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Transition-Metal Carbonyl Derivatives of the Germanes. 15.[1] Reaction of Digermane and Related Species with Cobalt Carbonyl: Formation of $Ge_2Co_6(CO)_{20}$ and Its Conversion to a Closed Cluster, $[\mu_4\text{-}GeCo(CO)_4]_2Co_4(CO)_{11}$

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All Ge–Ge and Ge–H bonds are cleaved in the reaction of polygermanes or silylgermanes with $Co_2(CO)_8$. Ge_2H_6 gives the known $(\mu_4\text{-}Ge)[Co_2(CO)_7]_2$ and the new compound $Ge_2Co_6(CO)_{20}$. $Me_2Si(GeH_3)_2$ gives $Ge_2Co_6(CO)_{20}$ in high yield. Me_3GeGeH_3 and Me_3SiGeH_3 form mainly $(\mu_4\text{-}Ge)[Co_2(CO)_7]_2$ and $Me_3MCo(CO)_4$. At 50–60 °C, $Ge_2Co_6(CO)_{20}$ loses CO quantitatively to give $Ge_2Co_6(CO)_{19}$, which crystallizes in the orthorhombic space group *Cmca* (a = 17.902 (3) Å, b = 12.783 (2) Å, c = 26.456 (3) Å, V = 6054 Å^3, and Z = 8). The structure shows a quadrilateral of Co atoms, bicapped by $\mu_4\text{-}GeCo(CO)_4$ groups and having one $Co(CO)_2\text{–}Co(CO)_2$ edge symmetrically bridged, the opposite $Co(CO)_3\text{–}Co(CO)_3$ edge unbridged, and the other two edges semibridged by CO.

Introduction

The formation of Ge–Co bonds by reaction of Ge–H with $Co_2(CO)_8$ was first used to make a small cluster containing a $GeCo_2$ triangle, by Fieldhouse et al.[2] in 1969 with the synthesis of $Co_2(\mu\text{-}GePh_2)(\mu\text{-}CO)(CO)_6$ from Ph_2GeH_2. Soon after, Graham and his colleagues[3] reported the similar synthesis of $Co_2[\mu\text{-}Ge(Ph)Co(CO)_4](\mu\text{-}CO)(CO)_6$ from $PhGeH_3$. They also explored the CO addition and elimination reactions of this species. More recently $MeGeH_3$ has given[4] the methyl analogue of Graham's complex, which undergoes quantitative decarbonylation to the closed cluster[5] $Co_3(\mu_3\text{-}GeMe)(CO)_9$.

When the reaction of GeH_4 with $Co_2(CO)_8$ was examined,[6,7] the product, $(\mu_4\text{-}Ge)[Co_2(CO)_7]_2$, contained two $GeCo_2$ triangles linked through the common spiro Ge. Carbon monoxide was readily lost at 50 °C to give the pyramidal Co_3Ge cluster[7] first published by Schmid[8] (eq 1).

$$GeH_4 + 2Co_2(CO)_8 \rightarrow 2H_2 + 2CO + (\mu_4\text{-}Ge)[Co_2(CO)_7]_2 \rightarrow CO + [\mu_3\text{-}(CO)_4CoGe]Co_3(CO)_9 \quad (1)$$

If the Ge atom is already bonded to a transition metal, its Ge–H groups behave analogously. Thus, $(CO)_4CoGeMeH_2$ gives[4] the same final product with $Co_2(CO)_8$ as does $MeGeH_3$, while $(CO)_5MnGeH_3$ forms[9] $[\mu_3\text{-}(CO)_5MnGe]Co_3(CO)_9$ at room temperature presumably via addition and subsequent condensation. Under the mild conditions used for all these reactions the Ge–H bonds are all readily replaced while Ge–C bonds are unaffected.

These observations suggested that examination of the reactions of polygermanes with $Co_2(CO)_8$ would be of interest. The use of species with more Ge–H bonds might well give a larger cluster, but it was less clear whether Ge–Ge bonds would be retained. The disilane $Me_2HSiSiHMe_2$ reacted[10] in a complex manner with $Co_2(CO)_8$ to give some products retaining Si–Si, like $(CO)_4CoSiMe_2SiMe_2Co(CO)_4$, and others involving Si–Si cleavage such as $(\mu\text{-}SiMe_2)_2Co_2(CO)_6$. Reactions of digermanes with $Ru_3(CO)_{12}$ or of disilanes with $Mn_2(CO)_8(PPh_3)_2$ led[11,12] to Ge–Ge or Si–Si cleavage, respectively, though the conditions were more vigorous.

Table I. Incondensable Gases Formed from Ge_2H_6 (1.84 mmol) plus $Co_2(CO)_8$ (5.51 mmol)

time, h	mmol H_2	mmol CO	time, h	mmol H_2	mmol CO
0.5	1.49	3.42	72	4.52	6.46
1.5	2.52	5.10	252	5.74	6.66
19.5	3.26	3.72	348	5.89	6.86

In the work reported here, we investigated the reaction of Me_3GeGeH_3 with $Co_2(CO)_8$ to see whether it behaved as an analogue of $MeGeH_3$ or whether the Ge–Ge bond cleaved. The study was then extended to Ge_2H_6 and other related species.

Experimental Section

Compounds were handled under nitrogen or by standard vacuum-line methods. Known compounds were established spectroscopically. Instruments were a Perkin-Elmer 180 (infrared) a JEOL C60HL (^1H NMR), and a Varian CH5 (mass spectra). All mass spectra were run at the minimum probe temperature needed to give the spectrum (usually 20–30 °C).

Me_3GeGeH_3, Me_3SiGeH_3, and $Me_2Si(GeH_3)_2$ were prepared[13,14] by reacting the appropriate chloride with dry GeH_3Na in absence of solvent.

Reactions with $Co_2(CO)_8$ were carried out in dry hexane in sealed ampules of ca. 50-mL capacity at room temperature. Ampules were opened onto a vacuum line, and total volatiles (H_2 + CO) were transferred to a gas buret by using a Toepler pump; approximate proportions were derived by weighing a standard volume to obtain the average molecular weight of the gaseous mixture.

Me_3GeGeH_3 and $Co_2(CO)_8$. Me_3GeGeH_3 (95 mg, 0.49 mmol) and $Co_2(CO)_8$ (0.29 g, 0.85 mmol) were reacted for 4 days. The IR spectrum of the product mixture showed $Me_3GeCo(CO)_4$,[15] $(\mu_4\text{-}Ge)[Co_2(CO)_7]_2$,[6] traces of $Co_4(CO)_{12}$, and a new species absorbing at 2087 cm^{-1}. Unreacted Me_3GeGeH_3 and solvent were pumped off, and $Me_3GeCo(CO)_4$ (87 mg, 0.30 mmol) was recovered by sublimation at 25 °C and 0.1 torr. Pure $(\mu_4\text{-}Ge)[Co_2(CO)_7]_2$ (209 mg, 0.298 mmol) was recovered from the residue by recrystallization from hexane. Yields of $Me_3GeCo(CO)_4$ and $(\mu_4\text{-}Ge)[Co_2(CO)_7]_2$ were each 61% on the basis of starting Me_3GeGeH_3 and were estimated to be ca. 90% on the basis of consumed Me_3GeGeH_3. The 2087-cm^{-1} species remained in the less soluble residue.

Further reactions in 1:2 ratio for longer periods gave similar results. A 2:1 ratio yielded a complex mixture of largely unidentified products.

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Me_3SiGeH_3 and $Co_2(CO)_8$. After 18 days, Me_3SiGeH_3 (115 mg, 0.773 mmol) and $Co_2(CO)_8$ (530 mg, 1.55 mmol) gave $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ (453 mg, 0.646 mmol, 83%) after recrystallization from hexane. $Me_3SiCo(CO)_4$,[16] a trace of $HCo(CO)_4$, and unreacted Me_3SiGeH_3 were removed with the solvent but not measured. Small quantities of $Co_4(CO)_{12}$ and the 2087-cm^{-1} species were detected.

Ge_2H_6 and $Co_2(CO)_8$. After Ge_2H_6 (97 mg, 0.64 mmol) and $Co_2(CO)_8$ (660 mg, 1.92 mmol) had reacted for 4 weeks, volatiles were removed and Ge_2H_6 (7 mg, 0.05 mmol) was recovered. The residue was extracted with CH_2Cl_2 (15 mL), and recrystallization from CH_2Cl_2/hexane at −16 °C gave a pure sample of the 2087-cm^{-1} species, shown below to be $Ge_2Co_6(CO)_{20}$ (240 mg, 0.226 mmol, 38% based on Ge_2H_6 consumed). Further $Ge_2Co_6(CO)_{20}$ remained but could not be separated from $GeCo_4(CO)_{14}$, minor amounts of $Co_4(CO)_{12}$, and a new species absorbing at 2094 cm^{-1}.

Repeat runs for times from 2 to 5 weeks and at 1:3, 1:4, or 1:2 molar ratios gave similar results with minor variations in the ratio of $Ge_2Co_6(CO)_{20}$ to $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$. Small quantities of a product with ν(CO) at 2106 w, 2088 s, 2040 m, 2034 ms, 2024 sh, 2019.5 vs, 2008 m, 2002 sh, vw, and 1971 vw cm^{-1} were sublimed from the 1:2 system. Monitoring of incondensable gas evolution from a 1:3 run gave the results shown in Table I.

Spectroscopic Properties of $Ge_2Co_6(CO)_{20}$. The pure, orange solid had a mass spectrum with a parent ion envelope at m/e 1066–1054 with the intensity pattern appropriate to 2Ge ($C_{20}Co_6{}^{70}Ge_2O_{20}$ = 1054); 80% of the ion current was carried by the $(P - n\text{CO})^+$ series whose relative intensities from n = 0 to 20 were 26, 19, 39, 100, 14, 17, 31, 76, 97, 61, 70, 63, 82, 66, 58, 62, 60, 43, 40, 41, and 61. Other significant ions: $Ge_2Co_5(CO)_n{}^+$ for n = 1 (18) and 0 (36); $Ge_2Co_4(CO)_n{}^+$ for n = 1 (9) and 0 (29); $Ge_2Co_3(CO)_n{}^+$ for n = 1 (14) and 0 (24); $Ge_2Co_2(CO)_n{}^+$ for n = 1 (12) and 0 (24); $GeCo_4{}^+$ (10); $GeCo_2(CO)_n{}^+$ for n = 3 (15), 2 (21), 1 (20), 0 (46). In the infrared spectrum, carbonyl stretching bands are as follows (hexane): 2087 s, 2068 vs, 2054 s, 2050 sh, 2040 w, 2033 mw, 2027 m, 2003 w, 1848 sh, 1844 mw cm^{-1}.

$(GeH_3)_2SiMe_2$ and $Co_2(CO)_8$. $(GeH_3)_2SiMe_2$ (0.188 g, 0.90 mmol) and $Co_2(CO)_8$ (1.08 g, 3.16 mmol) were reacted for 2.5 weeks. Soluble products were extracted with hexane (10 mL), and the residue was recrystallized from CH_2Cl_2/hexane to give $Ge_2Co_6(CO)_{20}$ (0.86 g, 91%) together with some $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ (<5%). A 1:5 reactant mixture behaved similarly.

The hexane solution gave, as the major fraction, a sample showing ν(CO) bands (hexane) at 2103 w, 2098 mw, 2048 vs, 2042 sh, 2034 s, 2013 w, and 2002 m cm^{-1}. This was inseparable from unreacted $Co_2(CO)_8$ or from a little $Co_4(CO)_{12}$ (2062 m, 2052 m, 1866 mw cm^{-1}). These frequencies match, in intensity and frequency, those reported[17] for $R_2SiCo_4(CO)_{14}$ (R = Ph, Et) and are attributed to the methyl analogue,[18] $(CO)_4CoSiMe_2OCCo_3(CO)_9$. A minor component (2092 w, 2029 s, 2006 w, 1995 m cm^{-1}) was probably $Me_2HSiCo(CO)_4$.

GeH_4 and $Co_2(CO)_8$. GeH_4 (1.45 mmol) and $Co_2(CO)_8$ (1.45 mmol) were reacted for 21 days. Recrystallization of the crude product from CH_2Cl_2/hexane gave $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ (0.656 mmol, 90%). GeH_4 (0.67 mmol) was recovered.

When the 1:1 reaction was repeated for times up to 14 weeks, or when a 1:2 ratio was used, $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ was still the major product although significant amounts of $Ge_2Co_6(CO)_{20}$ (up to 20%) were also formed.

GeH_4 and $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$. $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ (0.20 g, 0.28 mmol) and GeH_4 (0.082 g, 1.07 mmol) were reacted for 6 weeks. Unreacted GeH_4 (0.076 g, 0.99 mmol, 92%) was recovered. The residue gave recovered $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ (0.172 g, 86%) together with traces of $Ge_2Co_6(CO)_{20}$ among other products, all in very low yield.

Thermolysis of $Ge_2Co_6(CO)_{20}$. $Ge_2Co_6(CO)_{20}$ (0.36 g, 0.34 mmol) in hexane was heated at 60 °C for 14 days. Evolution of CO was monitored and reached a plateau after 8–10 days at 0.37 mmol (1.09 mol/mol of starting material). From the residue a small amount of $[\mu_3\text{-GeCo}(CO)_4]Co_3(CO)_9$[8] was removed with CH_2Cl_2 to leave black sparsely soluble crystals of $[\mu_4\text{-GeCo}(CO)_4]_2Co_4(CO)_{11}$, showing ν(CO) (CH_2Cl_2) at 2100 s, 2065 w, sh, 2050 s, 2037 vs, 2014 m, 2003 w, sh, 1990 w, sh, and 1844 w, br cm^{-1}. This product was characterized by X-ray crystallography.

Crystal Structure of $[\mu_4\text{-GeCo}(CO)_4]_2Co_4(CO)_{11}$. A black diamond-shaped platelike crystal of dimensions 0.3 mm × 0.3 mm × 0.07 mm was obtained from hot CH_2Cl_2 and sealed in a thin-walled glass capillary. Preliminary precession photography indicated an orthorhombic crystal class with space group either *Cmca* or *Aba2*; the success of the refinement showed the former to be correct. An Enraf-Nonius CAD4 diffractomer, with monochromated Mo Kα X-rays, was used to determine accurate cell dimensions and to obtain data.

Table II. Final Positional Parameters for $Ge_2Co_6(CO)_{19}$ ($\times 10^4$)

atom	x/a	y/b	z/c
Ge(1)	4164 (1)	2451 (2)	1245 (1)
Co(1)	5000	2970 (4)	577 (2)
Co(2)	5000	3848 (4)	1495 (2)
Co(3)	5000	1941 (4)	1927 (2)
Co(4)	5000	1108 (4)	976 (2)
Co(5)	2829 (2)	2341 (3)	1153 (1)
C(11)	4263 (14)	3414 (20)	242 (10)
C(14)	5000	1569 (29)	274 (14)
C(21)	4287 (16)	4415 (23)	1836 (10)
C(22)	5000	4648 (28)	981 (13)
C(31)	4280 (17)	2289 (27)	2344 (12)
C(32)	5000	665 (36)	1939 (16)
C(41)	4249 (16)	277 (21)	929 (9)
C(51)	2903 (17)	1414 (24)	1672 (10)
C(52)	1851 (20)	2248 (26)	1177 (12)
C(53)	2970 (15)	1756 (19)	567 (10)
C(54)	2907 (19)	3696 (26)	1143 (11)
O(11)	3724 (11)	3676 (15)	−37 (8)
O(14)	5000	1209 (20)	−84 (11)
O(21)	3794 (13)	4807 (17)	2050 (9)
O(22)	5000	5459 (25)	719 (12)
O(31)	3791 (15)	2431 (20)	2648 (11)
O(32)	5000	−273 (26)	2033 (12)
O(41)	3753 (12)	−419 (17)	919 (8)
O(51)	2910 (13)	832 (17)	1984 (8)
O(52)	1166 (14)	2198 (18)	1192 (9)
O(53)	3023 (10)	1335 (15)	161 (7)
O(54)	2949 (12)	4649 (18)	1046 (8)

Table III. Selected Bond Lengths and Bond Angles for $Ge_2Co_6(CO)_{19}$

Bond Lengths (Å)

Ge(1)–Co(1)	2.406 (4)	Co(2)–Co(3)	2.693 (8)
Ge(1)–Co(2)	2.423 (4)	Co(3)–Co(4)	2.735 (7)
Ge(1)–Co(3)	2.434 (5)	Co(1)–C(14)	1.95 (4)
Ge(1)–Co(4)	2.390 (5)	Co(4)–C(14)	1.94 (4)
Ge(1)–Co(5)	2.405 (4)	C(14)–O(14)	1.07 (4)
Co(1)–Co(2)	2.671 (7)	Co(2)–C(22)	1.70 (4)
Co(1)–Co(4)	2.604 (7)	Co(3)–C(32)	1.66 (5)

all other Co–C distances 1.71 (3)–1.80 (3)
all other C–O distances 1.13 (3)–1.23 (3)

Bond Angles (deg)

Co(1)–Ge(1)–Co(2)	67.2 (2)	Co(2)–Co(1)–Co(4)	91.1 (2)
Co(1)–Ge(1)–Co(3)	103.5 (1)	Ge(1)–Co(1)–Ge(1)′	77.0 (2)
Co(1)–Ge(1)–Co(4)	65.8 (2)	Ge(1)–Co(2)–Ge(1)′	76.3 (2)
Co(1)–Ge(1)–Co(5)	124.1 (1)	Ge(1)–Co(3)–Ge(1)′	75.9 (2)
Co(2)–Ge(1)–Co(3)	67.4 (2)	Ge(1)–Co(4)–Ge(1)′	77.6 (2)
Co(2)–Ge(1)–Co(4)	103.0 (1)	Co(1)–C(14)–O(14)	139 (3)
Co(2)–Ge(1)–Co(5)	133.3 (2)	Co(4)–C(14)–O(14)	136 (3)
Co(3)–Ge(1)–Co(4)	69.1 (2)	Co(2)–C(22)–O(22)	161 (3)
Co(3)–Ge(1)–Co(5)	132.0 (2)	Co(3)–C(32)–O(32)	168 (3)
Co(4)–Ge(1)–Co(5)	123.3 (2)	Ge(1)–Co(5)–C(51)	84 (1)
Co(1)–Co(2)–Co(3)	90.3 (2)	Ge(1)–Co(5)–C(52)	173 (1)
Co(1)–Co(4)–Co(3)	90.8 (2)	Ge(1)–Co(5)–C(53)	89 (1)
Co(2)–Co(3)–Co(4)	87.9 (2)	Ge(1)–Co(5)–C(54)	83 (1)

all other Co–C–O angles 172 (3)–179 (3)

Crystal Data: $C_{19}Co_6Ge_2O_{19}$, M_r = 1030.95, orthorhombic, space group *Cmca*, a = 17.902 (3) Å, b = 12.783 (2) Å, c = 26.456 (3) Å, V = 6054 Å^3, D_c = 2.26 g cm^{-3} for Z = 8; F(000) = 3935, $\bar{\mu}$(Mo Kα) = 50.7 cm^{-1}, λ(Mo Kα) = 0.7107 Å, T = 23 °C.

Intensity data were collected in the range 1° < θ < 20.5° with an ω–2θ scan and with a horizontal counter aperture and ω-scan angle of (0.80 + 0.35 tan θ) mm and (1.7 + 1.2 tan θ)°, respectively. This gave 1227 unique reflections, which were corrected for Lorentz and polarization effects and for absorption (on the basis of a series of ϕ scans). The 871 reflections for which $F^2 > 2\sigma(F^2)$ were used in all calculations.

The structure was solved by direct methods (MULTAN) to reveal the metal core. All subsequent calculations were carried out by using the SHELX 76 programs. A difference map revealed all other atoms. The final cycles of full-matrix least-squares refinement, with anisotropic temperature factors for the Ge and Co atoms and isotropic temperature factors

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for the C and O atoms, converged at $R = 0.064$ and $R_w = 0.070$, where $w = 1.00[(\sigma(F))^2 + 0.0085F^2]^{-1}$. There was no evidence for extinction, and a final difference map gave no significant residual electron density. Neutral-atom scattering factors were taken from Cromer and Mann[19] and included anomalous dispersion effects.

Final atomic coordinates are listed in Table II, and bond lengths and selected bond angles are given in Table III. Thermal parameters and structure factors have been deposited as supplementary information.

Results

Although the reactant ratio was appropriate for Ge–H substitution, the reaction of Me_3GeGeH_3 with $Co_2(CO)_8$ at room temperature involved cleavage of Ge–Ge as well as of Ge–H bonds (eq 2). The two metal-containing products were recovered in

$$Me_3GeGeH_3 + {}^5/_2[Co_2(CO)_8] \rightarrow Me_3GeCo(CO)_4 + (\mu_4\text{-Ge})[Co_2(CO)_7]_2 + {}^3/_2H_2 + 2CO \quad (2)$$

equal amounts in good yields. Traces of $Co_4(CO)_{12}$ and the new species identified later as $Ge_2Co_6(CO)_{20}$ were also formed. An excess of Me_3GeGeH_3 gave a different, but complex and unmanageable, product mixture. A brief study showed that the stronger Si–Ge bond in Me_3SiGeH_3 was similarly cleaved in a reaction analogous to (2). The recovery of $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ corresponded to the stoichiometry of (2), and $Me_3SiCo(CO)_4$ was observed but not quantified.

When no blocking methyl groups are present, reaction follows eq 3. The new species, which has a characteristic infrared band

$$^3/_2Ge_2H_6 + 5Co_2(CO)_8 \rightarrow (\mu_4\text{-Ge})[Co_2(CO)_7]_2 + Ge_2Co_6(CO)_{20} + {}^3/_2H_2 + 6CO \quad (3)$$

at 2087 cm^{-1}, was formed in a 50:50 ratio with $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ when the Ge_2H_6:$Co_2(CO)_8$ ratio was 1:3 and in a 40:60 ratio when the starting materials were in the ratio 1:4. Since $Ge_2Co_6(CO)_{20}$ is less soluble than the other products, pure samples could be isolated from these reactions although with sacrifice of material.

When the Ge_2H_6:$Co_2(CO)_8$ ratio was 1:2, the proportion of $Ge_2Co_6(CO)_{20}$ was enhanced, but with the formation of other products including a sublimable compound whose infrared spectrum closely matches those found[20] for $RSn[Co(CO)_4]_3$ species. This latter compound was also found when the $Ge_2H_6/Co_2(CO)_8$ (1:3) reaction was conducted under CO (1 atm) although no other differences were found compared with the evacuated reaction system.

The best route to the new $Ge_2Co_6(CO)_{20}$ complex is by the addition of $Co_2(CO)_8$ to $(GeH_3)_2SiMe_2$. After recrystallization, more than 90% of the initial germanium was found as $Ge_2Co_6(CO)_{20}$ with only ca. 5% as $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$. The major silicon product was not isolated pure but was probably $(CO)_4CoSiMe_2OCCo_3(CO)_9$, and traces of $HMe_2SiCo(CO)_4$ were also indicated.

Reexamination of the reaction[6] of GeH_4 with $Co_2(CO)_8$ showed the main fraction was always $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ and this was unaffected by removal of H_2 and CO or by addition of 1 atm of CO. However, in the presence of excess GeH_4 over that required by eq 1, $Ge_2Co_6(CO)_{20}$ and other species are formed in minor amounts.

Characterization of $Ge_2Co_6(CO)_{20}$. Single crystals of this compound could not be obtained, and characterization depends on spectroscopic properties. The mass spectrum (see Experimental Section) is dominated by the ions arising from CO loss, $(P - nCO)^+$ (n = 0–20), as expected for the formulation $Ge_2Co_6(CO)_{20}$. No ions of higher mass were detected up to the instrument limit (m/e ca. 1200).

The carbonyl stretches in the infrared spectrum are qualitatively similar for $Ge_2Co_6(CO)_{20}$ and $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$. Small solvent shifts allow a total of 12 terminal $\nu(^{12}CO)$ modes to be tentatively identified of which 8 are well-resolved maxima, as well as the μ-CO mode. Thus, $Ge_2Co_6(CO)_{20}$ and $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$ both show carbonyl stretching patterns that are compatible with respectively three and two $(CO)_3Co(\mu\text{-X})_2Co(CO)_3$ units, as discussed by Bor.[21] This formulation, $[(CO)_7Co_2](\mu_4\text{-Ge})[Co_2(CO)_6](\mu_4\text{-Ge})[Co_2(CO)_7]$, for $Ge_2Co_6(CO)_{20}$ is also compatible with the $Ge_2Co_n^+$ and $GeCo_n^+$ fragments in the mass spectrum.

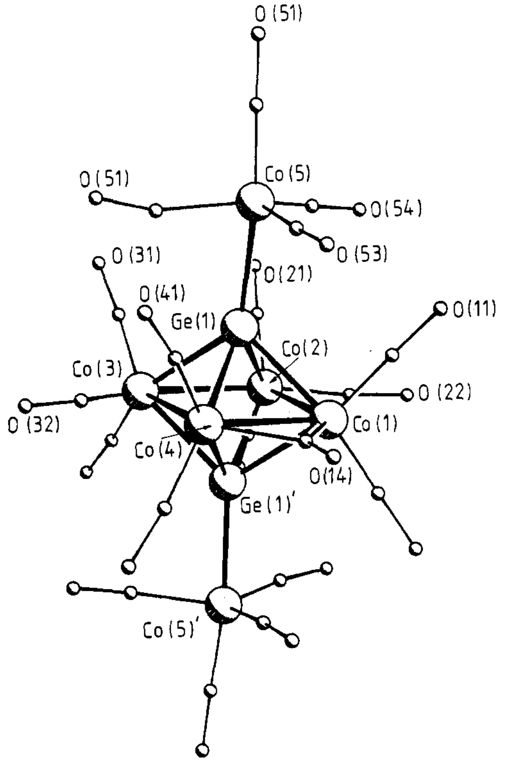

Figure 1. Structure of $Ge_2Co_6(CO)_{19}$ showing the atom labeling scheme. A crystallographic mirror plane contains the four equatorial cobalt atoms.

Decarbonylation of $Ge_2Co_6(CO)_{20}$. Further confirmation of the $Ge_2Co_6(CO)_{20}$ formula is given by following the CO evolution over 10–20 days at 60 °C in hexane. The orange starting material turns black, and the CO evolution reaches a plateau after 8–10 days corresponding to ca 1 CO per $Ge_2Co_6(CO)_{20}$. A little unchanged $Ge_2Co_6(CO)_{20}$ was recovered, and the product is the new complex characterized as $Ge_2Co_6(CO)_{19}$ by crystallography. Traces of the smaller $[\mu_4\text{-GeCo(CO)}_4]Co_3(CO)_9$ cluster were also found.

Crystal Structure of $Ge_2Co_6(CO)_{19}$. The structure of $Ge_2Co_6(CO)_{19}$ is shown in Figure 1. Four of the cobalt atoms lie on a crystallographic mirror plane and form a quadrilateral bicapped by quadruply bridging germanium atoms, thus generating an irregular square-bipyramidal core. There is a further terminal $-Co(CO)_4$ group bonded to each of the germanium atoms to give a total of five Ge–Co bonds about each germanium, in a distorted square-pyramidal configuration.

Each of the core cobalt atoms carries two "axial" carbonyl ligands, actually at 45–55° to the Co_4 plane. The three remaining CO groups, which lie in the mirror plane, are bridging although each in a different manner. The shortest edge, Co(1)–Co(4), is symmetrically bridged while the two edges adjacent to this are semibridged. The shorter semibridged edge, Co(1)–Co(2), has a less unsymmetrical configuration [Co(2)–C(22) = 1.70 (4), Co(1)···C(22) = 2.39 (4) Å] than the longer edge, Co(3)–Co(4) [Co(3)–C(32) = 1.66 (5), Co(4)···C(32) = 2.61 (4) Å]. This semibridging is undoubtedly to compensate for the electronic inequivalence of Co(1) and Co(4) (with 2.5 CO groups each) compared with Co(2) and Co(3) (with 3 CO ligands each); the differences in the two semibridges must arise from packing effects since the halves of the molecule are otherwise equivalent. The remaining Co(2)–Co(3) bond is nonbridged but is, suprisingly, not the longest.

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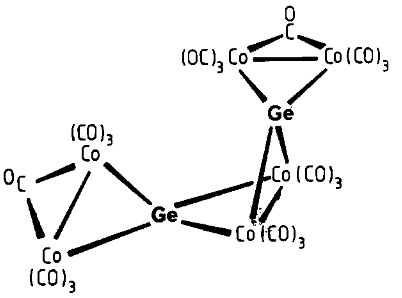


Figure 2. Proposed structure for $Ge_2Co_6(CO)_{20}$.

All the Ge–Co distances fall within the limited range 2.39–2.43 Å, including the bond to the external $-Co(CO)_4$ group. In this the Ge_2Co_4 cluster differs from the smaller closed cluster, $[\mu_4\text{-}GeCo(CO)_4]Co_3(CO)_9$, where the external Ge–Co bond is 0.17 Å shorter than the average of the cluster Ge–Co distances.[8]

Discussion

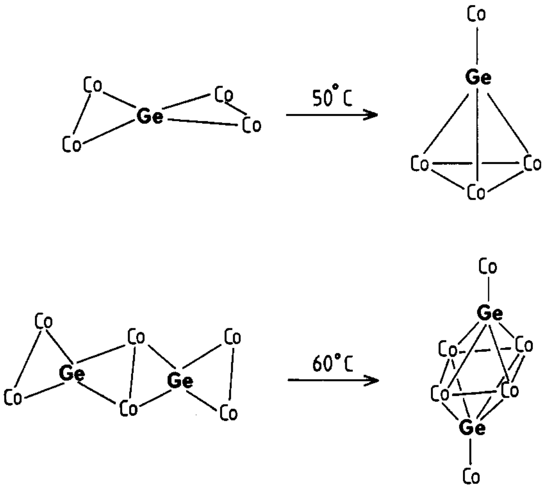
Characterization of $Ge_2Co_6(CO)_{20}$. The quantitative decarbonylation of $Ge_2Co_6(CO)_{20}$ to give $Ge_2Co_6(CO)_{19}$ confirms the mass spectrometric formula $Ge_2Co_6(CO)_{20}$. The spectroscopic evidence, together with the observation that no initial Ge–Ge bond is needed, suggests that a reasonable structure is that of the next homologue of $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$, namely $[(CO)_7Co_2]_2(\mu_4\text{-Ge})[Co_2(CO)_6](\mu_4\text{-Ge})[Co_2(CO)_7]$ (Figure 2). If this has dihedral angles about Co–Co of around 100°, similar to those usually found for $(\mu\text{-X})_2Co_2(CO)_6$ units, the molecule will have approximate C_{2v} symmetry, neglecting the bridging carbonyls. This would lead to 14 infrared-active terminal CO stretches. Since the energy difference between "cisoid" and "transoid" arrangements of the bridging carbonyls at either end of the molecule is probably negligible, both forms may exist together, possibly accounting for difficulties in procuring single crystals. Although no direct analogue of this structure is known, it may be noted that species such as $[PbFe_3(CO)_{12}]_n$ are thought to consist of linked three- and four-membered rings as in $(\mu_4\text{-Sn})[Fe_2(CO)_8]_2$ and $Me_4Sn_3Fe_4(CO)_{16}$.[22,23]

An alternative structure based on that of $Ge_2Co_6(CO)_{19}$ (see below) with an extra CO ligand can be excluded because of the light color (the *closo*-Ge_2Co_4 core is an intense chromophore) and the infrared spectrum, which is more complex than that expected for the higher symmetry alternative.

The course of the reactions leading to $GeCo_2$ triangles is not obvious. The more detailed survey of incondensable gas evolution during the reaction of Ge_2H_6 with $Co_2(CO)_8$ shows that CO evolution predominates in the early stages, while complete loss of all the hydrogen takes 2–3 times longer. Similar results were noted for the GeH_4 reaction. This could indicate an initial addition of Ge–H (or Ge–Ge) across the Co–Co bond with concomitant loss of CO to give a Ge–Co–Co–H sequence. A subsequent, slower, loss of H_2 intra- or intermolecularly would form a Co_2Ge triangular unit; repetition of the sequence would account in a general way for the observed products. The reaction with Ge_2H_6 suggests that the Ge–Ge bond cleaves early in the reaction sequence for about one-third of the molecules. For the remainder, the formation of $Ge_2Co_6(CO)_{20}$ suggests the two Ge atoms remain close together until later so that both are incorporated in the same resultant molecule. Similarly, the nearly quantitative yield of $Ge_2Co_6(CO)_{20}$ from $(H_3Ge)_2SiMe_2$ supports a model where Co_2Ge frameworks build up on each Ge, with their contiguity leading to the linkage to the common Co_2 moiety on expulsion of Me_2Si.

Formation of $Ge_2Co_6(CO)_{19}$. The decarbonylation of $Ge_2Co_6(CO)_{20}$ to give, virtually quantitatively, $Ge_2Co_6(CO)_{19}$ represents a remarkable rearrangement involving cleavage of two Co–Co bonds and formation of three new Co–Co bonds, together with the relocation of several CO ligands. We note the interesting parallel with the reaction of eq 1 by which open chains based on linked $GeCo_2$ triangles lose CO under mild conditions and condense to closed clusters with apical $Ge-Co(CO)_4$ units (Scheme I). Under these conditions the Ge–Co bonds are obviously nonlabile and so permit specific rearrangements of the cobalt–carbonyl groups about the germanium atoms without fragmentation.

Scheme I



The resulting $Ge_2Co_6(CO)_{19}$ cluster is of particular interest. It incorporates germanium atoms that are bonded to five other metal atoms. Although five-coordinate germanium is fairly well established for inorganic complexes of simple ligands, there is only one previous example[24] involving five germanium–metal bonds, namely $[GeCo_5(CO)_{17}]^-$.

There are a number of clusters containing a square-bipyramidal core E_2M_4 where E is a group 15 or 16 atom[32] and M is Co or Fe; some recent examples are $(\mu_4\text{-PhP})_2Co_2Fe_2(CO)_{11}$,[25] $(\mu_4\text{-PhP})_2Co_4(CO)_{11}$,[26] $(\mu_4\text{-RP})_2Fe_4(CO)_x$, x = 11, 12,[27] and $(\mu_4\text{-S})_2Co_4(CO)_{10}$.[28] Of these, the P_2Co_4 species have been shown to give efficient hydroformylation and carbon monoxide hydrogenation catalysis.[29] The Ge_2Co_4 core of $Ge_2Co_6(CO)_{19}$ is the only representative from among the group 14 elements so far, although there are a few variations in the apical group. Thus, we have also reported $(\mu_4\text{-MeGe})_2Co_4(CO)_{11}$,[30] and Vahrenkamp and co-workers have independently synthesized $(RGe)_2Co_4(CO)_{11}$ (R = *t*-Bu or Ph).[31] For all these species, the quadruply bridging main-group atoms confer marked stability to the clusters, suggesting that the E–M bonds are nonlabile. The presence of such linking main-group atoms may be the key to cluster catalysis without the complications of fragmentation to monometallic units.

Conclusion

$Ge_2Co_6(CO)_{20}$, which has been characterized, is probably the

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(32) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

first homologue of $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$. Gentle decarbonylation of $Ge_2Co_6(CO)_{20}$ gives the new $[\mu_4\text{-}(CO)_4CoGe]_2Co_4(CO)_{11}$ cluster, a group 14 example in the octahedral $E_2M_4(CO)_n$ series.

Acknowledgment. We thank the New Zealand University Grants Committee for equipment grants, the University of Waikato for a studentship (S.P.F.), Dr. Pat Holland of the Ruakura Agricultural Research Centre for mass spectra and Dr. Tony Jones, University of Auckland, for X-ray data.

Registry No. $Co_2(CO)_8$, 15226-74-1; Me_3GeGeH_3, 20478-15-3; $Me_3GeCo(CO)_4$, 52637-40-8; $(\mu_4\text{-Ge})[Co_2(CO)_7]_2$, 77018-35-0; Me_3SiGeH_3, 18365-18-9; Ge_2H_6, 13818-89-8; $Ge_2Co_6(CO)_{20}$, 84664-74-4; $(GeH_3)_2SiMe_2$, 20576-05-0; $(CO)_4CoSiMe_2OCCo_3(CO)_9$, 72622-29-8; GeH_4, 7782-65-2; $[\mu_4\text{-}GeCo(CO)_4]_2Co_4(CO)_{11}$, 94890-86-5; Co, 7440-48-4; Ge, 7440-56-4.

Supplementary Material Available: Listings of thermal parameters and of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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Two Compounds Containing the Tris(μ-chloro)hexakis(tetrahydrofuran)divanadium(II) Cation. Preparation, Structures, and Spectroscopic Characterization

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The reduction of $VCl_3(THF)_3$ with metallic zinc, as reported several years ago by Hall, Schmulbach, and Soby, affords a bright green compound that we have shown, by elemental analysis (including X-ray fluorescence measurements) and X-ray crystallography, to be $[V_2(THF)_6(\mu\text{-Cl})_3]_2[Zn_2Cl_6]$ (**1**). This compound can be converted to $[V_2(THF)_6(\mu\text{-Cl})_3]BPh_4$ (**2**), also light green. X-ray crystallographic studies of both of these compounds have shown that the dinuclear, unipositive cation consists of two *fac*-$VCl_3(THF)_3$ octahedra with a common triangular Cl_3 face. The V–V distance (in **1**) is 2.993 (1) Å. The two crystalline compounds are characterized by the following crystallographic constants: For **1** at −105 °C, the triclinic unit cell (space group $P\bar{1}$) has the dimensions $a = 11.485$ (4) Å, $b = 15.312$ (2) Å, $c = 10.786$ (2) Å, $\alpha = 71.07$ (2)°, $\beta = 99.10$ (2)°, $\gamma = 104.41$ (2)°, $V = 1731$ (1) Å^3, and $Z = 2$. For **2** at 22 °C, the monoclinic unit cell (space group $P2_1/c$) has dimensions $a = 16.67$ (1) Å, $b = 16.77$ (1) Å, $c = 19.21$ (1) Å, $\beta = 110.93$ (2)°, $V = 5019$ (12) Å^3, and $Z = 4$. The dinuclear cation has an electronic spectrum that is solvent dependent (for **1**). In the presence of THF it exhibits remarkable, intense double spin-flip transitions of a type previously seen only in an unusual solid-state situation.

Introduction

The report by Hall, Schmulbach, and Soby[1] in 1981 that reduction of vanadium(III) chloride in THF by metallic zinc afforded a vanadium(II) chloride compound attracted interest in this laboratory several years ago. The product of this reduction, which was presumed to be $VCl_2{\cdot}2THF$, proved to be a convenient starting material for the synthesis of other vanadium(II) and vanadium(III) compounds. However, in the course of our work with it we had occasion to question its proposed formulation. We also obtained excellent crystals, serendipitously by slow solvolysis of phosphine adducts. The combined results of the X-ray crystallographic study and X-ray fluorescence analysis for vanadium and zinc led us to the unequivocal identification of the compound as $[V_2(THF)_6(\mu\text{-Cl})_3]_2(Zn_2Cl_6)$, and we presented a brief but definitive report of this result in 1983.[2]

We have since done a great deal of additional work with this compound, in some of which it has been used as a preparative starting material from which products containing either vanadium alone[3,4] or vanadium and zinc together[5,6] have been obtained. We have also extended our studies of the $[V_2(THF)_6(\mu\text{-Cl})_3]^+$ ion itself,[7] and in this paper we shall describe the properties of this dinuclear cation in more detail.

Experimental Section

All operations were performed under an atmosphere of argon by using standard Schlenk techniques and a double-manifold vacuum line. Tetrahydrofuran, benzene, and hexane were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless-steel canulae and/or syringes. Sodium tetraphenylboron was deaerated under vacuum at room temperature.

Elemental analyses were performed by Galbraith Microanalytical Laboratories. Source-excited X-ray fluorescence analysis was done with a 100-mCi ^{241}Am excitation source. X-rays emitted from the sample were detected and analyzed by a KEVEX lithium-drifted silicon detector [Si(Li)]. Detector output pulses were digitized and evaluated with a Nuclear Data ND66 pulse height analyzer. We thank Professor Emil Schweikert of this department for the X-ray fluorescence analysis. The UV–visible spectra were measured on a Cary 17D spectrometer at room temperature. The IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer.

$[V_2(\mu\text{-Cl})_3(THF)_6]_2(Zn_2Cl_6)$ (1). This compound was prepared according to the published procedure.[1,2] The purity of the bulk, bright green $[V_2(\mu\text{-Cl})_3(THF)_6]_2(Zn_2Cl_6)$ was checked by elemental analyses, X-ray fluorescence measurements for V and Zn, and infrared spectroscopy.

Anal. Calcd for $C_{48}H_{96}Cl_{12}O_{12}V_4Zn_2$: C, 35.47; H, 5.95; Cl, 26.18. Found: C, 35.89; H, 5.92; Cl, 26.71.

X-ray fluorescence for a 2:1 atom ratio of V to Zn: calcd, 1.56; found, 1.49.

IR (KBr, cm^{-1}): 2960 (s), 2880 (s), 1450 (s), 1340 (m), 1290 (m), 1248 (m), 1178 (m), 1025 (vs), 913 (m), 870 (s), 680 (m).

Vis λ, nm (ϵ, given per mole of $V_2Cl_3(THF)_6^+$): (CH_2Cl_2) 695 (13), 450 (10.5), 410 (8), 400 (sh) (6), 345 (4.5); (CH_2Cl_2 + THF, 9:1) 625 (13), 430 (sh) (14), 405 (35), 395 (23), 630 (21).

Crystallographic quality crystals of $[V_2(\mu\text{-Cl})_3(THF)_6]_2(Zn_2Cl_6)$ were obtained by a two-step procedure. First, $[V_2(\mu\text{-Cl})_3THF)_6]_2(Zn_2Cl_6)$ was reacted with PPh_3 in benzene to give $[V_2(\mu\text{-Cl})_3(THF)_5(PPh_3)]_2(Zn_2Cl_6)$, which in turn was dissolved in THF and carefully layered with hexane. Under these conditions the PPh_3 ligand is slowly displaced by THF to give excellent quality crystals of $[V_2(\mu\text{-Cl})_3(THF)_6]_2(Zn_2Cl_6)$.

$[V_2(\mu\text{-Cl})_3(THF)_6]B(C_6H_5)_4$ (2). To a slurry of $[V_2(\mu\text{-Cl})_3(THF)_6]_2(Zn_2Cl_6)$ (1.20 g, 0.74 mmol) in 75 mL of THF, prepared in a 250-mL Schlenk tube equipped with a magnetic stirrer, was added $NaB(C_6H_5)_4$ (0.51 g, 1.49 mmol). The solution became immediately clear and bright green in color. Stirring of the reaction mixture was continued at room temperature for 12 h, after which a flocculent white precipitate was formed. The solution was filtered through Celite 545 (Fisher Scientific Co.), carefully covered with ~150 mL of hexane, and placed in a refrigerator at 0 °C for several days. Green crystals were obtained that were isolated by filtration, washed three times with hexane,

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