# Reaction of Octacarbonyldicobalt with Organo-silanes, -germanes, and -stannanes: Formation, Properties, and Vibrational Spectra of Trimethylgermyltetracarbonylcobalt and Related Complexes

By **Geraldine F. Bradley** and **Stephen R. Stobart,*** Department of Chemistry, Queen's University, Belfast BT9 5AG

The hydrides $R_3MH$ (R = Me, M = Si, Ge, or Sn; R = Et, M = Ge) react exothermically with $Co_2(CO)_8$ at 20 °C affording in high yield the complexes $R_3MCo(CO)_4$ [R = Me, M = Si (I); M = Ge (II); M = Sn (III); and R = Et, M = Ge (IV)]. Conversion of (I) to (II) or (III) and of (II) to (III) occurs on reaction with $Me_3MH$ (M = Ge or Sn), and (II) can also be prepared from (I) with $Me_3GeBr$. The Ge–Co bond in (II) is cleaved by HCl or $HgCl_2$; (II) with $Et_3N$ or piperidine forms tetracarbonylcobaltate adducts. The vibrational spectra of (II)—(IV) are reported, with ν(M–Co) assigned to polarised Raman shifts respectively at 192, 177, and 188 $cm^{-1}$. Variation with M of the vapour-phase i.r.-intensity of one of the two $a_1$ CO stretching fundamentals expected for $C_{3v}$ symmetry points to a significant out-of-plane displacement of equatorial carbonyl groups in the direction of the silicon atom in (I), but with no analogous effect in (II) or (III). Deviations from $C_{3v}$ selection rules observed in the solid state for (II) and (III) are also discussed.

CATALYTIC activity of octacarbonyldicobalt in reactions involving organosilicon hydrides has recently been established,[1,2] and has led to continuing interest in the chemistry of complexes with silicon–cobalt bonds.[3] Formation of the latter directly from $Co_2(CO)_8$ was investigated by Chalk and Harrod in their study of silane addition to 1-olefins, and identification of hydridotetracarbonylcobalt as an initial product prompted them to suggest[4] that the observed reaction (1) could be represented as a combination of (2) and (3), involving $HCo(CO)_4$ as intermediate. This has been confirmed by subsequent work, and it has also been established that formation of the hydridocarbonyl is crucial to the catalysis by cobalt carbonyl of hydrosilation and related silylation reactions.[2,5] Baay and MacDiarmid have examined reaction (1) in more detail for R = Me, and have discovered[5] that while the reaction is rapid in the liquid phase, (3) does not occur between $Me_3SiH$ and $HCo(CO)_4$ in the gas phase. Analogously, while hydrosilation of ethylene by $Me_3SiH$ is catalysed in the liquid phase by $HCo(CO)_4$ to give the expected product ethyltrimethylsilane, different products including $Me_3SiCo(CO)_4$ are formed from these reactants in the gaseous state.

$$2R_3SiH + Co_2(CO)_8 \longrightarrow 2R_3SiCo(CO)_4 + H_2 \qquad (1)$$

$$R_3SiH + Co_2(CO)_8 \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4 \qquad (2)$$

$$R_3SiH + HCo(CO)_4 \longrightarrow R_3SiCo(CO)_4 + H_2 \qquad (3)$$

Reaction (1) has thus found considerable application as a synthetic approach to a variety of tetracarbonylcobalt–silanes,[4-6] but by contrast although corresponding germanium and tin species are known their isolation from reactions related to (1) has received scant attention.[3] Exploration of such a route to complexes with bonds from cobalt to these two heavier Group IV elements is described in this paper, and has afforded the hitherto unreported trimethylgermyltetracarbonylcobalt. A full comparison of the latter with the known silicon[5] and tin[7] analogues has therefore become possible, particularly in relation to spectroscopic properties as a reflection of structural and bonding characteristics. Interconversion of the three compounds by exchange reactions at the M–Co bond (M = Si, Ge, or Sn) has also been investigated, together with some other aspects of the chemistry of the germane.

Trimethyl- and triethyl-germane and trimethylstannane react with resublimed octacarbonyldicobalt in the liquid phase in a manner apparently identical to trimethylsilane, to give metal–cobalt complexes according to equation (4). Properties of the products of these reactions are collected in Table 1. Reaction was

$$2R_3MH + Co_2(CO)_8 \longrightarrow 2R_3MCo(CO)_4 + H_2 \qquad (4)$$

---

[1] J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 1965, **87**, 1133.

[2] A. J. Chalk, *Chem. Comm.*, 1970, 847.

[3] F. Glockling and S. R. Stobart, *M.T.P. Internat. Rev. Sci., Inorg. Chem. Ser.* 1, 1972, **6**, 63.

[4] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1967, **89**, 1640.

[5] Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, 1969, **8**, 986.

[6] A. J. Chalk, *J. Organometallic Chem.*, 1970, **21**, 207; L. H. Sommer and J. E. Lyons, *J. Amer. Chem. Soc.*, 1968, **90**, 4197.

[7] S. Breitschaft and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 2702.

judged to be somewhat slower for M = Ge or Sn, but yields of $R_3MCo(CO)_4$ [R = Me, M = Si (I); M = Ge (II); M = Sn (III). R = Et, M = Ge (IV)] did not appear to vary significantly (Table 1). An excess of organometallic hydride was used throughout, with the result that $HCo(CO)_4$ was not observed, but its involvement in reaction (4) in a general sense [*cf.* reactions (2) and (3)] seems likely, a view supported [2] by its appearance in a number of cleavage reactions of compound (II).

Table 1

Physical and $^1H$ n.m.r. data

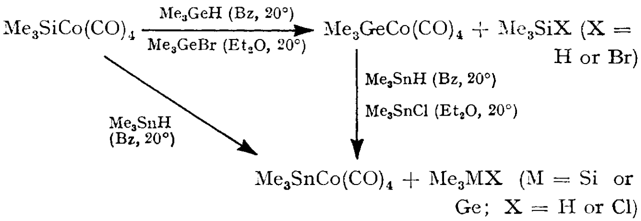
| | Appearance | M.p. ($t$/°C) | $M$ [a] | $\tau CH_3$ | Yield (%) [b] |
|---|---|---|---|---|---|
| (I) $Me_3SiCo(CO)_4$ | White solid | 52—53 dec. | 244 | 9·73 [c] | 90 |
| (II) $Me_3GeCo(CO)_4$ | Very pale yellow solid | 57—58 | 290 | 9·56 [c] | 79 |
| (III) $Me_3SnCo(CO)_4$ | Ivory needles | 67—68 [d] | 336 | 9·37 [e] | 60 |
| (IV) $Et_3GeCo(CO)_4$ | Pale yellow liquid | < −25 | 332 | 8·77 [f] | 94 |

[a] Molecular weight found (mass spectrum). [b] This work, from $R_3MH + Co_2(CO)_8$. [c] Cyclohexane soln.; in benzene = 9·41 for $Me_3GeCo(CO)_4$. [d] 74·5 °C, ref. 7. [e] Ref. 19. [f] $CDCl_3$ soln.

Exothermic formation of cobalt-substituted germanes and stannanes at 20 °C contrasts strikingly with the low reactivity of $Me_3MH$ (M = Ge or Sn) towards binuclear carbonyls of manganese or rhenium,[8] with which silanes do react [9] although usually only at elevated temperatures. Correspondingly, in a preliminary experiment only 6% of a tin–molybdenum complex was isolated from reaction (5). These observations emphasise the recognised high reactivity of the Co–Co bond in $Co_2(CO)_8$,

$$2Me_3SnH + [(\pi\text{-}C_5H_5)(CO)_3Mo]_2 \longrightarrow 2Me_3SnMo(\pi\text{-}C_5H_5)(CO)_3 + H_2 \qquad (5)$$

and analogously the M–Co bond (M = Si, Ge, or Sn) in compounds (I)—(III) very readily undergoes metal exchange in a similar way to that demonstrated for certain related intermetallic complexes.[3] Thus compound (I) reacts completely with $Me_3MH$ (M = Ge or Sn) to give respectively (II) or (III) and trimethylsilane, these and associated reactions (Scheme) following the established pattern of attachment of the transition-metal atom to the heavier Group IVB element. The reaction of compound (I) with dimethylchloroarsine to give a polymeric compound with As–Co bonds has been reported elsewhere,[5] so that exchange might also be expected to occur with halogeno–Group IVB derivatives. Accordingly, the germyl complex (II) was obtained in good yield on treatment of (I) with $Me_3GeBr$, while no reaction occurred between (II) and $Me_3SiCl$ under identical conditions (see Scheme). Similarly facile replacement reactions take place between Group IVB–iridium complexes and Group IVB organometallic hydrides; [10] more vigorous conditions are required to exchange ruthenium derivatives [11] and pentacarbonylmanganese species are virtually unreactive in this sense.[8] A contribution to ease of substitution by a molecular mechanism of the lower co-ordination number of the transition metal atom in the cobalt and iridium compounds is suggested, and additional evidence for this is found in recent observations concerning reactivity of alkyl–transition metal species. Thus while reaction of $Me_3SnH$ with $(Ph_2PCH_2PPh_2)PtMe_2$ is rapid [12] at 20 °C to give $(Ph_2PCH_2PPh_2)Pt(H)(SnMe_3)_3$, 93% recovery of $MeW(CO)_3(\pi\text{-}C_5H_5)$ was made [13] from $Me_3SnH$ after 6 days at 50 °C.



Scheme

Compounds (I)—(III) are physically very similar to one another and may readily be handled by trap-to-trap vacuum manipulations. Unlike its monogermyl relative $GeH_3Co(CO)_4$, the trimethylgermyl complex (II) does not darken noticeably on exposure to daylight, but, like the former [14] and compounds (I) and (III) in air, rapid decomposition occurs probably to $Co_2(CO)_8$. No evidence for thermal instability of (II) at 20 °C was forthcoming either during handling or from mass spectroscopy, in contrast to (I) which [5,15] slowly releases $(Me_3Si)_2O$, but above 80 °C in glass sample tubes rapid deposition of a black mirror was apparent.

Quantitative cleavage of the metal–metal bond in (II) resulted from treatment either with HCl or $HgCl_2$, to give $HCo(CO)_4$ and $Hg[Co(CO)_4]_2$ respectively as cobalt-containing products. Recovery of 50% of (II) from methanol solution after 26 h without evidence for the formation of $Me_3GeOMe$ (although the latter is known) contrasts with rapid and complete methanolysis [5] of (I) according to reaction (6), and may be compared with a similarly much increased resistance to protolysis of $Me_3SnMn(CO)_5$ over the corresponding silane.[8] In common with (I) and with $MH_3Co(CO)_4$ (M = Si [16] or

---

[8] R. A. Burnham, F. Glockling, and S. R. Stobart, *J.C.S. Dalton*, 1972, 1991; R. A. Burnham and S. R. Stobart, unpublished observations.

[9] B. K. Nicholson and J. Simpson, *J. Organometallic Chem.*, 1971, **32**, C29; A. D. Berry and A. G. MacDiarmid, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 601.

[10] F. Glockling and J. G. Irwin, *Inorg. Chim. Acta*, 1972, **6**, 355.

[11] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559.

[12] F. Glockling and R. J. I. Pollock, unpublished work.

[13] R. A. Burnham, C. M. Regan, and S. R. Stobart, unpublished results.

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

[15] F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 1970, **92**, 2324.

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

Ge[14]), compound (II) reacted immediately with triethylamine to give a carbonyl complex with $\nu$(CO) lowered in wavenumber to 1890 cm$^{-1}$ and therefore identifiable as a germylammonium salt [*cf.* $Na^+Co(CO)_4^-$, $\nu$(CO) 1883 cm$^{-1}$]. With piperidine the adduct formed was, curiously, a liquid, which also showed $\nu$(CO) 1890 cm$^{-1}$ and which with dry HCl rapidly formed $HCo(CO)_4$ but not $Me_3GeCl$, the germanium remaining as an uncharacterised involatile solid with a complex i.r. spectrum. Like the adducts formed by $MH_3Co(CO)_4$ (M = Si or Ge), these germanium-containing carbonylcobalt species were more ill defined stoicheiometrically than the silylammonium tetracarbonylcobaltates investigated by Bald and MacDiarmid.[17]

$$Me_3SiCo(CO)_4 + MeOH \longrightarrow Me_3SiOMe + HCo(CO)_4 \quad (6)$$

Examination of compounds (I)—(III) using $^1H$ n.m.r. spectroscopy revealed a minor downfield trend in $\tau CH_3$, as expected from electronegativity considerations (Table 1). For the potentially more interesting triethylgermyl complex (IV), at 60 MHz the methyl and methylene resonances overlapped to give a complicated signal dominated by an asymmetric triplet [apparent $J$ 3·5 Hz, centred 0·8 p.p.m. to low field of $CH_3$ in compound (II)].

Mass spectroscopy was used to confirm the identity and monomeric character of (I)—(III) and of $Et_3GeCo(CO)_4$ (Table 1). Fragmentation patterns for all four compounds were similar with ion abundances comparable with those tabulated elsewhere[15] for (I). A marked increase in abundance of ions resulting from methyl loss was evident in the order M = Sn > Ge > Si, similar to the situation found for related pentacarbonylmanganese complexes,[18] but otherwise little change with M was noted.

*Vibrational Spectra.*—I.r. and Raman data for compounds (II)—(IV) are listed, together with approximate descriptions of bands attributable to fundamentals in Supplementary Publication No. 20854 (3 pp.).* Wavenumbers for certain i.r. bands in the spectrum of the trimethyltin complex (III) have been measured previously, but these are dispersed among several sources;[7,19-21] likewise, partial i.r. (but not Raman) frequencies for (IV) have been recorded and assigned elsewhere.[22] By contrast, related silanes have received very much more attention:[5,16,22,23-25] for (I), vapour and solid phase i.r. and solid-state Raman spectra have been discussed[25] on the basis of $C_{3v}$ molecular symmetry, and augment the present data for the series of compounds (I)—(III). The $C_{3v}$ model for interpretation of the vibrational spectra of the silyl cobalt carbonyl derivatives is supported by $X$-ray[26,27] and electron diffraction[28] structure determinations, and has therefore been used in arriving at the proposed assignments.

Metal–metal stretching vibrations ($a_1$) are observed for (II)—(IV) as polarised Raman shifts at 175—195 cm$^{-1}$, having much enhanced intensities over $\nu$(Si–Co) in (I);[25] a similar situation was found for related pentacarbonylmanganese complexes.[18] Calculation of approximate metal–metal stretching force constants, the character and limitations of which have been described in previous papers,[18,29] affords the data of Table 2.

TABLE 2

Metal–metal stretching frequencies/cm$^{-1}$ and force-constants/mdyn Å$^{-1}$

| Compound | $\nu_{obs}$(M–M) | $F_{M-M}$(DA) [a] | $F_{M-M}$(PDA) [a] |
|---|---|---|---|
| $Me_3SiCo(CO)_4$ | 292 [b] | 0·95 | 2·57 |
| $Me_3GeCo(CO)_4$ | 192 | 0·71 | 1·51 |
| $Et_3GeCo(CO)_4$ | 188 | 0·69 | 1·71 |
| $Me_3SnCo(CO)_4$ | 177 | 0·73 | 1·54 |

[a] See refs. 18 and 29. [b] Ref. 25.

The small wavenumber variation for $\nu$(Ge–Co) between (II) and (IV) is also reflected in the $F_{M-M}$(DA) values, suggesting that this vibration is relatively free from interaction with other $a_1$ fundamentals, of which those involving bond stretching are in any case considerably higher in energy. This in turn indicates that in compound (III), $\nu$(Sn–Co) should be a comparatively unmixed vibration. The same conclusion has been reached for $\nu$(Sn–Co) in $Cl_3SnCo(CO)_4$ through detailed normal co-ordinate calculations,[24] but the metal–metal stretching frequency is here 204 cm$^{-1}$, 27 cm$^{-1}$ (or 15%) higher that that for (III). It therefore seems at least possible that this increase reflects an increase in tin–cobalt bond strength as a result of the well attested strong $\pi$-acceptor character of the $Cl_3Sn$ grouping.[30] It can also be noted that the Raman spectrum of (III) confirms the earlier tentative assignment[20] of a rather poorly resolved far-i.r. absorption to $\nu$(Sn–Co).

The possible sensitivity of carbonyl stretching fre-

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full-size copies.

[17] J. F. Bald and A. G. MacDiarmid, *J. Organometallic Chem.*, 1970, **22**, C22.

[18] R. A. Burnham and S. R. Stobart, *J.C.S. Dalton*, 1973, 1269.

[19] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1967, **6**, 981.

[20] N. A. D. Carey and H. C. Clark, *Inorg. Chem.*, 1968, **7**, 94.

[21] A. D. Beveridge and H. C. Clark, *J. Organometallic Chem.*, 1968, **11**, 601.

[22] O. Kahn and M. Bigorgne, *J. Organometallic Chem.*, 1967, **10**, 137.

[23] A. P. Hagan and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 687.

[24] K. L. Watters, J. N. Brittain, and W. M. Risen, *Inorg. Chem.*, 1969, **8**, 1347.

[25] J. R. Durig, S. J. Meischen, S. E. Hannum, R. R. Hitch, S. K. Gondal, and C. T. Sears, *Appl. Spectroscopy*, 1971, **25**, 182.

[26] K. Emerson, P. R. Ireland, and W. T. Robinson, *Inorg. Chem.*, 1970, **9**, 436.

[27] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 1208.

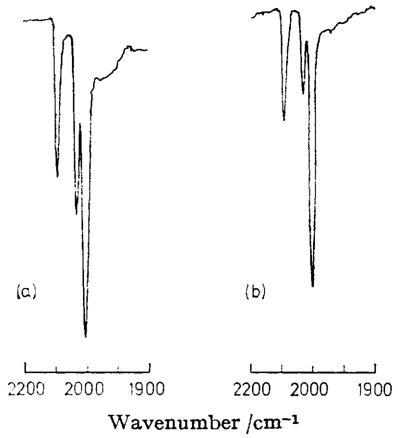
[28] A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. M. Campbell, *J. Organometallic Chem.*, 1968, **14**, 279.

[29] K. M. Mackay and S. R. Stobart, *J.C.S. Dalton*, 1973, 214.

[30] G. W. Parshall, *J. Amer. Chem. Soc.*, 1966, **88**, 704; V. I. Baranowskii, V. P. Sergeev, and B. E. Dzevitskii, *Doklady Akad. Nauk S.S.S.R.*, 1969, **184**, 632; D. D. Spencer, J. L. Kirsch, and T. L. Brown, *Inorg. Chem.*, 1970, **9**, 235; J. D. Graybeal, S. D. Ing, and M. W. Hsu, *ibid.*, p. 678.

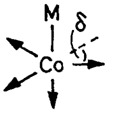
quencies (and derived parameters) to changes in the characteristics of transition-metal to substituent bonding is a subject which has been well ventilated, especially recently in relation to metal–metal bonded carbonyl derivatives.[31] Stone and co-workers have found[32] that simplified CO stretching force constants for complexes $R_3MCo(CO)_4$ (M = Si, Ge, Sn, or Pb) show a linear dependence on the Taft polarity constants ($\sigma^*$) for the substituent R on M, and similar relationships have been identified[22] by Kahn and Bigorgne; the CO stretching frequency data for (I)—(IV) can be shown to support these earlier inferences and require no further comment.

Assignment of observed i.r. bands attributable to the $2a_1 + e$ fundamentals predicted for carbonyl stretching in $R_3MCo(CO)_4$ complexes assuming $C_{3v}$ symmetry has been carried out using the method of oscillating dipoles, developed for systems of this type by Orgel[33] and by El-Sayed and Kaesz,[34] and subsequently adopted by others.[19,23,35] The relative intensities of the $a_1^{(2)}$ (equatorial), $a_1^{(1)}$ (axial), and $e$ modes have also been rationalised on this basis, resonance interaction between the two $a_1$ vibrations resulting in a non-zero intensity in the i.r. for that at higher energy (equatorial).[19,23] More recently, structural studies of tetracarbonylcobalt–silanes have revealed significant displacement of equatorial carbonyl groups towards the silyl substituent.[36] This has been interpreted in terms of a bonding interaction between the silicon and $C_{eq}$ atoms, with which orbital overlap calculations and electron impact fragmentation data are also consistent. In the light of the present investigation and certain earlier observations,[14,16,19,23] it now seems possible to unite these structural conclusions with i.r. intensity considerations.

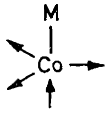


Vapour-phase i.r. spectra for (a) $Me_3GeCo(CO)_4$, (b) $Me_3SnCo(CO)_4$ (note scale change at 2000 cm$^{-1}$)

A conspicuous feature of the vapour-phase i.r. spectra of (I)—(III) is the variation in intensity of the band attributable to the $a_1^{(1)}$ carbonyl stretching mode. This is shown in the Figure, and by comparison of the latter with Figure 2 of ref. 25, where the corresponding contour for compound (I) is reproduced. Earlier discussion of band intensities for related molecules has assumed[19] coupling of the two predicted $a_1$ vibrations to give combinations which can be represented by



(A)



(B)

where (A) is the $a_1^{(2)}$ (equatorial) and (B) the $a_1^{(1)}$ (axial) mode. Both of these will be i.r.-active, and the expression derived by Bor[37] relating their intensities for a general $XCo(CO)_4$ system can be applied. This is

$$\left(\frac{I_A}{I_B}\right)^{\frac{1}{2}}_{a_1} = \frac{\sqrt{1-\cos\beta} - \sqrt{3(1+\cos\beta)}\,.\,\sin\delta}{\sqrt{1+\cos\beta} + \sqrt{3(1-\cos\beta)}\,.\,\sin\delta} \qquad (7)$$

where cos β is a variable relating the symmetrised $F$-matrix elements generated in a limited force-constant treatment of the carbonyl stretching vibrations, and δ is the displacement angle shown in (A). Calculation of the Cotton–Kraihanzel type force constants $f_{eq}$, $f_{ax}$, $f_{11}$, and $f_{12}$ defined by Bor leads, by graphical examination of their inter-relationship, to $0\cdot3 \leqslant \cos\beta \leqslant 0\cdot5$ as reasonable limits for (I)—(III), whence substitution with observed intensity ratios into (7) affords values for δ as presented in Table 3. These data suggest that while in (I) there is a significant tilt (7½ ± 2°) of the three equatorial carbonyl groups towards the silicon atom, by contrast for (II) and (III) the M–Co–$C_{eq}$ angles are quite similar and represent a small displacement in the opposite sense. The calculated bond angle of 82½° for the silyl complex is consistent with those of 85½°

TABLE 3

I.r. intensity ratios for $a_1$ carbonyl stretching modes and derived displacement angles δ

| | $(I_A/I_B)^{\frac{1}{2}}$ [a] | δ | | | Calc. M–Co–$C_{eq}$ angle [b] |
|---|---|---|---|---|---|
| cos β | | 0·3 | 0·4 | 0·5 | |
| (I) $Me_3SiCo(CO)_4$ [c] | 0·35 | +9° 25′ | +7° 38′ | +5° 37′ | 82½ |
| (II) $Me_3GeCo(CO)_4$ | 0·90 | −3° 6′ | −4° 48′ | −6° 25′ | 94½ |
| (III) $Me_3SnCo(CO)_4$ | 1·10 | −6° 40′ | −8° 20′ | −10° 15′ | 98½ |

[a] Values estimated to *ca.* ±0·07 from integrated band-intensities $I_A$, $I_B$ in vapour-phase spectra. [b] Degrees, ±2. [c] Force constants used to define cos β calculated from ν(CO) frequencies of ref. 23.

---

[31] J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2744 and references therein; F. T. Delbeke, E. G. Claeys, G. P. Van der Kelen, and R. M. de Caluwe, *J. Organometallic Chem.*, 1970, **23**, 497.

[32] J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1199.

[33] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

[34] M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectroscopy*, 1962, **9**, 310.

[35] A. R. Manning and J. R. Miller, *J. Chem. Soc.* (*A*), 1966, 1521.

[36] A. D. Berry, E. R. Corey, A. P. Hagan, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, 1970, **92**, 1940.

[37] G. Bor, *Inorg. Chim. Acta*, 1967, **1**, 81.

determined by *X*-ray crystallography for the related species $X_3SiCo(CO)_4$ ($X = F$ [26] or Cl [27]); unfortunately we have been unable to find any similar structural data for tetracarbonylcobalt-germanes or -stannanes in the literature, so that further comparisons are not possible. It should also be emphasised that the values of Table 3 are calculated from i.r. data measured in the vapour phase, where molecular distortion due to crystal packing and other intermolecular effects should be minimal; a gas-phase structural determination by electron diffraction revealed [28] a $Si-Co-C_{eq}$ angle reduced to $81\frac{1}{2}$° for $H_3SiCo(CO)_4$.

It may be tentatively concluded that the $M-Co-C_{eq}$ bond angles calculated from relative i.r. band intensities (Table 3) provide support for the idea [36] of a bonding interaction between the silicon and equatorial carbon atoms in $Me_3SiCo(CO)_4$, but indicate that similar effects in the corresponding germane and stannane are negligible. Orbital overlap calculations indicate [36] that the most significant contribution to $Si-C_{eq}$ interaction involves carbon $2p_z$ and silicon $3s$ and $3p_z$ orbitals. Lower $M-C_{eq}$ overlap energies due to less effective participation of $4(s,p_z)$ and $5(s,p_z)$ orbitals for M = Ge and Sn could account for the calculated structural changes, and indeed ineffective competition with a weak $C_{eq}-C_{ax}$ bonding interaction, which was also suggested [36] from overlap population analysis, could lead to $\delta$ negative, as predicted in Table 3 for M = Sn. Since involvement of silicon $3d$ orbitals appeared to supplement the $Si-C_{eq}$ bonding by only 20% or so, relative ($p$–$d$) overlap for Si, Ge, and Sn (a contentious subject in any argument [38]) should not be an important factor.

Further indirect evidence for $Si-C_{eq}$ bonding has been adduced [36] from fragmentation patterns of $RCo(CO)_4$ complexes. While similar examination of ion abundances does lead to higher $Co(CO)_n^+/Me_3MCo(CO)_{n-1}^+$ ratios for (II) and (III) than for (I), particularly when $n = 4$ or 3, the differences are not especially convincing. However, the intensity change for the $a_1^{(1)}$ CO stretch in the i.r., with its possible structural implications, does seem to be general and is noticeable for example between $H_3SiCo(CO)_4$ [16] ($Si-Co-C_{eq}$ angle = 81°) and $D_3GeCo(CO)_4$ [14,39] [for the hydridic analogue of the latter the $\nu$(GeH) and $\nu$(CO) bands are not completely resolved].

Splitting of degenerate fundamentals by static field effects was observed [25] for (I), consistent with site symmetry $C_1$ and suggesting [24,25] a structure identical with that of $Cl_3SiCo(CO)_4$. Clear splitting of the $e$ carbonyl stretching mode into components at 1984, 1979 $cm^{-1}$ was similarly observed in the Raman spectrum of a solid sample of (II), and under the same conditions a low-frequency shoulder was resolved on the corresponding shift for (III). Durig *et al.* have reported [25] that immediate decomposition of a solution of (I) in cyclohexane resulted on laser illumination at 632·8 nm. While similar difficulties were encountered here with (II) and (III), the liquid triethylgermyl complex (IV) was more amenable to Raman investigation, even at 488·0 nm, and reproducible polarisation data could be measured. Shifts due to the carbonyl stretching vibrations of highest (2094 $cm^{-1}$) and lowest energy (1987 $cm^{-1}$) were found to have depolarisation ratios $\rho$ of *ca.* 0·05 and *ca.* 0·8 respectively, confirming their assignment as $a_1$ and $e$ modes assuming $C_{3v}$ symmetry: unexpectedly, however, the remaining band at 2033 $cm^{-1}$ had $\rho$ *ca.* 0·8, conflicting with its assignment as the $a_1^{(1)}$ vibration. Lowering of symmetry through non-threefold orientation of the ethyl groups (or less likely by adoption of the $C_{2v}$ axially substituted configuration) [19,23] should leave this as a totally symmetric mode, with $\rho$ *ca.* 0. This suggests that an alternative explanation of the observed $\rho$ value is required, and it seems possible that while the two $a_1$ modes interact to give (A) and (B), the latter also gains intensity from the $e$ mode by some other (*e.g.* rotation–vibration) interaction, resulting in a depolarised Raman shift, a conclusion in exact agreement with the predictions of El-Sayed and Kaesz.[34] Such an interpretation is also consistent with the further observation that, while the spectra obtained were not very satisfactory, the corresponding Raman bands at 2022 and 2016 $cm^{-1}$ respectively for (II) and (III) appeared not to be conspicuously polarised in cyclohexane solution.

## EXPERIMENTAL

Standard vacuum-line techniques were used for the manipulation of volatile materials, reactions being carried out in evacuated break-seal tubes or similar demountable vessels. I.r. spectra were measured using Perkin-Elmer 457 and Grubb–Parsons Spectromajor instruments, Raman spectra from 488·0 nm (Ar ion laser) with a Cary 83 spectrometer, and $^1H$ n.m.r. and mass spectra respectively with Varian A60-D and A.E.I. MS 902 spectrometers. Octacarbonyldicobalt was resublimed immediately before use. Trimethyl-silane, -germane, and -stannane were synthesised by $LiAlH_4$ reduction of the halogeno-derivatives, and triethylgermane was prepared similarly from a commercial sample of $Et_3GeCl$. Other reagents were purified by standard procedures.

*Reaction of Octacarbonyldicobalt.—With trimethylsilane.* $Me_3SiH$ (0·275 g, 3·71 mmol) was condensed onto $Co_2(CO)_8$ (0·391 g, 1·15 mmol) in a 10·0 ml reaction tube fitted with a greaseless tap. On warming to room temperature reaction was accompanied by bubbling in the liquid phase and evolution of heat, as described by Baay and MacDiarmid; removal of hydrogen at −196 °C followed by fractionation of volatiles yielded *trimethylsilyltetracarbonylcobalt* (0·503 g, 2·06 mmol) as a white solid in a trap at −45 °C, identified by its gas-phase i.r. spectrum.

*With trimethylgermane.* Reaction of $Me_3GeH$ (0·456 g, 3·85 mmol) with $Co_2(CO)_8$ (0·502 g, 1·47 mmol) under conditions identical to those described above appeared to be much slower to start. Evolution of non-condensible material ceased after *ca.* 1·5 h at 20 °C, when fractionation afforded unreacted $Me_3GeH$ (0·106 g, 0·90 mmol) condensed at −196 °C and *trimethylgermyltetracarbonylcobalt* (0·672 g,

---

[38] E. A. V. Ebsworth in 'Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, vol. 1, part 1, ch. 1 and references therein.

[39] R. D. George, Ph.D. Thesis, University of Nottingham, 1969.

2·32 mmol) at $-45$ °C, as an almost colourless crystalline solid (Found: C, 28·6; H, 2·95. Calc. for $C_7H_9CoGeO_4$: C, 29·15; H, 3·15%).

*With triethylgermane.* A similar exothermic reaction between $Et_3GeH$ (0·431 g, 2·68 mmol) and $Co_2(CO)_8$ (0·440 g, 1·29 mmol) followed by prolonged pumping through a trap maintained at 0 °C (Hg diff. pump vacuum) condensed out a very pale yellow liquid. After recovery from the trap under an atmosphere of dry nitrogen gas, this was identified as *triethylgermyltetracarbonylcobalt* (0·79 g, 2·4 mmol) (Found: C, 36·5; H, 4·7. Calc. for $C_{10}H_{15}CoGeO_4$: C, 36·3; H, 4·55%).

*With trimethylstannane.* An excess of $Me_3SnH$ (0·470 g, 2·84 mmol) and $Co_2(CO)_8$ (0·342 g, 1·00 mmol) were allowed to react as above for 2 h, when fractionation yielded *trimethylstannyltetracarbonylcobalt* (0·403 g, 1·20 mmol) as a white solid collected at $-45$ °C and identified spectroscopically.

*Reactions of Trimethylgermyltetracarbonylcobalt.—With hydrogen chloride.* The complex (43·4 mg, 0·15 mmol) was treated with an excess of dry HCl for 5 h. Incondensible gas was formed and volatile products were $HCo(CO)_4$ and $Me_3GeCl$, identified by gas-phase i.r. spectroscopy, and from a mixture of which pure $Me_3GeCl$ (14·7 mg, 0·10 mmol) was separated.

*With methanol.* An excess of degassed AnalaR methanol was added to the complex (45·5 mg, 0·16 mmol). After 26 h a clear deep yellow solution yielded on fractionation $Me_3GeCo(CO)_4$ (23·0 mg, 0·08 mmol) and unidentified involatile material.

*With mercuric chloride.* The complex (71·0 mg, 0·25 mmol), $HgCl_2$ (45 mg, 0·17 mmol), and THF (2·0 ml) reacted immediately at room temperature to give a yellow solid. After 14 days the tube was opened and $Me_3GeCl$ was identified (i.r.) in the volatiles. Washing the residue with THF gave insoluble yellow $Hg[Co(CO)_4]_2$ (69 mg, 0·13 mmol) (i.r.).

*With triethylamine, and with piperidine.* Reaction of the complex with an excess of either $NEt_3$ or $C_5H_{11}N$ led to rapid formation of involatile products showing i.r. bands at 1890vs,br cm$^{-1}$ and 550vs cm$^{-1}$ as well as those attributable to presence of the base. Treatment of the colourless *liquid* adduct from the piperidine reaction with an excess of dry HCl afforded $HCo(CO)_4$ approximately stoicheiometrically.

*Exchange Reactions between Trimethyl-Group* IVB–*Cobalt complexes and Trimethyl-Group* IVB *Hydrides and Halides.*—A series of reactions between $Me_3MCo(CO)_4$ (M = Si, Ge, or Sn) and $Me_3MH$ (M = Ge or Sn) or $Me_3MX$ (M = Si or Sn, X = Cl; M = Ge, X = Br) was carried out, of which the following are typical. (*i*) Dry benzene (2·0 ml), $Me_3SiCo(CO)_4$ (122 mg, 0·50 mmol), and $Me_3SnH$ (82 mg, 0·50 mmol) were allowed to react at 20 °C for 24 h. Fractionation afforded $Me_3SiH$ (30 mg, 0·41 mmol) and $Me_3SnCo(CO)_4$ (identified by its i.r. spectrum); no $Me_3SnH$ or $Me_3SiCo(CO)_4$ could be detected. (*ii*) Excess of $Me_3GeBr$ was condensed on to $Me_3SiCo(CO)_4$ (180 mg, 0·74 mmol) in dry ether (2·0 ml). The resulting colourless solution gradually turned brown, and after 3 days $Me_3GeCo(CO)_4$ (162 mg, 0·56 mmol) was recovered from the mixture. No unchanged $Me_3SiCo(CO)_4$ was found. (*iii*) A similar reaction to (*ii*) between $Me_3SiCl$ (23 mg, 0·19 mmol) and $Me_3GeCl(CO)_4$ (50 mg, 0·17 mmol) in ether gave after 3 days 72% recovery of unchanged germyl-cobalt complex. Results of related experiments are summarised elsewhere (see Scheme).

*Reaction of Bis(cyclopentadienyltricarbonylmolybdenum) with Trimethylstannane.*—$[Mo(\pi\text{-}C_5H_5)(CO)_3]_2$ (400 mg, 0·82 mmol), $Me_3SnH$ (267 mg, 1·62 mmol), and ether (1·5 ml) afforded after 17 days at room temperature a small amount of incondensible gas, and *trimethylstannyl(cyclopentadienyl)-tricarbonylmolybdenum* (39 mg, 0·10 mmol), separated from unreacted dimer by sublimation and characterised by comparison of its i.r. spectrum with that of an authentic sample.

[3/1421 *Received, 9th July,* 1973]