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Preparation and structures of mixed silicon-cobalt carbonyl clusters with Si–H, Si–O or Si–S bonds

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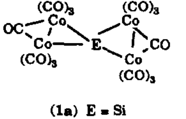
Abstract

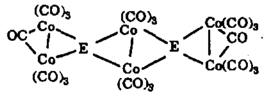
Reaction of Si_2H_6 with $\geq$ 3 molar equivalents of $Co_2(CO)_8$ in hexane gives the *closo*-cluster $Co_4(\mu_4\text{-}SiCo(CO)_4)(CO)_{11}$, while with < 3 molar equivalents the partially substituted cluster $H_2Si_3Co_6(CO)_{20}$ is formed. An X-ray crystal structure determination shows the latter to be relatively open, with linked $SiCo_2$ triangles and retention of Si–H bonds on two of the silicon atoms. With $O(SiH_3)_2$, $Co_2(CO)_8$ gives mainly the mono-silyl complex $\mu_4\text{-}Si[Co_2(CO)_7]_2$, together with an unstable species tentatively identified as $O\{Si[Co(CO)_4]Co_2(CO)_7\}_2$. Reaction of $S(SiH_3)_2$ with $Co_2(CO)_8$ gives $Co_4(\mu_4\text{-}S)_2(CO)_{11}$ and the novel cluster $SSi_2Co_2(CO)_{14}$; the latter was shown crystallographically to contain a $Co_2(CO)_6$ unit doubly-bridged by two silicon atoms that are in turn linked by the sulphur atom. There is also a terminal $Co(CO)_4$ group attached to each silicon atom. The most notable feature of this structure is an acute Si–S–Si bond angle of 70.3° which leads to a very short formally non-bonded Si ··· Si distance of 2.498 Å.

1. Introduction

The hydrogen-elimination reaction between a group 14 hydride and cobalt carbonyl is a useful general route to E–Co (E = Si, Ge) bonds under mild conditions [1]. Germanium hydrides have been extensively studied. Thus GeH_4 and $Co_2(CO)_8$ give $\mu_4\text{-}Ge[Co_2(CO)_7]_2$ **(1b)** [2], while Ge_2H_6 and Ge_3H_8 give the extended chain-of-triangles clusters $Ge_2Co_6(CO)_{20}$ **(2)** [3] and $Ge_3Co_8(CO)_{26}$ [4], respectively, among other products [3]. These relatively open clusters that are initially formed condense on gentle heating to a variety of *closo*-clusters [2,3]. Alkyl substituents are unchanged in these reactions, and so serve to block sites on the germanium atom, giving some control over the size of the clusters formed. Thus $RGeH_3$ with $Co_2(CO)_8$ gives $Co_2\{\mu\text{-}Ge(R)Co(CO)_4\}(CO)_7$, which can be decarbonylated to give $RGeCo_3(CO)_9$ [5], or $Co_2[\mu\text{-}Ge(R)Co(CO)_4]_2(CO)_6$ [5], which rearranges to $Co_4(\mu_4\text{-}GeR)_2(CO)_{11}$ [6]. The hydride R_2GeH_2 reacts with $Co_2(CO)_8$ to give $Co_2(\mu\text{-}GeR_2)(CO)_7$ or $Co_2(\mu\text{-}GeR_2)_2(CO)_6$ [7]. In the case of silicon hydrides relatively few of the analogous reactions have been reported. Silane SiH_4, reacts with $Co_2(CO)_8$ completely analogously to germane, to give $\mu_4\text{-}Si[Co_2(CO)_7]_2$, **(1a)** [8], and $RSiH_3$ has been briefly reported to give $RSiCo_3(CO)_n$ [$n = 11$ or 9] [5,9]. However, prior to our preliminary communication [10], no accounts of reactions of Si_2H_6 or higher hydrides with $Co_2(CO)_8$ had been reported. Reactions of siloxanes or silylthianes with $Co_2(CO)_8$ were also unknown, although partially methylated siloxanes such as $Me_2HSiOSiMe_2H$ had been shown to produce interesting compounds on treatment with other metal reagents by reaction of the Si–H bonds [11].



(1a) E = Si
(1b) E = Ge



(2) E = Ge
(3) E = Si

This paper reports the reactions of the simplest disilicon species Si_2H_6, $O(SiH_3)_2$, and $S(SiH_3)_2$ with cobalt carbonyl.

2. Experimental section

General procedures have been detailed elsewhere [12]. Disilane [13] was prepared by $LiAlH_4$ reduction

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* Dedicated to Mike Lappert on the occasion of his 65th birthday. BKN enjoyed his time in Lab 3 at Sussex.

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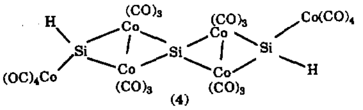
of Si_2Cl_6 (Petrach). Disiloxane was prepared via the sequence (i) $SiH_4 + Br_2 \rightarrow SiH_3Br$ (care is needed, as this is a potentially explosive reaction), (ii) $SiH_3Br + HgO \rightarrow H_3SiOSiH_3$ [14]. Disilylthiane was prepared by the sequence: $PhSiH_3 + HI \rightarrow H_3SiI$; $H_3SiI + HgS \rightarrow H_3SiSSiH_3$ [15]. All silicon hydrides were handled on a conventional vacuum line and purified by trap-to-trap distillation. Purity was checked by infrared spectroscopy.

2.1. Reaction of Si_2H_6 with $Co_2(CO)_8$

2.1.1. At lower Si : Co ratios

$Co_2(CO)_8$ (2.00 g, 5.85 mmol) and hexane (25 ml) were placed in a 100 ml vessel fitted with a greaseless tap. Si_2H_6 (0.146 g, 2.34 mmol) was condensed into the vessel and the mixture was left at 4°C for 8 days. Incondensable gases were removed and analysed after 4 h, 24 h, and 8 days. The initial evolution was of CO (83%) and H_2 (17%). The proportion of hydrogen increased with time, and formed 27% of a total of *ca.* 6 mmol of gas evolved after 8 days. The volatile components were removed under vacuum and shown by infrared spectroscopy to contain small amounts of SiH_4 and $HCo(CO)_4$ mixed with the solvent. The residue was extracted with hexane (20 ml) and an infrared spectrum of this extract showed that little unreacted $Co_2(CO)_8$ (or its condensation product $Co_4(CO)_{12}$) was present. The presence of the previously reported μ_4-$Si[Co_2(CO)_7]_2$ (**1a**) [8] was indicated by the spectra (ν(CO), hexane, 2085s, 2065s, 2044m, 2037s, 2026m, 2007w, 1847w,br), together with two new species, characterised below as $H_2Si_3Co_6(CO)_{20}$ (**4**) and $Si_2Co_6(CO)_{20}$ (**3**). Cooling of the extract gave **4** as yellow rectangular crystals. The supernatant liquid was concentrated and cooled to give yellow star-shaped crystals of **3**. More **4** was obtained by extracting the original residue with CH_2Cl_2/toluene and recrystallisation from toluene. The total estimated yield of **4** was 40–50% based on silicon.

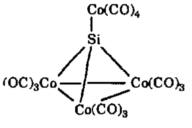


(4)

When the reaction was repeated on a half-scale in a closed ampoule for three weeks **1a** and **4** were found to be present in similar quantities while **3** made up *ca.* 15% of the product mixture.

2.1.2. At higher Si : Co ratios

$Co_2(CO)_8$ (0.718 g, 2.1 mmol), Si_2H_6 (0.038 g, 0.60 mmol) and hexane (10 ml) were sealed in a 50 ml ampoule. After six months the ampoule was opened and the contents were transferred to a Schlenk flask, the ampoule being washed out with CH_2Cl_2. Solvents were evaporated under vacuum. The residue was extracted with hexane (20 ml then 3 × 10 ml) and this extract was shown by infrared spectroscopy to contain mainly $(OC)_4CoSiCo_3(CO)_9$ (**5**) [16] with traces of $Co_2(CO)_8$ and $Co_4(CO)_{12}$. The total amount of hexane soluble products was 0.462 g, *ca.* 60% yield of **5** based on Si_2H_6. The hexane-insoluble reaction residue was extracted with CH_2Cl_2 to give on evaporation of the solvent pure $Co_4[\mu_4\text{-}SiCo(CO)_4]_2(CO)_{11}$ (**6**) 0.203 g, 36% based on Si_2H_6; ν(CO), CH_2Cl_2, 2102s, 2075w, 2054s sh, 2043vs, 2021s sh, 2006m sh, cm^{-1}. This compound was characterised by a single crystal X-ray structure determination, details of which have been published elsewhere [10].



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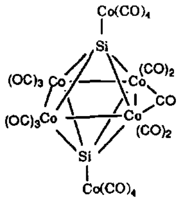
2.2. Characterisation of $H_2Si_3Co_6(CO)_{20}$ (4)

This compound formed yellow crystals which could be stored indefinitely at −25°C and handled in air for brief periods without decomposition, although its solutions were air-sensitive. The crystalline solid decomposed during a week at room temperature even in the absence of air. An infrared spectrum showed carbonyl-stretching peaks 2101w, 2082m, 2069s, 2054s, 2046m, 2030vs, 2004w. The overall pattern is similar to that of $Me_2Ge_3Co_6(CO)_{20}$ [17]. The full characterisation of **4** was by an X-ray structure analysis, see below.

2.3. Tentative characterisation of $Si_2Co_6(CO)_{20}$ (3)

This yellow compound showed ν(CO), hexane, 2112w, 2095s, 2074vs, 2061s, 2054vs, 2031s, 2008w, 1842mw, *cf.* the germanium analogue 2085s, 2068vs, 2054s, 2050s sh, 2040w, 2033mw, 2027m, 2003w, 1844mw cm^{-1} [3]. Definitive characterisation was hampered by the ready decarbonylation of **3** to give the *closo* cluster **6**.



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2.4. Reaction of $H_3SiOSiH_3$ with $Co_2(CO)_8$

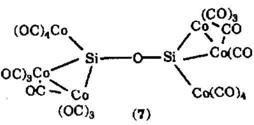
Disiloxane (0.0763 g, 0.975 mmol) was condensed into a 50 ml ampoule which contained $Co_2(CO)_8$ (1.00

g, 2.92 mmol) in hexane (10 ml). The ampoule was left in the dark at room temperature for 4 months, after which it contained a dark-brown solution and a brown precipitate. The ampoule was opened and the contents were transferred to a Schlenk flask, the ampoule being washed out with CH_2Cl_2. The solvents and any $HCo(CO)_4$ were removed under vacuum and some unchanged $Co_2(CO)_8$ was sublimed on to a cold finger. The residue was dissolved in hexane and an infrared spectrum indicated a mixture of $Co_2(CO)_8$, $Co_4(CO)_{12}$, μ_4-Si[$Co_2(CO)_7$]$_2$ (**1a**), $(OC)_4CoSiCo_3(CO)_9$ (**5**), and a new brown species, tentatively characterised as

TABLE 1. Final positional parameters for $H_2Si_3Co_6(CO)_{20}$ (4)

Atom	x	y	z	Atom	x	y	z
Co(11)	0.4734(1)	0.9762(1)	0.2622(1)	Co(21)	0.5035(1)	0.4800(1)	0.8606(1)
Co(12)	0.5650(1)	0.8291(1)	0.3336(1)	Co(22)	0.7447(1)	0.4219(1)	0.8730(1)
Co(13)	0.8992(1)	0.9699(1)	0.1978(1)	Co(23)	0.7606(1)	0.6312(1)	0.6830(1)
Co(14)	0.8485(1)	0.0423(1)	0.2891(1)	Co(24)	0.7283(1)	0.4828(1)	0.6689(1)
Co(15)	0.2697(1)	0.9051(1)	0.4648(1)	Co(25)	0.4698(1)	0.2059(1)	0.9459(1)
Co(16)	0.9617(1)	1.2399(1)	0.0955(1)	Co(26)	1.1412(1)	0.5704(1)	0.5979(1)
Si(11)	0.6956(2)	0.9567(1)	0.2704(1)	Si(21)	0.6854(2)	0.5030(1)	0.7716(1)
Si(12)	0.4632(2)	0.9282(1)	0.3770(1)	Si(22)	0.5634(2)	0.3424(1)	0.8680(1)
Si(13)	0.8424(2)	1.1111(1)	0.1756(1)	Si(23)	0.9308(2)	0.5396(1)	0.6743(1)
C(11)	0.5228(8)	0.9955(5)	0.1733(4)	C(21)	0.5369(9)	0.5914(5)	0.8541(4)
O(11)	0.5502(6)	1.0096(4)	0.1167(3)	O(21)	0.5560(7)	0.6608(4)	0.8505(3)
C(12)	0.4506(8)	1.0830(5)	0.2628(4)	C(22)	0.3688(9)	0.4862(5)	0.8154(4)
O(12)	0.4334(6)	1.1537(4)	0.2594(3)	O(22)	0.2789(7)	0.4908(4)	0.7899(3)
C(13)	0.3108(8)	0.9258(5)	0.2710(4)	C(23)	0.4146(9)	0.4366(5)	0.9484(4)
O(13)	0.2101(6)	0.8931(4)	0.2745(3)	O(23)	0.3604(7)	0.4092(4)	1.0036(3)
C(14)	0.669(1)	0.7840(5)	0.3939(4)	C(24)	0.845(1)	0.3405(5)	0.8550(4)
O(14)	0.7324(8)	0.7507(4)	0.4342(4)	O(24)	0.9166(7)	0.2890(4)	0.8450(3)
C(15)	0.6265(8)	0.7910(5)	0.2646(4)	C(25)	0.8701(9)	0.5069(5)	0.8582(4)
O(15)	0.6624(7)	0.7668(4)	0.2213(3)	O(25)	0.9515(8)	0.5554(4)	0.8538(3)
C(16)	0.4183(9)	0.7535(5)	0.3715(4)	C(26)	0.7070(8)	0.3985(5)	0.9644(4)
O(16)	0.3324(7)	0.7019(4)	0.3970(3)	O(26)	0.6919(7)	0.3904(4)	1.0196(3)
C(17)	0.9287(8)	0.8619(6)	0.2561(5)	C(27)	0.585(1)	0.6580(5)	0.6846(4)
O(17)	0.9448(6)	0.7954(4)	0.2927(4)	O(27)	0.4732(7)	0.6707(4)	0.6858(4)
C(18)	1.0761(9)	1.0063(5)	0.1604(4)	C(28)	0.8307(9)	0.7048(5)	0.5970(4)
O(18)	1.1850(6)	1.0272(4)	0.1377(3)	O(28)	0.8772(7)	0.7521(4)	0.5450(3)
C(19)	0.8449(9)	0.9494(6)	0.1307(5)	C(29)	0.827(1)	0.6813(5)	0.7314(4)
O(19)	0.8178(8)	0.9349(5)	0.0876(4)	O(29)	0.8734(8)	0.7168(4)	0.7599(3)
C(110)	0.7409(8)	1.1230(5)	0.3051(4)	C(210)	0.7980(8)	0.3785(5)	0.6936(4)
O(110)	0.6730(6)	1.1707(4)	0.3204(3)	O(210)	0.8363(7)	0.3100(4)	0.7092(3)
C(111)	0.8374(9)	0.9630(5)	0.3733(4)	C(211)	0.552(1)	0.4562(5)	0.6805(4)
O(111)	0.8318(7)	0.9202(4)	0.4284(3)	O(211)	0.4426(7)	0.4353(4)	0.5846(3)
C(112)	1.0244(9)	1.0761(5)	0.2806(4)	C(212)	0.7483(8)	0.5274(5)	0.5775(4)
O(112)	1.1333(6)	1.0913(4)	0.2801(3)	O(212)	0.7500(6)	0.5521(4)	0.5208(3)
C(113)	0.1684(9)	0.8508(6)	0.4285(4)	C(213)	0.5193(9)	0.2193(5)	1.0180(4)
O(113)	0.0942(7)	0.8167(5)	0.4110(3)	O(213)	0.5492(7)	0.2218(4)	1.0655(3)
C(114)	0.134(1)	0.8946(6)	0.5360(5)	C(214)	0.3956(9)	0.0956(5)	0.9915(4)
O(114)	0.0472(7)	0.8888(5)	0.5794(4)	O(214)	0.3515(7)	0.0261(4)	1.0173(3)
C(115)	0.286(1)	1.0215(6)	0.4332(5)	C(215)	0.3144(9)	0.2542(5)	0.9231(4)
O(115)	0.2932(8)	1.0964(4)	0.4139(4)	O(215)	0.2153(7)	0.2827(4)	0.9103(3)
C(116)	0.388(1)	0.8425(6)	0.5115(5)	C(216)	0.596(1)	0.1719(5)	0.8911(4)
O(116)	0.4650(8)	0.8023(5)	0.5405(3)	O(216)	0.6763(8)	0.1503(4)	0.8551(3)
C(117)	1.1250(9)	1.2162(5)	0.1196(4)	C(217)	1.1495(9)	0.6466(6)	0.6387(5)
O(117)	1.2300(7)	1.2056(4)	0.1309(3)	O(217)	1.1558(7)	0.6960(5)	0.6641(4)
C(118)	0.844(1)	1.2870(5)	0.1452(4)	C(218)	1.318(1)	0.5885(6)	0.5552(5)
O(118)	0.7691(7)	1.3195(4)	0.1744(3)	O(218)	1.4286(7)	0.5967(5)	0.5314(4)
C(119)	0.911(1)	1.1914(6)	0.0408(4)	C(219)	1.0689(9)	0.5993(5)	0.5221(5)
O(119)	0.8797(9)	1.1629(5)	0.0048(3)	O(219)	1.0308(7)	0.6155(4)	0.4731(3)
C(120)	1.0198(9)	1.3452(6)	0.0285(5)	C(220)	1.1543(9)	0.4556(6)	0.6394(5)
O(120)	1.0512(7)	1.4102(4)	−0.0127(4)	O(220)	1.1648(7)	0.3828(4)	0.6636(4)

O{Si[Co(CO)$_4$]Co$_2$(CO)$_7$}$_2$ (7) (*ca.* 25%, based on siloxane) ν(CO), hexane, 2101w, 2089s, 2061s, 2046m, 2036sh, 2030vs, 2021m, 1846m, cm^{-1}.



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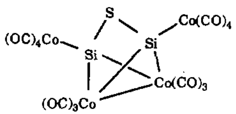
When the reaction was repeated with a lower Co$_2$(CO)$_8$: siloxane ratio (2 : 1) the same products were found together with a yellow-brown CH$_2$Cl$_2$-soluble species, (ν(CO), CH$_2$Cl$_2$, 2101w, 2072s, 2042vs, 2028s, 1848w br, cm^{-1}) which could not be characterised.

2.5. *Thermal rearrangement of putative O{Si[Co(CO)$_4$]-Co$_2$(CO)$_7$}$_2$ (7)*

A crude sample of **7** in hexane was heated at 50°C for 0.5 h. The solution became deep red as the infrared spectral peaks due to **7** diminished and strong new peaks at 2054m, 2030vs cm^{-1} developed. The product could not be isolated from the solution.

2.6. *Reaction of H$_3$SiSSiH$_3$ with Co$_2$(CO)$_8$*

Disilane (0.0979 g, 1.04 mmol) was condensed into a 50 ml ampoule which contained Co$_2$(CO)$_8$ (1.00 g, 2.92 mmol) in hexane (10 ml). The ampoule was left in the dark at room temperature for 3 weeks. A brown solution and a black precipitate formed and on opening the ampoule only traces of volatile silicon hydrides were found. The contents were transferred to a Schlenk flask and the solvent was removed under vacuum. The residue was extracted with hexane (3 × 10 ml), leaving a black precipitate. The hexane-soluble fraction contained Co$_2$(CO)$_8$ and Co$_4$(CO)$_{12}$, together with a new species characterised as SSi$_2$Co$_4$(CO)$_{14}$ (**8**). The hexane solution was cooled to -25°C to give a precipitate of crude **8**, which was recrystallised from toluene at -25°C to provide yellow-orange diamond-shaped crystals (0.32 g, 43%), ν(CO), hexane, 2104s, 2072s, 2056m sh, 2046vs, 2038s, 2024m, 2014w, cm^{-1}. Full characterisation was by an X-ray crystallographic study, see below.



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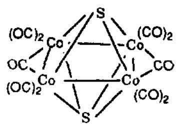

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The black precipitate left after hexane extraction was crystallised from CH$_2$Cl$_2$ and shown to be the well-known compound (μ_4-S)$_2$Co$_4$(CO)$_{10}$ (**9**) [18] from its infrared spectrum and an X-ray crystal structure determination [19].

The reaction was repeated under various conditions: (i) a reaction time of two years at room temperature gave 10% **8** and 30–40% **9**; (ii) a low temperature run, 5°C for 2 months, gave 40–50% **8** and only a small amount of **9**; (iii) a higher temperature run, 50°C for 10 days, gave no **8** and 94% of **9** based on the S content of S(SiH$_3$)$_2$, together with minor amounts of **5**. In all cases unchanged Co$_2$(CO)$_8$ and/or Co$_4$(CO)$_{12}$ were present, which necessitated fractional crystallisations to allow isolation of the pure clusters.

2.7. *X-ray crystallography*

The structures of clusters **4** and **8** were determined by X-ray crystallography. For each the crystal quality and space group were established by precession photography. Accurate cell parameters and intensity data were obtained on a Nicolet P3 diffractometer using monochromated Mo Kα X-rays. Absorption corrections were applied based on a series of azimuthal scans. The structures were solved by direct methods and refined by least-squares using the SHELX programs [20]. For both compounds complete lists of bond lengths and angles and tables of thermal parameters have been

TABLE 2. Selected bond lengths (Å) and angles (°) for H$_2$SI$_3$Co$_6$(CO)$_{20}$ (4)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Bond lengths					
Si(1)–CO(1)	2.282(2)	2.314(2)	Si(3)–Co(3)	2.281(2)	2.281(2)
Si(1)–Co(2)	2.321(2)	2.303(2)	Si(3)–Co(4)	2.315(2)	2.301(3)
Si(1)–Co(3)	2.291(2)	2.301(2)	Co(1)–Co(2)	2.618(2)	2.615(2)
Si(1)–Co(4)	2.293(3)	2.315(3)	Co(3)–Co(4)	2.615(2)	2.602(2)
Si(2)–Co(1)	2.298(2)	2.288(2)	Si(2)–Co(5)	2.374(2)	2.355(2)
Si(2)–Co(2)	2.289(3)	2.310(3)	Si(3)–Co(6)	2.371(2)	2.360(2)
Bond angles					
Co(1)–Si(1)–Co(2)	69.3(1)	69.0(1)	Co(1)–Si(2)–Co(2)	69.6(1)	69.3(1)
Co(3)–Si(1)–Co(4)	69.6(1)	68.5(1)	Co(3)–Si(3)–Co(4)	69.4(1)	69.2(1)
Co(1)–Si(2)–Co(5)	128.6(1)	130.3(1)	Co(2)–Si(2)–Co(5)	128.1(1)	127.7(1)
Co(3)–Si(3)–Co(6)	128.7(1)	128.6(1)	Co(4)–Si(3)–Co(6)	129.4(1)	130.6(1)

TABLE 3. Final positional parameters for $SSi_2Co_4(CO)_{14}$ (**8**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.34901(3)	0.18691(6)	0.21643(4)	Co(2)	0.48101(3)	0.25158(6)	0.56674(4)
Co(3)	0.31860(3)	0.16693(5)	0.44677(4)	Co(4)	0.34588(3)	0.36721(5)	0.41012(4)
Si(1)	0.36870(7)	0.2188(1)	0.33896(8)	Si(2)	0.41691(7)	0.2472(1)	0.46353(8)
S(1)	0.46851(6)	0.1906(1)	0.36688(7)	C(11)	0.3920(3)	0.0611(5)	0.2296(3)
O(11)	0.4190(2)	−0.0171(4)	0.2368(3)	C(12)	0.3923(3)	0.3118(5)	0.2092(3)
O(12)	0.4190(2)	0.3922(4)	0.2038(2)	C(13)	0.2646(3)	0.1844(5)	0.2381(3)
O(13)	0.2115(2)	0.1814(5)	0.2495(3)	C(14)	0.3390(3)	0.1722(5)	0.1177(3)
O(14)	0.3335(3)	0.1649(4)	0.0554(2)	C(21)	0.5368(3)	0.3203(5)	0.5080(3)
O(21)	0.5723(2)	0.3683(4)	0.4725(2)	C(22)	0.4647(3)	0.1098(5)	0.5642(3)
O(22)	0.4522(2)	0.0198(3)	0.5636(2)	C(23)	0.4231(3)	0.3369(5)	0.6132(3)
C(24)	0.5349(3)	0.2445(5)	0.6462(3)	O(24)	0.5673(2)	0.2418(4)	0.6960(2)
C(31)	0.3064(3)	0.1671(5)	0.5441(3)	O(31)	0.2996(2)	0.1651(4)	0.6069(2)
C(32)	0.2342(3)	0.1788(4)	0.4206(3)	O(32)	0.1813(2)	0.1870(4)	0.4088(2)
C(33)	0.3473(3)	0.0351(4)	0.4267(3)	O(33)	0.3668(2)	−0.0500(3)	0.4146(2)
C(41)	0.3133(3)	0.4266(4)	0.4929(3)	O(41)	0.2911(2)	0.4661(4)	0.5442(3)
C(42)	0.2846(3)	0.4039(5)	0.3456(3)	O(42)	0.2477(2)	0.4291(4)	0.3025(3)
C(43)	0.4123(3)	0.4460(4)	0.3821(4)	O(43)	0.4545(2)	0.4982(4)	0.3634(3)

deposited at the Cambridge Crystallographic Data Centre.

2.7.1. X-Ray structure of 4

Crystal data: $C_{20}H_2Co_6O_{20}Si_3$, M 1000.07, triclinic, space group $P\bar{1}$, *a* 10.061(7), *b* 16.458(19), *c* 21.592(15) Å, α 69.00(7), β 78.98(5), γ 88.70(7)°, *U* 3272(5) Å^3. D_c 2.03 g cm^{-3} for $Z = 4$, $F(000)$ 1944, μ(Mo Kα) 30 cm^{-1}, T 163 K. Yellow crystals from hexane, crystal size 1.0 × 0.3 × 0.3 mm. 11484 unique reflections collected for $4° < 2\theta < 50°$, $T_{max,min}$ 0.938, 0.792. For the refinement 7578 reflections with $I > 2\sigma(I)$ were used, all non-H atoms anisotropic, H atoms not located or included. Refinement (based on F) converged with R 0.0529, R_w 0.0460, where $w = [\sigma^2(F) + 0.000353\, F^2]^{-1}$. Largest final Δ/σ 0.02, largest features in a final difference map were *ca.* 1.0 e Å^{-3}, adjacent to Co atoms. There were no peaks obviously assignable to the H atoms on silicon and so these were not included in the refinement. Atom coordinates are given in Table 1 and selected bond parameters in Table 2.

2.7.2. X-ray structure of 8

Crystal data: $C_{14}Co_4O_{14}SSi_2$, M 716.11, orthorhombic, space group *Pbcn*, *a* 20.834(6), *b* 12.345(3), *c* 18.147(11) Å, *U* 4667(3) Å^3. D_c 2.04 g cm^{-3} for $Z = 8$, $F(000)$ 2784, μ(Mo Kα) 29 cm^{-1}, T 173 K. Yellow-orange crystals from toluene, crystal size 0.7 × 0.5 × 0.4 mm. A total of 4575 unique reflections was collected for $4° < 2\theta < 52°$, $T_{max,min}$ 0.962, 0.497. For the refinement 3390 reflections with $I > 2\sigma(I)$ were used, all atoms anisotropic. Refinement (based on F) converged with R 0.0401, R_w 0.0455, where $w = [\sigma^2(F) + 0.003\, F^2]^{-1}$. Largest final Δ/σ 0.02, largest feature in a final difference map 0.8 e Å^{-3}, adjacent to a cobalt atom. Atom coordinates are given in Table 3 and selected bond parameters in Table 4.

3. Results and discussion

Disilane reacts with > 3 mol equivalent of $Co_2(CO)_8$ in hexane at room temperature according to eqn. (1):

$$\begin{aligned} &Si_2H_6 + Co_2(CO)_8 \longrightarrow \\ &\qquad \underset{\mathbf{6}}{Co_4[\mu_4\text{-}SiCo(CO)_4](CO)_{11}} + \underset{\mathbf{1a}}{\mu_4\text{-}Si\{Co_2(CO)_7\}_2}, \\ &\qquad + \underset{\mathbf{5}}{(OC)_4CoSiCo_3(CO)_9} + 3H_2 + nCO \end{aligned} \qquad (1)$$

TABLE 4. Selected bond lengths (Å) and angles (°) for $SSi_2Co_4(CO)_{14}$ (**8**)

Bond lengths					
Co(3)–Co(4)	2.623(1)	Si(1)–Co(1)	2.295(2)	Si(1)–Co(3)	2.308(2)
Si(1)–Co(4)	2.291(2)	Si(2)–Co(2)	2.301(2)	Si(2)–Co(3)	2.296(2)
Si(2)–Co(4)	2.307(2)	Si(1)–S(1)	2.169(2)	Si(2)–S(1)	2.173(2)
Si(1)···Si(2)	2.498(2)				
Bond angles					
Co(1)–Si(1)–Co(3)	133.9(1)	Co(1)–Si(1)–Co(4)	130.3(1)	Co(3)–Si(1)–Co(4)	69.5(1)
Co(1)–Si(1)–S(1)	111.7(1)	Co(2)–Si(2)–Co(3)	129.5(1)	Co(2)–Si(2)–Co(4)	134.4(1)
Co(3)–Si(2)–Co(4)	69.5(1)	Co(2)–Si(2)–S(1)	112.2(1)	Si(1)–S(1)–Si(2)	70.3(1)

1a and its condensation product **5** are the products of a similar reaction with SiH_4 [8], and arise in the present system from cleavage of the disilane leaving the silicon atoms in separate clusters. In the case of **6** cleavage of the Si–Si bond has again taken place, but now both silicon atoms are in the same cluster. In various runs, 30–40% of the silicon ends up in **6**, with the remainder in the mono-silicon species **1a** and **5**. Although no intermediates on the way to **6** were detected in the room temperature reaction, by analogy with the corresponding digermane reaction [3] it is reasonable to propose that the open chain $Si_2Co_6(CO)_{20}$ (**3**) is initially formed and subsequent loss of CO and rearrangement leads to **6**. This suggestion was supported by the results of a reaction carried out for 8 days at 4°C, from which a yellow product with an infrared spectrum similar to that of $Ge_2Co_6(CO)_{20}$ was detected. Further characterisation of **3** was hampered by conversion to **6**, which occurs more readily than the corresponding rearrangement of the germanium analogue.

The characterisation of **6**, the first silicon example of the extensive *closo*-E_2M_4 family, was by comparison of spectroscopic features with those for the analogous germanium compound [3] and by a single crystal X-ray crystal structure determination, details of which have been given elsewhere [10].

When the reaction at a lower Co : Si ratio was examined at 4°C for 8 days **1a** and **3** were found, together with a new product accounting for about 40% of the silicon. This species had not been detected in any of the other silane reactions, and no directly analogous species had been isolated from digermane systems. Initial indication of the overall structure was provided by the similarity of the infrared spectrum to that of $Me_2Ge_3Co_6(CO)_{20}$ [17], and it was fully characterised crystallographically as $H_2Si_3Co_6(CO)_{20}$, (**4**), an open, linked-triangle cluster. The structure is discussed in detail below, but the most interesting feature is the retention of Si–H groups in a cluster, since Si–H bonds are reactive and so provide sites for subsequent modification and extended cluster-building reactions.

It is evident that there are several parallel reactions which occur simultaneously in the reactions of disilane with $Co_2(CO)_8$. The reactions are relatively slow at room temperature and all the products initially involve the replacement of Si–H bonds with Si–$Co(CO)_4$ ones. With an excess of $Co_2(CO)_8$ at lower temperatures and with shorter reaction times, there is early cleavage of the Si–Si bond to give mainly the mono-silicon species **1a** together with late cleavage of the Si–Si leading to incorporation of both Si atoms in the same cluster, giving initially **3**. At higher temperatures and/or over longer reaction times increasing amounts of **5** and **6** (the decarbonylation products of **1a** and **3** respectively) are formed.

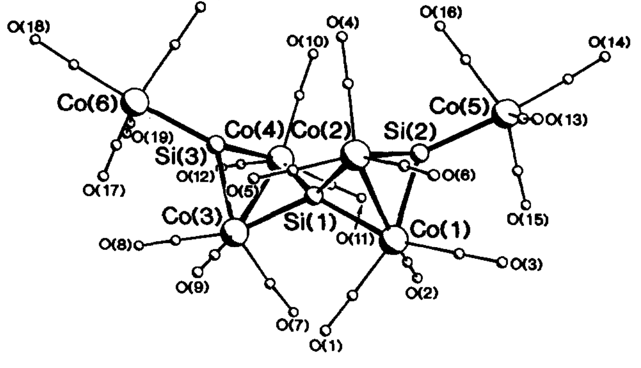

Fig. 1. A perspective view of one of the two independent molecules of $H_2Si_3Co_6(CO)_{20}$, (**4**) showing atom labelling.

When there is insufficient $Co_2(CO)_8$ to replace all the Si–H bonds then the new cluster **4** can be isolated. This has three silicon atoms incorporated in it, and is perhaps a surprising species to be formed from a reaction of a disilane precursor. However a trigermanium cluster $Ge_3Co_8(CO)_{26}$ has been isolated from the reaction of digermane with $Co_2(CO)_8$, so there is some precedent for this type of assembly [3]. Routes to **4** can only be speculative at this stage, but again there are hints from the germanium system, where it was shown that either or both of the μ-CO groups of μ_4-$Ge[Co_2(CO)_7]_2$ can be replaced by μ-GeR_2 groups when H_2GeR_2 is used [21]. If the reaction between Si_2H_6 and $Co_2(CO)_8$ led to a mixture of $Si[Co_2(CO)_7]_2$ and $H_3SiCo(CO)_4$, combination of these by a similar reaction could give **4**.

The crystal structure of **4** showed that there are two independent molecules in the asymmetric unit but the only significant difference between them is in the relative orientation of the $Co(CO)_4$ group attached to Si(2). The following discussion is based on average values for the bond parameters. Figure 1 gives the atom labelling scheme and shows that the structure is based on four $SiCo_2$ triangular units, linked alternately through the Si apices and the Co–Co edges. Each of the outer silicon atoms is bonded to a terminal $Co(CO)_4$ unit. The hydrogen atoms were not located in the X-ray structure analysis, but there are obvious empty sites on the outer silicon atoms where they will lie (see Fig. 2).

The only other linked-triangular $SiCo_2$ cluster structurally-defined is **1a**, [8] although for germanium examples of clusters with two (μ_4-$Ge[Co_2(CO)_7]_2$ [2]), four ($Ge[Co_2\{GeMe_2\}(CO)_6]_2$ [21]) and six ($Ge_3Co_8(CO)_{26}$ [4]) $GeCo_2$ triangles are established crystallographically. Complex **4** can be regarded as a derivative of **1a**,

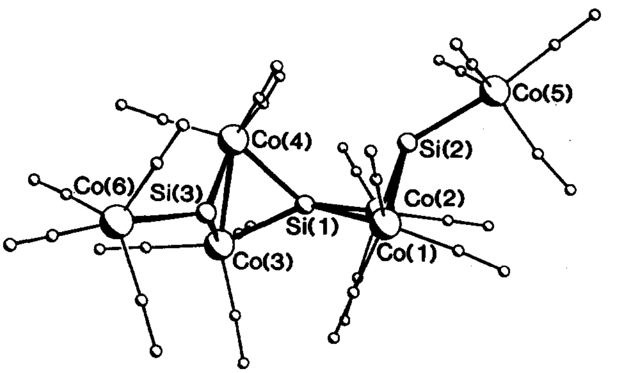

Fig. 2. An alternative view of $H_2Si_3Co_6(CO)_{20}$, (4) showing the apparently vacant sites on Si(2) and Si(3) where the H atoms will be bonded.

with the two μ-CO groups replaced by μ-Si(H)Co $(CO)_4$. Three distinct isomers of **4** can be envisaged, depending on the relative orientations of the H and $Co(CO)_4$ groups on the outer silicon atom; the crystal structure shows the least sterically hindered one, with the two Si–H bonds directed towards the centre of the molecule and the two Si–$Co(CO)_4$ groups directed outwards.

The Si–Co bonds within the triangular units of **4** lie in the range 2.281–2.321 Å, with no significant differences between the inner and outer triangles. The average distance, 2.298 Å, is marginally longer than the Si–Co distance (average 2.289 Å) in **1a**, probably reflecting a more crowded molecule overall. The outer Si–Co bonds to the $Co(CO)_4$ groups average 2.365 Å, longer than the intra-triangle distances, and also longer than the Si–Co(terminal) distance in $(OC)_4SiCo_3(CO)_9$ (2.288 Å) [16] and that involving the five-coordinate silicon in **6** [10]. The average Co–Co bond length (2.613 Å) is longer than that in **1a** (2.528 Å), but that is expected because of the presence of two μ-Si atoms in **4** compared to one μ-Si and one μ-C across the Co–Co bonds of **1a**.

The dihedral angle between the two $SiCo_2$ triangles with a common silicon apex is 81° which is essentially the same as in **1a**. The dihedral angles between triangles with common Co–Co edges vary from 96.7 to 98.7°, maintaining Si ··· Si non-bonded distances of 2.83–2.86 Å, which are less than twice the Van der Waals radius of silicon, and are only marginally longer than the Si ··· Si distance in **6** [10], for which a weak bonding interaction is assumed by comparison with similar P_2Fe_4 clusters for which detailed calculations are available [22].

The two H-sites are well protected by the neighbouring CO groups and are well separated from each other. Thus elimination of H_2, or further reaction of Si–H to form Si–Co (and ultimately $Si_3Co_8(CO)_{26}$) is minimised, thus accounting for the isolation and relative stability of **4**.

3.1. *The reaction of $(H_3Si)_2O$ with $Co_2(CO)_8$*

Silanes of the type $RSiH_3$ react with $Co_2(CO)_8$ to give initially the partially closed cluster $RSi[Co(CO)_4]$-$Co_2(CO)_7$, which on mild heating loses CO to give $RSiCo_3(CO)_9$ [9]. It was therefore of interest to see if $(H_3Si)_2O$ would give two of these units combined through a Si–O–Si link. When $(H_3Si)_2O$ and $Co_2(CO)_8$, were allowed to react in hexane a number of products was formed. Apart from unchanged $Co_2(CO)_8$ and $Co_4(CO)_{12}$, the only positively identified species was μ_4-$Si[Co_2(CO)_7]_2$ (**1a**), which incorporated up to 60% of the silicon. This mono-silicon species was unexpected, since its formation must result from cleavage of the very strong Si–O bond in the siloxane under very mild conditions. Possibly the cobalt carbonyl catalyses the disproportionation of eqn. (2):

$$2H_3SiOSiH_3 \longrightarrow 3SiH_4 + SiO_2 \qquad (2)$$

with the SiH_4 forming **1a**. Greene and Curtis have reported Si–O bond rearrangements under mild conditions catalysed by the complex $(Ph_3P)_2(H)(CO)\overline{IrSiMe_2OSiMe_2}$, containing a four membered Ir–Si–O–Si cycle, so there is some precedent [11].

The only other silicon-containing product was a light-brown compound that could not be isolated in a form suitable for full characterisation. The infrared spectrum of this species (ν(CO) 2101w, 2089s, 2061s, 2046m, 2036sh, 2030vs, 2021m, 1846m) is similar to that of the fully characterised $PhGe[Co(CO)_4]Co_2(CO)_7$ (ν(CO) 2104w, 2082s, 2056s, 2044w, 2036s, 2025m, 2014m, 1998w, 1850w, 1835sh); the peak at 1846 cm^{-1} is especially characteristic of a $Co_2(CO)_7$ moiety [5]. We therefore tentatively suggest that this compound is the double cluster species **7**. Further support for this comes from the results of gentle heating. The light brown solution becomes deep red, and the infrared spectrum simplifies to give essentially only two strong peaks in the ν(CO) region, at 2054 and 2030 cm^{-1}. These compare with the strongest two peaks for $MeCCo_3(CO)_9$ [23] at 2052 and 2039 cm^{-1} and for $MeGeCo_3(CO)_9$ [24] at 2055 and 2045 cm^{-1}. The infrared data and deep red colour are therefore quite consistent with this compound being $O[SiCo_3(CO)_9]_2$, the expected decarbonylation product of **7**. However, once again attempts to isolate a pure sample were unsuccessful, so the assignment must remain tentative.

3.2. *The reaction of $(H_3Si)_2S$ with $Co_2(CO)_8$*

Reaction of the disilylthiane with cobalt carbonyl followed a completely different course from that found

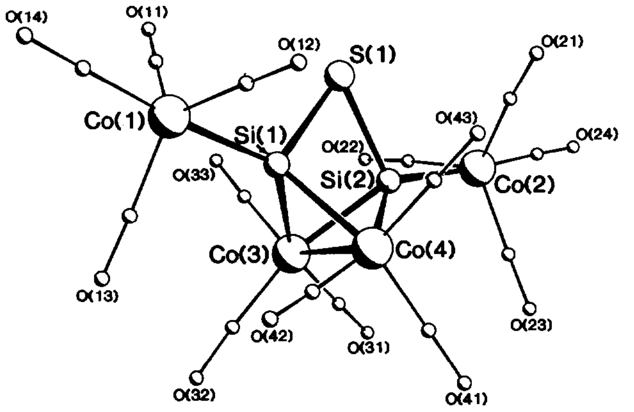

Fig. 3. The structure of $SSi_2Co_4(CO)_{14}$, (**8**).

for the disiloxane. Two clusters were formed, with relative yields that depended on the conditions. With longer reaction times or at higher temperatures up to 94% of the sulphur ended up in the well-known [18,19] cluster $(\mu_4\text{-}S)_2Co_4(CO)_{10}$. This compound has been isolated from various systems containing cobalt carbonyls and various sulphur-containing substrates so its presence here is not surprising. The other product, the formation of which is favoured by shorter reaction times, lower temperatures, and lower Co:Si ratios in the reaction mixture, was the novel cluster $SSi_2Co_4(CO)_{14}$, (**8**), which was characterised crystallographically. Figure 3 shows it to have a central "sawhorse" $Co_2(CO)_6$ unit doubly bridged by two silicon atoms, which are in turn linked by the sulphur atom. Each of the silicon atoms also carries a terminal $Co(CO)_4$ group. The doubly silicon-bridged Co–Co bond is 2.623 Å, longer, as expected, than the Co–Co distance in μ_4-Si $[Co_2(CO)_7]_2$ (**1a**) of 2.528 Å [8], but shorter than the doubly germanium-bridged bond in $Co_2[Ge(Me)Co(CO)_4]_2(CO)_6$ of 2.733 Å [6]. The internal Si–Co bonds average 2.301 Å, similar to those in the $SiCo_2$ triangles of **3** discussed above, while the external Si–Co bonds to the terminal $Co(CO)_4$ groups are 2.297 Å, which is significantly shorter than the corresponding bond in **4**. The most remarkable feature of the structure of **8** is the geometry of the SSi_2 unit. The S–Si bonds are 2.171 Å, slightly longer than usual (*ca.* 2.15 Å), while the Si–S–Si angle is an exceptionally acute 70.3°. In $S(SiH_3)_2$ the corresponding angle is 97.4° [25], and it is even larger for other disilylthianes such as $S(SiPh_3)_2$ (112°) [26]. The smallest Si–S–Si angle that has been previously reported is, to our knowledge, that in tetramethylcyclodisilyldithiane [27], where the constraints of the four-membered ring give a value of 82.5°, still much larger than that one in **8**. The acute angle at S in **8** means that the formally non-bonded Si · · · Si distance is a remarkable 2.498 Å, not much longer than the Si–Si bond in Si_2H_6 (2.32 Å) [28], and much shorter than the Si–Si bond in $Si_2{}^tBu_6$ (2.679 Å) [29]. The closest example in the literature for comparison is $Cp_2\overline{MoSiMe_2SSiMe_2}$, which has a much longer Si · · · Si distance of 2.87 Å and a Si–S–Si angle of 82.5° [30]. Even in metallocycles, such as $\overline{(dppe)PtSiMe_2OSiMe_2}$ [31] or $(Ph_3P)_2(H)(CO)\overline{IrSiMe_2OSiMe_2}$ [11], that are bridged by the smaller oxygen atom, the Si · · · Si distance is larger (2.549 and 2.567 Å, respectively) and the Si–O–Si angles are more normal (97.8 and 99.7° respectively). It appears therefore that there is a nett bonding interaction between the two silicon atoms in **8**, since if the interaction between them was repulsive they could move apart, at the same time relieving the apparently strained bond angle at the S atom, without any obvious adverse steric consequences in the rest of the molecule. Other examples of the SSi_2Co_2 core, and detailed calculations will be needed to provide full understanding of this so far unique cluster. The geometry adopted by **8** means that the sulphur atom is well exposed, and interesting donor behaviour may be expected.

The marked difference found for the reactions of $Co_2(CO)_8$ with $E(SiH_3)_2$ for E = O or S is interesting. In the E = O reactions there was no indication of any $(\mu_4\text{-}O)_2Co_4(CO)_{10}$ (an as-yet unknown cluster) nor of an analogue of **8**. Similarly in the E = S system there was no sign of $S[Si\{Co(CO)_4\}Co_2(CO)_7]_2$ (*cf.* **7**). One possible explanation relates to the preferred geometry of the Si–E–Si linkage. For Si–O–Si wide angles are normally found (*e.g.* 142° for $O(SiH_3)_2$ [32], or even 180° for $O(SiPh_3)_2$ [33] or $O[Si(Me)F\{Fe(CO)_2Cp\}]_2$ [34]) which would favour compounds such as **7** but which would not be accommodated so readily in a structure related to **8**. Conversely Si–S–Si bond angles are usually relatively acute, even in sterically crowded species (*e.g.* 110.5° in $S[Si(O^tBu)_3]_2$ [35] or 112° in $S(SiPh_3)_2$ [26]), so the Si–S–Si group can perhaps be incorporated more readily into a structure of type **8** than into an analogue of **7**.

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