

## Structure of Bis[ $\mu$ -carbonyl-bis(tricarbonylcobaltio)(Co–Co)]silicon(4 Co–Si)

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**Abstract.**  $\text{Si}[\text{Co}_2(\text{CO})_7]_2$ ,  $M_r = 655.97$ , monoclinic,  $C2/c$ ,  $a = 13.687(1)$ ,  $b = 12.602(1)$ ,  $c = 12.429(1)$  Å,  $\beta = 100.85(1)^\circ$ ,  $V = 2105.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.07$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 31$  cm<sup>-1</sup>,  $F(000) = 1272$ ,  $T = 296$  K,  $R = 0.027$  for 1561 observed reflections. The discrete molecules contain two near-perpendicular [dihedral angle  $80.92(2)^\circ$ ]  $\text{SiCo}_2$  triangles sharing the Si apex, which lies on a crystallographic diad. The Co–Co bonds are bridged by a carbonyl ligand, and each Co is bonded to three terminal carbonyl groups. Si–Co (average) =  $2.288(1)$ , Co–Co =  $2.528(1)$  Å.

**Introduction.** The structure of the complex  $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$  has served as a benchmark for a variety of novel clusters derived from it (Gerlach, Mackay, Nicholson & Robinson, 1981; Duffy, Mackay, Nicholson & Robinson, 1981; Croft, Duffy & Nicholson, 1982). The silicon analogue was assigned a similar structure on spectroscopic evidence (Mackay & Ngo, 1982) but since it was not isomorphous, and since the  $\text{SiCo}_2$  closed triangular unit had not previously been characterized structurally, it was decided a full X-ray structure analysis was merited.

**Experimental.** Prepared by the reaction of  $\text{SiH}_4$  with  $\text{Co}_2(\text{CO})_8$  in hexane (Mackay & Ngo, 1982). Moderately air-sensitive, red-orange crystals were obtained from  $\text{CH}_2\text{Cl}_2$  and embedded in epoxy resin for data collection. Precession photography showed systematic absences  $hkl$   $h + k \neq 2n$ ,  $h0l$   $l \neq 2n$  consistent with  $Cc$  or  $C2/c$ , the latter confirmed by the  $E$  statistics and the refinement. Enraf–Nonius CAD-4 automated diffractometer, graphite monochromator, lattice parameters from 25 automatically centred reflections,  $22 < 2\theta < 34^\circ$ ; 2049 unique reflections,  $0 < 2\theta < 54^\circ$ , collected with an  $\omega$ – $\theta$  scan,  $-16 < h < 16$ ,  $0 < k < 15$ ,  $0 < l < 15$ ; three standard reflections monitored every hour of exposure, random fluctuations of  $ca$  1% during collection; 1561 data [ $I \geq 3\sigma(I)$ ] corrected for Lorentz and polarization effects; empirical absorption correction applied based on  $\psi$  scans of each of three reflections, normalized transmission factors between 1.00 and 0.92. Structure solved by direct methods; full-matrix least-squares refinement based on  $F$  with all atoms anisotropic:  $R = 0.027$ ,  $wR = 0.027$ ,  $w =$

$1.0966[\sigma^2(F_o) + 0.000368F_o^2]^{-1}$ ,  $\Delta_{\text{max}}/\sigma = 0.01$ , final difference Fourier map peaks  $< 10.5$  e Å<sup>-3</sup>, no evidence for extinction; atomic scattering factors and  $f'$ ,  $f''$  values from *International Tables for X-ray Crystallography* (1974).<sup>\*</sup> Calculations involved the *SHELX76* suite of programs (Sheldrick, 1976); e.s.d.'s on dihedral angles calculated using *PARST* (Nardelli, 1982).

**Discussion.** The structure of  $\text{Si}[\text{Co}_2(\text{CO})_7]_2$  is shown in Fig. 1, the atomic parameters in Table 1 and bond lengths and selected angles in Table 2. The discrete molecules (shortest intermolecular  $\text{O}\cdots\text{O} = 3.00$  Å) contain a spiro Si atom linking two symmetry-equivalent  $\text{SiCo}_2$  triangles related by a crystallographic diad through the Si atom. Each Co is attached to three terminal CO groups while the Co–Co bond is bridged by a further CO ligand. An alternative description is in terms of two  $\text{Co}_2(\text{CO})_8$  molecules with one  $\mu$ -CO on each replaced by a common Si atom. The overall structure therefore conforms with the germanium analogue (Gerlach *et al.*, 1981) although there are some significant structural differences.

The Si–Co bond lengths are  $ca$  0.07 Å shorter than the equivalent bonds in  $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$  matching the

<sup>\*</sup> Lists of structure factors, anisotropic thermal parameters, bond angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43547 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

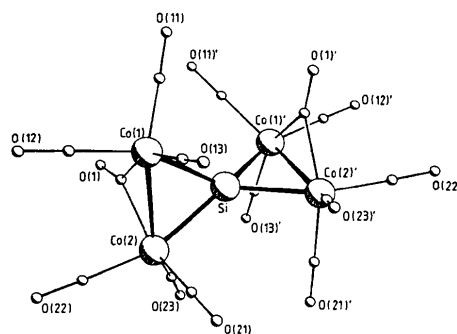


Fig. 1. A view of the molecule showing the labelling scheme. The numbering of the C atoms follows that of the attached O atoms.

difference in the relative atom sizes. A similar difference is observed in the  $M'$ -Co bonds in  $(\text{CO})_4\text{Co}M'\text{Co}_3$  ( $\text{CO})_9$ ,  $M' = \text{Si, Ge}$  (Schmid, Etzrodt & Batzel, 1976; Schmid & Etzrodt, 1977). The effect of the smaller Si atom in  $\text{Si}[\text{Co}_2(\text{CO})_7]$  is to increase the terminal  $\text{O}\cdots\text{O}$  interactions between the two halves of the molecule, with  $\text{O}(11)\cdots\text{O}(11)' = 2.93$ ,  $\text{O}(13)\cdots\text{O}(23)' = 2.97$  Å. For the germanium species there are no intramolecular  $\text{O}\cdots\text{O}$  interactions less than 3.0 Å. The twisting of the two  $\text{SiCo}_2$  triangles from a mutually perpendicular orientation to give a dihedral angle between them of  $80.92(2)^\circ$  can be seen as an attempt to minimize these  $\text{O}\cdots\text{O}$  interactions.

The two independent Si-Co distances are significantly different [ $\Delta = 0.025(2)$  Å] while the Co(1)C(1)-Co(2) triangle is asymmetric in the opposite sense. This movement of the bridging atoms in opposite directions serves to increase the  $\text{Si}\cdots\text{C}(1)$  non-bonded distance, which at 2.60 Å is still well within the sum of the van

der Waals radii. The equivalent distortion in  $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$  is more pronounced (Gerlach *et al.*, 1981) as expected for a larger central atom. The relative sizes of the Si and Ge atoms also account for the smaller  $\text{SiCo}(1)\text{Co}(2)/\text{Co}(1)\text{Co}(2)\text{C}(1)$  dihedral angle of  $99.08(2)^\circ$  compared with the equivalent in the germanium analogue of  $107^\circ$ .

The Co(1)-Co(2) bond length is essentially the same as in  $\text{Co}_2(\text{CO})_8$  (2.529 Å, Sumner, Klug & Alexander, 1964; Leung & Coppens, 1983), which suggests that Si is of a similar size to CO as a bridging moiety; the Co-Co distance in closed  $M\text{Co}_2$  triangles varies from this value, through 2.56 ( $M = \text{Ge}$ ), 2.63 ( $M = \text{Sn}$ ) (Ball & Hall, 1973) to 2.75 Å ( $M = \text{Hg}$ ) (Croft *et al.*, 1982) as the bridging atom becomes larger.

The six terminal carbonyl ligands on the two unique Co atoms fall into three distinctly different pairs. The average Co-C distance for the carbonyls pseudo-*trans* to the Co-Co bond is 1.785(4) Å, for the groups opposite the bridging carbonyl 1.815(4) Å, and for the CO's opposite the Co-Si bond it is 1.828(4) Å. These differences clearly indicate varying  $\pi$  bonding in the Co-C bonds, but a more specific discussion is hindered by the large distortions from octahedral coordination about the Co atom. For  $\text{Co}_2(\text{CO})_8$  the smaller distinction between the pseudo-axial Co-C [1.815(1) Å] and equatorial Co-C [1.832(4) Å] was only apparent with low-temperature data (Leung & Coppens, 1983).

The asymmetric  $\text{SiCo}_2$  triangles, the asymmetric bridging CO, and the dihedral angles at Si and across Co-Co of  $\text{Si}[\text{Co}_2(\text{CO})_7]_2$  can thus be understood in terms of a small atom bridging two bulky groups which undergo shifts from regularity to minimize intramolecular congestion.

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Table 1. Final positional and equivalent isotropic thermal parameters for  $\text{Si}[\text{Co}_2(\text{CO})_7]_2$

	x	y	z	$U_{\text{eq}}^*(\text{Å}^2)$
Si(1)	0.0	0.2390 (1)	0.25	0.033
Co(1)	0.11381 (3)	0.15729 (4)	0.16280 (4)	0.038
Co(2)	0.00391 (3)	0.30982 (4)	0.08241 (4)	0.039
C(1)	-0.0087 (3)	0.1562 (3)	0.0571 (3)	0.044
O(1)	-0.0644 (2)	0.0990 (2)	0.0057 (2)	0.066
C(11)	0.1083 (3)	0.0299 (3)	0.2257 (4)	0.059
C(12)	0.1828 (3)	0.1284 (3)	0.0537 (3)	0.053
C(13)	0.2184 (3)	0.2204 (3)	0.2510 (3)	0.055
C(21)	0.0775 (3)	0.4190 (3)	0.1504 (3)	0.055
C(22)	0.0386 (3)	0.3253 (4)	-0.0517 (3)	0.059
C(23)	-0.1230 (3)	0.3494 (3)	0.0544 (3)	0.059
O(11)	0.1088 (3)	-0.0500 (3)	0.2655 (3)	0.091
O(12)	0.2246 (2)	0.1124 (3)	-0.0144 (3)	0.081
O(13)	0.2866 (2)	0.2551 (3)	0.3032 (3)	0.092
O(21)	0.1251 (3)	0.4853 (3)	0.1938 (3)	0.085
O(22)	0.0600 (3)	0.3327 (4)	-0.1336 (3)	0.101
O(23)	-0.2017 (2)	0.3793 (3)	0.0330 (3)	0.096

\* The equivalent isotropic temperature factor  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. Bond lengths (Å) and selected angles and dihedral angles ( $^\circ$ ) for  $\text{Si}[\text{Co}_2(\text{CO})_7]_2$

Si(1)-Co(1)	2.301 (1)	Co(2)-C(22)	1.828 (4)
Si(1)-Co(2)	2.276 (1)	Co(2)-C(23)	1.777 (4)
Co(1)-Co(2)	2.528 (1)	C(1)-O(1)	1.151 (4)
Co(1)-C(1)	1.926 (3)	C(11)-O(11)	1.121 (5)
Co(1)-C(11)	1.794 (4)	C(12)-O(12)	1.126 (5)
Co(1)-C(12)	1.828 (4)	C(13)-O(13)	1.122 (5)
Co(1)-C(13)	1.814 (4)	C(21)-O(21)	1.133 (5)
Co(2)-C(1)	1.964 (4)	C(22)-O(22)	1.115 (5)
Co(2)-C(21)	1.816 (5)	C(23)-O(23)	1.126 (5)
Co(1)-Si(1)-Co(2)	67.0 (1)	Si(1)-Co(2)-Co(1)	57.0 (1)
Si(1)-Co(1)-Co(2)	56.0 (1)	Co(1)-Co(2)-C(1)	48.8 (1)
Si(1)-Co(1)-C(1)	75.2 (1)	Si(1)-Co(2)-C(1)	75.1 (1)
Co(2)-Co(1)-C(1)	50.1 (1)	Co(1)-C(1)-Co(2)	81.1 (1)
Co(1)-C(1)-O(1)	141.6 (3)	Co(2)-C(1)-O(1)	137.4 (3)
SiCo(1)Co(2)/SiCo(1)'Co(2)'	80.92 (2)		
SiCo(1)Co(2)/Co(1)Co(2)C(1)	99.08 (2)		

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## Structure of Pentacarbonyl(tribromophosphine)chromium(0)

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**Abstract.**  $[\text{Cr}(\text{CO})_5(\text{PBr}_3)]$ ,  $M_r = 462.75$ , triclinic,  $P\bar{1}$ ,  $a = 6.695$  (1),  $b = 6.823$  (1),  $c = 13.641$  (3) Å,  $\alpha = 88.07$  (1),  $\beta = 87.16$  (1),  $\gamma = 87.73$  (1)°,  $Z = 2$ ,  $V = 621.5$  (2) Å<sup>3</sup>,  $D_x = 2.47$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 112.9$  cm<sup>-1</sup>,  $T = 293$  K,  $F(000) = 428$ ,  $R = 7.12\%$  for 1901 unique observed reflections. The structure displays a slightly distorted octahedral geometry about the Cr atom with five carbonyl C atoms and the P atom of  $\text{PBr}_3$  occupying the coordination sites. The Cr–P, Cr–CO (*trans*) and average Cr–CO (*cis*) distances are 2.263 (3), 1.892 (11) and 1.903 (11) Å, respectively.

**Introduction.** There remains considerable interest in the synergic  $\sigma$ -donor/ $\pi$ -acceptor characteristics of phosphine ligands toward low-valent-metal carbonyl fragments. Previous studies (Plastas, Stewart & Grim, 1973; Cotton, Darensbourg & Isley, 1981) have suggested that there is an approximate correlation between  $\nu_{\text{CO}}(E \text{ mode})$  and  $M$ –P bond distances in metal carbonyl phosphine complexes which should make comparative predictions on the nature of new phosphine–metal interactions in  $X_3PM(\text{CO})_5$  ( $M = \text{Cr, Mo}$  and  $\text{W}$ ;  $X = \text{halide, hydride, alkoxide, alkyl}$  and *aryl*) possible. Utilizing this correlation and published infrared spectra (Fischer & Knauss, 1969) it would be expected that the  $X_3\text{PCr}(\text{CO})_5$  ( $X = \text{halide}$ ) complexes should display some of the shortest metal–phosphine bond distances. The crystal-structure determination of the title compound was undertaken to partially test this prediction.

**Experimental.** The complex was prepared by literature techniques (Fischer & Knauss, 1969) and air-sensitive orange crystals were obtained by sublimation. Crystal  $0.1 \times 0.3 \times 0.4$  mm (glass capillary); Syntex *P3/F* diffractometer,  $\text{Mo K}\alpha$  radiation, graphite monochromator; cell parameters from a least-squares fit of 25 reflections with  $10 < 2\theta < 32^\circ$ , space group  $P\bar{1}$ ; no

absorption correction was applied; data collected to  $2\theta_{\text{max}} = 55^\circ$  with  $\pm h, \pm k, \pm l$  ranges 0 to 8, 8 and 17 respectively;  $\theta$ – $2\theta$  scan mode,  $1.2^\circ$  range,  $4$ – $30^\circ$  min<sup>-1</sup> speed; three standard reflections monitored every 141 reflections, 20% intensity variation; rapid crystal deterioration after 48 h of exposure necessitated the merging of data sets for two crystals; 7861 reflections measured,  $R_{\text{int}} 4.4\%$ ; 2870 unique data, 1901 data with  $F > 5\sigma(F)$  used in solution and refinement (based on  $F^2$ s); structure solved by direct methods; blocked-cascade least-squares refinement using anisotropic thermal parameters for all atoms, 136 parameters,  $R = 0.071$ ,  $wR_F = 0.068$ ,  $w = 1/[\sigma^2(F_o) + 0.00095 F_o^2]$ ,  $S = 1.624$ ,  $(\Delta/\sigma)_{\text{max}} = -0.091$  for  $U(11)$  of C(2); max. and min. heights in final difference Fourier synthesis 1.64 and  $-1.46$  e Å<sup>-3</sup>; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs from *SHELXTL* (Sheldrick, 1981). The relatively high  $R$  index reflects the instability of the compound during X-ray exposure.

**Discussion.** Atom coordinates are given in Table 1 and bond distances and angles in Table 2.† A view of the molecular structure and a stereoview of the unit-cell contents are shown in Figs. 1 and 2. The Cr atom displays pseudooctahedral symmetry and it is bonded to the C atom of five terminal CO ligands and the P atom of  $\text{PBr}_3$ . The Cr–P bond distance is, indeed, short compared to Cr–P distances found in  $\text{Cr}(\text{CO})_5\text{-P}(\text{C}_6\text{H}_5)_3$  2.422 (1),  $\text{Cr}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$  2.309 (1) (Plastas *et al.*, 1973),  $\text{Cr}(\text{CO})_5\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$  2.364 (1) (Cotton *et al.*, 1981) and  $\text{Cr}(\text{CO})_5\text{P}(\text{CH}_3)_2\text{-}(\text{SH})$  2.344 (2) Å (Meier, Strähle & Lindner, 1976). Construction of a plot of  $d_{\text{Cr-P}}$  vs  $\nu_{\text{CO}}(E)$  utilizing the

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43462 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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