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TRANSITION METAL CARBONYL DERIVATIVES OF THE GERMANES

XIV *. STUDIES OF MIXED COBALT CARBONYL/MANGANESE CARBONYL SUBSTITUTED GERMANES INCLUDING $[(CO)_5MnGeCo_3(CO)_9]$, μ_3-(PENTACARBONYLMANGANESEGERMYLIDYNE)CYCLOTRIS-(TRICARBONYLCOBALT)(3*Co—Co*)

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Summary

$[Mn(CO)_5GeH_3]$ reacts smoothly with $Co_2(CO)_8$ to form the $[(CO)_5MnGeCo_3(CO)_9]$, which is also produced by the reaction of $Mn(CO)_5^-$ with $[(CO)_4CoGeCo_3(CO)_9]$. $[Mn(CO)_5GeMeH_2]$ similarly reacts with $Co_2(CO)_8$ to give $[\{Mn(CO)_5\}\{Co_2(CO)_7\}GeMe]$. The products were characterised spectroscopically and the ESR spectrum of the radical ion of the title compound is presented.

Introduction

Germanes react under mild conditions with $Co_2(CO)_8$ to yield germanium-polycobalt species in which each Ge—H has been replaced by a Ge—Co bond. Germanium is usually found in a bridging position, where this is possible. Thus GeH_4 [1] yields $[Ge\{Co_2(CO)_7\}_2]$, and $RGeH_3$ give $[\{Co(CO)_4\}\{Co_2(CO)_7\}GeR]$ for R = Ph [2] or Me [3]. The latter compound also results when $Co_2(CO)_8$ reacts with $[Co(CO)_4GeMeH_2]$ [3]. It was of interest to examine whether Ge—H bonded to other metals reacted similarly, providing a route to mixed-metal species. Manganese was chosen as the second metal since alternative syntheses of manganese/cobalt germanes are also possible using the established displacement reaction [3,4] of $Co(CO)_4^-$ by $Mn(CO)_5^-$.

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* For part XIII see ref. 1.

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Results and discussion

Over a range of reaction ratios, $[Mn(CO)_5GeH_3]$ reacts with $Co_2(CO)_8$ to give only one major product, $[Mn(CO)_5GeCo_3(CO)_9]$, together with varying amounts of $Co_4(CO)_{12}$. There were no high molecular weight residues and only traces of possible alternative products. When the ratio of GeH to Co was greater than 1/1, unreacted pentacarbonyl(germyl)manganese was recovered. Incondensables were not measured directly, but in terms of pressure in a fixed volume over the reaction mixture held in liquid N_2. As the vapour pressure of CO varies very rapidly with temperature around —196° C, the measurements are subject to some uncertainty. However, all the observations are compatible with eq. 1 being the principal reaction. Byproducts include a small amount of $HMn(CO)_5$ when the Co ratio is low, and small amounts of two different secondary products, one of which may contain a $GeCo_2(CO)_7$ unit. Thus, even using a marked deficit of $Co_2(CO)_8$, the major reaction proceeds with full replacement of all the GeH bonds and complete condensation to the $GeCo_3$ cluster.

$$[Mn(CO)_5GeH_3] + 1.5\ Co_2(CO)_8 \rightarrow 1.5\ H_2 + 3\ CO + [Mn(CO)_5GeCo_3(CO)_9] \quad (1)$$

With a methylgermyl group on manganese, a very similar substitution is seen with the major reaction as in eq. 2. Again, there is complete substitution of Ge—H and the product contains no $Co(CO)_4$ units. Only minor amounts of other products were observed.

$$[Mn(CO)_5GeMeH_2] + Co_2(CO)_8 \rightarrow H_2 + CO + [Mn(CO)_5Ge(Me)Co_2(CO)_7] \quad (2)$$

Thus the addition of GeH bonds to $Co_2(CO)_8$ occurs when the germanium is also bonded to manganese, and essentially proceeds with complete substitution of all the GeH, eq. 1 and 2. The germanium ends up in a μ_2 or μ_3 configuration as observed in the reactions of the parent germanes. This route therefore serves as an approach to mixed-metal carbonyl derivatives of the germanes.

The reaction of the germanium tetracobalt species $[Ge\{Co_2(CO)_7\}_2]$ [1] with $(PPN)^+\ Mn(CO)_5^-$ provides an alternative synthesis of $[Mn(CO)_5GeCo_3(CO)_9]$ and may be formulated in three steps.

$$[Ge\{Co_2(CO)_7\}_2] \rightarrow [Co(CO)_4GeCo_3(CO)_9] + CO \quad (3a)$$

$$[Co(CO)_4GeCo_3(CO)_9] + Mn(CO)_5^- \rightarrow [Mn(CO)_5GeCo_3(CO)_9] + Co(CO)_4^- \quad (3b)$$

$$Co(CO)_4^- + [Ge\{Co_2(CO)_7\}_2] \rightarrow [GeCo_5(CO)_{16}]^- + 2\ CO \quad (3c)$$

Reactions 3a [1] and 3c [5] have been established separately. Reaction 3b then amounts to substitution of the terminal Ge—$Co(CO)_4$ group by $Mn(CO)_5^-$, a displacement which is well established for simple germanes $RGeH_2Co(CO)_4$ (R = H, alkyl, GeH_3) [3,4]. There was no indication of any tendency to displace a further cobalt from the $GeCo_3$ cluster unit.

The spectroscopic properties of $[Mn(CO)_5GeCo_3(CO)_9]$ are consonant with the formulation, Table 1A. The simplicity of the infrared spectrum can be accounted for by overlapping of bands. Thus the strongest band at 2041 cm^{-1} will include the strong bands expected about 2055 and 2030 cm^{-1} for a $GeCo_3(CO)_9$ moiety [6,7] and that about 2035 cm^{-1} of the $GeMn(CO)_5$ unit [8]. A very similar situation pertains for $[Co(CO)_4GeCo_3(CO)_9]$ which also shows

TABLE 1

INFRARED-ACTIVE CARBONYL STRETCHING MODES (cm^{-1}).

All measurements in hexane solution

A. Species containing the $GeCo_3(CO)_9$ moiety

$[Mn(CO)_5GeCo_3(CO)_9]$	$[Co(CO)_4GeCo_3(CO)_9]$ [6]	$[MeGeCo_3(CO)_9]$ [7]
2115 w	2111 vw	2105 m
2078 m	2082s	2082 s
		2056 s
2041 vs	2044 vs	2046 sh
		2030 s
2022 ms	2027 mw	2025 m

B. Species containing the $MeGeCo_2(CO)_7$ moiety

$[Mn(CO)_5\{Co_2(CO)_7\}GeMe]$	$[Co(CO)_4\{Co_2(CO)_7\}GeMe]$ [17]	$[\{Co_2(CO)_7\}GeMe_2]$ [9]
2109 w	2105 m	
2076 s	2082 s	2087 s
2049 s	2056 s	2048 vs
	2046 sh	
2030 s	2030 s	
2020 vs	2025 m, br	2025 vs
2014 s	2007 w	2008 vs
2002 w	1998 w	1998 sh
		1965 w
	1850 m	
1836 mw	1838 w	1840 m

[6] a very simple four-band carbonyl region in the infrared spectrum. The mass spectrum similarly shows strong resemblances between the $[LGeCo_3(CO)_9]$, L = $Mn(CO)_5$ or $Co(CO)_4$ species. In each case, $[P - n\ CO]^+$ fragments are relatively weak for $n = 0, 3, 4$ and 5 while the metal core, Co_4Ge^+ or Co_3MnGe^+, ions are extremely strong and Co_3Ge^+ is very strong. However, the $GeCo_4$ species differs in showing a few $GeCo_3(CO)^+_n$ ions (n = 3, 2, 1) while no $GeCo_3$ or $GeCo_2Mn$ species retaining CO groups are seen for the manganese derivative.

The spectroscopic properties of $[Mn(CO)_5\{Co_2(CO)_7\}GeMe]$ again compare well with those of the "all-cobalt" analogue [1,7] $[Co(CO)_4Ge(Me)Co_2(CO)_7]$, and related species [8,9], see Table 1B.

Reduction of $[Mn(CO)_5GeCo_3(CO)_9]$ in THF by a sodium mirror was rapid, as evidenced by a colour change from purple to brown. The paramagnetic species formed, assumed to be $[Mn(CO)_5GeCo_3(CO)_9]^{\cdot-}$, displayed a symmetrical 22-line ESR spectrum in solution consistent with hyperfine coupling of the unpaired electron to three equivalent cobalt atoms [$a(^{59}Co) = 33$ G, $I = \frac{7}{2}$]. Coupling to the apical Ge atom, or to the Mn atom attached to the $GeCo_3$ unit, was not observed. The radical anion has a half-life of ca. 2 h at 295 K in THF. The ESR features are therefore very similar to those of related $[RCCo_3(CO)_9]^{\cdot-}$ [10] and the neutral paramagnetic $ECo_3(CO)_9$ (E = S, Se [11]), and it can be concluded, by comparison with these earlier studies, that the unpaired electron in $[Mn(CO)_5GeCo_3(CO)_9]^{\cdot-}$ is in a weakly antibonding orbital localised on the Co_3 triangle, with negligible contribution from the apical Ge atom.

Conclusions

The hydride-elimination reaction of $Co_2(CO)_8$ with Ge—H bonds attached to metal-carbonyl groups proceeds predictably to give Ge—Co bonds. Similar species can be generated by displacement of terminal $Co(CO)_4$ groups attached to Ge by more nucleophilic groups, such as $Mn(CO)_5$, leaving Co groups which are part of cluster units untouched. Both these routes have potential in the rational synthesis of mixed-metal derivatives of germanium.

Experimental

All compounds were handled under vacuum or under dry nitrogen: other experimental methods were as reported in previous parts [1].

$[Mn(CO)_5GeH_3]$ plus $[Co_2(CO)_8]$. The reagents (1.07 mmol + 0.47 mmol) were sealed with hexane (3 ml) and allowed to react for 5 h at room temperature by which time bubbling had ceased and the solution was very dark red. There were recovered incondensable gases, unreacted $[Mn(CO)_5GeH_3]$ (0.58 mmol), $[Mn(CO)_5H]$ (trace) and involatile species. Extraction with hexane (20 ml) followed by CH_2Cl_2 (20 ml) completely dissolved the residue. The infrared spectrum showed a trace of $[Mn(CO)_5GeH_3]$, $Co_4(CO)_{12}$, an unidentified species with a band at 2008 cm^{-1} and the main product in the hexane fraction while the CH_2Cl_2 fraction contained $Co_4(CO)_{12}$ and the main product, in similar quantities.

The experiment was repeated using (0.98 mmol + 0.94 mmol) of the two reagents and yielded incondensable gases, a small amount of unreacted $[Mn(CO)_5GeH_3]$ in the hexane fraction together with main product, a smaller amount of $Co_4(CO)_{12}$, and a trace of a species with a bridging carbonyl frequency at 1842 cm^{-1}.

With a reactant composition of (1.28 mmol + 2.02 mmol), incondensables yielded mostly the main product together with a little $Co_4(CO)_{12}$, and traces of starting material and the 1842 cm^{-1} species.

The ratio of incondensables for the three reaction ratios was 1.0/2.2/4.8. The main product was identified as $[(CO)_5MnGeCo_3(CO)_9]$ (see below).

$[Mn(CO)_5GeMeH_2]$ plus $Co_2(CO)_8$. The reagents were allowed to react similarly in a proportion of 0.93 to 1.0 mmol. There were recovered, incondensable gases (relative proportion 1.2), unreacted $[Mn(CO)_5GeMeH_2]$ (0.25 mmol), $HMn(CO)_5$ (trace), $Co_4(CO)_{12}$, an unidentified species with CO stretches at 2082 and 2006 cm^{-1}, and the major product. This showed a singlet in the ^1H NMR spectrum at τ 8.51. The infrared bands in the carbonyl stretching region at (cm^{-1}) 2076s, 2049s, 2020vs, 2014s, 2002w and 1836mw may reasonably be assigned to a $\{Co_2(CO)_7\}GeMe$ moiety while 2109w and 2030s, together with a contribution to the 2020vs absorption, correspond to vibrations expected for a $(CO)_5MnGe$ unit, see Table 1B. The mass spectrum also supports a formulation as $[\{Co_2(CO)_7\}\{Mn(CO)_5\}GeMe]$ showing the series $(P - n\ CO)^+$ of relative intensities w, m, m, vvw, vw, w, ms, s, ms, m, vs (base peak), ms and s for $n = 0$ to 12 respectively, together with $MnCo_2Ge^+$(s), Co_2Ge^+(w) and $Mn(CO)_5Ge^+$(m).

$[Ge\{Co_2(CO)_7\}_2]$ plus $Mn(CO)_5^-$. No reaction occurred between

$[Ge\{Co_2(CO)_7\}]_2$ (0.5 mmol) and $Mn(CO)_5^-$ (0.5 mmol, as PPN^+ salt) at room temperature in CH_2Cl_2. However, after $2\frac{1}{2}$ h gentle reflux, while the mixture passed through a purple stage and evolved CO, reaction was complete and new infrared carbonyl stretches had appeared including 1887(s, br) cm^{-1} ascribed to $Co(CO)_4^-$. When hexane was added, ionic species (identified as traces of $Co(CO)_4^-$ plus $GeCo_5(CO)_{16}^-$ which forms [5] from the reaction of $Co(CO)_4^-$ on $[Ge\{Co_2(CO)_7\}_2]$) were precipitated leaving $Mn_2(CO)_{10}$ and product in solution. The solvents were evaporated, $Mn_2(CO)_{10}$ was sublimed out at room temperature leaving a deep purple solid which was recrystallised from hexane and identified as $[\{Mn(CO)_5\}GeCo_3(CO)_9]$ (see below).

Characterisation of $[\{Mn(CO)_5\}GeCo_3(CO)_9]$. The main product from the reaction $[Mn(CO)_5GeH_3]$ with $[Co_2(CO)_8]$ had identical spectra to that resulting from $[Ge\{Co_2(CO)_7\}_2]$ plus $Mn(CO)_5^-$. The formulation is based mainly on the mass spectrum which showed all the ions of the $(P - n\ CO)^+$ series with relative intensities 17/47/23/6/3/25/88/100/63/74/63/90/54/56/94 for $n = 0$ to 14 respectively. Also observed $GeCo_3^+$ (73) and $GeCo_2^+$ (6). The sample from (A) also showed ions ascribable to a trace of $Co_4(CO)_{12}$ and a medium-weak fragment at m/e = 296—288 assigned as $Co_2(CO)_6Ge^+$ which may possibly arise from the minor product showing the bridging carbonyl frequency.

The vibrational spectrum is relatively simple, showing only four ^{12}CO modes, Table 1A. However, the latter two have widths of 6 and 10 cm^{-1} respectively at half-maximum and undoubtedly include more than one component.

Reduction of $[Mn(CO)_5GeCo_3(CO)_9]$. A solution of $[Mn(CO)_5GeCo_3(CO)_9]$ in THF was passed over a sodium mirror in an evacuated ampoule with a 4 mm o.d. side tube (cf. ref. 10). The ESR spectrum of the resulting brown solution was recorded on a Varian E104A spectrometer at ambient temperatures.

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