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Preliminary communication

DIGERMANIUM POLYCOBALT CARBONYLS FORMED BY ADDITION REACTIONS OF Ge—H BONDS: $[Co_4(CO)_{13}Ge(GeMe_2)]$ AND $[Co_6(CO)_{20}Ge_2]$

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Summary

$GeMe_2H_2$ reacts under mild conditions with $[\{Co_2(CO)_7\}_2Ge]$ to replace one bridging CO and give $[Co_4(CO)_{13}Ge(GeMe_2)]$. GeH_4 similarly yields a trace of $[Co_6(CO)_{20}Ge_2]$, which may be made in high yield from $[Co_2(CO)_8]$ and Ge_2H_6 or $Me_2Si(GeH_3)_2$. Spectroscopic evidence suggests structures of linked $GeCo_2$ triangles.

$[\{Co_2(CO)_7\}_2Ge]$ is formed [1] in a smooth reaction under mild conditions between GeH_4 and $[Co_2(CO)_8]$, and a similarly facile reaction between $[Co_2(CO)_8]$ occurs for other germanes, e.g. with $GeMeH_3$ or $[Co(CO)_4GeMeH_2]$ [2] or $[Mn(CO)_5GeH_3]$ [3]. Since the $Co_2(CO)_7$ units in $[\{Co_2(CO)_7\}_2Ge]$ are structurally very similar [1] to $[Co_2(CO)_8]$, it appeared possible that a similar reaction would occur with Ge—H bonds to give controlled syntheses of larger polymetallic species.

A hexane solution of $GeMe_2H_2$ and $[\{Co_2(CO)_7\}_2Ge]$ (mole ratio 1.5/1) was held in a sealed tube in the dark for 40—60 days. The recovery of volatiles was in accord with eq. 1. The orange-red solid product was stable indefinitely under

$$GeMe_2H_2 + [\{Co_2(CO)_7\}_2Ge] \rightarrow [Co_4(CO)_{13}Ge_2Me_2] + CO + H_2 \qquad (1)$$

N_2 at 4°C, and was moderately air-stable. Under similar conditions, it was possible to detect the analogous reaction of GeH_4, eq. 2, but this proceeded only to a very minor extent.

$$GeH_4 + [\{Co_2(CO)_7\}_2Ge] \rightarrow [Co_6(CO)_{20}Ge_2] + CO + H_2 \qquad (2)$$

The product of reaction 2 results in much higher yields when Ge_2H_6 was treated with $[Co_2(CO)_8]$, cf. the synthesis [1] of $[\{Co_2(CO)_7\}_2Ge]$, eq. 3. The relative yields of the two products varied with mole ratio, but both always oc-

$$Ge_2H_6 + [Co_2(CO)_8] \rightarrow [\{Co_2(CO)_7\}_2Ge] + [Co_6(CO)_{20}Ge_2] + CO + H_2 \qquad (3)$$

curred. Extraction of a pure sample of $[Co_6(CO)_{20}Ge_2]$ involved much sacrifice of yield. A pure sample was readily prepared in essentially quantitative yield by reaction 4.

$$\begin{aligned} &Me_2Si(GeH_3)_2 + [Co_2(CO)_8] \rightarrow [Co_6(CO)_{20}Ge_2] + \\ &\qquad [Co(CO)_4SiMe_2H] + [(CO)_9Co_3OSiMe_2Co(CO)_4] + CO + H_2 \end{aligned} \qquad (4)$$

$[Co_6(CO)_{20}Ge_2]$ forms orange crystals which are reasonably stable in air.

The principal spectroscopic properties of the new compounds are summarised in Table 1. They are compatible with the structures shown in the Fig. 1,

TABLE 1

CHARACTERISING SPECTROSCOPIC PROPERTIES

(a) Principal features of mass spectrum

$[Co_4(CO)_{13}Ge(GeMe_2)]$:	Main current carriers $(P-nCO)^+$ with intensities w, mw, w, w, w, m, s, s, ms, w, m, ms, s for $n = 0$ to 13 respectively $(P-Me-nCO)^+$ vw to w, except $MeGe_2Co_4^+$ ms. $(P-2Me-nCO)^+$ w, except $Ge_2Co_4^+$ ms $Me_xGe_2Co_3^+$ w, $(x = 0, 1, 2)$
$[Co_6(CO)_{20}Ge_2]$:	Main current carriers $(P-nCO)^+$ with intensities mw, w, vw, m, vw, mw, w, m, m, mw, m, mw, m, m, s, ms, m, m, m, m, ms for $n = 0$ to 20 respectively $(P-Co-nCO)^+$ medium $Co_4Ge_2^+$ s; Co_4Ge^+ s; Co_3Ge^+ w.

(b) Carbonyl stretches in the infrared (cm^{-1})

$[Co_4(CO)_{13}Ge(GeMe_2)]$	$[Co_6(CO)_{20}Ge_2]$	$[\{Co_2(CO)_7\}_2Ge]$ (ref. 1)
2095 m	2087 s	2079 s
2064 vs	2068 vs	2061 vs
2054 s	2053 s	
2043 vs		
	2040 w	2040 mw
	2033 sh	
2025 m	2027 m	2032 m
2019 sh	2021 sh	2023 mw
2015 ms		
	1848 sh	
1843 m	1843 mw	1848 m

which are based on that [1] of $[\{Co_2(CO)_7\}_2Ge]$ and assume similar dihedral angles. $GeMe_2H_2$ reacts with $[\{Co_2(CO)_7\}_2Ge]$ to replace one μ-CO by a μ-$GeMe_2$ unit alternatively regarded as forming a new $GeCo_2$ triangle sharing a Co—Co edge. In reaction 2, we might expect a similar species to form initially, with the Ge—H bonds of the μ-GeH_2 group reacting further. In reactions 3 and 4, a stepwise building process is readily envisaged with the second Ge held in a favourable position in the reaction intermediate.

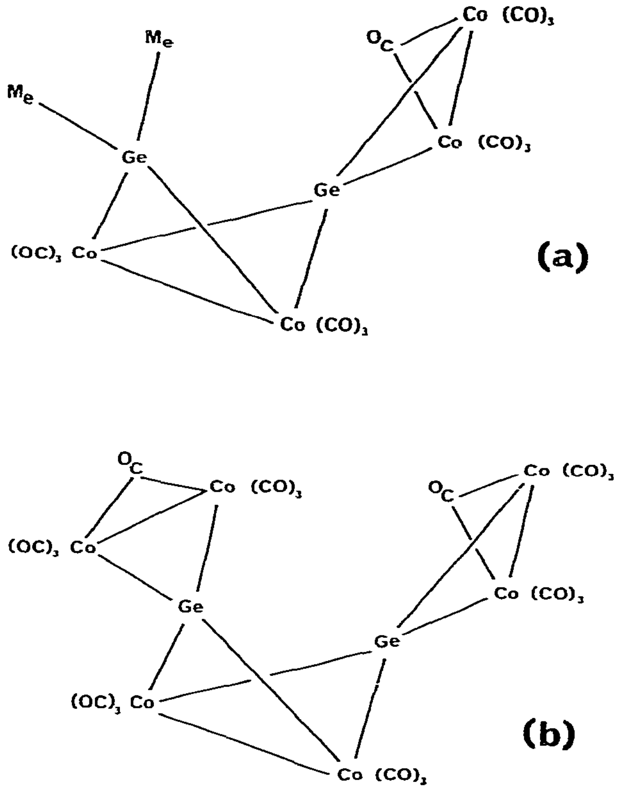

Fig. 1. Structures of (a) [Co$_4$(CO)$_{13}$Ge(GeMe$_2$)] and (b) [(Co$_6$(CO)$_{20}$Ge$_2$].

While it has proved impossible to procure suitable single crystals of [Co$_6$(CO)$_{20}$Ge$_2$], crystallographic studies are proceeding on the dimethyl product. Initial solution confirms the heavy atoms lie in the positions for [{Co$_2$(CO)$_7$}Ge{Co$_2$(CO)$_6$(μ-GeMe$_2$)}] as postulated, though problems with pseudosymmetry in the unit cell have prevented full refinement to date.

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