Preparation of Hexacarbonyldicobalt-Complexed 1,3-Dioxa-2-silacycloheptynes

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The reaction between 2-butyne-1,4-diol-hexacarbonyldicobalt and a series of dichlorodialkylsilanes (R = Me, Et, CH=CH$_2$, and Ph) in the presence of triethylamine results in the formation of the corresponding cobalt-complexed 1,3-dioxa-2-silacycloheptynes, **3**−**7**, as the major products. Complexed silacyclononynes, **8** and **9**, and a spirocyclic analogue **10**, have also been prepared and characterized. The solid-state structures of **3** and **10** have been determined by X-ray diffraction studies.

Introduction

The preparation of polymers that contain pendant and/or backbone transition-metal fragments has recently received much attention, since these materials often possess unique physical and chemical properties.[1] Recently we reported the preparation of novel transition-metal-functionalized alkynylsilane-based oligomers and polymers, which were efficiently assembled in an iterative manner via hydrosilylation.[2] The molecular weights that could be achieved using this approach were limited by the degree to which the stoichiometric ratio of the difunctional starting materials could be matched. In an attempt to develop alternative routes to such materials, and with the specific goal of preparing higher molecular weight polymers, we sought to prepare monomeric ring systems that could be subjected to traditional ring-opening polymerization techniques.

The facile reaction between octacarbonyldicobalt and alkynes, yielding pseudo-tetrahedral dimetallic clusters, is a well-defined facet of organometallic chemistry,[3] which has been exploited both in the protection of alkynes[4] and as a means of favorably effecting geometric distortions in these moieties.[5] Extending this methodology to the formation of metal-complexed silacycloalkynes from coordinated diols and dichlorodialkylsilanes represents an attractive route to a variety of organometallic rings comprising silicon and cobalt. Moreover, oxidative decomplexation of the metal fragment in these molecules would provide an efficient synthetic pathway to an interesting class of heteroatom-substituted cycloalkynes.

Cragg et al. previously reported that the use of alkyne complexation to facilitate ring formation, in the synthesis of cobalt-complexed 1,3-dioxa-2-silacycloheptynes **1**, leads rather to the generation of *dimeric* 14-membered ring species, analogous to **2** in Scheme 1.[6] The potential utility of compounds such as **1**, and the hope that we could develop synthetic routes to favor the formation of **1**, prompted us to reexamine their work. Herein we report the synthesis and characterization of a series of cobalt-complexed 1,3-dioxa-2-silacycloheptynes.

Results and Discussion

The desired cobalt-complexed 1,3-dioxa-2-silacycloalkynes were successfully prepared using synthetic methods similar to those detailed by Cragg and coworkers.[6] In the presence of triethylamine, treatment of 2-butyne-1,4-diol-hexacarbonyldicobalt with the appropriate dichlorodialkylsilane resulted in facile ring closure, producing compounds **3**−**7** as the major products (Chart 1). These compounds were accompanied by the formation of small quantities of nine-membered ring siloxanes (**8** in the preparation of **3**) that likely result

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Scheme 1. Synthesis and Dimerization of Cobalt-Complexed 1,3-Dioxa-2-silacycloheptynes

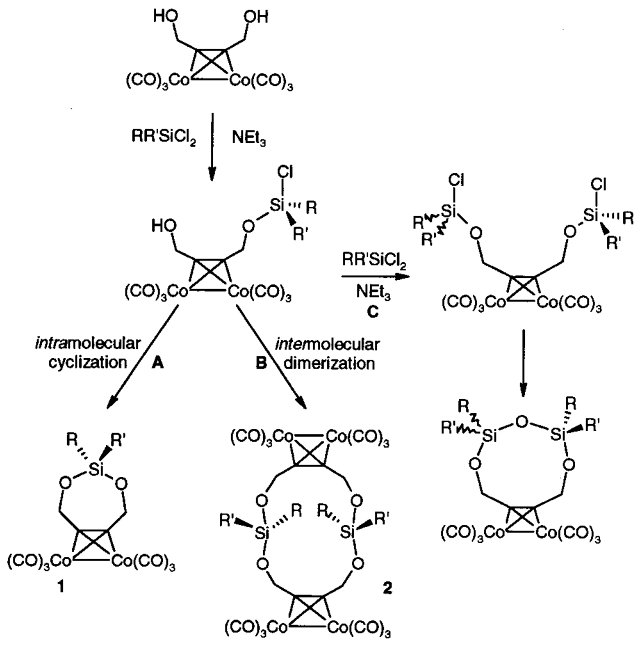
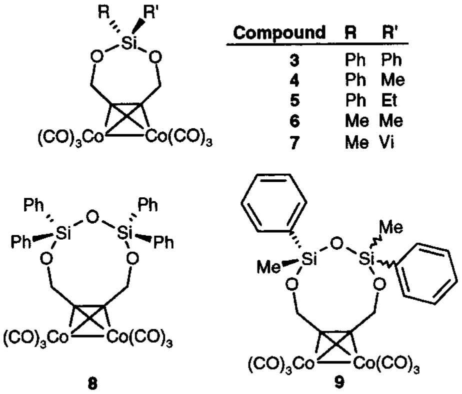


Chart 1



Compound	R	R'
3	Ph	Ph
4	Ph	Me
5	Ph	Et
6	Me	Me
7	Me	Vi

from competitive silylation of the second oxygen prior to cyclization (Scheme 1C). In the case of **9**, the presence of both *meso*- and *d*,*l*-products (a consequence of stereogenic silicon centers) could be rationalized on the basis of ^{1}H NMR spectral data, but these could not be separated by standard chromatographic techniques. This proposal was further substantiated by independent preparation of the racemic product mixture **9** from 2-butyne-1,4-diol-hexacarbonyldicobalt and racemic $(ClMePhSi)_2O$. With the exception of the asymmetrical nine-membered ring, **9**, the seven- and nine-membered ring compounds were readily purified by column chromatography and isolated in acceptable yields as analytically pure materials.

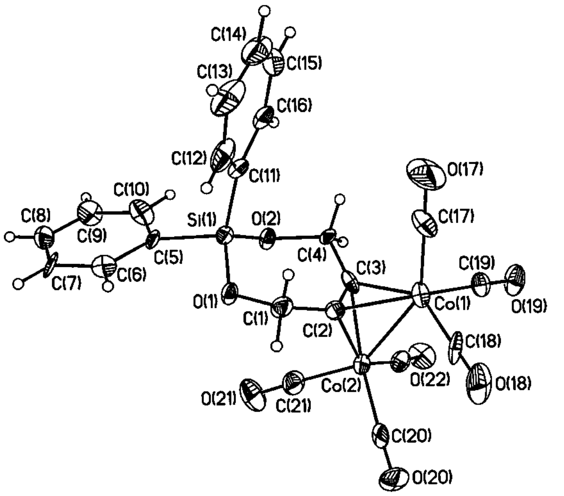


Figure 1. Crystallographically determined structure of **3** (shown with 30% thermal displacement ellipsoids).

Table 1. Crystal Data and Structure Refinement Parameters for 3 and 10

	3	10
empirical formula	$C_{22}H_{14}Si_1Co_2O_8$	$C_{20}H_8Si_1Co_4O_{16}$
mol wt	552.28	768.07
description	red prism	red plate
temp, K	213(2)	213(2)
wavelength, Å	(Mo Kα) 0.710 73	(Mo Kα) 0.710 73
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a, Å	14.8904(7)	25.614(5)
b, Å	6.8276(3)	16.959(3)
c, Å	23.854(1)	12.777(3)
β, deg	105.883(2)	100.62(3)
volume, Å^3	2332.6(2)	5455(2)
Z	4	8
calcd density, g/cm^3	1.573	1.870
scan mode	ω-scans	ω-scans
F(000)	1112	3024
θ-range for collection, deg	1.46–22.00	1.45–23.00
index ranges	$-16 \le h \le 16$ $-7 \le k \le 6$ $-26 \le l \le 26$	$-28 \le h \le 33$ $-20 \le k \le 8$ $-16 \le l \le 15$
no. of reflns collected	9793	9960
no. of unique reflns	2856	3946
no. of data/restraints/params	2833/0/299	3939/0/370
goodness-of-fit on F^2	1.034	0.838
final *R* indices ($I > 2s(I)$)[a]	R1 = 0.0878; wR2 = 0.1523	R1 = 0.0547; wR2 = 0.1190
R indices (all data)[a]	R1 = 0.1975; wR2 = 0.2006	R1 = 0.1155; wR2 = 0.1435
mean shift/error	<0.002	0.002
max. shift/error	<0.002	0.011
transmission (max., min.)	0.943, 0.833	0.682, 0.301
largest diff peak, e/Å^3	0.48	0.65
largest diff hole, e/Å^3	−0.47	−0.71

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

Given that the symmetry of species such as **1** and **2** makes them difficult to unambiguously differentiate by use of standard spectroscopic methods,[6-8] we chose to definitively characterize **3** by use of X-ray diffraction techniques; the structure of **3** is presented as Figure 1, and relevant data are collected in Tables 1 and 2. The crystallographically determined structure of **3** serves to identify the monomeric nature of the product unequivocally. In the solid state, **3** exists in a chairlike conformation and contains a pseudo-mirror-plane which bisects the C(2)–C(3) bond and contains the cobalt and silicon atoms. This geometry parallels that of related heterocyclic systems, including 1,3-dioxa-2,2-diphenyl-2-sila-5,6-benzocycloheptane, described by Hanson and co-workers.[7] On the basis of this crystallographic structure and mass spectral data, we infer that the remaining compounds, **4**–**7**, are also seven-membered

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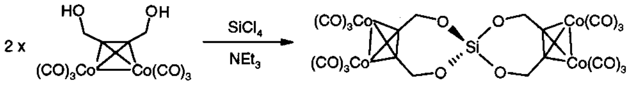
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3 and 10

3		10	
Si(1)−O(1)	1.652(9)	Si(1)−O(1)	1.615(5)
Si(1)−O(2)	1.645(8)	Si(1)−O(2)	1.609(5)
Co(1)−C(2)	1.940(9)	Si(1)−O(3)	1.620(4)
Co(1)−C(3)	1.961(9)	Si(1)−O(4)	1.627(4)
Co(2)−C(2)	1.961(9)	Co(1)−Co(2)	2.467(1)
Co(2)−C(3)	1.951(9)	Co(3)−Co(4)	2.456(1)
Co(1)−Co(2)	2.480(3)	C(2)−C(3)	1.335(9)
C(2)−C(3)	1.36(2)	C(6)−C(7)	1.349(8)
C(1)−C(2)-C(3)	135.4(9)	C(1)−C(2)-C(3)	137.3(6)
C(2)−C(3)-C(4)	138.1(9)	C(2)−C(3)-C(4)	135.6(6)
O(1)−Si(1)-O(2)	113.5(5)	C(5)−C(6)-C(7)	137.0(6)
C(5)−Si(1)-C(11)	113.7(6)	C(6)−C(7)-C(8)	137.8(6)
C(11)−Si(1)-O(1)	108.8(6)	O(1)−Si(1)-O(2)	115.5(2)
C(11)−Si(1)-O(2)	110.3(6)	O(3)−Si(1)-O(4)	114.4(2)

Scheme 2. Synthetic Route to the Spirocyclic Product, 10



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rings. However, it is important to recognize that crystallographic evidence does exist for the formation of the cyclic dimers referred to herein. Cragg and coworkers reported that treatment of the phenyl-substituted derivative of **2** with 2 equiv of triphenylphosphine affords a mixture of phosphorus-substituted seven- and 14-membered-ring species, the latter of which has been structurally characterized.[6]

In the pursuit of monomeric species that would have the capacity to act as cross-linking agents,[9] the spirocyclic compound **10** was prepared (Scheme 2). By use of the methodology detailed above, 2 equiv of 2-butyne-1,4-diol-hexacarbonyldicobalt was allowed to react with freshly distilled tetrachlorosilane in the presence of triethylamine. After purification by column chromatography, **10** was isolated as a red crystalline solid that was characterized by the use of a variety of spectroscopic techniques and X-ray crystallography; the molecular structure of **10** is presented as Figure 2. Compound **10** consists of two monomeric (i.e., seven-membered) spirocyclic rings and possesses structural features that closely parallel those previously discussed for **3**.

In light of the fact that our synthetic approach differs only modestly from that employed by Cragg et al., perhaps the most intriguing aspect of these results is the complete absence of evidence for the formation of dimeric products, which were previously reported to predominate in these hexacarbonyldicobalt-based systems.[6] Despite numerous synthetic trials utilizing a variety of experimental conditions, including a direct repetition of the procedure employed by Cragg, followed by careful chromatographic separation on silica, we were unable to obtain any experimental data in support of the formation of dimeric products analogous to **2**. Indeed, the mass spectra obtained for compounds **3**−**7** are consistent with monomeric species, in that no higher molecular weight peaks are observed.

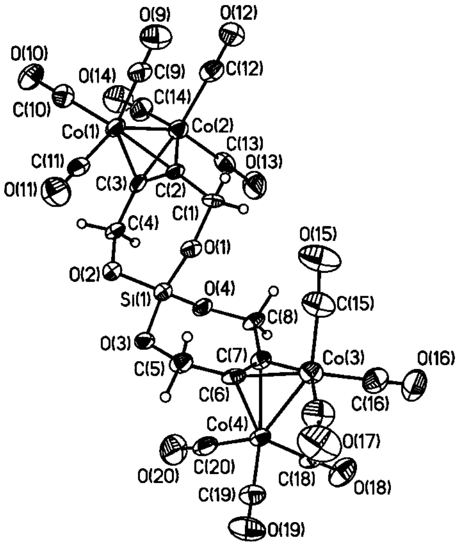

Figure 2. Crystallographically determined structure of **10** (shown with 30% thermal displacement ellipsoids).

The equilibration of 1,3-dioxa-2-silacycles can be facile, as elegantly demonstrated by Cragg and coworkers.[8a] Many catalysts facilitate this process, particularly acids and silaphilic nucleophiles,[10] and in the absence of steric constraints arising from substituents on either the silicon or the cyclic unit, metathesis leading to larger rings may proceed without catalysis, a situation we have observed firsthand.[11] It remains to be determined whether the serendipitous presence of other catalysts, possibly present during workup or chromatographic purification, may have played a role in facilitating the isolation of the monomeric species described herein. Nevertheless, these results clearly demonstrate that, in contrast to previous reports,[6] cobalt-complexed 1,3-dioxa-2-silacycloheptynes can be efficiently prepared and isolated as monomeric species.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen at ambient temperature using standard Schlenk techniques, unless otherwise stated. Solvents were dried according to established procedures. NMR spectra were recorded on Bruker AC-200, AC-300, and DRX-500 spectrometers, with ^{1}H, ^{13}C, and ^{29}Si chemical shifts reported relative to tetramethylsilane. IR spectra were obtained on a Bio-Rad FTS-40 spectrometer, using NaCl windows. Mass spectra were obtained on a VG Analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10 000. Microanalytical data were obtained from Guelph Chemical Laboratories, Guelph, Ontario, Canada. Octacarbonyldicobalt (Strem), 2-butyne-1,4-diol (Aldrich), and dichlorodialkylsilanes (Gelest) were used without purification, while 2-butyne-1,4-diol−hexacarbonyldicobalt was prepared using a previously published method.[12]

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X-ray Crystallography. Crystallographic data[13] for **3** and **10** were collected from single-crystal samples, which were mounted on a glass fiber. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (using the program SMART) and a rotating anode using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, utilizing 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 4.5° scan in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected, to better than 0.8 Å resolution. Processing was carried out by use of the program SAINT, which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the Patterson method in the Siemens SHELXTL program library and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the attached carbon.

General Preparation of Compounds 3−9. To a round-bottom flask containing 2-butyne-1,4-diol-hexacarbonyldicobalt (200 mg, 0.54 mmol) and triethylamine (120 mg, 0.17 mL, 1.18 mmol) in either toluene or CH_2Cl_2 (30 mL) was added the dichlorodialkylsilane (0.65 mmol (compound **8**: 0.55 mmol)). The dark red solution was stirred at room temperature for 1 h, poured into acidified water (30 mL, pH 6, acidified with acetic acid), and extracted three times with CH_2Cl_2 (20 mL). The organic phase was then dried over Na_2SO_4, and after removal of the solvent, the residue was subjected to flash chromatography on silica gel. Elution with hexane/CH_2Cl_2 (∼1:1) yielded the desired product, which was dried under vacuum.

2,2-Diphenyl-1,3-dioxa-2-silacyclohept-4-yne-hexacarbonyldicobalt (3). **3** was isolated as red crystals (65% yield), mp 102 °C (with decomposition). Anal. Calcd for $C_{22}H_{14}Co_2O_8Si$: C, 47.83; H, 2.55. Found: C, 48.08; H, 2.61. ^1H NMR (500 MHz, acetone-d_6): δ 5.36 (s, 4H, CH_2), 7.45 (m, 6H, phenyl), 7.69 (m, 4H, phenyl). ^{13}C NMR (50 MHz, CD_2Cl_2, ^1H decoupled): δ 67.14 (CH_2), 96.25 ($C\equiv C$), 128.74 (phenyl), 131.33 (phenyl), 132.25 (phenyl), 135.09 (phenyl), 199.41 ($C\equiv O$). ^{29}Si NMR (99.36 MHz, acetone-d_6): δ −23.2. IR (neat): ν/cm^{-1} 1083, 2028, 2056, 2098, 2855, 3010, 3072. MS (DEI, m/z (%)): 468 (48, $[M - 3CO]^+$), 440 (30, $[M - 4CO]^+$), 413 (40, $[M - 5CO]^+$), 384 (100, $[M - 6CO]^+$). MS (CI, m/z (%)): 570 (39, $[MNH_4]^+$), 553 (25, $[MH]^+$), 525 (31, $[MH - CO]^+$), 469 (100, $[MH - 3CO]^+$), 441 (33, $[MH - 4CO]^+$), 413 (25, $[MH - 5CO]^+$), 385 (50, $[MH - 6CO]^+$). MS (ES, m/z (%)): 552.9 (30, $[MH]^+$), 524.8 (20, $[MH - CO]^+$), 469.0 (35, $[MH - 3CO]^+$). MS (MS/MS, m/z (%)): 469.1 (80, $[MH - 3CO]^+$), 441.1 (100, $[MH - 4CO]^+$), 412.9 (70, $[MH - 5CO]^+$), 384.9 (55, $[MH - 6CO]^+$). MS (DEI, m/z, high resolution): calcd for $C_{19}H_{14}Co_2O_5Si$ ($[M - 3CO]^+$) 467.9274, obsd 467.9282. Single crystals suitable for X-ray diffraction analysis (0.06 × 0.04 × 0.03 mm^3) were grown from hexane.

2-Methyl-1,3-dioxa-2-phenyl-2-silacyclohept-4-yne-hexacarbonyldicobalt (4). **4** was isolated as red crystals (52% yield), mp 48 °C (with decomposition). Anal. Calcd for $C_{17}H_{12}Co_2O_8Si$: C, 41.65; H, 2.47. Found: C, 42.15; H, 2.75. ^1H NMR (500 MHz, acetone-d_6): δ 0.38 (s, 3H, CH_3), 5.23 (s, 4H, CH_2), 7.43 (m, 3H, phenyl), 7.67 (m, 2H, phenyl). ^{13}C NMR (125 MHz, acetone-d_6, ^1H decoupled): δ −3.85 (CH_3), 66.65 (CH_2), 97.38 ($C\equiv C$), 129.06 (phenyl), 131.47 (phenyl), 134.10 (phenyl), 134.84 (phenyl), 200.55 ($C\equiv O$). ^{29}Si NMR (99.36 MHz, acetone-d_6): δ −9.04. IR (neat): ν/cm^{-1} 1088, 1260, 2024, 2057, 2096, 2851, 2952, 3075. MS (DEI, m/z (%)): 406 (35, $[M - 3CO]^+$), 378 (21, $[M - 4CO]^+$), 350 (31, $[M - 5CO]^+$), 322 (100, $[M - 6CO]^+$). MS (CI, m/z (%)): 491 (25, $[MH]^+$), 463 (25, $[MH - CO]^+$), 407 (100, $[MH - 3CO]^+$), 379 (58, $[MH - 4CO]^+$), 351 (29, $[MH - 5CO]^+$); MS (ES, m/z (%)): 490.8 (100, $[MH]^+$), 462.9 (20, $[MH{-}CO]^+$), 406.9 (10, $[MH{-}3CO]^+$). MS (DEI, m/z, high resolution): calcd for $C_{14}H_{12}Co_2O_5Si$ ($[M{-}3CO]^+$) 405.9138, obsd 405.9118.

2-Ethyl-1,3-dioxa-2-phenyl-2-silacyclohept-4-yne-hexacarbonyldicobalt (5). **5** was isolated as red crystals (50% yield), mp 49 °C (with decomposition). Anal. Calcd for $C_{18}H_{14}Co_2O_8Si$: C, 42.87; H, 2.80. Found: C, 43.10; H, 2.79. ^1H NMR (500 MHz, acetone-d_6): δ 0.86 (q, 2H, CH_2CH_3, J = 6.3 Hz), 0.98 (t, 3H, CH_2CH_3, J = 6.3 Hz), 5.25 (s, 4H, CH_2), 7.45 (m, 3H, phenyl), 7.68 (m, 2H, phenyl). ^{13}C NMR (50 MHz, acetone-d_6, ^1H decoupled): δ 6.07 (CH_2CH_3), 6.39 (CH_2CH_3), 66.81 (OCH_2), 97.30 ($C\equiv C$), 129.16 (phenyl), 131.47 (phenyl), 132.66 (phenyl), 135.27 (phenyl), 200.43 ($C\equiv O$). IR (neat): ν/cm^{-1} 1087, 1247, 2019, 2060, 2097, 2869, 2957, 3022, 3076. MS (DEI, m/z (%)): 420 (50, $[M - 3CO]^+$), 364 (39, $[M - 5CO]^+$), 336 (100, $[M - 6CO]^+$); MS (CI, m/z (%)): 505 (42, $[MH]^+$), 477 (25, $[MH - CO]^+$), 421 (100, $[MH - 3CO]^+$), 393 (17, $[MH - 5CO]^+$). MS (DEI, m/z, high resolution): calcd for $C_{15}H_{14}Co_2O_5Si$ ($[M - 3CO]^+$) 419.9274, obsd 419.9280.

2,2-Dimethyl-1,3-dioxa-2-silacyclohept-5-yne-hexacarbonyldicobalt (6). **6** was previously reported by Cragg and co-workers[6] and isolated as a viscous red oil (40% yield). ^1H NMR (200 MHz, acetone-d_6): δ 0.20 (s, 6H, CH_3), 5.09 (s, 4H, CH_2). ^{13}C NMR (50 MHz, acetone-d_6, ^1H decoupled): δ −3.82 (CH_3), 66.98 (CH_2), 97.75 ($C\equiv C$), 200.40 ($C\equiv O$). ^{29}Si NMR (99.36 MHz, acetone-d_6): δ 5.96. IR (neat): ν/cm^{-1} 1091, 1261, 2025, 2057, 2097, 2852, 2929. MS (DEI, m/z (%)): 344 (50, $[M - 3CO]^+$), 288 (60, $[M - 5CO]^+$), 260 (100, $[M - 6CO]^+$); MS (CI, m/z (%)): 429 (100, $[MH]^+$), 401 (60, $[MH - CO]^+$). MS (DEI, m/z, high resolution): calcd for $C_9H_{10}Co_2O_5Si$ ($[M - 3CO]^+$) 343.8961, obsd 343.8970.

2-Methyl-1,3-dioxa-2-sila-2-vinylcyclohept-4-yne-hexacarbonyldicobalt (7). **7** was isolated as a viscous red oil (52% yield). Anal. Calcd for $C_{13}H_{10}Co_2O_8Si$: C, 35.47; H, 2.29. Found: C, 35.52; H, 2.35. ^1H NMR (200 MHz, acetone-d_6): δ 0.23 (s, 3H, CH_3), 5.15 (s, 4H, CH_2), 6.11 (m, 3H, $CH{=}CH_2$). ^{13}C NMR (50 MHz, acetone-d_6, ^1H decoupled): δ −4.23 (CH_3), 66.36 (CH_2), 97.51 ($C\equiv C$), 133.19 ($CH{=}CH_2$), 136.97 ($CH{=}CH_2$), 200.26 ($C\equiv O$). ^{29}Si NMR (99.36 MHz, acetone-d_6): δ −9.68. IR (neat): ν/cm^{-1} 1090, 1264, 2024, 2057, 2097, 2852, 2950, 3060. MS (DEI, m/z (%)): 384 (22, $[M - 2CO]^+$), 356 (27, $[M - 3CO]^+$), 328 (40, $[M - 4CO]^+$), 300 (71, $[M - 5CO]^+$), 272 (100, $[M - 6CO]^+$); MS (CI, m/z (%)): 441 (100, $[MH]^+$), 413 (9, $[MH - CO]^+$), 385 (10, $[MH - 2CO]^+$), 357 (22, $[MH - 3CO]^+$). MS (DEI, m/z, high resolution): calcd for $C_{11}H_{10}Co_2O_6Si$ ($[M - 2CO]^+$) 383.8911, obsd 383.8920.

2,2,4,4-Tetraphenyl-1,3,5-trioxa-2,4-disilacyclonon-6-yne-hexacarbonyldicobalt (8). **8** was isolated as a byproduct by column chromatography as a viscous red oil (10% yield). Anal. Calcd for $C_{34}H_{24}Co_2O_9Si_2$: C, 54.40; H, 3.23. Found: C, 54.14; H, 3.41. ^1H NMR (200 MHz, acetone-d_6): δ 5.22 (s, 4H, CH_2), 7.45 (m, 12H, phenyl), 7.73 (m, 8H, phenyl). ^{13}C NMR (50 MHz, acetone-d_6, ^1H decoupled): δ 65.37 (CH_2), 95.78 ($C\equiv C$), 128.84 (phenyl), 131.52 (phenyl), 133.88 (phenyl), 135.52 (phenyl), 200.49 ($C\equiv O$). ^{29}Si NMR (99.36 MHz, acetone-d_6): δ −36.0. IR (neat): ν/cm^{-1} 1084, 2031, 2054, 2094, 2844, 2933, 2963, 3015, 3071. MS (CI, m/z (%)): 751 (24, $[MH]^+$), 667 (100, $[MH - 3CO]^+$), 639 (52, $[MH - 4CO]^+$), 611 (100, $[MH - 5CO]^+$), 583 (95, $[MH - 6CO]^+$).

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(13) (a) *SMART 1996*, Release 4.05; Siemens Energy And Automation Inc.: Madison, WI 53719, 1996. (b) *SAINT 1996*, Release 4.05; Siemens Energy and Automation Inc.: Madison, WI 53719, 1996. (c) Sheldrick, G. *SADABS* (Siemens Area Detector Absorption Corrections), 1996. (d) *SHELXTL 1994*, Version 5.03; Siemens Crystallographic Research Systems: Madison, WI 53719, 1994.

2,4-Dimethyl-1,3,5-trioxa-2,4-diphenyl-2,4-disilacyclonon-6-yne-hexacarbonyldicobalt (9). **9** was isolated as a viscous red oil (71% yield). Anal. Calcd for $C_{24}H_{20}Co_2O_9Si_2$: C, 46.01; H, 3.22. Found: C, 46.23; H, 3.00. ^{1}H NMR (200 MHz, acetone-d_6): δ 0.34 (s, 3H, CH_3), 0.47 (s, 3H, CH_3), 5.07 (s, 2H, CH_2), 5.11 (s, 2H, CH_2), 7.39 (m, 6H, phenyl), 7.70 (m, 4H, phenyl). ^{13}C NMR (50 MHz, acetone-d_6, ^{1}H decoupled): δ −1.81 (CH_3), −1.77 (CH_3), 64.45 (CH_2), 64.59 (CH_2), 96.11 (C≡C), 96.33 (C≡C), 128.87−135.94 (phenyl), 200.63 (C≡O). ^{29}Si NMR (99.36 MHz, acetone-d_6): δ −23.2, −22.7. IR (neat): ν/cm^{-1} 1082, 1261, 2023, 2055, 2093, 2843, 2933, 2966, 3023, 3073. MS (CI, *m*/*z* (%)): 627 (53, $[MH]^+$), 599 (10, $[MH - CO]^+$), 543 (100, $[MH - 3CO]^+$), 515 (20, $[MH - 4CO]^+$), 487 (47, $[MH - 5CO]^+$), 459 (16, $[MH - 6CO]^+$). MS (DEI, *m*/*z*, high resolution): calcd for $C_{21}H_{20}Co_2O_6Si$ ($[M - 3CO]^+$) 541.9462, obsd 541.9463.

Spirobicycloheptyne-bis(hexacarbonyldicobalt) (10). To a flask containing 2-butyne-1,4-diol-hexacarbonyldicobalt (300 mg, 0.8 mmol) in CH_2Cl_2 (30 mL) was added triethylamine (0.33 g, 3.28 mmol, 0.45 mL). Freshly distilled $SiCl_4$ (70 mg, 0.4 mmol, 0.046 mL) was diluted to 1 mL (CH_2Cl_2) and added dropwise to the solution of the diol. The dark red solution was stirred for 30 min, then poured into water (pH 6, acidified with acetic acid and saturated with NaCl). After extracting the aqueous phase three times with CH_2Cl_2 (30 mL), the combined organic phases were dried over $NaSO_4$ and evaporated to give the crude product, which was chromatographed on silica gel (CH_2Cl_2/hexanes, 3:1) and isolated as red crystals (16% yield). Anal. Calcd for $C_{20}H_8Co_4O_{16}Si$: C, 31.26; H, 1.05. Found: C, 31.52; H, 0.83. Mp: decomposes between 90 and 110 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 5.23 (s, 8H, CH_2). ^{13}C NMR (50 MHz, acetone d_6, ^{1}H decoupled): δ 66.68 (CH_2), 95.18 (C≡C), 199.70 (C≡O). ^{29}Si NMR (99.36 MHz, acetone-d_6): δ −70.2. IR (neat): ν/cm^{-1} 2021, 2060, 2098. Single crystals suitable for X-ray diffraction analysis ($0.30 \times 0.20 \times 0.08$ mm^3) were grown from CH_2Cl_2.

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Supporting Information Available: Atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **3** and **10** (12 pages). Ordering information is given on any current masthead page.

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