Preparation and Carbonyl-substitution Reactions of Hexacarbonyldicobalt-complexed 1,3-Dioxa-2-silacyclohept-5-ynes and 1,3,8,10-Tetraoxa-2,9-disilacyclotetradeca-5,12-diynes. X-Ray Crystal Structure of $[(Ph_3P)(OC)_5Co_2\{\mu\text{-}(C_2CH_2OSiPh_2OCH_2)_2\}Co_2(CO)_5(PPh_3)]$†

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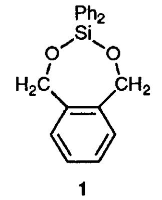
Reactions between $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)L^1L^2(CO)_4]$ [$L^1 = L^2 = CO$ or $L^1\text{–}L^2$ = bis(diphenylphosphino)methane (dppm)] and $SiR^1(R^2)Cl_2$ ($R^1 = R^2$ = Me or Ph; R^1 = Me, R^2 = Ph) afford hexacarbonyldicobalt-complexed 1,3-dioxa-2-silacyclohept-5-ynes which undergo carbonyl substitution in the case of $L^1 = L^2 = CO$ with PPh_3 or dppm. Fast-atom-bombardment (FAB) mass spectral evidence indicates that the 2,2-diphenyl-1,3-dioxa-2-silacyclohept-5-yne complex and its monophosphine-substituted derivative are dimers which is confirmed by the X-ray crystal structure of the latter, $[(Ph_3P)(OC)_5Co_2\{\mu\text{-}(C_2CH_2OSiPh_2OCH_2)_2\}Co_2(CO)_5(PPh_3)]$, in which the phosphine ligands occupy axial positions on opposite sides of the fourteen-membered ring. Only monomers are identified in the mass spectra of the other compounds, but evidence for unseparated higher oligomers as minor products is found in the NMR spectra of the 2,2-dimethyl-1,3-dioxa-2-silacyclohept-5-yne complex and its monophosphine and dppm derivatives.

When an alkyne co-ordinates to a mono- or poly-nuclear metal centre it undergoes geometric distortions. The acetylenic bond distance increases and the substituents bend back from their linear positions to give a cisoid structure in accord with the substantial perturbation caused by the bonding interaction to the metal centre or centres.[1] This deviation from linearity can have important consequences if the alkyne carries functional substituents. We have recently shown that co-ordination of the acetylenic bond of bis(diphenylphosphino)acetylene (dppa) to a tungsten centre enables the thereby distorted dppa to chelate *via* its phosphorus atoms to a $Mo(CO)_4$ fragment.[2]

In order to establish whether this effect has general utility we decided to investigate whether it could be applied to the synthesis of 1,3-dioxa-2-silacycloalkynes from co-ordinated acetylenic diols. The formation of 1,3-dioxa-2-silacycloalkanes from alkanediols and dichlorosilanes has been studied in considerable detail.[3] Many diols such as catechol, ethane-1,2-diols, propane-1,3-diols and butane-1,4-diols afford both monomeric and dimeric products which can, in favourable cases, be separated.[4] The relative stability of the cyclic products depends on the ring sizes involved as well as the substituents present on both the silicon and other ring positions. In general, bulky substituents are found to favour smaller ring sizes.

Of particular relevance to the work described in this paper are the compounds **1** and **2** formed by the reaction of benzene-1,2-dimethanol with dichlorodiphenylsilane.[4] Separation of **1** and **2** can be achieved by fractional crystallisation of the less-soluble dimer and the structures of both compounds have been established by X-ray crystallography.[5] Analogous reactions with dichloromethylphenylsilane and dichlorodimethylsilane afford mainly monomeric products.[4] It is found for 1,3-dioxa-2-silacycloheptanes that dimers are only isolated for 2,2-diphenyl compounds which are also the most stable monomers and it is assumed that two phenyl groups on the silicon atom confer stability by steric crowding or stabilisation of the silicon–oxygen bonds. The 2,2-dimethyl-1,3-dioxa-2-silacycloheptanes show a marked tendency to dimerise which is diminished by phenyl substitution at the silicon. The 2,2-diphenyl-substituted dimers are considered to have been produced during the initial reaction rather than by subsequent dimerisation of the monomers, *i.e.* the product distribution is under kinetic rather than thermodynamic control.[4]



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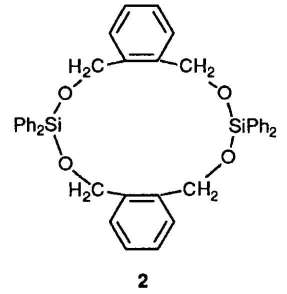

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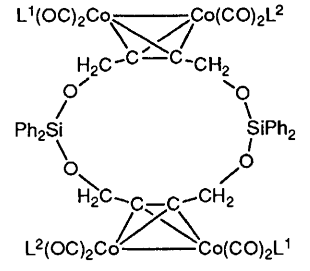
† μ-[1,2(5,6-η):3,4(12,13-η)-2,2,9,9-Tetraphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne]-bis[decacarbonyl-$1\kappa^3C,2\kappa^2C,3\kappa^3C,4\kappa C^2$-bis(triphenylphosphine)-$2\kappa P,4\kappa P$-tetracobalt($Co^1\text{–}Co^2,Co^3\text{–}Co^4$)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

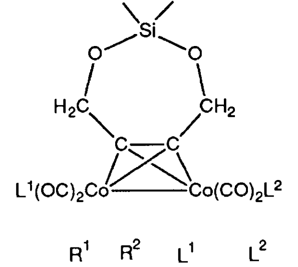
Table 1 Analytical[a] and physical data

Compound	Colour	Yield (%)	$\nu_{max}(CO)/cm^{-1}$	Analysis (%) C	Analysis (%) H
3	Red-orange	59	2097w, 2060s, 2034vs, 2018w[b]	47.8 (47.8)	2.4 (2.6)
4	Red-orange	48	2063s, 2014vs, 2000s, 1966w[c]	58.7 (59.6)	3.9 (3.7)
5	Purple	27	2017s, 1987vs, 1959s[c]	65.9 (65.6)	4.4 (4.4)
6	Red-orange	76	2026s, 1997vs, 1970s[c]	61.5 (61.4)	4.4 (4.1)
7	Red-orange	19	2026s, 1996vs, 1970s[c]	58.4 (58.7)	4.2 (4.2)
8	Red-orange[d]	68	2096m, 2059vs, 2034vs, 2029s, 2016w[b]		
9	Red-orange	35	2063s, 2015s, 1967w[c]	52.6 (52.6)	3.9 (3.8)
10	Purple	17	2017s, 1987vs, 1959vs[c]	61.0 (61.6)	4.4 (4.5)
11	Red-orange	29	2026s, 1996vs, 1969s[c]	54.8 (55.6)	4.0 (4.3)

[a] Calculated values are given in parentheses. [b] In light petroleum. [c] In dichloromethane. [d] Oil.



3 $L^1 = L^2 = CO$
4 $L^1 = CO$, $L^2 = PPh_3$



	R^1	R^2	L^1	L^2
5	Ph	Ph	PPh_3	PPh_3
6	Ph	Ph	$Ph_2PCH_2PPh_2$	
7	Ph	Me	$Ph_2PCH_2PPh_2$	
8	Me	Me	CO	CO
9	Me	Me	CO	PPh_3
10	Me	Me	PPh_3	PPh_3
11	Me	Me	$Ph_2PCH_2PPh_2$	

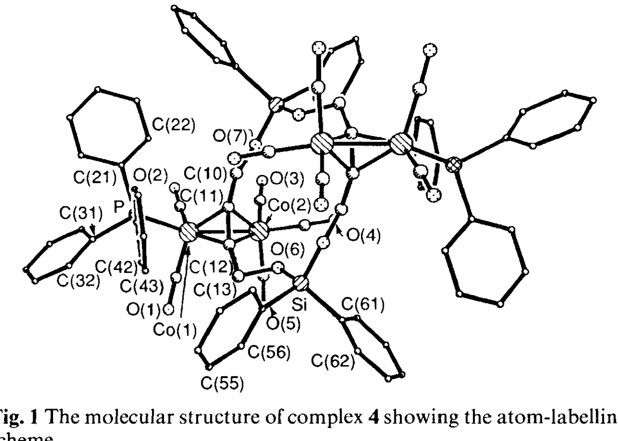


Fig. 1 The molecular structure of complex **4** showing the atom-labelling scheme

We decided to investigate whether 1,3-dioxa-2-silacycloheptynes could be formed from co-ordinated but-2-yne-1,4-diol. The complex $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(CO)_6]$ was chosen owing to its ready preparation[6] and the possibility of decomplexing the hexacarbonyldicobalt unit after cyclisation. A preliminary account has been made of some of the results described in this paper.[7]

Results and Discussion

The linear nature of but-2-yne-1,4-diol thwarts attempts to form cyclic products. For example, the reaction of bis(diethylamino)diphenylsilane with but-2-yne-1,4-diol in refluxing benzene results in the formation of an intractable polymer.

In contrast, reaction of equimolar quantities of $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(CO)_6]$ and $SiPh_2Cl_2$ at room temperature in the presence of 2 equivalents NEt_3 affords compound **3** in a yield of 59% after work-up (see Experimental section). Analytical and IR data for the new compounds are given in Table 1. The solution IR spectrum of **3** recorded in light petroleum is typical of $[Co_2(\mu\text{-alkyne})(CO)_6]$ derivatives.[8] The NMR spectra are also readily interpreted and show only one oligomer to be present (Table 2). The ^1H NMR spectrum contains a singlet at δ 5.26 assigned to the eight methylene protons which integrates in the expected ratio with the twenty aromatic protons. The $^{13}C\text{-}\{^1H\}$ NMR spectrum contains resonances at δ 66.6 assigned to the methylene carbons, δ 95.7 assigned to the acetylenic carbons and a broad resonance at δ 198.7 ppm assigned to the carbonyl ligands as well as aromatic resonances. The fast-atom-bombardment (FAB) mass spectrum of compound **3** shows an isotope envelope centred at m/z 1020 assigned to $[M - 3CO]^+$ and further carbonyl-loss peaks $M - n$CO (n = 6, 7, 9, 10 or 12) as well as m/z 553 $[\frac{M}{2} + H]^+$ and $[\frac{M}{2} - nCO]^+$ (n = 3–6), the base peak being $[\frac{M}{2} - 3CO]^+$. Similarly the electron-impact (EI) mass spectrum contains peaks due to the dimeric formulation, $M - n$CO (n = 6–12), and the monomeric formulation, $\frac{M}{2} - n$CO (n = 0–6). Cleavage of dimers to monomers is often observed in the mass spectra of 1,3-dioxa-2-silacycloalkanes.[9] Indeed, with 1,3-dioxa-2-silacyclohexanes the mass spectra of dimers only show monomeric peaks;[10] however monomers are rarely observed in the spectra of dimeric 1,3-dioxa-2-silacycloheptanes.[4]

Refluxing compound **3** with 2 equivalents of PPh_3 in benzene affords a mixture of **4** and **5** which can be separated by column chromatography (see Experimental section). Solution IR analysis indicates that **4** contains $Co_2(\mu\text{-alkyne})(CO)_5(PPh_3)$ units while **5** contains $Co_2(\mu\text{-alkyne})(CO)_4(PPh_3)_2$ units.[11] NMR measurements indicated that **4** and **5** are single isomers and will be discussed in detail after the crystal structure of **4**. Selected structural parameters for compound **4** are listed in Table 3 and the molecular structure is shown in Fig. 1. The molecule is dimeric with a crystallographically imposed inversion centre at the centre of the ring and can be viewed as a

Table 2 Hydrogen-1 and carbon-13 NMR data[a]

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
3	7.9–7.1 (m, 20 H, Ph), 5.26 (s, 8 H, CH_2)	198.7 (CO), 135–128 (Ph), 95.7 (C_2), 66.6 (CH_2)
4	7.6–7.2 (m, 50 H, Ph), 4.98 [d, 4 H, CH_2, *J*(HH) 15], 4.70 [d, 4 H, CH_2, *J*(HH) 15]	204.8 [Co(CO)$_2$], 201.3 [Co(CO)$_3$], 135–127 (Ph), 91.0 (C_2), 65.8 (CH_2)
5	7.4–7.2 (m, 40 H, Ph), 4.63 (s, 4 H, CH_2)	206.1 (CO), 136–127 (Ph), 90.8 (C_2), 65.8 (CH_2)
6	7.7–7.2 (m, 30 H, Ph), 5.22 [t, 4 H, CH_2, *J*(PH) 3], 3.28 [t, 2 H, PCH_2P, *J*(PH) 10]	204.4 (CO), 137–127 (Ph), 96.7 (C_2), 67.8 (CH_2), 41.2 [t, PCH_2P, *J*(PC) 20]
7	7.7–7.2 (m, 25 H, Ph), 5.13 (s, 4 H, CH_2), 3.32 [t, 2 H, PCH_2P, *J*(PH) 10], 0.46 (s, 3 H, Me)	204.6 (CO), 137–128 (Ph), 96,8 (C_2), 67.3 (CH_2), 41.4 [t, PCH_2P, *J*(PC) 20], −4.4 (Me)
8[d]	5.00 (s, 4 H, CH_2), 0.21 (s, 6 H, Me)	199.4 (CO), 96.0 (C_2), 65.4 (CH_2), −4.1 (Me)
9[d]	7.5–7.3 (m, 15 H, Ph), 4.85 [d, 2 H, CH_2, *J*(HH) 14], 4.41 [dd, 2 H, CH_2, *J*(HH) 14, *J*(PH) 2], 0.06 (s, 3 H, Me), −0.04 (s, 3 H, Me)	204.9 [Co(CO)$_2$], 201.4 [Co(CO)$_3$], 135–128 (Ph) 91.7 (C_2), 64.8 (CH_2), −2.4, −5.1 (Me)
10	7.6–7.2 (m, 30 H, Ph), 4.44 (s, 4 H, CH_2), −0.31 (s, 6 H, Me)	206.1 (CO), 136–128 (Ph), 91.3 (C_2), 64.7 (CH_2), −3.3 (Me)
11[d]	7.4–7.1 (m, 20 H, Ph), 4.98 [t, 4 H, CH_2, *J*(PH) 3], 3.31 [t, 2 H, PCH_2P, *J*(PH) 10], 0.22 (s, 6H, Me)	204.6 (CO), 138–128 (Ph), 97.0 (C_2), 66.8 (CH_2), 41.6 [t, PCH_2P, *J*(PC) 20], −3.8 (Me)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. [b] Measured in $CDCl_3$. [c] Measured in $CDCl_3$, hydrogen-1 decoupled. [d] Minor isomers present (see text).

Table 3 Selected internuclear distances (Å) and angles (°) for complex **4**. Atoms generated by symmetry are indicated by the suffix A

Co(1)–Co(2)	2.470(1)	C(10)–C(11)	1.478(6)	C(1)–O(1)	1.130(8)	Co(2)–C(5)	1.782(6)
Co(1)–C(2)	1.780(5)	C(12)–C(13)	1.483(6)	C(4)–O(4)	1.116(5)	Si–O(6)	1.599(3)
Co(2)–C(3)	1.800(5)	Co(1)–P	2.199(1)	C(10)–O(7)	1.394(6)	C(2)–O(2)	1.132(7)
Co(2)–C(11)	1.961(3)	Co(1)–C(11)	1.958(4)	C(13)–O(6)	1.419(5)	C(5)–O(5)	1.130(8)
Si–O(7A)	1.646(4)	Co(2)–C(4)	1.786(4)	Co(1)–C(1)	1.789(6)	C(11)–C(12)	1.324(6)
C(3)–O(3)	1.124(7)	Co(2)–C(12)	1.976(3)	Co(1)–C(12)	1.934(3)	O(7)–SiA	1.646(4)
Co(2)–Co(1)–C(11)	51.0(1)	Co(1)–C(12)–C(13)	140.4(3)	Co(1)–C(11)–C(10)	143.1(2)	C(61)–Si–O(7A)	109.8(1)
Co(1)–Co(2)–C(11)	50.9(1)	C(12)–C(13)–O(6)	109.7(4)	Co(2)–C(11)–C(12)	70.9(2)	Co(2)–C(3)–O(3)	178.6(4)
O(6)–Si–C(51)	112.6(1)	Co(2)–Co(1)–C(12)	51.6(1)	Co(1)–C(12)–C(11)	71.1(2)	C(11)–C(10)–O(7)	112.8(3)
O(6)–Si–O(7A)	109.0(2)	Co(1)–Co(2)–C(12)	50.1(1)	Co(2)–C(12)–C(13)	128.6(2)	Co(2)–C(11)–C(10)	132.5(2)
Co(1)–C(1)–O(1)	177.3(5)	O(6)–Si–C(61)	107.8(2)	Si–O(6)–C(13)	130.5(3)	C(10)–C(11)–C(12)	133.3(4)
Co(2)–C(4)–O(4)	178.7(4)	C(51)–Si–O(7A)	106.3(2)	C(11)–Co(1)–C(12)	39.8(2)	Co(2)–C(12)–C(11)	69.8(2)
Co(1)–C(11)–Co(2)	78.1(1)	Co(1)–C(2)–O(2)	178.1(5)	C(11)–Co(2)–C(12)	39.3(2)	C(11)–C(12)–C(13)	140.1(4)
Co(1)–C(11)–C(12)	69.1(2)	Co(2)–C(5)–O(5)	174.9(5)	C(51)–Si–C(61)	111.3(2)	C(10)–O(7)–SiA	124.1(3)
Co(1)–C(12)–Co(2)	78.3(1)						

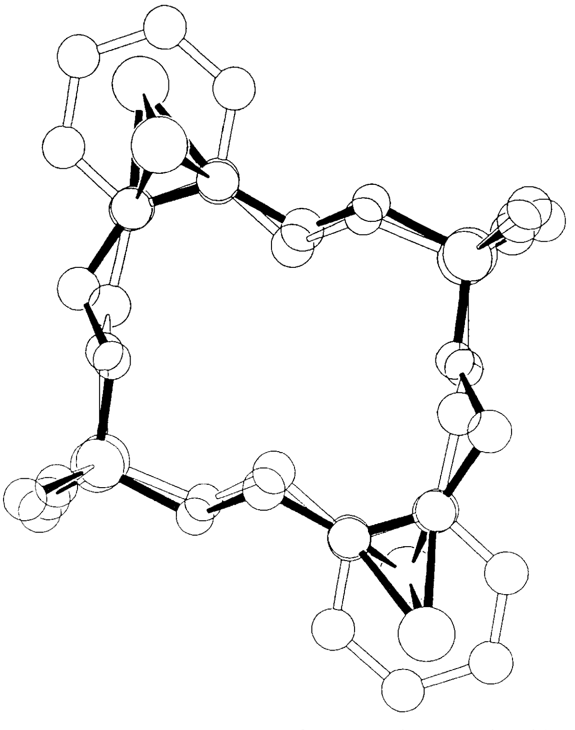


Fig. 2 Comparison of the structures of compounds **2** (open bonds) and **4** (filled bonds)

cyclic dimer of 2,2-diphenyl-1,3-dioxa-2-silahept-5-yne in which the acetylenic bonds are ligated to $Co_2(CO)_5(PPh_3)$ groups.

The phosphines occupy axial positions as expected for [Co_2(μ-alkyne)$(CO)_5$L] derivatives[11] and recently confirmed in the case of [Co_2{μ-HC≡CCH(OH)Ph}$(CO)_5(PPh_3)$].[12] The phosphine groups are positioned on opposite sides of the fourteen-membered ring to minimise steric interactions. All the bond lengths and angles about the pseudo-tetrahedral Co_2C_2 cores are within the ranges normally expected for these structures,[12–15] although the conformation of the ring results in the alkyne bend-back angles at C(11) [133.3(4)°] and C(12) [140.1(4)°] being somewhat disparate. Fig. 2 illustrates the similarity between the conformations of compounds **2** and **4** and highlights the similarity in geometries of benzene-1,2-dimethanol and the co-ordinated but-2-yne-1,4-diol. The major differences are caused by the Co_2C_2 tetrahedra being forced out of plane by the steric bulk of the triphenylphosphine groups.

The FAB mass spectrum of compound **4** contains a peak at *m*/*z* 1574 assigned to $[M + H]^+$ and carbonyl-loss peaks corresponding to $[M - n\mathrm{CO}]^+$ (n = 3–8). Peaks were also observed corresponding to the monomer at $[\frac{M}{2} - n\mathrm{CO}]$ (n = 0, 3–5). The NMR spectra show that the ring has conformational mobility in solution. Hence all four methylene groups are chemically equivalent, but the hydrogen atoms on each methylene are inequivalent producing an AB pattern in the ^{1}H NMR spectrum. No evidence is found in the NMR spectra for the presence of any other isomers or oligomers. Either FAB mass spectrometry is the only technique used which resolves the oligomers or, as seems more likely in the light of results discussed below, the compound fragments in the mass spectrometer.

Compound **5** also only shows one set of resonances in the NMR spectra, but in this case using FAB mass spectroscopy peaks at *m*/*z* 992 $[M - CO]^+$ and $[M - nCO]^+$ (n = 2–4) due to the monomeric formulation depicted could be detected with no evidence for higher oligomers. The similarity of the IR spectrum of **5** to other known $[Co_2(\mu\text{-alkyne})(CO)_4L_2]$ derivatives[11] suggests that the phosphine ligands occupy the two axial positions as observed in the X-ray structure of $[Co_2(\mu\text{-}HCCH)(CO)_4(PMe_3)_2]$.[14] The presence of bulky triphenylphosphine groups in both axial positions would favour fragmentation of the dimer to a monomer and it is assumed that this oligomer gives rise to the observed NMR signals. The other, less likely, possibility is that **5** is purely dimeric in solution, but fragments entirely in the mass spectrometer.

The hexacarbonyldicobalt complex **3** is not very thermally robust as indicated by the formation of **4** and **5** when only **4** would be expected from the reaction stoichiometry.[11] Attempts to produce a monosubstituted triphenylphosphine derivative of **3** were unsuccessful. Reaction of compound **3** with 1 mole equivalent of PPh_3 in refluxing benzene for 10 min affords a solution whose IR spectrum suggests the presence of $Co_2(CO)_6$ and $Co_2(CO)_5(PPh_3)$ units, but chromatography results in the isolation of **4** and unreacted **3**.

Reaction of $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(\mu\text{-dppm})(CO)_4]$ (dppm = $Ph_2PCH_2PPh_2$) with $SiPh_2Cl_2$ affords compound **6** which again exists in solution as a single isomer and FAB mass spectrometry detects monomeric ions at $[M + H - nCO]^+$ (n = 0 or 1) and $[M - nCO]^+$ (n = 2–4). The dppm ligand in $[Co_2(\mu\text{-alkyne})(\mu\text{-dppm})(CO)_4]$ derivatives is known to occupy two equatorial positions.[11,15] The NMR spectra of **6** indicate that an effective mirror plane containing the silicon atom and the Co–Co bond is generated on the NMR time-scale as has been observed in other $[Co_2(\mu\text{-alkyne})(\mu\text{-dppm})(CO)_4]$ derivatives.[16] Phosphorus coupling is observed to the methylene resonance which occurs at δ 5.22 [*J*(PH) 3 Hz]. Substitution of two carbonyl ligands by dppm in compound **3** affords a product indistinguishable from **6** and reaction of **3** with only 1 equivalent of dppm affords a mixture of **6** and unreacted **3**. Reaction of $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(\mu\text{-dppm})(CO)_4]$ with $SiMe(Ph)Cl_2$ affords **7** in a similar manner to **6**, again as a single apparently monomeric, isomer.

In contrast the dimethylsilane derivatives **8**–**10** show the presence of more than one oligomer in their NMR spectra even after work-up (see Experimental section). For example, reaction of $SiMe_2Cl_2$ with $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(CO)_6]$ followed by slow column chromatography of the residue using a Florisil support eluting with light petroleum affords **8** as a red-orange oil. The mass spectrum of compound **8** contains a peak at *m*/*z* 428 corresponding to the molecular ion and successive carbonyl-loss peaks are also observed. No peaks significantly above noise level are detected at higher mass, however, the ^1H NMR spectrum reveals the presence of more than one oligomer. The major constituent of the mixture (*ca.* 80%) has a resonance due to the four equivalent methylene protons at δ 5.00 and a resonance due to the six equivalent methyl protons at δ 0.21 (Table 2). Two other sets of resonances at δ 4.96 and 0.20 and at δ 4.93 and 0.14 account for approximately 15 and 5% of the product distribution respectively. It is postulated that these signals are due to the presence of oligomers, possibly a dimer and trimer of **8**. A shift to high field of approximately 0.2 ppm of the methylene resonances has been observed for 1,3-dioxa-2-silacyclohexanes upon dimerisation.[10] The $^{13}C\text{-}\{^1H\}$ NMR spectrum also shows a mixture of products. The major isomer has resonances assigned to the methylene carbons at δ 65.4 and methyl carbons at −4.1 ppm as well as acetylenic carbon resonances at δ 96.0 and the carbonyl ligands at 199.4 ppm. The minor components display methylene resonances at δ 63.4 and 63.2 ppm and methyl resonances at δ −3.3 and −1.4 ppm, again to high field of the monomer. Only one additional acetylenic resonance is observed at δ 94.8 ppm possibly due to overlap or the difficulty of detecting these weak signals, and no additional carbonyl resonances are observed, presumably due to overlap of these characteristically broad signals.

Reaction of compound **8** with 1 equivalent of triphenylphosphine in refluxing benzene results in the formation of a separable mixture of **9** and **10**. Only the monomeric formulation depicted could be detected in the FAB mass spectrum of **9**, but again NMR spectroscopy shows that the monomer only accounts for *ca.* 80% of the sample. In addition to the signals in Table 2, the ^1H NMR spectrum contains a second distinctive set of methylene resonances, δ 4.57 [d, *J*(HH) 13] and 4.26 [dd, *J*(HH) 13, *J*(PH) 2 Hz], to high field of the signals assigned to the monomer. In an analogous fashion to **5**, compound **10** appears to be a single isomer as indicated by NMR spectroscopy and only peaks assignable to the monomer are observed in the FAB mass spectrum.

Compound **11** is prepared in a similar manner to **6** and **7**. Unlike the last two compounds this dppm-substituted derivative shows two isomers in its ^1H NMR spectrum, although again only a monomer was detected by FAB mass spectroscopy. The second isomer is characterised by a methylene resonance at δ 4.83 [*J*(PH) 3 Hz] which is 0.15 ppm to high field of the monomer (Table 2) and is assumed to be a dimer. Integration of the spectrum indicates that the dimer accounts for *ca.* 6% of the total sample. Interestingly the methylene resonance of the dppm in the dimer occurs at δ 3.59 [*J*(PH) 6 Hz], shifted by *ca.* 0.3 ppm from the position in the monomers **6**, **7** and **11**, and also the coupling constant is reduced from 10 Hz in the other three compounds. Compound **11** was chosen to study the possible interconversion of oligomers in these systems because the bridging dppm ligands confer extra thermal stability compared to the other derivatives.[17] Refluxing **11** in benzene for 1 h, filtering the solution through a Florisil pad, and re-recording the ^1H NMR spectrum results in a small decrease in the amount of dimer to *ca.* 5%. Such a change is small compared to the accuracy of the integration and it is unclear whether it is due to isomerisation or selective decomposition of the dimer. The ^1H NMR spectrum recorded in C_6D_6 is found to be unchanged when recorded at 60 °C or upon standing for several weeks. It is concluded that isomerisation in these systems is slow or possibly non-existent and that the product distribution is determined by kinetic factors.

Attempts to remove the dicobalt fragments from the acetylenic bonds of compound **3** using Ce^{4+} or Me_3NO[18] have not facilitated the isolation of the metal-free heterocycle. Dialkylsilyl groups are used as protecting groups for diols and are readily removed under mild conditions, possibly accounting for the failure of these reactions.[19]

Experimental

The experimental techniques used and the instrumentation employed have been described previously.[20] The compound $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(CO)_6]$ was prepared by a literature method[6] from $[Co_2(CO)_8]$ purchased from Strem, while the dichlorosilanes were purchased from Aldrich. Analytical and other data for the new compounds are given in Tables 1 and 2.

Preparation of $[Co_4\{\mu\text{-}(C_2CH_2OSiPh_2OCH_2)_2\}(CO)_{12}]$.—To a solution of $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(CO)_6]$ (0.46 g, 1.24 mmol) in toluene (15 cm^3) was added NEt_3 (0.34 cm^3, 2.44 mmol) and $SiPh_2Cl_2$ (0.26 cm^3, 1.23 mmol). The mixture was stirred for 0.5 h and then filtered through a Florisil pad (1.5 × 3 cm) before removing the solvent *in vacuo*. Chromatography of the residue on a Florisil column (1.5 × 15 cm) eluting with light petroleum (b.p. 40–60 °C) afforded a red eluate which upon removal of the solvent *in vacuo* gave compound **3** (0.40 g, 0.36 mmol).

Reaction of $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(CO)_6]$ *with* $SiMe_2Cl_2$.—To a solution of $[Co_2(\mu\text{-}HOCH_2C_2CH_2OH)(CO)_6]$ (0.32 g, 0.86 mmol) in toluene (20 cm^3) was added

Table 4 Atomic positional (fractional coordinates) parameters (× 10^4) with estimated standard deviations in parentheses, for compound **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	756(1)	6 744(1)	8 254(1)	C(26)	−3 244(4)	4 623(3)	5 516(3)
Co(2)	2 561(1)	8 690(1)	9 297(1)	C(31)	−1 753(3)	4 057(3)	6 988(3)
P	−1 404(1)	5 550(1)	7 420(1)	C(32)	−2 591(4)	3 331(3)	7 344(3)
Si	132(1)	9 619(1)	12 060(1)	C(33)	−2 855(5)	2 195(4)	6 932(4)
C(1)	1 182(5)	5 887(3)	8 779(4)	C(34)	−2 307(5)	1 783(4)	6 168(4)
O(1)	1 437(5)	5 367(3)	9 144(3)	C(35)	−1 474(6)	2 479(4)	5 819(4)
C(2)	1 379(4)	6 571(4)	7 140(3)	C(36)	−1 165(5)	3 630(3)	6 234(3)
O(2)	1 786(4)	6 493(4)	6 438(3)	C(41)	−2 656(3)	5 738(3)	8 144(2)
C(3)	3 380(4)	8 969(4)	8 336(4)	C(42)	−2 587(4)	5 615(3)	9 054(3)
O(3)	3 899(5)	9 166(3)	7 747(3)	C(43)	−3 471(4)	5 822(3)	9 637(3)
C(4)	2 954(4)	10 114(3)	10 142(3)	C(44)	−4 419(5)	6 158(3)	9 345(3)
O(4)	3 176(4)	11 001(3)	10 662(3)	C(45)	−4 497(4)	6 298(3)	8 457(3)
C(5)	3 596(4)	8 338(4)	10 036(4)	C(46)	−3 617(4)	6 089(3)	7 852(3)
O(5)	4 173(4)	8 093(3)	10 537(3)	C(51)	−1 377(3)	8 534(3)	12 190(2)
C(10)	−252(4)	8 745(3)	8 541(3)	C(52)	−2 677(4)	8 506(3)	12 055(3)
C(11)	571(3)	8 171(3)	8 767(3)	C(53)	−3 785(4)	7 673(3)	12 135(3)
C(12)	763(3)	7 863(3)	9 513(3)	C(54)	−3 625(4)	6 838(3)	12 353(3)
C(13)	392(4)	7 953(3)	10 489(3)	C(55)	−2 347(4)	6 838(3)	12 478(3)
O(6)	678(3)	9 095(2)	11 103(2)	C(56)	−1 235(4)	7 673(3)	12 405(3)
O(7)	393(3)	9 469(2)	8 100(2)	C(61)	1 591(3)	10 357(3)	13 215(2)
C(21)	−2 084(3)	5 543(3)	6 212(2)	C(62)	1 340(4)	10 550(3)	14 170(3)
C(22)	−1 459(4)	6 472(3)	6 001(3)	C(63)	2 397(5)	11 103(3)	15 046(3)
C(23)	−2 025(5)	6 450(4)	5 084(3)	C(64)	3 730(5)	11 480(3)	14 984(3)
C(24)	−3 164(5)	5 526(4)	4 398(3)	C(65)	4 027(4)	11 312(4)	14 066(4)
C(25)	−3 774(4)	4 609(4)	4 610(3)	C(66)	2 956(4)	10 747(3)	13 183(3)

NEt_3 (0.24 cm^3, 1.73 mmol) and $SiMe_2Cl_2$ (0.105 cm^3, 0.86 mmol). The mixture was stirred for 0.5 h and then filtered through a Celite pad. The solvent was removed *in vacuo* and the residue chromatographed on a Florisil column (1.5 × 15 cm) eluting with light petroleum. Removal of the solvent *in vacuo* from the red-orange eluate afforded an orange oil (0.25 g) containing compound **8** and related oligomeric species.

Carbonyl Substitution Reactions.—A solution of compound **3** (0.16 g, 0.14 mmol) and PPh_3 (0.08 g, 0.29 mmol) in benzene was stirred for 0.5 h after which time solution IR spectra showed that all the starting material had been consumed. The solvent was removed *in vacuo* and the residue chromatographed on a Florisil column (1.5 × 15 cm). Elution with light petroleum–dichloromethane (4:1) afforded a red-orange band followed by a purple-red band. Removal of the solvent *in vacuo* from the first band followed by crystallisation from CH_2Cl_2–light petroleum afforded crystals of compound **4** (0.11 g, 0.07 mmol). Similar work-up of the second band afforded crystals of **5** (0.08 g, 0.04 mmol). The carbonyl-substitution reactions of **8** were performed in a similar manner.

Preparation of $[Co_2\{\mu\text{-}C_2CH_2OSiPh_2OCH_2\}(\mu\text{-dppm})(CO)_4]$.—Carbonyl substitution of $[Co_2\{\mu\text{-}HOCH_2C_2CH_2OH\}(CO)_6]$ by dppm was performed by refluxing equimolar quantities of the aforementioned compounds in benzene for 0.5 h. To a solution of $[Co_2\{\mu\text{-}HOCH_2C_2CH_2OH\}(\mu\text{-dppm})(CO)_4]$ (0.20 g, 0.29 mmol) in toluene (20 cm^3) was added NEt_3 (0.08 cm^3, 0.58 mmol) and $SiPh_2Cl_2$ (0.06 cm^3, 0.29 mmol). After stirring for 0.25 h the solution was filtered through a Florisil pad and the solvent removed *in vacuo*. The residue was chromatographed on a Florisil column (1.5 × 15 cm) eluting with light petroleum–CH_2Cl_2 (1:1). The red eluate was concentrated to *ca.* 1 cm^3 and addition of light petroleum (*ca.* 20 cm^3) afforded crystals of compound **6** (0.19 g, 0.22 mmol). The compounds **7** and **11** were prepared in a similar manner.

Crystal Structure Determination of $[(Ph_3P)(OC)_5Co_2\{\mu\text{-}(C_2CH_2OSiPh_2OCH_2)_2\}Co_2(CO)_5(PPh_3)]$ **4**.—Crystals of complex **4** were obtained by solvent diffusion from light petroleum–CH_2Cl_2 as black prisms with crystal dimensions *ca.* 0.61 × 0.52 × 0.42 mm. Data were collected using a Nicolet *P*3 diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å). Of the 7087 data collected (Wyckoff ω-scans, $2\theta \leqslant 50°$), 4815 unique data had $F \geqslant 5\sigma(F)$, and only these were used for the structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects the latter by a method based upon azimuthal scan data.[21]

Crystal data. $C_{78}H_{58}Co_4O_{14}P_2Si_2$, $M = 1573.2$, triclinic, space group $P\bar{1}$, $a = 10.748(3)$, $b = 13.969(4)$, $c = 14.509(4)$ Å, $\alpha = 110.80(2)$, $\beta = 95.46(2)$, $\gamma = 111.48(2)°$, $U = 1829.8(8)$ Å^3, $Z = 1$, $D_c = 1.43$ g cm^{-3}, $F(000) = 804$, μ(Mo-Kα) = 10.3 cm^{-1}.

The structure was solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. The complex has crystallographically imposed $\bar{1}$ symmetry. All non-hydrogen were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (U = 0.08 Å^2). Refinement by full-matrix least squares led to $R = 0.039$ ($R' = 0.041$) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.7 or < -0.3 e Å^{-3}.

All calculations were performed on a Digital Micro Vax computer with the SHELXTL system of programs.[21] Scattering factors with corrections for anomalous dispersion were taken from ref. 22. Atom coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles. Structure factors are available from the authors.

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