Oligo(alkynylsilanes): Templates for Organometallic Polymers

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A series of compounds containing alkynylsilane and arylsilane groups, including oligomers and polymers, were used as transition-metal ligands. The alkyne groups could be complexed by dicobalt hexacarbonyl. Alternatively, complexation of the aryl groups by chromium tricarbonyl readily took place. The molecular weights of these complexes ranged up to 155 000 for a silicone polymer derived complex. Mixed-metal clusters containing Cr/Mo and Cr/Co could be made by modifying the chromium derivatives with $Mo_2Cp_2(CO)_6$ and $Co_2(CO)_8$, respectively. The model compound **20** shows an interesting self-assembly of the metals (Co and Cr, respectively) in the crystal.

Introduction

The preparation of organometallic polymers has recently received much attention, since the presence of a metal can dramatically affect the properties of the material, particularly its optical and conductive properties.[1] The polymeric nature of such systems confers greater stability and better processability in comparison to those of analogous small molecules. Some noteworthy examples include the poly(ferrocenylsilanes) of Manners and co-workers,[2] the ferrocenylsilicones of Cuadrado and co-workers,[3] the cobalt and iron cyclobutadiene complexes of Bunz and of Gleiter,[4] the chromium complexes that Corriu and co-workers used to embed chromium in ceramics,[5] the cobalt-containing dendrimers of Seyferth *et al.*[6a] and Cuadrado et al.,[6b,c] the polyalkynyl architectures of Diederich and co-workers.[7]

On the basis of the premise that the combination of different metals could affect the properties of a compound cooperatively, as has been seen with short dimetal oligoalkynes,[8] we chose to devise ligands that (i) could readily be prepared as small molecules or polymers, (ii) lend themselves to the selective binding of several different transition metals, and (iii) utilize the flexibility of organosilane chemistry.

The ligands of interest for this project were those possessing alkynyl and aryl groups that provide sites of attachment for organometallic moieties containing molybdenum, cobalt, or chromium. In recent years, we have reported the syntheses of a variety of metal complexes of alkynes, monosilyl- and disilylalkynes, and arylsilanes.[9−11] Similarly, Corriu *et al.*[12] and others[13,14] have described linear polymers, while Seyferth and co-workers have reported dendrimeric complexes of this type.[6] Complexes of $Cp_2Mo_2(CO)_4$ with trimethylsilyl-terminated alkynes and diynes also are readily prepared.[15,16] For the aryl complexes, Corriu and co-workers[5] and McGlinchey and co-workers[11] have shown that such ligands are compatible with the presence of $Cr(CO)_3$ groups. Indeed, Manners recently reported a compound in which a chromium atom was sandwiched between two aryl groups bound to a single silicon (Ar−SiR_2−Ar).[17]

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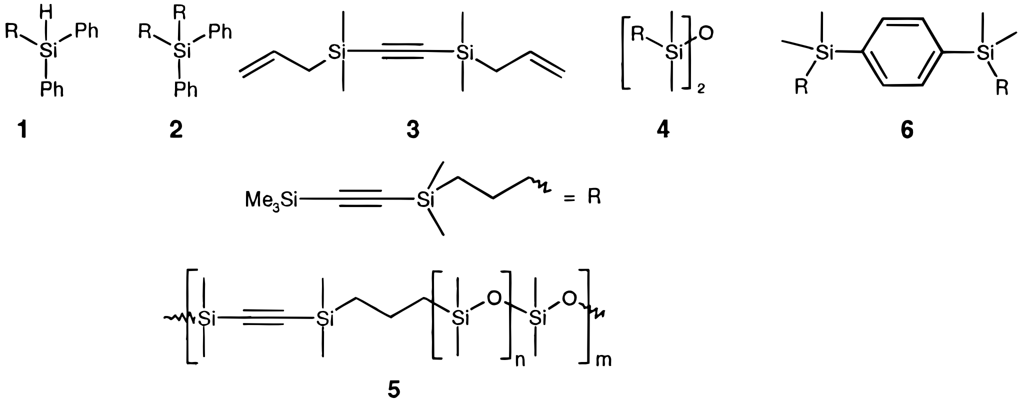
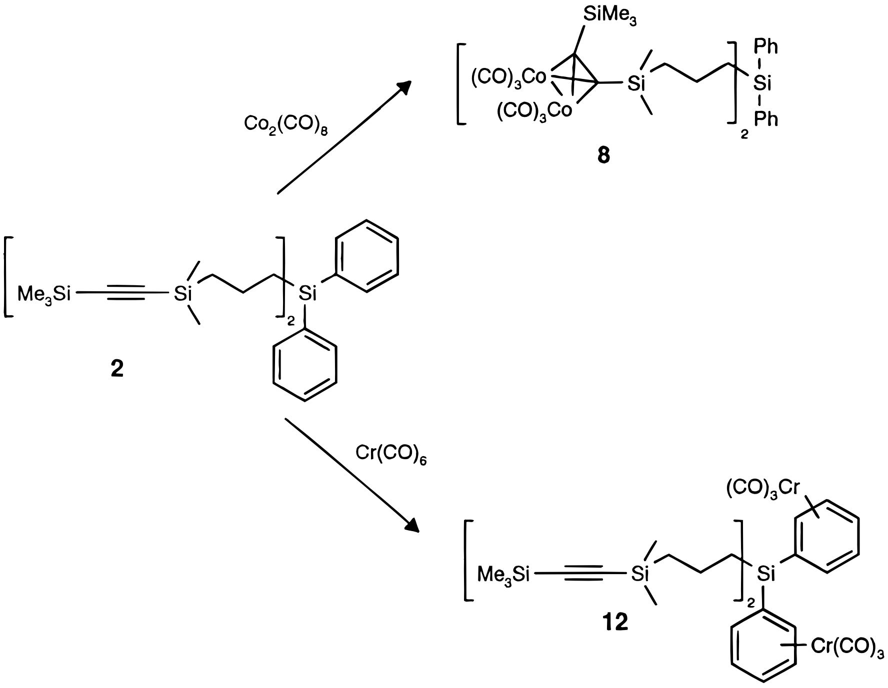
Chart 1



Scheme 1



It is hoped that judiciously selected combinations of organometallic moieties will lead to materials similar to those noted above, but with tunable properties. We report herein our model synthetic studies in this area.

Results and Discussion

The ligands from which we chose to make polymeric materials are the silanes **1**−**6**, as shown in Chart 1.[18] These all contain two potential sites for transition-metal coordination, namely the alkynyl and aryl groups. Smaller molecules, such as $Me_3SiC{\equiv}CSiMe_2(CH_2)_3Si(H)Ph$ (**1**) and $(Me_3SiC{\equiv}CSiMe_2(CH_2)_3)_2SiPh_2$ (**2**), were used to establish the conditions necessary to selectively attach a transition-metal fragment to one of the two potential ligand binding sites. Subsequently, the conditions were established whereby the second organometallic moiety could be incorporated without decomplexing the first.

Complexes Possessing a Single Type of Organometallic Moiety. Cobalt. The preparation and utilization of dicobalt complexes of alkynylsilanes owes much to the pioneering work of Seyferth,[19] Markó,[20] and their respective co-workers. Many other workers have also contributed to this area.[21] Following these precedents, the hexacarbonyldicobalt complexes **7**−**11** (see eqs 1−4 and Scheme 1) were prepared by stirring the appropriate precursors **1**−**5**, respectively, with $Co_2(CO)_8$ in freshly distilled tetrahydrofuran at room temperature. Beautiful deep red complexes were obtained in excellent yield. Especially noteworthy are the silicone-based compounds **10** and **11** ($\bar{M}_w = ca.$ 50 000), which, unlike the other cobalt complexes, are fluids. Although $Co_2(CO)_8$ will react with Si−H compounds, this reaction did not accompany the conversion of **1** to **7**.[10] We ascribe

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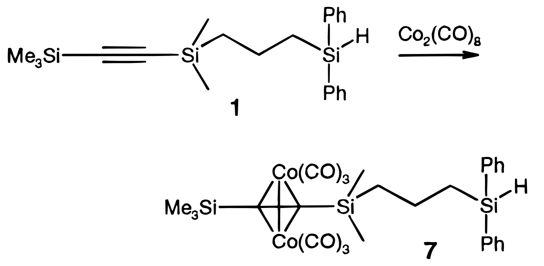
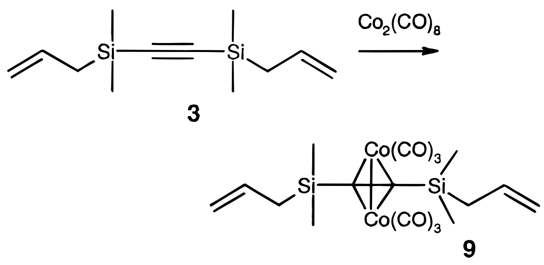


(1)



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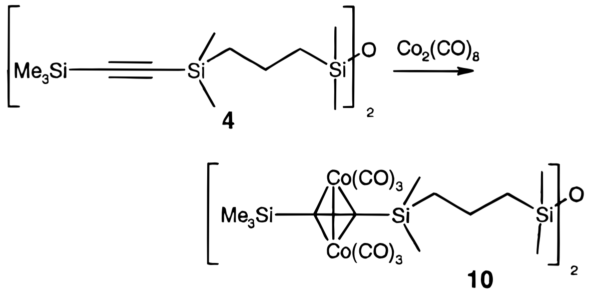

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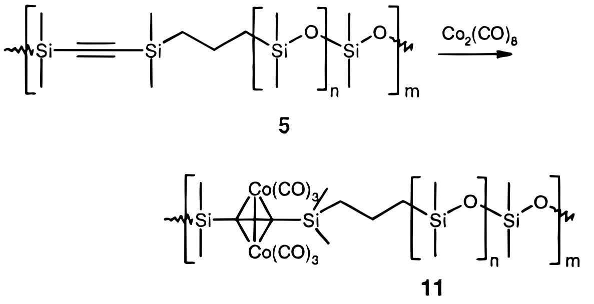

(4)

this to the steric encumbrance provided by the flanking phenyl groups.[22]

Chromium. The incorporation of tricarbonylchromium units into arylsilanes is well-established,[5,11,23] and the alkynylarylsilanes **2** and **6** react with chromium hexacarbonyl to yield the chromium complexes **12** and **13**, respectively (see Schemes 1 and 2). To complement the usual analytical and spectroscopic data, **12** was also characterized by X-ray crystallography. The molecular structure appears in Figure 1, and the relevant crystallographic data are collected in Tables 1 and 2. The molecular geometry reveals no unusual features but serves to identify the product unequivocally. However, the conformation adopted, at least in the solid state, leaves the alkynyl groups relatively unencumbered and readily available for coordination to a dicobalt or dimolybdenum fragment.

In contrast, attempts to perform the analogous complexation reaction with the model compound **1**, which possesses only a single alkynyl unit but also contains an Si−H linkage, led to unexpected results. When **1** was heated at reflux with $Cr(CO)_6$ in di-*n*-butyl ether, the product was initially assumed to be **14**, analogous to **12**. The compound exhibited the expected number of ^1H and ^{13}C NMR resonances, and the mass spectrum and microanalytical data also were consistent with this formulation (see Scheme 3). However, the purported Si−*H* absorption at 7.77 ppm in the proton NMR spectrum was considerably deshielded relative to its normal resonance position. Moreover, the 2D $^{29}Si-^{1}H$ NMR (HMBC) demonstrated unequivocally that this proton *was coupled to all three silicon atoms*, eliminating **12** as the correct structure. We were alerted to the possibility of an intramolecular hydrosilation (to give **15**) when a search of the literature revealed that the alkene proton in trisilylated ethenes is generally found in the range δ 7.1−7.3.[24] The particular absorption, at δ 7.77 ppm, was further deshielded from these values by approximately 0.5 ppm. To clarify this point, and to establish the molecular connectivity definitively, an X-ray crystal structure determination was undertaken. Figure 2 depicts the molecule **15** and confirms the cyclic nature of the product. It is evident that *cis* addition of the Si−H moiety across the alkynyl linkage has occurred. The X-ray data also provide a rationale for the strongly deshielded character of the alkene proton at δ 7.77 ppm. Relevant crystallographic data are collected in Tables 1 and 3.

The diamagnetic anisotropy of inorganic or organometallic fragments, such as metal−metal triple bonds,[25] ferrocenyl units,[26] and metal carbonyl linkages,[27] has been the subject of numerous studies. In particular, the Cr−C≡O linkage behaves analogously to the alkynyl group in that protons lying close to the C_∞ axis are markedly shielded while those hydrogens more nearly perpendicular to the M−C≡O bond are strongly deshielded. The incremental shift, σ, in parts per million, is given by the formula $\sigma = \chi_{CrCO}(1 - 3\cos^2\theta)/((3R^3)4\pi)$, where R is the distance from the proton to the center of the C≡O bond and θ is the angle made by R with the Cr−C≡O axis.[27] In the case at hand, the values of R and θ were obtained from the X-ray crystal structure of **15**, and χ_{CrCO} was taken as -490×10^{-36} m^3/molecule.[28] These structural data predict that the ethene proton should be deshielded by 0.58 ppm. Subsequent decomplexation of the bis-$Cr(CO)_3$ complex **15** by photolysis in sunlight yielded the free ligand **16**, in which the ethene hydrogen now absorbed at approximately δ 7.3 ppm.

Initially, it was assumed that the hydrosilylation catalyst in this reaction was the added chromium agent, *i.e.* $Cr(CO)_6$, or an aryl−$Cr(CO)_3$ complex. However, it was discovered that a purified sample of **1** left at room temperature for a few months contained about 80% **16**.

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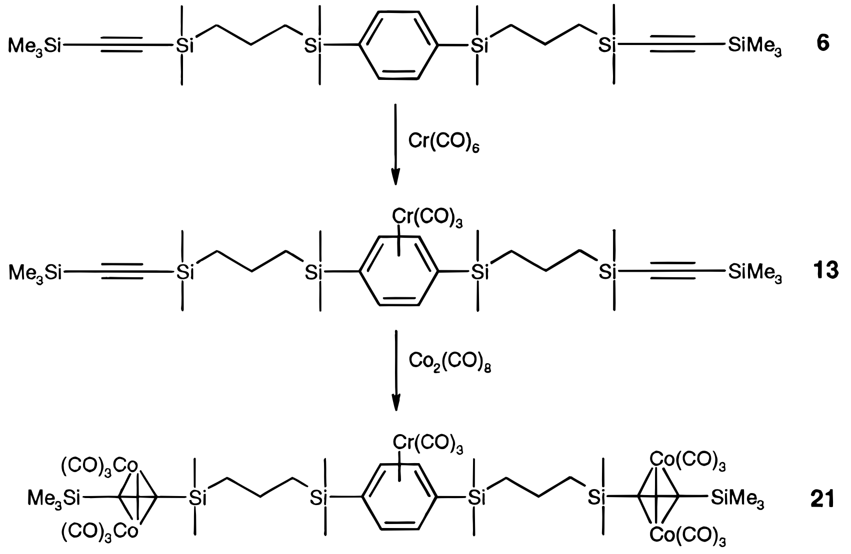
Scheme 2



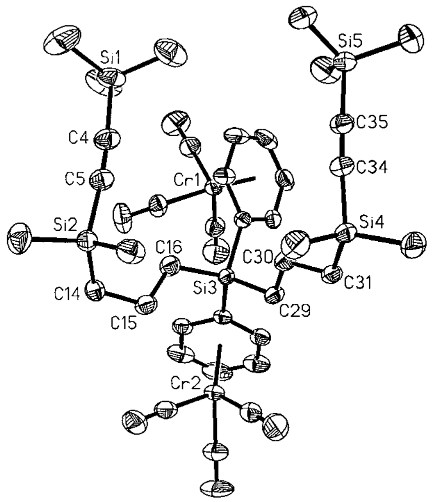


Figure 1. Molecular structure of **12** showing 30% probability ellipsoids.

Thus, in spite of purification of **1** by column chromatography, it is concluded that residual platinum from the initial preparation of **1** accounts for the hydrosilylation, both in the presence and absence of $Cr(CO)_6$, although thermal activation cannot be discounted. This is in accord with the observed intramolecular cyclization of a chromatographically purified sample of $Ph_2(H)Si(CH_2)_3SiMe_2C{\equiv}CSiMe_2(CH_2)_3Si(H)Ph_2$ (**17**) to **18** over a period of approximately 1 month. The structural isomers **17** and **18** were readily differentiated by use of a 2D $^{29}Si-^{1}H$ NMR (HMBC) experiment (eq 5).

The intramolecular hydrosilylation reaction of **1** was somewhat unexpected. Previous experiments with the related silylalkyne $(Me_3SiC{\equiv}C)_4Si$[9,29] showed it to be completely inert to the normal conditions used for the Pauson−Khand reaction,[30] to electrophilic attack by acid or nucleophilic attack by fluoride,[9,31] to Vollhardt cyclotrimerization, or to Diels−Alder reactions[32] with either electrophilic or electron-rich dienes. The lack of reactivity in these cases can be attributed to steric hindrance of the alkyne provided by the flanking groups. The bulk of these $SiMe_2R$ ligands in **1** can be seen from the ball-and-stick representation of the structure calculated using molecular mechanics (Figure 3). In contrast, the proximity of functional groups in **1** and the intramolecular nature of the hydrosilylation process to give **15** or **16** presumably enhances the reactivity in this particular case. The transition state leading to hydrosilylation was modeled by constraining the $Me_3Si\boldsymbol{C}\cdots\boldsymbol{H}SiPh_2$ distance to 3 Å and minimizing the structure. It can be appreciated from Figure 3 that, while steric hindrance is still significant, one of the flanking groups ($SiMe_2$) has adopted a conformation that minimizes the steric constraints allowing the intramolecular hydrosilylation to proceed.

Mixed-Metal Systems. Following a systematic evaluation, the most efficient sequence for the preparation of the mixed-metal systems proved to involve complexation of the aryl system prior to introduction of transition metals to the alkynyl moieties. Thus, the mixed molybdenum/chromium complex **19** was prepared by stirring the chromium complex **12** in di-*n*-butyl ether with $Mo_2Cp_2(CO)_4$. Analogously, the mixed chromium/cobalt compounds **20** and **21** (Schemes 2 and 4) were made by stirring **12** and **13**, respectively, with $Co_2(CO)_8$ in THF.

Single crystals suitable for X-ray crystallographic analysis were obtained of the chromium/cobalt complex **20**; relevant crystallographic data and the resulting structure appear in Tables 1 and 4 and Figure 4, respectively. While the organometallic fragments $Co_2(CO)_6$ and $Cr(CO)_3$ respectively show very typical structures, the overall conformation of an individual molecule looks rather awkward. An examination of the packing diagram along the *a* axis, however, shows that association of similar metal clusters, a type of self-assembly, is apparently driving the packing in the crystal. One can clearly observe repeating layers of cobalt−cobalt−

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Table 1. Crystal Data and Structure Refinement Details for 12, 15, and 20

	12	**15**	**20**
empirical formula	$C_{38}H_{52}Cr_2O_6Si_5$	$C_{28}H_{32}Cr_2O_6Si_3$	$C_{50}H_{52}Co_4Cr_2O_{18}Si_5$
mol wt	849.25	652.81	1421.09
descripn	yellow prism	yellow prism	red plate
dimens, mm	0.44 × 0.25 × 0.18	0.50 × 0.25 × 0.12	0.38 × 0.18 × 0.05
temp, K	293(2)	300(2)	300(2)
wavelength, Å	0.710 73 (Mo Kα)		
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a, Å	12.828(3)	18.910(2)	45.975(5)
b, Å	13.526(3)	10.533(2)	12.936(2)
c, Å	13.909(3)	16.532(2)	24.459(3)
α, deg	92.29(3)	90.000(0)	90.000(0)
β, deg	105.02(3)	109.51(1)	115.767(7)
γ, deg	100.22(3)	90.000(0)	90.000(0)
V, Å^3	2284.7(8)	3103.7(6)	13100(3)
Z	2	4	8
calcd density, g/cm^3	1.234	1.397	1.441
abs coeff, mm^{-1}	0.646	0.854	1.462
F(000)	892	1352	5776
θ range for collecn, deg	1.52−26.73	2.25−25.00	1.65−22.50
transmissn min	0.794	0.842	0.683
transmissn max	0.948	0.913	0.968
index ranges	$-16 \le h \le 16$	$-22 \le h \le 21$	$0 \le h \le 49$
	$-16 \le k \le 16$	$-12 \le k \le 1$	$0 \le k \le 13$
	$-14 \le l \le 17$	$-1 \le l \le 19$	$-26 \le l \le 23$
no. of rflns collected	18895	6896	8195
no. of indep rflns	8680	5478	8073
R(int)	0.0185	0.0470	0.0587
refinement method	full-matrix least squares on F^2		
no. of data/restraints/params	8680/0/461	5478/3/358	8073/0/712
goodness of fit on F^2	1.032	1.021	0.836
final *R* indices ($I > 2\sigma(I)$)[a]	R1 = 0.0380	0.0580	0.0818
	wR2 = 0.0993	0.1313	0.2107
R indices (all data)[a]	R1 = 0.0511	0.1013	0.1606
	wR2 = 0.1090	0.1569	0.2667
largest diff peak, e/Å^3	0.414	0.850	1.111
largest diff hole, e/Å^3	−0.335	−0.524	−0.740

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

Table 2. Selected Salient Bond Lengths (Å) and Angles (deg) for 12

Si(3)−C(29)	1.853(2)	Cr(1)-C(46)	1.802(3)
Si(3)−C(23)	1.881(2)	Cr(2)−C(47)	1.837(3)
C(35)−C(34)	1.198(4)	Si(4)−C(34)	1.837(3)
Si(4)−C(34)−C(35)	176.5(3)	C(17)−Si(3)−C(23)	105.97(10)
C(16)−Si(3)−C(17)	114.38(12)		

chromium lying in the *b*−*c* plane (Figure 5). We intend to examine the crystal packing in the related systems **19** and **21** to establish whether this is a general phenomenon.[33]

Having established that such mixed-metal systems may be readily prepared, we are in the process of preparing higher molecular weight, silicone-based systems with the goal of establishing the conditions under which the different organometallic fragments will act cooperatively.

Experimental Section

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AC-200 spectrometer (at 200.13 MHz for ^{1}H and 50.3 MHz for ^{13}C) or on a Bruker DRX 500 spectrometer with an 11.74 T superconducting magnet, equipped with a Bruker B-VT 2000 temperature controller and a 5 mm multinuclear inverse probe equipped with three-axis gradients. ^{1}H, ^{29}Si, and ^{13}C NMR data were obtained at 500.13, 99.36, and 125.76 MHz, respectively. All spectra, except for 2D experiments on the DRX 500, were recorded on spinning samples. Peaks were referenced to a residual proton signal of the solvent or to a ^{13}C solvent signal.

In some of the ^{13}C NMR spectra, it was not possible to observe the carbonyl peaks.

^{1}H-Detected ^{29}Si Multiple-Bond (HMBC) Correlation Experiment. The ^{29}Si spectral width was 5531.0 Hz with 2048 data points, zero-filled to 4096. The ^{1}H spectral width was 5952.4 Hz with 256 time increments and 64 scans per increment. A relaxation delay of 2 s between scans was used. Values of $^1J_{Si-H} = 224$ Hz and $^2J_{Si-H} = 6.7$ Hz were used to calculate Δ_1 and Δ_2 ($\Delta_1 = 1/[2(^1J_{Si-H})]$ and $\Delta_2 = 1/[2(^2J_{Si-H})]$).

Infrared spectra were obtained on a Bio-Rad FTS-40 spectrometer, using NaCl windows. Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. High-resolution mass spectra were determined in the EI mode on the same instrument.

The molecular weights of the hydrophobic polymers were analyzed using a Waters Gel Permeation Chromatograph (GPC) equipped with a Waters 510 HPLC pump and a Waters 410 differential refractive index detector. Two Jordi mixed-bed columns and one Waters 4E column in series were utilized with 1,1,1-trichloroethane as solvent flowing at 1 mL/min. Pretreatment of the HPLC grade 1,1,1-trichloroethane involved filtration through a 400 μm Teflon filter. Narrow-molecular-weight polystyrene and silicone standards from Scientific Polymer Products Inc. were used for calibration of the chromatographic system. While we recognize that neither standard will give an accurate molecular weight value for compounds **5** and **11**, comparison of the retention volumes of the standards and the known molecular weights of the starting materials with those of the products allows us to estimate the

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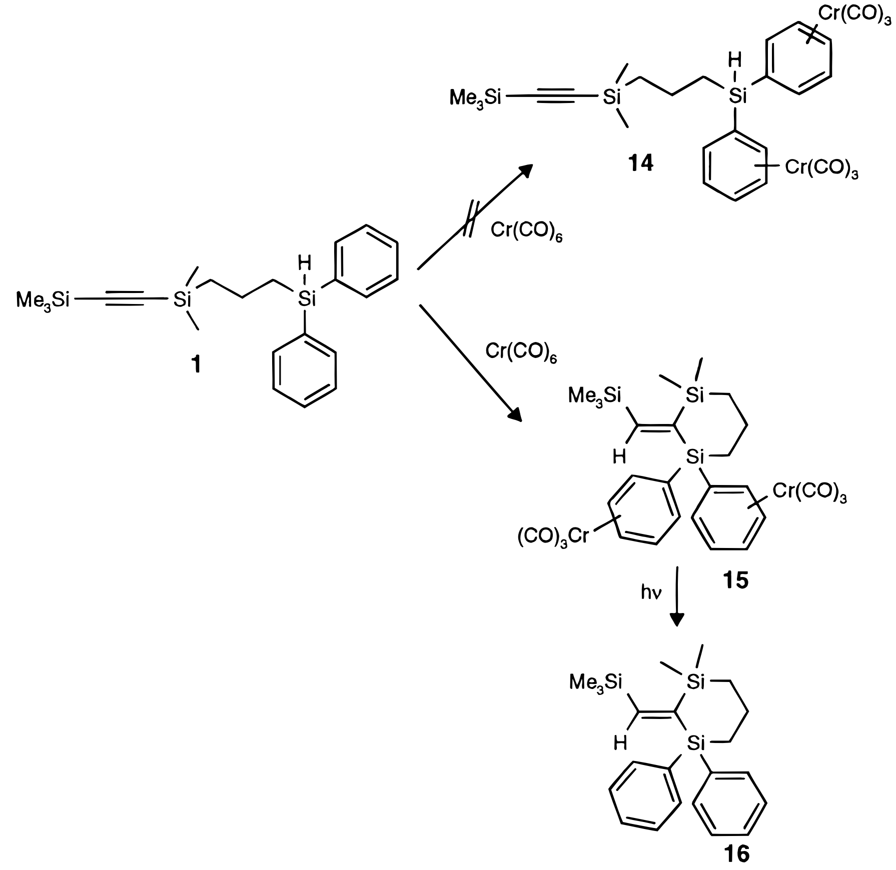
[33] For a recent discussion of organometallic crystal engineering, refer to: Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* **1996**, 571.

Scheme 3



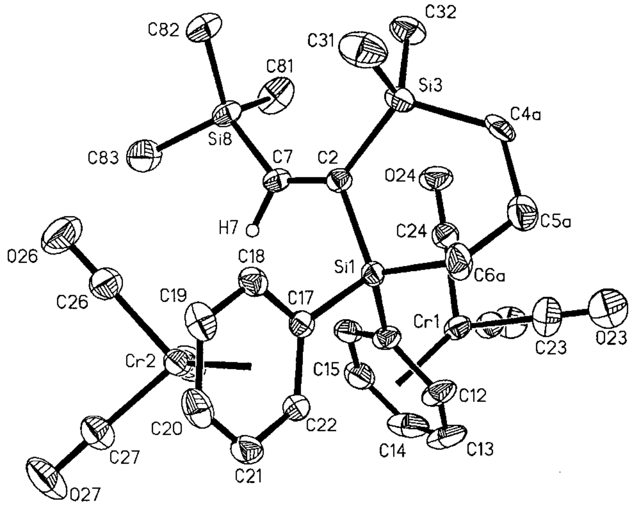


Figure 2. Molecular structure of **15** showing 30% probability ellipsoids.

Table 3. Selected Salient Bond Lengths (Å) and Angles (deg) for 15

C(2)−C(7)	1.344(7)	Si(3)−C(4A)	1.883(14)
Si(8)−C(7)	1.888(5)	Si(3)−C(2)	1.890(5)
Si(1)−C(17)	1.886(5)	Si(1)−C(2)	1.880(4)
Si(1)−C(11)	1.895(5)		
C(4A)−Si(3)−C(2)	112.6(5)	C(7)−C(2)−Si(1)	116.9(3)
C(5A)−C(4A)−Si(3)	121.2(10)	C(7)−C(2)−Si(3)	128.4(3)
Si(1)−C(2)−Si(3)	114.6(2)		

number of iterative hydrosilylations which occurred. Data manipulation was done using Waters Millenium Chromatography Manager software.

Crystal Structure Determinations. X-ray crystallographic data for **12** (Tables 1 and 2) were collected from a single-crystal sample, which was 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[34]) 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 determination was carried out by scanning 4.5° in 15 frames over 3 different parts of reciprocal space (45 frames,

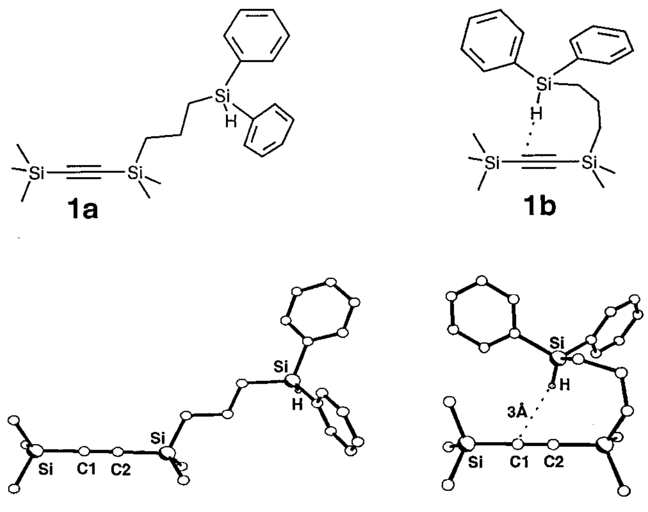


Figure 3. Structure of disilylalkynes **1a**,**b** (additional hydrogens omitted for clarity): **1a**, calculated using molecular mechanics (MM2); **1b**, calculated using MM2 with Me$_3$Si**C**···**H**SiPh$_2$ constrained to 3 Å.

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[34] SMART, Release 4.05; Siemens Energy and Automation, Inc., Madison, WI 53719, 1996.

Scheme 4

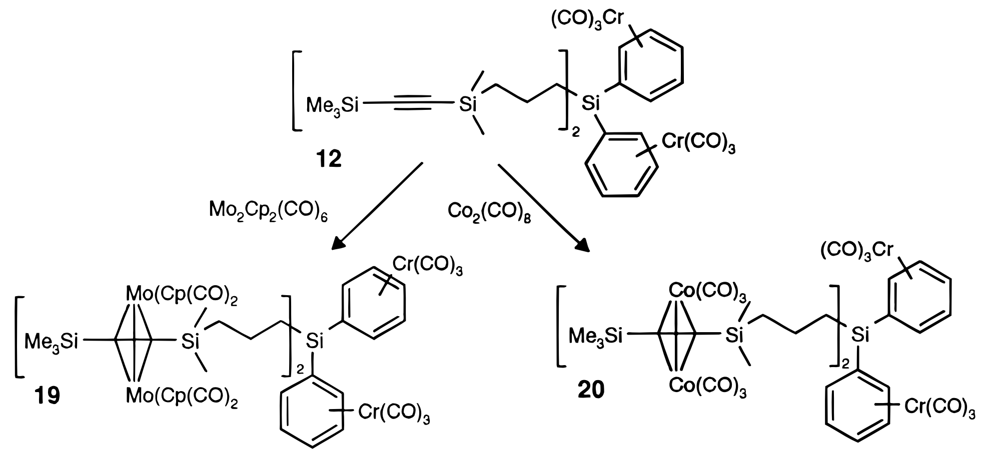

Table 4. Selected Salient Bond Lengths (Å) and Angles (deg) for 20

Co(3)−C(34)	1.997(12)	Si(3)−C(17)	1.889(12)
Co(3)−Co(4)	2.525(3)	Si(4)−C(34)	1.880(14)
Co(4)−C(34)	2.007(13)		
C(16)−Si(3)−C(23)	109.7(5)	C(34)−C(35)−Si(5)	142.6(13)
C(29)−Si(3)−C(23)	105.3(5)	Si(5)−C(35)−Co(4)	132.1(10)
C(29)−Si(3)−C(16)	112.5(5)	C(34)−C(35)−Co(3)	72.1(11)

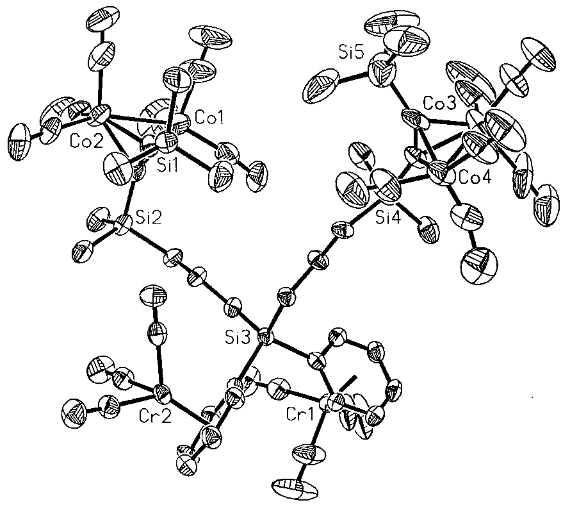

Figure 4. Molecular structure of **20** showing 30% probability ellipsoids.

180 reflections total). The strong reflections were then chosen and used in the determination of the unit cell. One complete hemisphere of data was collected, to better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were re-collected in order to improve the decay correction analysis. Processing was carried out by use of the program SAINT,[35] which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS[36] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structures were solved by using the direct methods procedure in the Siemens SHELXTL program library[37] and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were included as fixed contributors at calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of their attached atom.

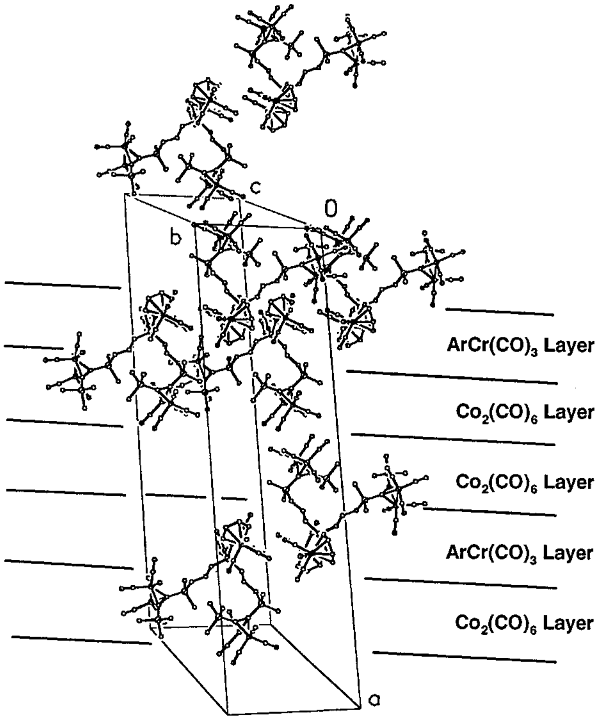

Figure 5. Crystal-packing diagram of **20** showing the cobalt- and chromium-rich layers.

X-ray crystallographic data for **15** and **20** were collected from single crystals, which were mounted on a glass fiber and transferred to a P4 Siemens diffractometer, equipped with a rotating anode and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Three standard reflections, which were measured after every 97 reflections, showed neither instrument instability nor crystal decay. Data were corrected for absorption using an empirical Ψ-scan method.[38] The structures were solved by using the direct-methods procedure in the Siemens SHELXTL program library[37] and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. With the exception of the vinylic and aromatic protons in **15**, all hydrogen atoms were included as fixed contributors at calculated positions. Crystallographic data collection parameters for **15** and **20** are summarized in Table 1.

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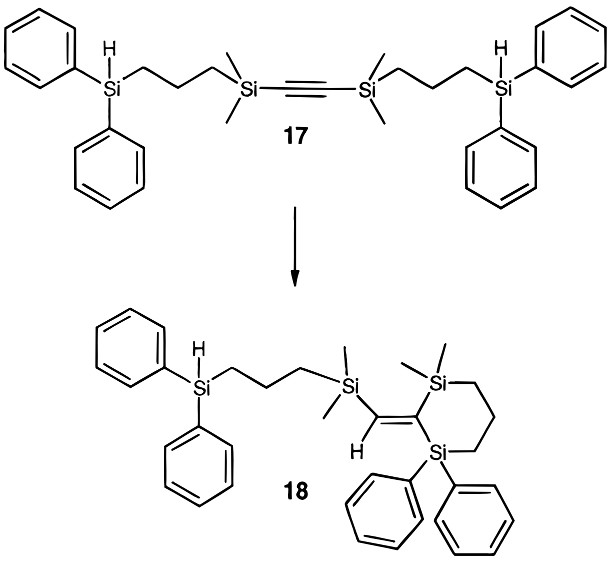
(35) SAINT, Release 4.05; Siemens Energy and Automation, Inc., Madison, WI 53719, 1996.

(36) Sheldrick, G. M. SADABS (Siemens Area Detector Absorption Corrections), 1996.

(37) Sheldrick, G. M. SHELXTL PC, Release 4.1; Siemens Crystallographic Research Systems, Madison, WI 53719, 1994.

(38) Sheldrick, G. M. XPREP, Version 5.03; Siemens Crystallographic Research Systems, Madison, WI 53719, 1994.



17

18

(5)

For **15**, the final refined structure was based on a disordered model in which the six-membered ring could exist in one of two nonplanar conformations. On the basis of the observed thermal displacement ellipsoids, it was assumed that only the positions of the three methylene carbon atoms of the ring were significantly affected by this disorder. The occupancy of the two conformations was refined as a free variable (the final ratio of approximately 56:44), and then hydrogen atoms for each unique component of the disorder were placed in calculated positions and refined on the basis of the carbon atom to which they were attached.

Molecular Mechanics Calculations. The structure of **15** was calculated using Hyperchem (Waterloo, Canada) with the MM2 parameter set on an IBM-compatible computer (Pentium processor under Windows 95). The structure in Figure 3, designed to model the approach to the transition state in the hydrosilylation reaction leading to the cyclic structure, was calculated using a fixed distance for $Me_3Si\boldsymbol{C}\cdots\boldsymbol{H}SiPh_2$ of 3 Å.

Materials. Tetrahydrofuran (Caledon) and di-*n*-butyl ether (Aldrich) were distilled from potassium/benzophenone. CH_2Cl_2 (Caledon) was distilled prior to use from P_4O_{10}. Methanol (Caledon) was distilled from Mg. Cyclohexane (Caledon), hexane (Caledon), and toluene (Caledon) were distilled prior to use. Only distilled water was used.

$Co_2(CO)_8$, $Mo_2Cp_2(CO)_6$, and $Cr(CO)_6$ were obtained from Strem and were used as supplied without further purification.

All experiments were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were dried according to standard procedures. For all hydrosilylations, 1 mol % of either Wilkinson's ($(Ph_3P)_3RhCl$, Aldrich) or Karstedt's catalyst ($(Pt_2(H_2C{=}CHSiMe_2OSiMe_2CH{=}CH_2)_n$, Gelest) was used. Unless otherwise specified, compounds were purified using flash chromatography. The eluents are provided in each experimental description.

Ligands 1−6. The preparation and characterization of these compounds has been discussed previously.[18]

General Procedure for the Preparation of Hexacarbonyldicobalt Derivatives. $Co_2(CO)_8$ (1 equiv, 0.4−1.7 g, *ca.* 1−5 mmol) was dissolved in THF (30 mL), and a solution of the alkyne (1 equiv) in THF (10 mL) was added dropwise over a period of 30 min at 25 °C. The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The mixture was then subjected to flash chromatography on silica gel using elution with nonpolar solvent mixtures.

$Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiPh_2H[Co_2(CO)_6]$ (7). $Co_2(CO)_8$ (0.39 g, 1.14 mmol) and ($Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiPh_2H$) (**1**; 0.35 g, 0.92 mmol) gave, after chromatography with cyclohexane/CH_2Cl_2 (90:10), **7** as a red waxy solid (0.52 g, 0.78 mmol; 85%). ^1H NMR (CD_2Cl_2, 200.13 MHz): δ 7.48 (m, 10H, aromatic), 4.77 (m, 1H, Si−*H*), 1.75 (m, 2H, $CH_2CH_2CH_2$), 1.21 (m, 2H, $SiPh_2CH_2$), 0.83 (m, 2H, $SiMe_2CH_2$), 0.21 (s, 6H, $Si(CH_3)_2$), 0.17 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 134.4, 130.2, 128.2 (aromatic), 21.2 ($CH_2CH_2CH_2$), 20.3 ($SiPh_2CH_2$), 18.4 ($SiMe_2CH_2$), 1.1 ($Si(CH_3)_2$), −0.6 ($Si(CH_3)_3$). IR (neat, cm^{-1}): ν_{CO} 2018 (sh), 2045 (m), 2083 (sh).

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)_2SiPh_2[Co_2(CO)_6]_2$ (8). $Co_2(CO)_8$ (0.60 g, 1.75 mmol) and $(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)_2SiPh_2$ (**2**; 1.00 g, 1.74 mmol) yielded the dark red waxy solid **8** (1.71 g, 1.49 mmol; 85%). ^1H NMR (CD_2Cl_2, 200.13 MHz): δ 7.40 (m, 10H, aromatic), 1.47 (m, 4H, $CH_2CH_2CH_2$), 1.22 (m, 4H, $SiMe_2CH_2$), 0.72 (m, 4H, $SiPh_2CH_2$), 0.13 (s, 12H, $Si(CH_3)_2$), 0.09 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 135.9, 135.2, 129.4, 128.1 (aromatic), 21.0 ($CH_2CH_2CH_2$), 19.0 ($SiPh_2CH_2$), 18.7 ($SiMe_2CH_2$), −0.5 ($Si(CH_3)_3$), −4.8 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ 0.5 ($SiPh_2$), −18.5 ($Si(CH_3)_3$), −19.6 ($Si(CH_3)_2$). IR (neat, cm^{-1}): ν_{CO} 2017 (m), 2045 (sh), 2083 (sh).

$CH_2{=}CHCH_2SiMe_2C{\equiv}CSiMe_2CH_2CH{=}CH_2[Co_2(CO)_6]$ (9). $Co_2(CO)_8$ (1.71 g, 5.00 mmol) and $CH_2{=}CHCH_2SiMe_2C{\equiv}CSiMe_2CH_2CH{=}CH_2$ (**3**; 1.11 g, 5.00 mmol) after chromatography with toluene/acetone (80:20) gave the desired compound **9** as a red waxy solid (2.21 g, 4.35 mmol; 87%).[21b] ^1H NMR (CD_2Cl_2, 200.13 MHz): δ 5.78 (m, 2H, $CH_2{=}CHCH_2$), 4.95 (m, 4H, $CH_2{=}CHCH_2$), 1.63 (m, 4H, $CH_2{=}CHCH_2$), 0.29 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 201.6 ($C{\equiv}O$), 133.6 ($CH_2{=}CHCH_2$), 114.6 ($CH_2{=}CHCH_2$), 25.2 ($CH_2{=}CHCH_2$), −1.0 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −0.8. IR (neat, cm^{-1}): ν_{CO} 2018 (sh), 2046 (m), 2085 (sh). Mass spectrum (DEI, *m/z* (%)): 467 (15) ($[M - C_3H_5]^+$), 424 (60) ($[M - 3(CO)]^+$), 396 (50) ($[M - 4(CO)]^+$), 368 (45) ($[M - 5(CO)]^+$), 340 (100) ($[M - 6(CO)]^+$). Anal. Calcd for $C_{18}H_{22}Co_2O_6Si_2$: C, 42.26; H, 3.69. Found: C, 42.53; H, 4.50.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiMe_2)_2O[Co_2(CO)_6]_2$ (10). $Co_2(CO)_8$ (1.10 g, 3.22 mmol) and $(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiMe_2)_2O$ (**4**; 0.81 g, 1.54 mmol) gave, after chromatography with hexanes, the desired compound (**10** as a red-brown oil (1.13 g, 1.03 mmol; 67%). ^1H NMR (CD_2Cl_2, 200.13 MHz): δ 1.44 (m, 4H, $CH_2CH_2CH_2$), 0.81 (m, 4H, $CH_2Si(CH_3)_2O$), 0.61 (m, 4H, $Si(CH_3)_2CH_2$), 0.30 (s, 18H, $Si(CH_3)_3$), 0.27 (s, 12H, $Si(CH_3)_2$), 0.03 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 200.9 ($C{\equiv}O$), 92.9, 92.0 (cluster carbons), 23.1 ($CH_2CH_2CH_2$), 22.8 ($CH_2Si(CH_3)_2O$), 18.0 ($Si(CH_3)_2CH_2$), 1.1, 0.5, −0.6 ($Si(CH_3)$'s). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ 0.7 ($Si(CH_3)_2$), 0.5 ($Si(CH_3)_3$), −6.4 ($Si(CH_3)_2O$). IR (neat, cm^{-1}): ν_{CO} 2084 (sh), 2046 (sh), 2020 (sh). Mass spectrum (DEI, *m/z* (%)): 644 (95), ($[M - (C_{12}O_{12}Co_2)]^+$), 585 (100) ($M$-$(C_{12}O_{12}Co_3)]^+$).

$-(Me_2Si(CH_2)_3Me_2SiC{\equiv}CSiMe_2(CH_2)_3(SiMe_2O)_nSiMe_2O)_m-[Co_2(CO)_6]_m$ (11). $Co_2(CO)_8$ (0.60 g, 1.75 mmol) and $-Me_2SiC{\equiv}CSiMe_2(CH_2CHCH_2)(SiMe_2O)_nSiMe_2OSiMe_2)_m-$ (1.0 g, $\bar{M}_w = 140\,000$, $\bar{M}_w/\bar{M}_n = 2.06$) after filtration though 25 g of silica gel afforded the red, highly viscous oil **11** (1.1 g). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 0.06 (broad, $Si(CH_3)$'s). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 1.0 ($Si(CH_3)$'s). IR (neat, cm^{-1}): ν_{CO} 2087 (m), 2047 (m), 2023 (sh). $\bar{M}_w = 155\,000$; $\bar{M}_w/\bar{M}_n = 2.51$.

General Procedure for the Preparation of Chromium Aryl Complexes. A 250 mL one-neck round-bottomed flask was charged with $Cr(CO)_6$, the arylsilane, and di-*n*-butyl ether (50 mL). After the mixture had stirred for 72 h at reflux, the solvent was removed by vacuum distillation. The residue was subjected to flash chromatography on silica gel. Elution with a nonpolar solvent gave the desired compound.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)_2SiPh_2[Cr(CO)_3]_2$ (12). A mixture of $Cr(CO)_6$ (0.76 g, 3.45 mmol), $(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)_2SiPh_2$ (**2**; 0.99 g, 1.72 mmol), and butyl ether was reacted as described above. Elution of the residue on silica with CH_2Cl_2 gave the crude desired compound, **12**. Further purification with methanol as recrystallization solvent yielded pure **12** as bright yellow crystals (mp 86 °C, 0.99 g, 1.17 mmol, 68%). ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ 5.65 (t, 2H, $^3J_{H-H}$ = 6.3 Hz, *para*), 5.49 (d, 4H, $^3J_{H-H}$ = 6.1 Hz, *ortho*), 5.21 (m, 4H, *meta*), 1.66 (m, 4H, $CH_2CH_2CH_2$), 1.22 (m, 4H, $SiPh_2CH_2$), 0.80 (m, 4H, $SiMe_2CH_2$), 0.15 (s, 12H, $Si(CH_3)_2$), 0.14 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 227.2 ($C\equiv O$), 100.0, 96.2, 95.4, 90.2 (aromatic), 20.7 ($CH_2CH_2CH_2$), 18.2 ($SiPh_2CH_2$), 15.5 ($SiMe_2CH_2$), −0.6 ($Si(CH_3)_2$), −2.2 ($Si(CH_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −4.4, −18.7, −19.7. IR (neat, cm^{-1}): ν_{CO} 1989 (sh), 1892 (sh). Anal. Calcd for $C_{38}H_{52}Cr_2O_6Si_5$: C, 53.76; H, 6.18. Found: C, 53.37; H, 5.93. For crystallographic data refer to Tables 1 and 2.

$(Me_3SiC\equiv CSiMe_2CH_2CH_2CH_2SiMe_2)_2Ph[Cr(CO)_3]$ (13). A mixture of $Cr(CO)_6$ (0.78 g, 3.55 mmol), $(Me_3SiC\equiv CSiMe_2CH_2CH_2CH_2SiMe_2)_2Ph$ (**6**; 1.56 g, 2.66 mmol), and butyl ether were reacted as described above. Elution of the residue with cyclohexane/CH_2Cl_2 (6:1) on silica gave the desired compound **13** as a yellow solid (mp 95 °C, 1.31 g, 1.81 mmol. 68%). ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ 5.34 (s, 4H, aromatic), 1.52 (m, 4H, $CH_2CH_2CH_2$), 0.88 (m, 4H, $Si(CH_3)_2Ph$), 0.67 (m, 4H, $SiMe_2CH_2$), 0.31 (s, 12H, $Si(CH_3)_2$), 0.15 (s, 12H, $Si(CH_3)_2$), 0.13 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 225.5 ($C\equiv O$), 115.0, 113.5 ($C\equiv C$), 102.4, 98.3 (aromatic), 20.8 ($CH_2CH_2CH_2$), 20.1 ($Si(CH_3)_2Ph$), 18.8 ($SiMe_2CH_2$), 0.2 ($Si(CH_3)_3$), −1.4 ($Si(CH_3)_2$), −3.2 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ 0.4, −18.4, −19.7. IR (neat, cm^{-1}): ν_{CO} 1966 (sh), 1893 (m). Mass spectrum (DEI, *m/z* (%)): 722 (20) ($[M]^+$), 638 (100) ($[M - 3(CO)]^+$), 331 (10) ($[C_{18}H_{31}Si_3]^+$), 255 (50) ($[C_{12}H_{27}Si_3]^+$). Anal. Calcd for $C_{33}H_{58}CrO_6Si_6$: C, 54.83; H, 8.09. Found: C, 54.62; H, 8.22.

$Me_3SiCHCSiMe_2CH_2CH_2CH_2SiPh_2[Cr(CO)_3]_2$ (15). A mixture of $Cr(CO)_6$ (2.33 g, 10.6 mmol), $Me_3SiC\equiv CSiMe_2CH_2CH_2CH_2SiPh_2H$ (**1**; 1.81 g, 4.77 mmol), and butyl ether were reacted as described above. Removal of volatile organics gave a yellow solid which was recrystallized from methanol to give **15** (mp 175 °C, 2.30 g, 3.53 mmol; 74%). ^{1}H NMR (CD_2Cl_2, 500.13 MHz): δ 7.77 (s, 1H, $C{=}CH$), 5.66 (t, 2H, $^3J_{H-H}$ = 6.4 Hz, *para*), 5.51 (d, 4H, $^3J_{H-H}$ = 6.1 Hz, *ortho*), 5.18 (m, 4H, *meta*), 2.02 (m, 2H, $CH_2CH_2CH_2$), 1.35 (m, 2H, $SiPh_2CH_2$), 0.86 (m, 2H, $SiMe_2CH_2$), 0.29 (s, 6H, $Si(CH_3)_2$), 0.22 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 125.03 MHz): δ 226.1 ($C\equiv O$), 172.9 ($C{=}CH$), 151.2 ($C{=}CH$), 101.6, 101.2, 97.1, 90.5 (aromatic), 18.4 ($CH_2CH_2CH_2$), 18.0 ($SiPh_2CH_2$), 15.6 ($SiMe_2CH_2$), 0.3 ($Si(CH_3)_2$ and $Si(CH_3)_3$). ^{29}Si NMR (CH_2Cl_2, 99.3 MHz): δ −18.5 ($Si(CH_3)_2$), −19.8 ($Si(CH_3)_3$), −24.1 ($SiPh_2$). IR (neat, cm^{-1}): ν_{CO} 1957 (m), 1882 (m), 1867 (sh). Mass spectrum (CI, *m/z* (%)): 652 (10) ($[M]^+$), 568 (40) ($[M - CO]^+$), 512 (15) ($[M - 5(CO)]^+$), 484 (100) ($[M - 6(CO)]^+$). Anal. Calcd for $C_{28}H_{32}Cr_2O_6Si_3$: C, 51.52; H, 4.94. Found: C, 50.92; H, 4.51. For crystallographic data, refer to Tables 1 and 3.

$Me_3SiHC{=}CSiMe_2CH_2CH_2CH_2SiPh_2$ (16). To a 25 mL vial charged with **15** (0.61 g, 0.94 mmol) was added a 1:1 mixture of hexane and CH_2Cl_2 (5 mL). After exposure to direct light for approximately 2 weeks, the crude mixture was subjected to flash chromatography on silica gel. Elution with CH_2Cl_2/hexane (50:50) gave the desired compound **16** as a clear colorless solid (0.31 g, 0.82 mmol; 88%). ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ 7.39 (m, 11H, aromatic and $Si{-}H$), 1.85 (m, 2H, $CH_2CH_2CH_2$), 1.26 (m, 2H, $SiPh_2CH_2$), 0.72 (m, 2H, $SiMe_2CH_2$), 0.14 (s, 6H, $Si(CH_3)_2$), 0.07 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 169.3 ($C{=}CH$), 163.0 ($C{=}CH$), 136.0, 135.5, 129.2, 127.6 (aromatic), 19.3 ($CH_2CH_2CH_2$), 18.4 ($SiPh_2CH_2$), 15.1 ($SiMe_2CH_2$), 0.5 ($Si(CH_3)_3$), −0.2 ($Si(CH_3)_2$. ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −8.3, −10.6, −11.5. IR (neat, cm^{-1}): ν 2954 (sh), 2898 (m), 2854 (m), 1427 (w). Mass spectrum (DEI, *m/z* (%)): 380 (5) ($[M]^+$), 365 (10) ($[M - CH_3]^+$), 303 (100) ($[M - C_6H_5]^+$), 198 (22) ($[M - Si(C_{12}H_{10}Si]^+$), 73 (76) ($[Si(CH_3)_3]^+$). Mass spectrum (high resolution, (DEI)): calculated mass for $^{12}C_{16}H_{32}Si_3$ ($[M]^+$), 380.1812 amu; observed, 380.1808 amu. Anal. Calcd for $C_{22}H_{32}Si_3$: C, 69.44; H, 8.48. Found: C, 69.39; H, 8.83.

$HPh_2Si(CH_2CH_2CH_2)SiMe_2C\equiv CSiMe_2(CH_2CH_2CH_2)SiPh_2H$ (17). To a mixture of diphenylsilane (4.14 g, 0.0225 mol) and $(H_2C{=}CHCH_2)Me_2SiC\equiv CSiMe_2(CH_2CH{=}CH_2)$ (2.5 g, 0.012 mol)[18] at −15 °C was added Karstedt's catalyst. After 1.5 h, the mixture was warmed to ambient temperature with stirring for an additional 18 h. The crude mixture was then subjected to flash chromatography on silica gel. Elution with pentane/CH_2Cl_2 (5:1) gave the desired compound **17** as a clear oil (6.6 g, 0.011 mol, 98%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.41 (m, 20H, aromatic), 4.90 (t, 2H, J = 3.6 Hz, $Si{-}H$), 1.65 (m, 4H, $CH_2CH_2CH_2$), 1.27 (m, 4H, $SiPh_2CH_2$), 0.74 (m, 4H, $SiMe_2CH_2$), 0.09 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 50.03 MHz): δ 135.8, 135.4, 135.1, 134.5 (aromatic), 113.8 ($C\equiv C$), 20.9, 20.0, 16.1 ($CH_2CH_2CH_2$), −1.7 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −10.7 ($PhSi$), −15.0 ($Si(CH_3)_2$). IR (neat): ν_{Si-H} 2116 cm^{-1}. Mass spectrum (DEI, *m/z* (%)): 365 (30) ($[C_{21}H_{29}Si_3]^+$), 283 (55) ($[C_{17}H_{23}Si_2]^+$), 183 (100) ($[C_{12}H_{11}Si]^+$). Mass spectrum (CI, NH_3, *m/z* (%)): 608 (10) ($[M + 18]^+$), 366 (100) ($[C_{21}H_{29}Si_3 + 1]^+$). Anal. Calcd for $C_{36}H_{46}Si_4$: C, 73.19; H, 7.85. Found: C, 73.40; H, 8.10.

$(HPh_2SiCH_2CH_2CH_2SiMe_2HC{=}CSiMe_2CH_2CH_2CH_2SiPh_2)$ (18). Spectroscopic studies of a sample of **17** (purified and characterized 1 month earlier) demonstrated that **17** had undergone a single intramolecular hydrosilylation to give **18**, in nearly quantitative yield. The cyclized product **18** was unambiguously characterized by use of HMBC multidimensional NMR (HMBC ^{29}Si−^{1}H 2D NMR, HSQC ^{13}C−^{1}H 2D NMR, HMBC ^{13}C−^{1}H 2D NMR, ^{1}H−^{1}H COSY). ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 7.90 (m, 10H, HPh_2Si), 7.74 (m, 10H, $SiPh_2$), 7.72 (s, 1H, $C{=}CH$), 5.32 (s, 1H, SiH), 2.35 (m, 2H, $CH_2CH_2CH_2$), 1.96 (m, 2H, $HPh_2SiCH_2CH_2CH_2$), 1.76 (m, 2H, $Si(CH_3)_2CH_2CH_2CH_2$), 1.63 (m, 2H, $HPh_2SiCH_2CH_2CH_2$), 1.22 (m, 2H, $HPh_2SiCH_2CH_2CH_2$), 1.19 (m, 2H, $Si(CH_3)_2CH_2CH_2CH_2$), 0.53 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 168.5 ($C{=}CH$), 163.6 ($C{=}CH$), 135.9, 135.4, 135.1, 134.6 (Ph_2SiH), 129.4, 129.0, 127.9, 127.6 (Ph_2Si), 21.0 ($HPh_2SiCH_2CH_2CH_2$), 19.2 ($Si(CH_3)_2CH_2CH_2CH_2$), 19.1 ($HPh_2SiCH_2CH_2CH_2$), 18.4 ($CH_2CH_2CH_2$), 16.6 ($HPh_2SiCH_2CH_2CH_2$), 15.0 ($Si(CH_3)_2CH_2CH_2CH_2$), 0.1 ($Si(CH_3)_2$), −1.2 ($HPh_2SiCH_2CH_2CH_2Si(CH_3)_2$). ^{29}Si NMR ($CH_2Cl_2$, 99.36 MHz): δ −9.8 ($Si(CH_3)_2$), −12.1 ($HPh_2SiCH_2CH_2CH_2Si(CH_3)_2$), −16.3 ($HPh_2Si$), −19.8 ($SiPh_2$). IR (neat): ν_{Si-H} 2116 cm^{-1}. Mass spectrum (DEI, *m/z* (%)): 590 (10) ($[M]^+$), 575 (15) ($[M - CH_3]^+$), 513 (25) ($[M - Ph]^+$), 365 (100) ($[C_{25}H_{29}Si_3]^+$). Mass spectrum (high resolution, (DEI)): calculated msas for $^{12}C_{36}H_{46}Si_4$ ($[M]^+$), 590.2677 amu; observed, 590.2665 amu. Anal. Calcd for $C_{36}H_{46}Si_4$: C, 73.19; H, 7.85. Found: C, 73.14; H, 8.12.

Preparation of Mixed-Metal Compounds. $(Me_3SiC\equiv CSiMe_2CH_2CH_2CH_2)_2SiPh_2[Cr(CO)_3]_2[Mo_2(CO)_4Cp_2]_2$ (19). A 250 mL one-necked round-bottomed flask was charged with $Mo_2Cp_2(CO)_6$ (0.98 g, 2.00 mmol) and di-*n*-butyl ether (50 mL). The mixture was stirred for 24 h at reflux to generate $Mo_2Cp_2(CO)_4$.[39] After cooling to room temperature, a solution of **12** (0.77 g, 0.91 mmol) in CH_2Cl_2 (10 mL) was added dropwise and the reaction mixture was stirred for 12 h. The solvent was removed by vacuum distillation and the residue subjected to flash chromatography on silica gel. Elution with cyclohexane/CH_2Cl_2 (9:1) gave the desired compound **19** as a red solid (50 °C, 1.10 g, 0.64 mmol; 70%). ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ 5.40 (m, 10H, aromatic), 5.23 (s, 20H, Cp *H*'s), 1.64 (m, 4H, $CH_2CH_2CH_2$), 1.23 (m, 4H, $SiPh_2CH_2$), 0.82 (m, 4H, $SiMe_2CH_2$), 0.26 (s, 12H, $Si(CH_3)_2$), 0.15 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 100.6, 96.8, 95.0, 90.9 (aromatic), 89.0 (Cp *C*'s), 21.2 ($CH_2CH_2CH_2$), 18.7 ($SiPh_2CH_2$), 16.2 ($SiMe_2CH_2$), 0.1 ($Si(CH_3)_3$), −1.7 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ 6.3, −18.7, −19.6. IR (neat, cm^{-1}): ν_{CO} 1970 (sh), 1893 (m).

For the following two compounds, the general method for the preparation of cobalt complexes was followed (see above).

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[39] Curtis, M. D.; Fotinos, N. A.; Messerle, L.; Sattelberger, A. P. *Inorg. Chem.* **1983**, *22*, 1559.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)_2SiPh_2[Cr(CO)_3]_2[Co_2(CO)_6]_2$ (20). $Co_2(CO)_8$ (0.81 g, 2.37 mmol) and **12** (1.00 g, 1.18 mmol) were reacted overnight at ambient temperature. Removal of volatile organics yielded a red solid, which was recrystallized from hexane to give dark red crystals of **20**, suitable for X-ray diffraction (mp 114 °C, 0.98 g, 0.69 mmol; 58%). ^1H NMR (CD_2Cl_2, 200.13 MHz): δ 5.66 (t, 2H, $^3J_{H-H}$ = 6.3 Hz, *para*), 5.48 (d, 4H, $^3J_{H-H}$ = 6.1 Hz, *ortho*), 5.22 (m, 4H, *meta*), 1.69 (m, 4H, $CH_2CH_2CH_2$), 1.23 (m, 4H, $SiPh_2CH_2$), 0.97 (m, 4H, $SiMe_2CH_2$), 0.32 (s, 12H, $Si(CH_3)_2$), 0.30 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.03 MHz): δ 225.5 (Cr−CO), 200.1 (Co−CO), 99.9, 96.3, 94.3, 90.3 (aromatic), 22.2 ($CH_2CH_2CH_2$), 18.4 ($SiPh_2CH_2$), 15.8 ($SiMe_2CH_2$), 0.6 ($Si(CH_3)_2$), −1.2 ($Si(CH_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ 0.6 (*Si*(CH$_3$)'s), 0.4 (*Si*Ph$_2$). IR (neat, cm^{-1}): ν_{CO} 2084 (sh), 2044 (sh), 2014 (m), 1970 (m), 1895 (sh). Anal. Calcd for $C_{50}H_{52}Co_4Cr_2O_{18}Si_5$: C, 42.26; H, 3.96. Found: C, 41.89; H, 3.45. For crystallographic data, refer to Tables 1 and 4.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiMe_2)_2C_6H_4[Cr(CO)_3][Co_2(CO)_6]_2$ (21). $Co_2(CO)_8$ (0.94 g, 2.75 mmol) and **13** (0.94 g, 1.30 mmol) were reacted overnight at ambient temperature. Elution with hexane/CH_2Cl_2 (7:1) gave the desired compound **21** as a red oil (1.50 g, 1.16 mmol, 89%). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 5.32 (s, 4H, aromatic), 1.53 (m, 4H, $CH_2CH_2CH_2$), 0.90 (m, 8H, $CH_2CH_2CH_2$), 0.34 (s, 12H, $Si(CH_3)_2$), 0.32 (s, 18H, $Si(CH_3)_3$), 0.28 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 225.4 (Cr−C≡O), 201.6 (Co−C≡O), 102.1, 100.3 (aromatic), 93.9, 92.8 (cluster carbons), 22.5 ($CH_2CH_2CH_2$), 20.6 ($SiPh_2CH_2$), 19.0 ($SiMe_2CH_2$), 1.3 ($Si(CH_3)_3$), 0.5 ($Si(CH_3)_2$), −3.4 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz) δ 0.4 (C_6H_4-$SiMe_3$), −18.4 (Me_2Si), −19.7 ($SiMe_3$). IR (neat, cm^{-1}): 2084 (sh), 2047 (sh), 2020 (m), 1965 (sh), 1893 (m).

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Supporting Information Available: Tables of thermal parameters, bond lengths, bond angles, and complete atomic coordinates for compounds **12**, **15**, and **20** and figures giving ^1H NMR and ^{13}C NMR spectra for compounds **7**, **8**, **10**, **11**, **19**, and **21** (34 pages). Ordering information is given on any current masthead page.

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