

**Preparation of Organosilicon Derivatives of Cobalt-complexed
But-2-yne-1,4-diol. X-Ray Crystal Structure of
[Co₂(CO)₅(PPh₃)₂{μ-C₂(CH₂)₂O₂(SiPh₂)₂O₂(CH₂)₂C₂}Co₂(CO)₅(PPh₃)₂]**

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Reactions of [Co₂(μ-HOCH₂C₂CH₂OH)(CO)₆] with diorganodichlorosilanes in the presence of triethylamine afford hexacarbonyldicobalt-complexed 1,3-dioxa-2-silacycloalkynes.

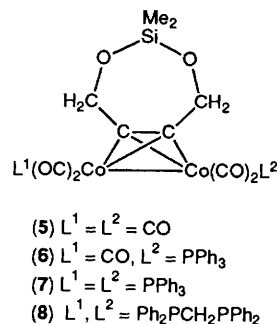
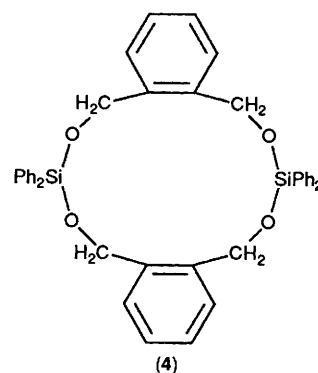
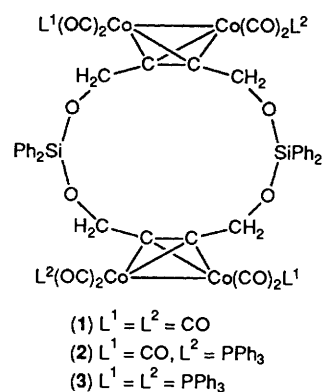
The nature of the compounds formed from the reactions of diols with dichlorosilanes has been studied in considerable detail.¹⁻⁴ Many diols such as catechol, ethane-1,2-diols, propane-1,3-diols, and butane-1,4-diols afford both monomeric and dimeric products which can, in favourable cases, be separated.¹⁻⁴ 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.

The linear nature of but-2-yne-1,4-diol thwarts attempts to form cyclic products. For example, the interaction of bis-diethylaminodiphenylsilane and this acetylenic diol in refluxing benzene results in the formation of an intractable polymer.

It is well known that co-ordinated alkynes are distorted from linear geometry and recently this distortion has been utilised in the formation of cyclic hydrocarbons⁵ and novel metallacyclic complexes.⁶ Reaction of [Co₂(μ-HOCH₂C₂CH₂OH)(CO)₆] with Ph₂SiCl₂ in the presence of NEt₃ affords (1). Refluxing (1) with PPh₃ in benzene affords a mixture of (2) and (3) which can be separated by column chromatography on Florisil.[†] The structure of (2) has been established by a single-crystal X-ray diffraction study and is shown in Figure 1.[‡] The molecule is dimeric, with a crystallographically imposed inversion centre at the centre of the ring and can be viewed as a cyclic dimer of 2,2-diphenyl-1,3-dioxa-2-silahept-5-yne in which the acetylenic bond is ligated to Co₂(CO)₅(PPh₃). The phosphines occupy axial positions as expected for [Co₂(μ-alkyne)(CO)₅(PR₃)] derivatives⁷ and the structure closely parallels that of (4)³ indicating a similarity

between the geometries of the co-ordinated alkyne and benzene-1,2-dimethanol. The FAB mass spectrum of (2) contains a peak at *m/z* 1574 assigned to (M + H)⁺.

In contrast, the complexes (5)–(8) obtained by analogous reactions with Me₂SiCl₂ only show peaks assignable to the monomeric formulation in their mass spectra. However, the presence in solution of isomers which are inseparable by column chromatography is revealed by NMR spectroscopy. For example, the ¹H NMR spectrum of (5) contains three methylene resonances at δ 5.00, 4.96, and 4.93 and three



[†] Selected spectroscopic data: Compound (1): ν_{CO} (light petroleum) 2097w, 2060s, 2034vs, and 2018w cm⁻¹; NMR: ¹H (CDCl₃), δ 7.9–7.1 (m, 20H, Ph) and 5.26 (s, 8H, CH₂); ¹³C{¹H} (CDCl₃), δ 198.7 (CO), 135–128 (Ph), 95.7 (C₂), and 66.6 (CH₂).

Compound (2): ν_{CO} (CH₂Cl₂) 2063s, 2014vs, 2000s, and 1966w cm⁻¹; NMR: ¹H (CDCl₃), δ 7.6–7.2 (m, 50H, Ph), 4.98 (d, 4H, CH₂, J_{HH} 15 Hz), and 4.70 (d, 4H, CH₂, J_{HH} 15 Hz); ¹³C{¹H} (CDCl₃), δ 204.8 [Co(CO)₂], 201.3 [Co(CO)₃], 135–127 (Ph), 91.0 (C₂), and 65.8 (CH₂).

Compound (3): ν_{CO} (CH₂Cl₂) 2017s, 1987vs, and 1959s cm⁻¹; NMR: ¹H (CDCl₃), δ 7.4–7.2 (m, 80H, Ph) and 4.63 (s, 8H, CH₂); ¹³C{¹H} (CDCl₃) δ 206.1 (CO), 136–127 (Ph), 90.8 (C₂), and 65.8 (CH₂).

[‡] Crystal data for (2): C₇₈H₅₈Co₄O₁₄P₂Si₂, M = 1573.2, triclinic, space group P1, a = 10.748(3), b = 13.969(4), c = 14.509(4) Å, α = 110.80(2), β = 95.46(2), γ = 111.48(2)°, U = 1829.8(8) Å³, Z = 1, D_c = 1.43 g cm⁻³, F(000) = 804, μ(Mo-Kα) = 10.3 cm⁻¹, R = 0.039 (R_w = 0.041) for 4815 unique absorption-corrected intensities [293 K, Wyckoff ω-scans, 2θ ≤ 50°, F ≥ 5σ(F), Mo-Kα X-radiation (λ = 0.71069 Å)]. Data were collected using a Nicolet P3 diffractometer and the structure was solved by Patterson and Fourier methods with full-matrix least-squares refinement. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1. Structure factors are available from the authors.

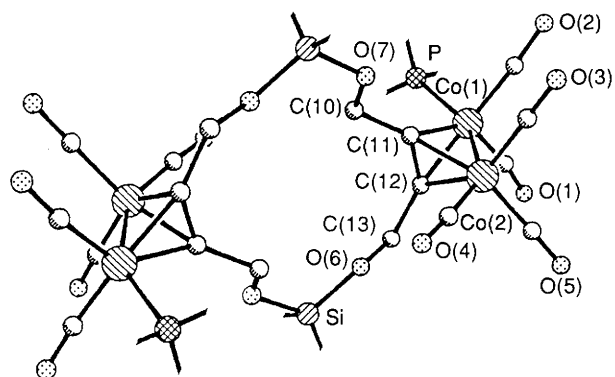


Figure 1. Molecular structure of (2). Phenyl groups omitted for clarity. Dimensions: Co(1)–Co(2) 2.470(1), Co(1)–P 2.199(1), Co(1)–C(11) 1.958(4), Co(1)–C(12) 1.934(3), Co(2)–C(11) 1.961(3), Co(2)–C(12) 1.976(3), Si–O(6) 1.599(3), Si–O(7) 1.646(4), C(10)–C(11) 1.478(6), C(11)–C(12) 1.324(6), C(12)–C(13) 1.483(6) Å; angles: O(6)–Si–O(7) 109.0(2), C(10)–C(11)–C(12) 133.3(4), C(11)–C(12)–C(13) 140.1(4)°.

corresponding methyl resonances at δ 0.21, 0.20, and 0.14 in the approximate ratio 16:3:1. It is postulated that the major isomer is a monomer while the other two are oligomers. Similar shifts to higher field upon dimerisation have been observed in the case of 2,2-diorgano-1,3-dioxo-2-silaheptanes.¹ As yet no evidence has been obtained for the interconversion of these isomers.

So far attempts to remove the dicobalt fragments from the acetylenic bonds of (1) using Ce^{4+} or Me_3NO 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.⁸ Research is currently in progress to use alkyne co-ordination complexes to prepare new macrocyclic ethers and thioethers which would be expected to decomplex cleanly.

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