Transition-metal Carbonyl Derivatives of the Germanes. Part 10.[1] Tetracarbonyldigermanylcobalt

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Digermanyl chloride reacts with $Na[Co(CO)_4]$ in diethyl ether to yield $[Co(CO)_4(Ge_2H_5)]$. The compounds Ge_2ClH_5 and $[Co(CO)_4(GeH_3)]$ yield an equilibrium mixture which lies largely to the side $[Co(CO)_4(Ge_2H_5)]$ plus $GeClH_3$. The ^1H n.m.r. vibrational, and mass spectra of the title compound are discussed. The Co–Ge bond is cleaved by $HgCl_2$, no reaction occurs with CCl_4 or $GeCl_4$, and $[Mn(CO)_5]^-$ displaces $[Co(CO)_4]^-$ yielding $[Mn(CO)_5(Ge_2H_5)]$, all these reactions paralleling those of $[Co(CO)_4(GeH_3)]$.

ALTHOUGH the chemistry of digermane has been briefly explored [2,3] its only transition-metal derivative is pentacarbonyldigermanylmanganese,[4] $[Mn(CO)_5(Ge_2H_5)]$. A related compound,[5] $[\{Mn(CO)_5\}_4(Sn_2H_2)]$ is by far the most stable distannane known. A few perorganodigermane [6] and -disilane [7] derivatives such as $[\{Fe(CO)_4(Ge_2Me_4)\}_2]$ and $[Mn(CO)_5(Si_2Me_5)]$ have also been reported, although frequently the reaction of a disilane with a metal carbonyl results in Si–Si cleavage as in the formation [8] of $[\{Me_3SiOs(CO)_3SiMe_2\}_2]$ from Si_2Me_5H.

Of the monogermane derivatives, $[Co(CO)_4(GeH_3)]$ [9] is less stable than the manganese compound [10] $[Mn(CO)_5(GeH_3)]$, and most of the known reactions of the cobalt species involve Ge–Co cleavage. A preliminary attempt to prepare $[Co(CO)_4(Ge_2H_5)]$ indicated low stability [11] in contact with the reaction mixture. We now report the preparation and characterisation of tetracarbonyldigermanylcobalt and a comparison of some of its reactions with those of the germyl species.

EXPERIMENTAL

All the manipulations were carried out using a vacuum line or in a nitrogen atmosphere with dried solvents. Spectroscopic measurements were made as reported [1,9] previously.

Preparation.—Digermanyl chloride, Ge_2ClH_5 (394.3 mg, 2.12 mmol) prepared by the action [12] of $SnCl_4$ on digermane, was condensed into $Na[Co(CO)_4]$, prepared by 1% sodium-

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[1] Part 9, A. Bonny and K. M. Mackay, *J.C.S. Dalton*, 1978, 1569.

[2] K. M. Mackay, P. Robinson, and R. D. George, *Inorg. Chim. Acta*, 1967, **1**, 236.

[3] R. D. George and K. M. Mackay, *J. Chem. Soc.* (*A*), 1969, 2122.

[4] S. R. Stobart, *Chem. Comm.*, 1970, 998.

[5] K. D. Bos, E. J. Bulten, J. G. Noltes, and A. L. Spek, *J. Organometallic Chem.*, 1975, **92**, 33.

[6] K. Triplett and M. D. Curtis, *Inorg. Chem.*, 1975, **14**, 2284.

[7] B. K. Nicholason, J. Simpson, and W. T. Robinson, *J. Organometallic Chem.*, 1973, **47**, 403; W. Malisch, *ibid.*, 1974, **85**, 185.

[8] A. Brookes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3469.

[9] R. D. George, K. M. Mackay, and S. R. Stobart, *J.C.S. Dalton*, 1972, 974.

[10] R. D. George, K. M. Mackay, and S. R. Stobart, *J.C.S. Dalton*, 1972, 1505.

[11] S. R. Stobart, personal communication, 1970.

[12] K. M. Mackay, *Inorganic Synth.*, 1974, **15**, 169.

amalgam reduction of $[Co_2(CO)_8]$ (1.063 g, 3.11 mmol), in dry diethyl ether. The mixture was shaken for 15 min at room temperature and then fractionated to give diethyl ether at −120 °C, trace amounts of Ge_2ClH_5 and $[Co(CO)_4H]$ at −45 °C, and $[Co(CO)_4(Ge_2H_5)]$ (576.4 mg, 1.79 mmol, 84.4% based on the Ge_2ClH_5 added) at −23 °C. The compound was identified as *tetracarbonyldigermanylcobalt*, by the mass of the parent ions in the mass spectrum (*m/e* 315—328: $^{12}C_4{}^1H_5{}^{59}Co^nGe_2{}^{16}O_4$ requires 328 for $n = 76$ to 316 for $n = 70$ with $P - H = 3\%\ P$). Further characterisation is provided by the fragmentation pattern (Table 1), the vibrational spectrum (Table 3), by the chemical reactions reported below, and by the ^1H n.m.r. spectrum. The latter shows an A_3B_2 pattern with $\tau(GeH_3)$ 6.51, $\tau(GeH_2)$ 6.25, and *J* 4.2 Hz.

The compound is a colourless liquid which turns orange-brown then dark brown in daylight with slow evolution of digermane and CO. These changes are very slow in the dark. It is just volatile in the vacuum line with a vapour pressure of *ca.* 0.1 mmHg at 20 °C:* 1—2 mmol may be transferred in 0.5 h at diffusion-pump pressures.

TABLE 1

Mass spectrum of $[Co(CO)_4(Ge_2H_5)]$ [a]

	$[Co(CO)_n(Ge_2H_x)]^+$							$[Co(CO)_n(GeH_x)]^+$						
		x							*x*				Relative intensity	
n	Relative intensity [b]	5	4	3	2	1	0	Relative intensity	3	2	1	0	$[Co(CO)_nH]^+$	$[Co(CO)_n]^+$
4	2.0	10	0	0	0	0	0	25	10	1	0	0	2.5	9.3
3	56	10	1	0	0	0	0	68	10	0	1	1	n.o.	1.7
2	100	4	2	10	0	0	0	90	5	1	10	1	0.8	21
1	70	0	0	0	0	10	3	83	0	0	10	3	0.8	20
0	94	0	0	0	0	10	8	77	1	2	10	8	0.8	10

n.o. = Not observed.

[a] For $[Ge_2H_x]^+$ and $[GeH_x]^+$ see text. For *m/e* 28 the relative intensity was 76 but this peak may include $[N_2]^+$ as well as $[CO]^+$.
[b] Intensities are relative to $[Co(CO)_2(Ge_2H_x)]^+$: for germanium species the intensities are summed over *x*. Intensities for *x* are relative to the strongest component = 10, values being rounded to the nearest unit.

Reactions.—Ge_2ClH_5 *and* $[Co(CO)_4(GeH_3)]$. Digermanyl chloride (22.5 mg, 0.121 mmol) and $[Co(CO)_4(GeH_3)]$ (38.4 mg, 0.155 mmol) were combined in benzene and the reaction followed by ^1H n.m.r. spectroscopy at room temperature. Product signals were detected after 15 min and changes ceased after 7 h when the reaction mixture (from relative intensities by integration) consisted of Ge_2ClH_5 (τ 6.71 and 4.98, 10%), $[Co(CO)_4(GeH_3)]$ (τ 6.27, 31%), $[Co(CO)_4(Ge_2H_5)]$ (τ 6.51 and 6.25, 31%), and $GeClH_3$ (τ 5.38, 29%). The tube was opened and fractionation yielded $[Co(CO)_4(Ge_2H_5)]$ (29.75 mg, 0.092 mmol, 76% of initial Ge_2ClH_5).

$[Co(CO)_4(Ge_2H_5)]$ *and* $HgCl_2$. The compound $[Co(CO)_4(Ge_2H_5)]$ (65.2 mg, 0.203 mmol) was drawn through a tube filled with $HgCl_2$ and the products collected at −196 °C. Fractionation yielded digermane with a trace amount of chlorogermane at −120 °C (1.5 mg, *ca.* 4%), Ge_2ClH_5 {33.0 mg, 0.18 mmol, 91% of initial $[Co(CO)_4(Ge_2H_5)]$} at −45 °C, and unchanged $[Co(CO)_4(Ge_2H_5)]$ (2.6 mg, *ca.* 4%) at −23 °C. A yellow layer, probably $Hg[Co(CO)_4]_2$, was left on the $HgCl_2$.

$[Co(CO)_4(Ge_2H_5)]$ *and* CCl_4 *or* $GeCl_4$. The compound $[Co(CO)_4(Ge_2H_5)]$ (0.14 mmol) and CCl_4 (0.10 mmol) were sealed with benzene in an n.m.r. tube. No change, apart from a slight yellowing, was observed over 7 d in subdued lighting. In a similar experiment with $GeCl_4$ no change was observed.

$[Co(CO)_4(Ge_2H_5)]$ *and* $[Mn(CO)_5]^-$. The compound $[Co(CO)_4(Ge_2H_5)]$ (337.7 mg, 1.049 mmol) was condensed onto a diethyl ether solution (5 cm³) of $Na[Mn(CO)_5]$, prepared using $[Mn_2(CO)_{10}]$ (585.0 mg, 1.5 mmol) and sodium amalgam. The reaction mixture was shaken for 15 min at room temperature and the volatiles removed. The compound $[Mn(CO)_5(Ge_2H_5)]$ (340.7 mg, 0.985 mmol, 93%), identified [4] by i.r. and n.m.r. spectroscopy, was found to be the only volatile product. All the $[Co(CO)_4(Ge_2H_5)]$ was consumed. A slightly yellow solid was left in the reaction vessel. When exposed to air this turned purple, characteristic of the reaction of $Na[Co(CO)_4]$.

RESULTS

Mass Spectrum.—All the mass spectra run were dominated by very strong $[Ge_2H_x]^+$ and $[GeH_x]^+$ envelopes, which varied in intensity relative to the other ions observed and were especially dominant with gas sampling. These ions thus arise mainly from decomposition, probably accelerated by contact with metal surfaces. The intensity pattern of the remaining ion envelopes remained consistent for gas- and liquid-sampled spectra (handled under an inert atmosphere). Thus the main features of the spectrum can be determined, and this is shown in Table 1.

The parent ion is relatively weak but all the other $[Co(CO)_n(Ge_2H_x)]^+$ ions are strong and 40% of the ion current (apart from $[Ge_2H_x]^+$ and $[GeH_x]^+$ arising from fragmentation) is carried by ions retaining $CoGe_2$. Hydrogen loss becomes significant only after two carbonyls are lost. The $[Co(CO)_n(GeH_x)]^+$ family carries most of the remaining ion current and $x = 3$ for the ions retaining most carbonyls, suggesting a GeH_2 elimination. The pattern of CO loss and hydrogen retention is broadly similar to that observed [9] for $[Co(CO)_4(GeH_3)]$. In contrast, hydrogen loss occurs readily [13] from digermane and the other polygermanes.

*Hydrogen-*1 *N.M.R. Spectrum.*—N.m.r. parameters are collected in Table 2. By coincidence, $[Co(CO)_4(Ge_2H_5)]$ and $[Mn(CO)_5(Ge_2H_5)]$ give almost exact mirror-image A_3B_2 spectra at 60 MHz with $\Delta/J = \pm 4.4$. The GeH_2 shifts parallel the chemical shifts of $[Co(CO)_4(GeH_3)]$ and $[Mn(CO)_5(GeH_3)]$.[10] The GeH_3 shifts are relatively unaffected by the change from cobalt to manganese but are significantly to low field of digermane, reflecting the effect of magnetic fields induced in the carbonyl moiety.

Vibrational Spectrum.—The observed absorptions are listed in Table 3 and assigned by comparison with $[Mn(CO)_5(Ge_2H_5)]$,[4] $[Co(CO)_4(GeH_3)]$,[9] Ge_2MeH_5,[3] and Ge_2ClH_5.[2]

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[13] K. M. Mackay and K. J. Sutton, *J. Chem. Soc.* (*A*), 1968, 2312.

Three strong carbonyl modes are seen in the gas and solution spectra in positions close to those found for $[Co(CO)_4(GeH_3)]$ so the spectrum is reflecting the local C_{3v} symmetry rather than the true C_s one. The phase shift is more marked than for $[Co(CO)_4(GeH_3)]$ and the lowest band splits into two strong components in the solid, perhaps corresponding to the a' and a'' equatorial stretches deriving from the C_{3v} e mode. However, the solid-state spectrum shows a much larger number of bands than the gas or solution spectra so the splitting may arise from crystal effects. Two clear bands in the deformation region are assigned as the prominent [2,3] GeH_3 symmetric deformation near 800 cm^{-1} and the strong GeH_2 wag at <700 cm^{-1}. The other deformations are clear in the solid-state spectrum. Since the compound is light sensitive and darkened rapidly in the laser beam only the low-frequency region was observed in the Raman. The polarised Co–C stretch at 415 cm^{-1} matches the very strong mode found [9] at 420 cm^{-1} for $[Co(CO)_4(GeH_3)]$. The metal–metal stretches are both polarised and occur at 269 and 205 cm^{-1}, compared with 268 cm^{-1} for digermane,[14] 228 cm^{-1} for $[Co(CO)_4(GeH_3)]$,[9] and values [4] for $[Mn(CO)_5(Ge_2H_5)]$ of 273 and 205 cm^{-1}. It is interesting that very similar frequencies are observed for both the cobalt and manganese compounds, with the antisymmetric stretch near ν(GeGe) of the polygermanes and the symmetric stretch at 10—15 cm^{-1} below the metal–germanium mode of the germyl compounds.

TABLE 2

Hydrogen-1 n.m.r. parameters of $[Co(CO)_4(Ge_2H_5)]$ and related species in *ca.* 5% benzene solutions

Compound	Chemical shifts (τ)		J/Hz
	GeH_3Ge	$M(GeH_n)$	
$[Co(CO)_4(Ge_2H_5)]$	6.51	6.20	4.2
$[Co(CO)_4(GeH_3)]$ [a]		6.27	
$[Mn(CO)_5(Ge_2H_5)]$ [b]	6.53	6.85	4.4
$[Mn(CO)_5(GeH_3)]$ [c]		6.72	
Ge_2H_6 [d]	6.92		

[a] This value was incorrectly reported in ref. 9. [b] Compare with values [4] in cyclohexane: τ 6.56, 6.91, J not given. [c] Same value as in ref. 10. [d] Compare with τ 6.76 in cyclohexane (E. A. V. Ebsworth, S. G. Frankiss, and A. R. Robiette, *J. Mol. Spectroscopy*, 1964, **12**, 299).

TABLE 3

Vibrational spectrum (cm^{-1}) of $[Co(CO)_4(Ge_2H_5)]$

Gas	Solution in cyclohexane	Solid	Tentative assignment	
2 104ms	2 097s	2 097s 2 089m	ν(CO)	a'
2 085mw	2 077m	2 078m 2 069mw	$\nu(^{13}CO)$	a'
2 074 (sh) 2 072m	2 064m	2 038m 2 032m	ν(GeH)	
		2 020w		
2 044s	2 035s	2 000s	ν(CO)	a'
2 020vs	2 008vvs	1 989vs 1 982vvs	ν(CO)	$a' + a''$
2 007w 1 990vw 1 983w	1 971w	1 970w 1 965vw 1 960w 1 959w 1 953w	$\nu(^{13}CO)$	
		920vvw,br		
876vw,br	872w	877m (sh) 873m 868w	$\delta_{asym}(GeH_3)$	$a' + a''$
864v,br		858m 852m	GeH_2 bend	a'
815vvw		799vvw		
791m	784m	784s 778s	$\delta_{sym}(GeH_3)$	a'
762vw				
749vw				
673m,br	667m	669m 667s 658m 649m	GeH_2 wag, twist (and rock?)	
556ms	551m	560m (sh) 549s	δ[Co(CO)]	a'
500vw,br	528w	512vw 508w 500vw		
478vw,br	474w	487w 475m 459w	GeH_3 rocks	
	Raman of neat liquid			
	415s,p	418w	ν(CoC)	a'
	269s,p		$\nu_{asym}(CoGeGe)$	a'
	205vs,p		$\nu_{sym}(CoGeGe)$	a'

Reactions.—Substitution of the Ge–H bond is not reported for $[Co(CO)_4(GeH_3)]$ while Co–Ge cleavage is characteristic.[9] The cleavage reaction with mercury(II) halides is essentially quantitative for $[Co(CO)_4(SiH_3)]$,[15] $[Co(CO)_4(GeH_3)]$,[9] and $[Co(CO)_4(GeMeH_2)]$ and appears to be a useful analytical reaction for such species. The digermane reacts similarly with a recovery of digermanyl

$$2[Co(CO)_4(Ge_2H_5)] + HgCl_2 \longrightarrow 2Ge_2ClH_5 + Hg[Co(CO)_4]_2 \tag{1}$$

chloride corresponding to 91% of the $[Co(CO)_4(Ge_2H_5)]$ consumed. A small proportion of digermane was found, as expected from the relatively low stability [2] of digermanyl chloride, but there was little indication of Ge–Ge cleavage. The colour was consistent with the formation of $Hg[Co(CO)_4]_2$ but this was not characterised.

In reactions with CCl_4 and $GeCl_4$, germylmanganese compounds give [10] extensive Ge–H substitution, but no reaction was observed for $[Co(CO)_4(Ge_2H_5)]$.

The metal-carbonyl exchange reaction (2) follows the

$$[Co(CO)_4(Ge_2H_5)] + [Mn(CO)_5]^- \longrightarrow [Mn(CO)_5(Ge_2H_5)] + [Co(CO)_4]^- \tag{2}$$

same course as that established [16] for the GeH_3 analogues. The digermanyl group is exchanged with no evidence of Ge–Ge cleavage and with a somewhat higher recovery of the manganese compound.

A 5 : 4 mixture of $[Co(CO)_4(GeH_3)]$ and Ge_2ClH_5 comes to

$$[Co(CO)_4(GeH_3)] + Ge_2ClH_5 \rightleftharpoons [Co(CO)_4(Ge_2H_5)] + GeClH_3 \tag{3}$$

equilibrium (3) after a few hours with the balance lying well in favour of the digermanylcobalt species.

DISCUSSION

The spectroscopic measurements and the chemical reactions, particularly (1), establish the existence of $[Co(CO)_4(Ge_2H_5)]$.

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[14] J. E. Griffiths and G. E. Walrafen, *J. Chem. Phys.*, 1964, **40**, 321.

[15] B. J. Aylett and J. M. Campbell, *J. Chem. Soc. (A)*, 1969, 1910.

[16] R. F. Gerlach, B. W. L. Graham, and K. M. Mackay, *J. Organometallic Chem.*, 1976, **118**, C23.

While most reported reactions of Ge_2H_6 involve Ge–Ge cleavage, and the halides Ge_2XH_5 all decompose at room temperature, the metal carbonyl derivatives of digermane are more resistant to decomposition or Ge–Ge cleavage. The compound $[Co(CO)_4(Ge_2H_5)]$ is more stable thermally than $[Co(CO)_4(GeH_3)]$, but both species darken when exposed to light. While the properties and reactions of $[Co(CO)_4(GeH_3)]$ and $[Co(CO)_4(Ge_2H_5)]$ are similar, the digermanyl system is favoured overall.

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