °C, these species are temperature invariant. As a result, we believe they probably exist in a degenerate, dynamic equilibrium in solution where the planar C_{2v} conformation is a transition state, as described by Scheme 4, and where the rate of exchange is faster than the NMR time-scale. The barrier for this process is estimated to be ($\lesssim$ 5 kcal mol^{-1}).[1] For asymmetrically substituted species (*e.g.* **6**–**15**) it is not possible to distinguish such equilibria since the methylenic protons are inequivalent in both the puckered *and* planar conformations.

In a *solid-state* single-crystal X-ray diffraction study we have recently observed[11] that 1,1-dibromo-3,4-dimethyl-1-germacyclopent-3-ene has a planar ground-state conformation consistent with the vibrational analysis of Laane and co-workers.[10] Molecular orbital calculations have shown that, regardless of the nature of the substituent in 1,1-disubstituted germacyclopent-3-enes [*e.g.* by $Mn(CO)_5$, H or Cl], the planar conformation has lower energy relative to puckered conformations.[11] However, the energy required to form a puckered conformation is lower (by $\approx$2 kcal mol^{-1} for δ = 30°) for $Mn(CO)_5$ substituents than for either H or Cl. Previous explanations for the apparent stability of the planar ground-state conformation in metallacyclopent-3-enes have been based

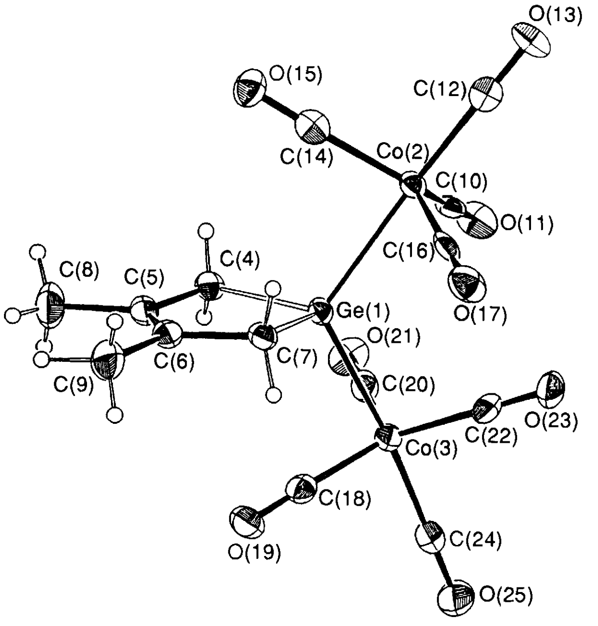


Fig. 1 The molecular structure of compound **5**, with 50% probability ellipsoids and arbitrary isotropic thermal parameters for the hydrogen atoms, showing the atom-numbering scheme

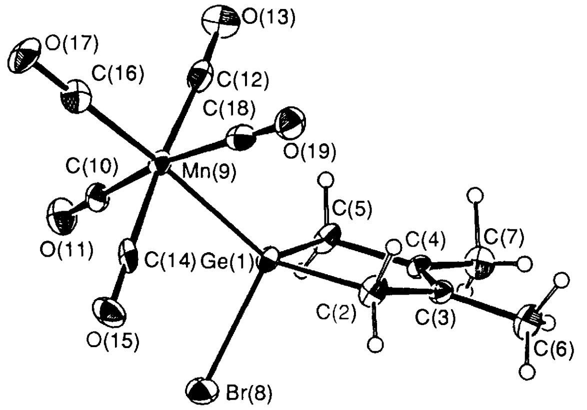


Fig. 2 The molecular structure of compound **7**; details as in Fig. 1

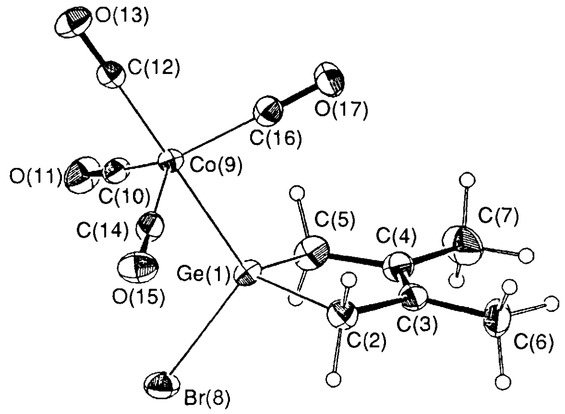


Fig. 3 The molecular structure of compound **11**; details as in Fig. 1

on the absence of eclipsing interactions due to the long Ge–C bonds relative to the C–C bonds of cyclopentene, which itself exists in a puckered conformation.[12] Others have proposed that the planar conformation may be stabilized by interaction of empty Group 14 element d orbitals with the p_π–p_π double bond of the ring.[13] However, we feel that the radial extension of the germanium d orbitals is probably too small to account for these observations.

Table 1 Fractional coordinates for compound **5**

Atom	*x*	*y*	*z*
Ge(1)	7 381.5(4)	1 411(1)	10 073.8(3)
Co(2)	8 782.6(5)	−354(1)	10 632.9(4)
Co(3)	6 558.0(5)	2 608(1)	11 003.5(4)
C(4)	6 565(4)	−5(9)	9 213(3)
C(5)	6 480(4)	1 392(10)	8 536(3)
C(6)	6 966(4)	3 037(10)	8 593(3)
C(7)	7 622(4)	3 506(10)	9 365(3)
C(8)	5 804(5)	750(14)	7 798(4)
C(9)	6 943(5)	4 556(12)	7 962(4)
C(10)	8 175(4)	−1 579(9)	11 229(3)
O(11)	7 803(3)	−2 386(7)	11 627(2)
C(12)	9 838(4)	−1 554(9)	11 077(3)
O(13)	10 498(3)	−2 263(7)	11 353(3)
C(14)	8 653(4)	−1 259(9)	9 655(4)
O(15)	8 593(3)	−1 863(7)	9 041(2)
C(16)	9 178(4)	2 180(10)	10 808(3)
O(17)	9 439(3)	3 761(7)	10 904(3)
C(18)	6 141(4)	4 304(10)	10 204(3)
O(19)	5 860(3)	5 368(7)	9 710(2)
C(20)	6 098(4)	129(10)	10 946(3)
O(21)	5 775(3)	−1 412(7)	10 908(3)
C(22)	7 604(4)	3 014(9)	11 684(3)
O(23)	8 263(3)	3 235(7)	12 133(2)
C(24)	5 892(4)	3 642(10)	11 622(3)
O(25)	5 476(3)	4 285(8)	12 004(3)

Table 2 Fractional coordinates for compound **7**

Atom	*x*	*y*	*z*
Ge(1)	7 788(1)	1 279(1)	889(1)
C(2)	8 716(5)	−635(12)	1 504(6)
C(3)	9 629(5)	160(11)	1 350(5)
C(4)	9 635(5)	1 889(11)	948(5)
C(5)	8 732(5)	3 070(11)	619(6)
C(6)	10 456(6)	−1 160(13)	1 697(6)
C(7)	10 489(6)	2 869(13)	768(7)
Br(8)	7 165(1)	−228(1)	−588(1)
Mn(9)	6 476(1)	2 379(2)	1 522(1)
C(10)	6 106(5)	3 586(12)	358(6)
O(11)	5 912(4)	4 366(9)	−336(4)
C(12)	7 095(5)	4 697(13)	1 932(5)
O(13)	7 438(4)	6 174(9)	2 167(4)
C(14)	5 946(5)	−12(14)	1 074(5)
O(15)	5 629(4)	−1 490(9)	806(4)
C(16)	5 449(6)	3 079(12)	1 965(5)
O(17)	4 817(4)	3 494(9)	2 236(4)
C(18)	7 068(5)	1 132(12)	2 626(6)
O(19)	7 435(4)	355(9)	3 290(4)

To shed further light on this matter, the derivatives **5**, **7** and **11** have been structurally characterized in the solid state; ORTEP plots are shown in Figs. 1, 2 and 3, respectively. The relevant bond distances and angles are given in Tables 5 and 6. The degree of puckering, δ, of the germacyclopent-3-ene rings is defined by the angle between the plane containing the four carbon atoms of the ring and that containing the germanium atom and the other two substituents (see Scheme 4). The puckering angles for **5**, **7** and **11** were approximately 8, 6 and 9°, respectively. These values are significantly smaller than those previously observed for **1** (δ = 30°) and for bis[3,4-dimethyl-1-(tetracarbonylferrio)-1-germacyclopent-3-ene] **18** (δ = 30°). As for **18**, no evidence for intermolecular interactions was found in the X-ray structural data for **5**, **7** and **11**. The Ge–Co distance of **11** [2.367(1) Å] is shorter than those of **5** [2.457(1) and 2.463(1) Å] probably as a result of the presence of an electronegative bromide substituent in **11**, but is considerably longer than the Ge–Co bond distance of $[GeCl_3\{Co(CO)_4\}]$.[14] Similarly, the Mn–Ge bond distance in **7** [2.461(1) Å] is significantly shorter than those of **1** [2.570(1) and 2.573 Å]. Similar trends are reflected in the Ge–C bond distances, shorter for the monobromo derivatives [**7**, Ge–C(2) 1.955(8), Ge–C(5) 1.963(7); **11**, Ge-C(2) 1.962(6), Ge–C(5) 1.950(6) Å] than for the dimetal-substituted derivatives [**1**, Ge–C(2) 1.980(4), Ge–C(5) 1.991(4); **5**, Ge–C(4) 1.972(6), Ge–C(7) 1.979(6) Å]. As expected, the X–Ge–X angles (where X = ML_n or halide) are larger for the dimetal-substituted species than for the monometal-substituted species. As the X–Ge–X angle increases the C–Ge–C angle decreases correspondingly. Other distances and angles within the germacyclopent-3-ene rings and the metal carbonyl substituents are unremarkable. A comparison of the metrical parameters for these and a number of other closely related derivatives is presented in Table 7. The reasons why some derivatives adopt a more puckered germacyclopent-3-ene conformation compared to others are not clear and probably reflect the small energy difference between different conformations. Inspection of the space-filling models of **5**, **7** and **11** shown in Fig. 4 is revealing in a number of ways. It seems unlikely that eclipsing interactions between the hydrogen atoms in the 2 or 5 position with the germanium halide or ML_n substituent are important, consistent with previous suggestions. Also an approximately planar ring conformation would appear to minimize steric repulsions between the germanium substituents and the germacyclopent-3-ene ring. The intermeshing of the carbonyl ligands is clearly visible in both **1** and **5**. However, it appears from the space-filling models that the interaction between the *carbonyl ligands* and the substituents in the 2 and 5 positions may be important. This interaction is apparent in the space-filling model of **5**, but appears to be

Table 3 Fractional coordinates for compound **11**

Atom	*x*	*y*	*z*
Ge(1)	5721(1)	1179.4(2)	5606(1)
C(2)	4478(10)	1776(2)	5001(9)
C(3)	6228(10)	2074(2)	6153(8)
C(4)	7991(10)	1896(2)	7340(9)
C(5)	8192(11)	1400(2)	7566(9)
C(6)	5786(14)	2564(2)	5878(11)
C(7)	9876(13)	2153(3)	8538(13)
Br(8)	3420(1)	787.9(2)	6986(1)
Co(9)	6510(1)	742.2(2)	3245(1)
C(10)	7595(9)	362(2)	5155(8)
O(11)	8325(8)	127(2)	6338(7)
C(12)	7176(9)	399(2)	1481(8)
O(13)	7583(8)	181(2)	397(6)
C(14)	3630(10)	772(2)	2117(8)
O(15)	1858(7)	797(2)	1396(7)
C(16)	8158(9)	1210(2)	3058(8)
O(17)	9216(8)	1507(2)	2941(7)

Table 4 Summary of crystallographic parameters for compounds **5**, **7** and **11** *

	5	**7**	**11**
T/°C	−155	−155	−131
M	496.68	429.63	405.61
a/Å	15.556(3)	14.825(2)	6.441(1)
b/Å	6.691(1)	6.781(1)	30.040(7)
c/Å	17.726(2)	14.765(2)	7.472(1)
β/°	104.23(1)	103.43(0)	106.38(1)
Z	4	4	4
U/Å^3	1788.21	1443.71	1387.05
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
D_c/g cm^{-3}	1.845	1.980	1.942
Crystal colour	Yellow	Colourless	Yellow
Crystal dimensions/mm	0.15 × 0.15 × 0.25	0.15 × 0.21 × 0.25	0.14 × 0.14 × 0.14
No. of reflections collected	2942	2174	4018
No. of reflections used in refinement [$F_o \geqslant 3\sigma(F_o)$]	2071	1672	2621
Limits of data collection/°	6–45	6–45	6–55
μ/cm^{-1}	35.157	56.560	61.850
R	0.0388	0.0423	0.0477
R′	0.0403	0.0432	0.0456

* Details in common: Mo-Kα radiation (λ = 0.710 69 Å); Picker four-circle goniostat with furnace monochromator and Picker X-ray generator interfaced to a TI980 computer.

Table 5 Relevant bond lengths (Å) for compounds **5**, **7** and **11**

5		**7**		**11**	
Ge(1)–Co(2)	2.463(1)	Ge(1)–Br(8)	2.392(1)	Ge(1)–Br(8)	2.346(1)
Ge(1)–Co(3)	2.457(1)	Ge(1)–Mn(9)	2.461(1)	Ge(1)–Co(9)	2.367(1)
Ge(1)–C(4)	1.972(6)	Ge(1)–C(2)	1.955(8)	Ge(1)–C(2)	1.962(6)
Ge(1)–C(7)	1.979(6)	Ge(1)–C(5)	1.963(7)	Ge(1)–C(5)	1.950(6)
Co(2)–C(10)	1.780(6)	Mn(9)–C(10)	1.867(8)	Co(9)–C(10)	1.808(6)
Co(2)–C(12)	1.823(6)	Mn(9)–C(12)	1.850(9)	Co(9)–C(12)	1.818(6)
Co(2)–C(14)	1.800(6)	Mn(9)–C(14)	1.855(9)	Co(9)–C(14)	1.810(6)
Co(2)–C(16)	1.804(7)	Mn(9)–C(16)	1.853(8)	Co(9)–C(16)	1.791(6)
Co(3)–C(18)	1.807(6)	Mn(9)–C(18)	1.865(9)	C(10)–O(11)	1.126(7)
Co(3)–C(20)	1.799(7)	C–O(av.)	1.14(1)	C(12)–O(13)	1.128(7)
Co(3)–C(22)	1.792(6)	C(2)–C(3)	1.522(11)	C(14)–O(15)	1.119(7)
Co(3)–C(24)	1.820(6)	C(3)–C(4)	1.315(11)	C(16)–O(17)	1.142(7)
C–O_{eq}(av.)	1.140(7)	C(3)–C(6)	1.509(11)	C(2)–C(3)	1.506(9)
C–O_{ax}(av.)	1.129(7)	C(4)–C(5)	1.538(10)	C(3)–C(4)	1.338(9)
C(4)–C(5)	1.501(9)	C(4)–C(7)	1.507(11)	C(3)–C(6)	1.502(9)
C(5)–C(6)	1.326(9)			C(4)–C(5)	1.501(9)
C(5)–C(8)	1.524(9)			C(4)–C(7)	1.502(9)
C(6)–C(7)	1.524(9)				
C(6)–C(9)	1.506(10)				

Table 6 Relevant bond angles (°) for compounds **5**, **7** and **11**

5		**7**		**11**	
Co(2)–Ge(1)–Co(3)	116.24(4)	Br(8)–Ge(1)–Mn(9)	107.72(4)	Br(8)–Ge(1)–Co(9)	110.14(4)
Co(2)–Ge(1)–C(4)	114.8(2)	Br(8)–Ge(1)–C(2)	102.8(3)	Br(8)–Ge(1)–C(2)	106.9(2)
Co(2)–Ge(1)–C(7)	108.0(2)	Br(8)–Ge(1)–C(5)	102.8(3)	Br(8)–Ge(1)–C(5)	108.9(2)
Co(3)–Ge(1)–C(4)	109.4(2)	Mn(9)–Ge(1)–C(2)	123.9(2)	Co(9)–Ge(1)–C(2)	119.6(2)
Co(3)–Ge(1)–C(7)	114.0(2)	Mn(9)–Ge(1)–C(5)	123.6(2)	Co(9)–Ge(1)–C(5)	116.6(2)
C(4)–Ge(1)–C(7)	92.0(3)	C(2)–Ge(1)–C(5)	92.7(3)	C(2)–Ge(1)–C(5)	93.2(3)
C(4)–C(5)–C(6)	121.3(5)	C(2)–C(3)–C(4)	118.9(7)	C(2)–C(3)–C(4)	120.0(6)
C(4)–C(5)–C(8)	114.6(6)	C(2)–C(3)–C(6)	114.8(7)	C(2)–C(3)–C(6)	115.0(6)
C(6)–C(5)–C(8)	124.1(6)	C(4)–C(3)–C(6)	126.3(7)	C(4)–C(3)–C(6)	125.0(6)
C(5)–C(6)–C(7)	118.9(5)	C(3)–C(4)–C(5)	120.7(7)	C(3)–C(4)–C(5)	120.0(6)
C(5)–C(6)–C(9)	126.5(6)	C(3)–C(4)–C(7)	124.5(7)	C(3)–C(4)–C(7)	125.7(7)
C(7)–C(6)–C(9)	114.6(6)	C(5)–C(4)–C(7)	114.8(7)	C(5)–C(4)–C(7)	114.3(6)

Table 7 Comparison of relevant bond lengths (Å) and angles (°) for transition metal-substituted germacyclopent-3-enes

Compound	Pucker (δ)	*D*(Ge–M)	*D*(Ge–Br)	*D*(Ge–C)	X–Ge–X	C–Ge–C	Ref.
1	29.7	2.570(1) 2.573(1)	—	1.980(4) 1.991(4)	120.5(1)	88.2(2)	1
18	30.2	2.483(1) 2.461(1)	—	1.978(2) 1.973(2)	105.24(3)	89.99(8)	1
5	8.3	2.457(1) 2.463(1)	—	1.979(6) 1.972(6)	116.24(4)	92.0(3)	This work
7	6.0	2.461(1)	2.392(1)	1.955(8) 1.963(7)	107.72(4)	92.7(3)	This work
11	9.2	2.367(1)	2.346(1)	1.962(6) 1.950(6)	110.14(4)	93.2(3)	This work
*	0	—	2.301(2)	1.94(2) 1.91(2)	106.4(1)	95.5(9)	11

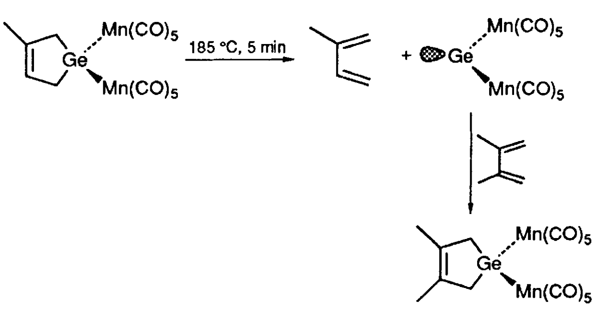
* 1,1-Dibromo-3,4-dimethyl-1-germacyclopent-3-ene.

Table 8 Kinetic data for the thermally induced decarbonylation of compound **5** according to equation (4)

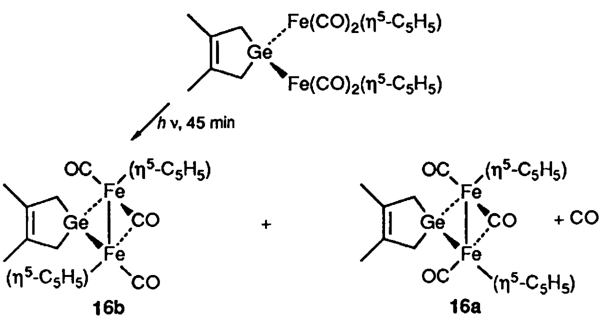
T/°C	Rate constant/s^{-1}
40	4.2×10^{-6}
50	1.5×10^{-5}
60	5.8×10^{-5}
70	2.0×10^{-4}
80	8.1×10^{-4}
90	2.1×10^{-3}

relieved to some extent in the case of **11**. The close proximity of the carbonyl ligands to the hydrogen atoms is consistent with the solution ^{1}H NMR data where the methylenic protons of disubstituted metal carbonyl germacyclopent-3-enes are markedly deshielded (by ≈0.5 ppm) compared to the dibromo analogues. A similar chemical shift difference is also apparent for the monobromomono(transition metal) carbonyl-substituted derivatives **7**–**11**. These observations are currently being tested by conformational studies of 2-alkyl-1,1-di(transition metal)-substituted germacyclopent-3-enes.

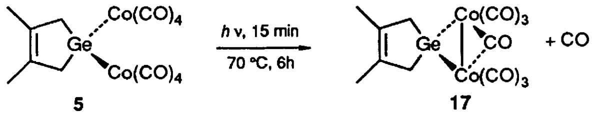
Reactivity Studies.—We have previously observed[5] that thermolysis of 1,1-bis(pentacarbonylmanganio)-substituted germacyclopent-3-enes results in cleavage of the Ge–C bonds, as shown in equation (2), where the presence of an excess of a different diene provides evidence consistent with extrusion of $\mathrm{:Ge\{Mn(CO)\}_2}$. However, in the case of other derivatives, thermolysis or photolysis results in loss of a *carbonyl ligand* and formation of a carbonyl-bridged metal–metal bond. Two examples are given in equations (3) and (4).



(2)



(3)



(4)

In the case of decarbonylation reaction (3) two isomers are formed. The germacyclopent-3-ene ring can be used as a subtle ^{1}H NMR probe of the symmetry of the metal carbonyl substituents in both the plane of the five-membered ring (depending on whether the methylene protons are diastereotropic or not) and perpendicular to it (using the olefin substituents). Based on these parameters, unambiguous distinction can be made between **16a** and **16b**. The *cis* isomer, **16a**, is preferred by about 4:1 over the *trans* isomer. Similar photolytic decarbonylation reactions have been studied with germanium-substituted cobalt and iron carbonyl compounds.[15–17] In particular, the photochemical decarbonylation of [GeMe$_2${Fe-

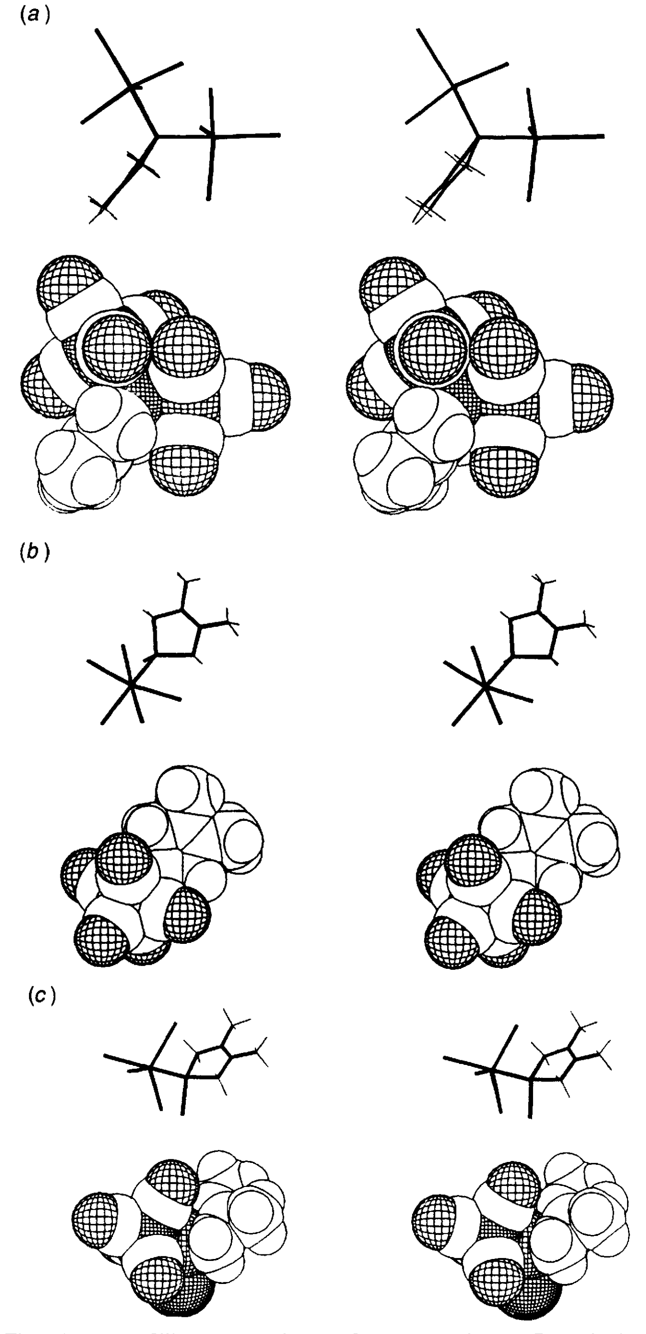


Fig. 4 Space-filling stereoviews of compounds **5**, **7** and **11**, emphasizing the steric interactions in these molecules

$(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ also resulted in formation of a 4:1 mixture of *cis* and *trans* isomers of $[GeMe_2\{Fe_2(CO)_3(\eta^5\text{-}C_5H_5)\}]$ respectively. However, thermolysis of this compound resulted mainly in formation of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$. When the mixture of **16a** and **16b** is heated no change in the ratio or the width of their cyclopentadienyl resonances was observed. These data are consistent with no exchange between *cis* and *trans* isomers on a rate comparable to the NMR time-scale and the absence of an equilibrium between these species between 23 and 60 °C. Photochemically induced ring closure was previously observed in the case of cobalt derivatives such as $[GeMe_2\{Co(CO)_4\}_2]$ to form $[GeMe_2\{Co_2(CO)_7\}]$ and carbon monoxide. The presence of only one type of alkylgermanium substituent was observed, as is the case here, probably as a result of carbonyl ligand exchange. The photochemical rearrangement of metal carbonyls is well known to proceed *via* loss of carbonyl ligands.[18–20]

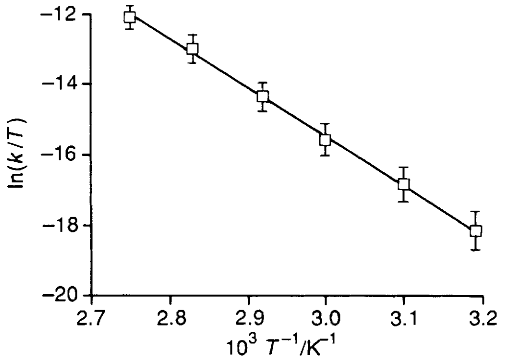


Fig. 5 Eyring plot for the thermally induced decarbonylation of compound **5**, according to equation (4)

The thermally induced reaction (4) has been the subject of a kinetic analysis, and the resulting Eyring plot is shown in Fig. 5. The decarbonylation of compound **5** was examined by ^1H NMR spectroscopy where the rate of loss of the reactant was monitored. Samples of **5** were dissolved in $[^2H_8]$toluene and sealed under vacuum at high dilution in order to minimize the reverse reaction of carbon monoxide with **17**. The reaction was monitored generally until completion or at least for three half-lives. Reaction (4) was found to be first order in reactant concentration over a temperature range 40–90 °C. The activation parameters for the decarbonylation of **5** at an average temperature of 70 °C were $\Delta G^\ddagger = +25.9$ kcal mol^{-1} $\Delta H^\ddagger = +27.6$ kcal mol^{-1} and $\Delta S^\ddagger = +5$ cal K^{-1} mol^{-1}. While the entropy of activation has a value that could simply reflect solvent reorganization, it seems likely that the transition state involves significant bond cleavage, but relatively little structural reorganization. The enthalpy of activation is close to the enthalpy of a Co–CO bond (≈ 32 kcal mol^{-1})[21] and is consistent with significant weakening of a Co–CO bond in the transition state.

Conclusion

A series of new transition-metal carbonylate-substituted germacyclopent-3-enes containing transition metal to germanium bonds have been prepared by simple salt-elimination reactions. Single-crystal X-ray diffraction studies of a number of derivatives show that in every case the ground-state conformation of the germacyclopent-3-ene ring is puckered, but that the degree of puckering, δ, varies over the range 6–30° including data for **18**. The variation in δ is believed to result from the different steric interactions of the carbonyl substituents with the germacyclopent-3-ene ring. Further studies are in progress to test this hypothesis. It has previously been shown that thermolysis of 1,1-bis(pentacarbonylmanganio)-substituted germacyclopent-3-enes results in cleavage of the five-membered ring. It is shown here that thermolysis and photolysis of cobalt and iron derivatives result in decarbonylation. These observations have been quantified by kinetic analysis of the decarbonylation of 3,4-dimethyl-1,1-bis(tetracarbonylcobaltio)-1-germacyclopent-3-ene, which shows that there is little entropy of activation, but significant enthalpy of activation in the transition state. It has also been demonstrated that reduction of Ge–Br bonds to form Ge–H bonds can be achieved without affecting either the olefinic bond or the metal carbonyl substituent. Further studies to investigate the degenerate rearrangement of this series of compounds are in progress.

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