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Metal-Mediated Allyl Transfers in (Alkynylallylsilane)$Co_2(CO)_6$ Complexes: A Synthetic and Structural Study

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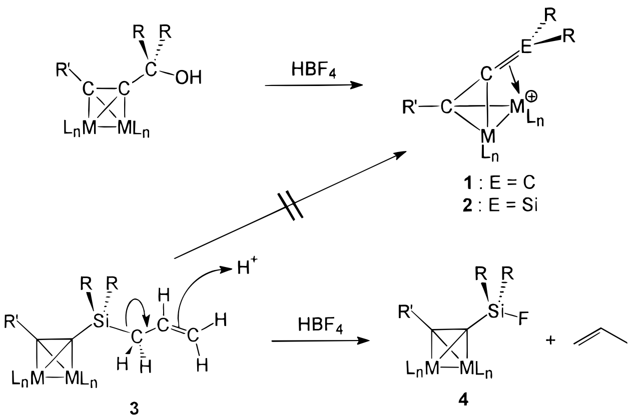
The alkyne complex $(CH_2{=}CHCH_2SiMe_2C{\equiv}CCMe_2OH)Co_2(CO)_6$, **5**, is a potential precursor to either a metal-stabilized silylium or carbenium species. Treatment with HBF_4 initially produces the cobalt-stabilized carbocation, which undergoes fluoride-promoted allyl migration to give $(FSiMe_2C{\equiv}CCMe_2CH_2CH{=}CH_2)Co_2(CO)_6$, **8**. $Fe(CO)_5$ reacts with **5** to yield the "dehydroxylated" iron−cobalt cluster $(CH_2{=}CHCH_2SiMe_2C{=}C{=}CMe_2)FeCo(CO)_6$, **13**, which upon addition of HBF_4 loses propene to give the corresponding fluorosilane cluster $(FSiMe_2C{=}C{=}CMe_2)FeCo(CO)_6$, **14**. This latter molecule has been characterized by X-ray crystallography and may be regarded as an excellent structural model for the analogous cationic dicobalt cluster.

Introduction

The synthetic utilization of metal cluster-stabilized propargyl cations, **1**, was pioneered by Nicholas and has since been exploited by many groups.[1] Thus, $Co_2(CO)_6$ moieties have been used not only as protecting groups[2] but also to allow geometrically disfavored cyclization reactions,[3] or to stabilize strained alkynes such as (hexafluorocyclohexa-3-ene-1-yne)$[Co_2(CO)_6]$.[4] In contrast to the normal linear arrangement of the R−C≡C−R′ grouping in free alkynes, complexation of the triple bond to a dimetallic fragment yields a bend angle in the range of 136−145°; this change in geometry brings the substituents closer together and enhances their ability to react with each other.

We have previously reported the syntheses of a series of metal cluster complexes **3**, which possess an Si-allyl unit.[5] However, attempts to generate the silicon analogue of **1**, i.e., a metal-stabilized silyl cation, **2**, from these compounds by protonation using HBF_4 led to cleavage of the silicon−α-carbon bond, subsequent loss of propene, and formation of the corresponding fluorosilanes, **4**, as depicted in Scheme 1. This reaction presumably occurs through an S_E2' process[6] via a β-silyl cation followed by nucleophilic displacement at silicon by fluoride. Lambert has used this approach to generate the trimesityl silylium ion from allyltrimesitylsilane;[7] however, in that case, $[B(C_6F_5)_4]^-$ was used as the nonnucleophilic counterion.

Scheme 1. Protonation of Metal Cluster Complexes of Alkynols and Alkynylallylsilanes



To further explore the formation of metal cluster-stabilized silylium ions (which can also be viewed as metal cation-stabilized silenes), we chose to incorporate potential precursors to silylium and carbenium centers in the same system. Two possible outcomes were envisaged in this competition process: in one scenario, attack of an external electrophile on the allyl group could form the silylium ion, whose intermediacy could be inferred as the result of a molecular rearrangement.[8] Although a silicon−hydrogen bond is weaker than a carbon−hydrogen bond by ≈6 kcal mol^{-1}, the formation of a metal-stabilized carbocation may be sufficient to allow this reaction to proceed. Alternatively, the propargyl cation, stabilized by the metal, could be used as

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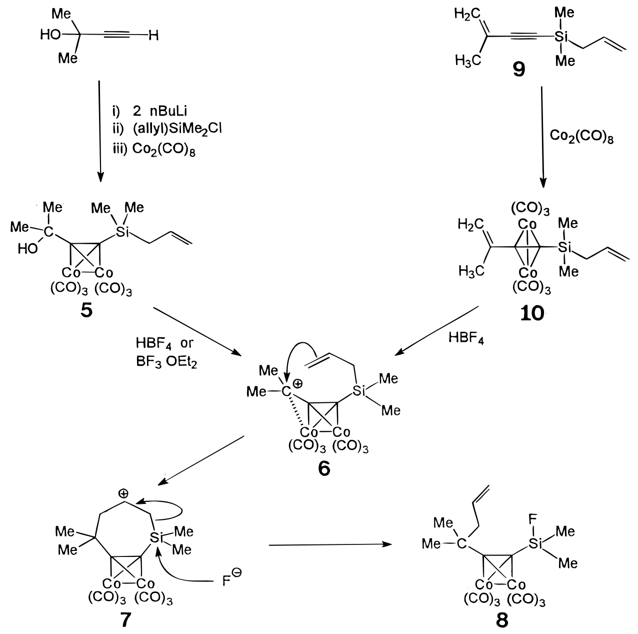
10.1021/om980267v CCC: $15.00

Scheme 2. The Fluoride-Mediated Allyl Migration Process



the internal electrophile to attack the allylsilane and generate the silylium ion.

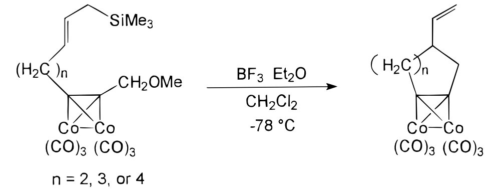
To address these possibilities, which would be expected to depend on the relative stabilities of the metal-stabilized carbenium and silylium ions, we have prepared the precursors **5** and **10** and have examined their reactivity in the presence of electrophiles.

Results and Discussion

Metal-Stabilized Carbocations versus Silylium Cations. Thus far, two approaches have been discussed whereby Si$-$CH$_2$CH$=$CH$_2$ and Si$-$H fragments have been considered as metal-stabilized silicon cation precursors.[5,9] In this study, we chose to incorporate an allylsilane functionality and a carbocation precursor (an alcohol or an alkene) into the same alkyne$-$dicobalt cluster. The synthesis of [(CH$_2$$=$CHCH$_2$)SiMe$_2C\equiv$CCMe$_2$-OH]Co$_2(CO)_6$, **5**, was accomplished by the route shown in Scheme 2. Double lithiation of 2-methyl-3-butyne-2-ol, treatment with allyldimethylchlorosilane, and addition of Co$_2$(CO)$_8$ furnished **5** in an overall yield of 92%. The final product was identified by its mass and NMR spectra, which are closely analogous to those of related systems, such as [(CH$_2$$=$CHCH$_2$)SiMe$_2C\equiv$CSiMe$_3$]Co$_2$-(CO)$_6$.[5]

In the expectation that protonation of **5** with HBF$_4$ could occur at either the allyl group (to yield ultimately a fluorosilane) or at the tertiary alcohol site (thus producing a carbocation), 1 equiv of tetrafluoroboric acid was added to **5**. Chromatographic separation yielded a product, **8**, whose mass and NMR spectra indicated loss of the alcohol functionality, retention of the allyl group, and formation of an SiMe$_2$F moiety. The presence of this latter fragment was unambiguously revealed by the fluorine-coupled doublet, $^1J_{\mathrm{Si-F}} = 251$ Hz, in the ^{29}Si NMR spectrum. The structure of **8**, together with its proposed mechanism of formation, is depicted in Scheme 2.

Scheme 3. The Cyclization of (Me$_3$SiCH$_2$CH$=$CH(CH$_2$)$_n$C$\equiv$CCH$_2$OMe)Co$_2$(CO)$_6$



The migration of the allyl fragment from silicon (in **5**) to carbon (in **8**) was established by means of a series of ^{1}H$-$^{1}H COSY, ^{1}H$-$^{13}C shift-correlated, and ^{13}C-DEPT NMR spectra. In particular, the ^{1}H$-$^{13}C shift-correlated NMR experiment revealed clear correlations from the geminal methyl protons to three carbon environments: one to their methyl partner at C(5), one to the quaternary carbon atom, C(4), to which both methyls are attached, and finally to C(3), the aliphatic methylene carbon resonance of the allyl unit. Additional evidence for the transfer of the allyl group from silicon to carbon is provided by the ^{1}H$-$^{13}C NMR correlations from the quaternary carbon atom at C(4) not only to the geminal dimethyl protons but also to the methylene protons at C(3) of the allyl fragment.

To verify that this allyl migration process occurs through initial formation of a cobalt-stabilized carbocation, **5** was treated with BF$_3$·etherate; this Lewis acid is known to react with propargylic alcohols or ethers to generate cobalt-stabilized carbocations, and indeed, **8** was again the major product. Moreover, the isopropenyl complex **10** (prepared by silylation of 2-methyl-1-buten-3-yne to give **9** and subsequent addition of Co$_2$(CO)$_8$) also led to the allyl transfer product **8** when treated with 1 equiv of HBF$_4$.

We conjecture that the favored site of proton attack on **5** or **10** is at the alcohol or the isopropenyl groups, respectively, to generate a cobalt-stabilized carbocation, **6**. Intramolecular electrophilic attack can then occur on the neighboring allyl group to give a β-silyl stabilized carbocation, **7**; subsequent nucleophilic attack by fluoride ion at the silicon center leads to cleavage of the Si$-$allyl linkage and generates the fluorosilane, **8**, as depicted in Scheme 2. It is presumably the formation of the silicon$-$fluorine bond that provides the overall thermodynamic driving force for the allyl migration.

It is, of course, well-known that intermolecular transfer of allyl groups from allylsilanes occurs with a wide variety of electrophiles;[6b] in seeking a precedent for such an allyl-transfer mechanism, we note that Schreiber[10] used a cobalt-stabilized cation (Scheme 3) to induce cyclization and subsequent loss of the silyl fragment. In contrast, in the current work, the silicon is a component of the cyclic cation and so is retained in the final structure.

Iron$-$Cobalt Clusters as Models of Dicobalt Cluster-Stabilized Cations. It has been shown, both by NMR data[11] and by calculations at the extended Hückel level,[12] that propargyl cations of the type [(R′C$\equiv$

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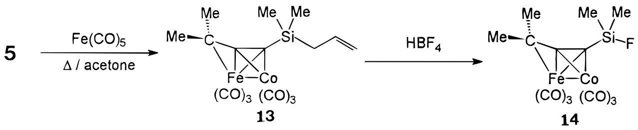
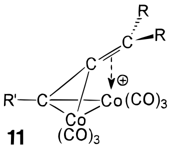
Scheme 4. Synthetic Route to 14



$CCR_2)Co_2(CO)_6]^+$, **11**, adopt a bent geometry such that the electron deficiency at the carbocationic center is alleviated by direct interaction with a metal. Until very recently,[13] no X-ray crystallographic data on such cobalt-stabilized cations had been reported, and it has been suggested[14] that isolobal replacement of a $Co(CO)_3^+$ vertex by an $Fe(CO)_3$ group should yield a neutral cluster with the same electron count and a similar structure. Experimental support for this proposal is based on the X-ray crystal structure of the iron−cobalt cluster $(MeC{\equiv}CCH_2)FeCo(CO)_5PPh_3$,[14] as well as the vinylidene clusters $Cp_2W_2(CO)_4Fe(CO)_3(C{=}CH_2)$ and $Co_2Ru(CO)_9(C{=}CH^tBu)$ reported by Stone and by Vahrenkamp, respectively.[15] In each of these molecules, the vinylidene moiety leans toward the $M(CO)_3$ vertex, where M = Fe or Ru.



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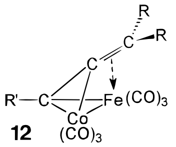

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The preparation of iron−cobalt clusters $(R'C{\equiv}CCR_2)$-$CoFe(CO)_6$, **12**, is readily achieved by the "dehydroxylation" of the corresponding propargyl alcohol complexes $(R'C{\equiv}CCR_2OH)Co_2(CO)_6$ with iron pentacarbonyl in refluxing acetone.[16,17] Accordingly, the reaction of **5** with iron pentacarbonyl in acetone under reflux gave the corresponding iron−cobalt cluster **13** (Scheme 4), which was fully characterized by NMR and mass spectrometry. The chiral nature of this cluster is reflected in the diastereotopic character of both the CMe_2 and $SiMe_2$ groups. Removal of the hydroxyl group, i.e. the potential carbocationic site, now leaves the allylsilane as the preferred site of attack by HBF_4 on **13** to give the fluorosilyl compound, **14**, which was characterized by X-ray crystallography. Figure 1 shows the structure of **14** and confirms its identity as a vinylidene complex.

The most relevant feature of the structure is the bending of the $C{=}CMe_2$ moiety toward the iron vertex; the Fe···CMe_2 distance of 2.335 Å reflects its character as a model for a tertiary carbocation stabilized by an organometallic unit. In other iron−cobalt cluster systems that we have characterized, the Fe···C distances range from 2.29 Å for CH_2 groups to 2.7 Å for "tertiary cations" of the CR_2 type.[17] This pattern follows that established for the molybdenum-stabilized system $[Cp_2Mo_2(CO)_4(HC{\equiv}CCR_2)]^+$, whereby the Mo···C distances range from 2.44 Å in primary cations (Mo···CH_2), to 2.61 Å in secondary cations (Mo···CHR), and to 2.75 in tertiary cations (Mo···CR_2).[18]

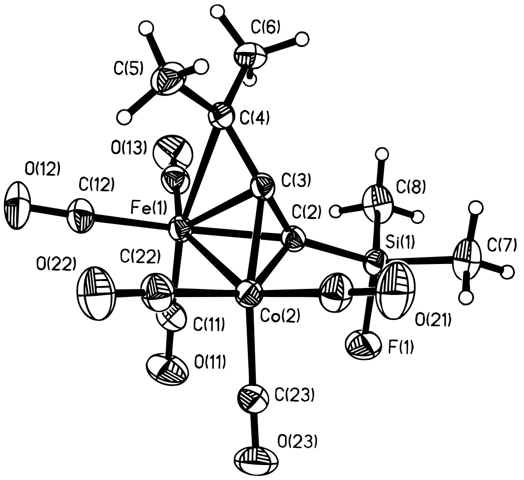

Figure 1. X-ray crystal structure of **14** showing 30% thermal probability ellipsoids. Salient bond lengths (Å): Fe(1)−Co(2) 2.5494(7), Co(2)−C(2) 2.015(3), Co(2)−C(3) 1.937(4), Fe(1)−C(2) 2.012(3), Fe(1)−C(3) 1.997(3), Fe(1)−C(4) 2.335(3), Si(1)−F(1) 1.601(3).

Conclusions

It is evident that HBF_4 reacts with allylsilane complexes, such as **3** to give fluorosilanes, with no evidence for the intermediacy of a silylium cation. However, when a more attractive site for protonation is available, such as an alcohol or an alkene at the other terminus of the alkyne, a different reaction pathway is followed such that the initially generated product is a metal-stabilized carbocation. The allyl group at the other terminus of the molecule behaves as the nucleophile and adds intramolecularly to the cationic center at the γ-carbon to form a seven-membered ring possessing a β-silyl-stabilized cation.[19] Finally, fluoride can now attack at the silicon center and generate a new C=C double bond; the overall result is to bring about migration of the allyl fragment from the silicon atom to the α-carbon atom at the other terminus of the complexed alkyne. Extension of this process to allyl migrations in steroidal and terpenoid systems will be the subject of a future report.

Experimental Section

All experiments were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded on a Bruker AC-200 or AC-300 or an Avance DRX-500 spectrometer. Proton spectra at 500 MHz were acquired using a 5 mm broadband inverse probe with triple axis gradient capability. Spectra were obtained with eight scans in 32K data points over a 3.788 kHz

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[13] The X-ray structure of the doubly complexed propargyl cation $[(^tBuC{\equiv}C)_3C\{Co_2(CO)_6\}_2]^+$ has very recently been reported: Melikyan, G. G.; Bright, S.; Monroe, T.; Hardcastle, K. I.; Ciurash, J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 161.

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[17] Recent results from this laboratory suggest that the process is in fact a decarboxylation: Dunn, J. D.; Britten, J. F.; McGlinchey, M. J. Manuscript in preparation.

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[19] The formation of cycloheptyne−cobalt complexes via intramolecular allylation of γ-carbonyl cations has been reported: Green, J. *Chem. Commun.*, in press.

spectral width (4.325 s acquisition time). The sample temperature was maintained at 30 °C by a Bruker Eurotherm variable-temperature unit. The free induction decay (FID) was processed using exponential multiplication (line broadening: 0.2 Hz) and was zero-filled to 64K before Fourier transformation.

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. Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Tetrahydrofuran (Caledon), acetonitrile (Caledon), and di-*n*-butyl ether (Aldrich) were distilled from potassium/benzophenone. CH_2Cl_2 (Caledon) was distilled prior to use from P_2O_5. Hexane (Caledon) and toluene (Caledon) were distilled prior to use. Only distilled water was used. Allyldimethylchlorosilane (Aldrich) was distilled prior to use. Otherwise, the compounds from Aldrich, *n*-butyllithium, 2-methyl-3-butyn-2-ol, 2-methyl-2-buten-3-yne, and BF_3·etherate, were used without further purification. $Co_2(CO)_8$ and $Fe(CO)_5$ were obtained from Strem Chemicals. The $Fe(CO)_5$ was distilled prior to use, and $Co_2(CO)_8$ was used as supplied without further purification.

X-ray Crystallography. X-ray crystallographic data for **14** were collected from a single-crystal sample which was mounted in a 0.2 mm sealed glass capillary. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (using the program SMART[20]) 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. Upon completion of the data collection, the first 50 frames were recollected in order to improve the decay corrections analysis. Processing was carried out by use of the program SAINT,[21] which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS[22] 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 direct methods procedure in the Siemens SHELXTL program library[23] and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic data are collected in Table 1.

Table 1. Crystal Data and Structure Refinement for 14

empirical formula	$C_{13}H_{12}SiFO_6CoFe$
mol wt	426.10
description	parallelepiped
dimens, mm	0.02 × 0.04 × 0.04
temp, K	300(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2_1/n$
Z	4
a, Å	8.2492(2)
b, Å	15.4888(2)
c, Å	13.6408(3)
β, deg	94.7430(10)
volume, Å^3	1736.92(6)
calcd density, g/cm^3	1.629
abs coeff, mm^{-1}	1.892
F(000)	856
θ-range for collection, deg	1.99−26.58
index ranges	$-10 \le h \le 10$, $-19 \le k \le 19$, $-16 \le l \le 16$
no. of reflns collected	14 037
no. of independent reflns	3375
R(int)	0.0470
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	3375/0/209
goodness-of-fit on F^2	1.059
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0396, wR2 = 0.0890
R indices (all data)*	R1 = 0.0622, wR2 = 0.1016
largest diff peak, e/Å^3	0.479
largest diff hole, e/Å^3	−0.360

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$.

Preparation of $(CH_2{=}CHCH_2)SiMe_2C{\equiv}CCMe_2OH$.[24] *n*-Butyllithium (125 mL, 1.6 M in hexane) was added dropwise to a solution of 2-methyl-3-butyn-2-ol (10 mL, 8.68 g, 0.10 mol) in diethyl ether/THF (30 mL) at −50 °C via syringe over 30 min. After stirring for 2 h at −50 °C a solution of allyldimethylchlorosilane (14.6 mL, 13.46 g, 0.10 mol) in diethyl ether (15 mL) was added dropwise. The solution was allowed to warm to room temperature slowly and stirred for 24 h. The crude mixture was extracted with water, and the separated organic phase was dried over $MgSO_4$. Removal of the solvent and other volatile organic components by rotary evaporation yielded $(CH_2{=}CHCH_2)SiMe_2C{\equiv}CC(CH_3)_2OH$ as a clear oil (16.7 g, 0.092 mol, 92%). ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 5.70 (m, 1H, $CH_2{=}CHCH_2$), 4.88 (m, 2H, $CH_2{=}CHCH_2$), 2.31 (s, 1H, O*H*), 1.62 (m, 2H, $CH_2{=}CHCH_2$), 1.48 (s, 6H, HO-$(CH_3)_2C$), 0.15 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 134.5 ($CH_2{=}CHCH_2$), 113.7 ($CH_2{=}CHCH_2$), 112.3, 84.5 ($C{\equiv}C$), 63.0 ($HO(CH_3)_2C$), 31.3 ($HO(CH_3)_2C$), 24.8 ($CH_2{=}CHCH_2$), −2.3 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 99.36 MHz): δ −17.9. IR (hexane) ν_{OH} at 3354, $\nu_{C\equiv C}$ at 2170 cm^{-1}. Mass spectrum: (DEI, *m/z* (%)) 165 (15) ($[M - OH]^+$), 99 (100) ($[CH_2{=}CHCH_2Si(CH_3)_2]^+$); (CI, *m/z* (%)) 200 (30) ($[M + NH_4]^+$), 182 (100) ($[M]^+$), 165 (35) ($[M - OH]^+$); (high resolution, DEI) calculated for mass $^{12}C_9H_{15}SiO$ ($[M - CH_3]^+$), 167.0892 amu; observed, 167.0898 amu. Anal. Calcd for $C_{10}H_{18}SiO$: C, 65.87; H, 9.95. Found: C, 66.01; H, 10.22.

Preparation of $[(CH_2{=}CHCH_2)SiMe_2C{\equiv}CCMe_2OH]Co_2(CO)_6$, (5). To a 250 mL round-bottom flask was transferred dicobalt octacarbonyl (1.90 g, 5.56 mmol) which had been dissolved in THF (30 mL). A solution of $(CH_2{=}CHCH_2)SiMe_2C{\equiv}CCMe_2OH$ (1.0 g, 5.95 mmol) in THF (30 mL) was next added dropwise over a 30 min period. The solution was allowed to stir for 24 h at room temperature. After removal of solvent in vacuo, the residue was subjected to flash chromatography on silica gel. Elution with hexane gave **5** as a dark red oil (2.39 g, 5.12 mmol; 92%). ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 5.86 (m, 1H, $CH_2{=}CHCH_2$), 4.96 (m, 2H, $CH_2{=}CHCH_2$), 1.83 (m, 2H, $CH_2{=}CHCH_2$), 1.60 (s, 6H, $C(CH_3)_2OH$), 0.33 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 200.7 ($C{\equiv}O$), 134.4 ($CH_2{=}CHCH_2$), 114.7 ($CH_2{=}CHCH_2$), 73.3 ($C(CH_3)_2OH$), 33.8 ($C(CH_3)_2OH$), 25.5 ($CH_2{=}CHCH_2$), −1.0 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 99.36 MHz): δ −1.1. IR (hexane): ν_{OH} at 3615, ν_{CO} at 2090, 2051, and 2025 cm^{-1}. Mass spectrum: (DEI, *m/z* (%)) 412 (50) ($[M - 2CO]^+$), 384 (70) ($[M - 3CO]^+$), 356 (80) ($[M - 4CO]^+$), 328 (70) ($[M - 5CO]^+$), 300 (100) ($[M - 4CO]^+$); (CI, NH_3, *m/z* (%)) 356 (100) ($[M - 4CO]^+$), 300 (20) ([M −

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[20] *SMART*, version 4.05; Siemens Energy and Automotive Analytical Instrumentation: Madison, WI 53719, 1996.

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$6CO]^+$), 182 (80) ($[CH_2{=}CHCH_2SiMe_2C{\equiv}CC(CH_3)_2OH]^+$). Anal. Calcd for $C_{16}H_{18}SiCo_2O_7$: C, 41.04; H, 3.87. Found: C, 41.33; H, 4.02.

Preparation of $(CH_2{=}CHCH_2)SiMe_2C{\equiv}CC(CH_3){=}CH_2$, (9). *n*-Butyllithium (49.3 mL, 1.6 M in hexane) was added dropwise to a solution of 2-methyl-2-buten-3-yne (7.5 mL, 5.2 g, 78.9 mmol) in diethyl ether (30 mL) at −78 °C via syringe over 30 min, after which the solution was allowed to warm to room temperature. After stirring for 2 h the solution was cooled to −78 °C, and allyldimethylchlorosilane (11.5 mL, 10.6 g, 78.9 mmol) in diethyl ether (15 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred for 24 h. The crude mixture was extracted with water, and the separated organic phase was dried over $MgSO_4$. Removal of the solvent and other volatile organic components by rotary evaporation yielded **9** as a clear oil (12.1 g, 73.3 mmol, 93%). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 5.78 (m, 1H, $CH_2{=}C\mathit{H}CH_2$), 5.28 (m, 2H, $\mathit{H}_2C{=}$), 4.90 (m, 2H, $C\mathit{H}_2{=}CHCH_2$), 1.86 (m, 3H, CH_3), 1.62 (m, 2H, $C\mathit{H}_2{=}CHCH_2$), 0.15 (s, 6H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 134.0 ($CH_2{=}\mathit{C}HCH_2$), 126.7 ($H_2\mathit{C}{=}$), 123.0 ($H_2C{=}\mathit{C}CH_3$), 113.8 ($\mathit{C}H_2{=}CHCH_2$), 107.2, 91.31 ($C{\equiv}C$), 23.9 ($CH_2{=}CH\mathit{C}H_2$), 23.3 (H_3C), −2.3 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 99.36 MHz): δ −18.5. Mass spectrum: (DEI, *m/z* (%)) 164 (10) ($[M]^+$), 149 (20) ($[M - CH_3]^+$), 123 (100) ($[M - CH_2CH{=}CH_2]^+$); (CI, *m/z* (%)) 165 (10) ($[M + 1]^+$). Anal. Calcd for $C_{10}H_{16}Si$: C, 73.09; H, 9.81. Found: C, 72.87; H, 9.67.

Preparation of $[(CH_2{=}CHCH_2)SiMe_2C{\equiv}CC(CH_3){=}CH_2]Co_2(CO)_6$, (10). Analogous to the synthesis of **5**, $CH_2{=}C(CH_3)C{\equiv}CSi(Me)_2(CH_2CH{=}CH_2)$ (1.0 g, 6.06 mmol) and dicobalt octacarbonyl (2.07 g, 6.06 mmol) yielded **10** as a dark red oil (2.46 g, 5.45 mmol; 90%). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 5.77 (m, 1H, $CH_2{=}C\mathit{H}CH_2$), 5.24 (m, 2H, $\mathit{H}_2C{=}CCH_3$), 4.86 (m, 2H, $C\mathit{H}_2{=}CHCH_2$), 2.03 (m, 3H, $H_2C{=}CC\mathit{H}_3$), 1.73 (m, 2H, $CH_2{=}CHC\mathit{H}_2$) 0.25 (s, 6H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 200.9 ($\mathit{C}{\equiv}O$), 142.2 ($H_2C{=}\mathit{C}CH_3$), 134.3 ($CH_2{=}\mathit{C}HCH_2$), 117.7 ($\mathit{C}H_2{=}CHCH_2$), 114.5 ($H_2\mathit{C}{=}CCH_3$), 25.3 ($CH_2{=}CH\mathit{C}H_2$), 24.8 ($H_2C{=}C\mathit{C}H_3$), −1.3 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 99.36 MHz): δ −0.9. IR (hexane) ν_{CO} at 2088, 2050, and 2021 cm^{-1}. Mass spectrum: (DEI, *m/z* (%)) 394 (60) ($[M - 2CO]^+$), 366 (35) ($[M - 3CO]^+$), 338 (35) ($[M - 4CO]^+$), 310 (40) ($[M - 5CO]^+$), 282 (70) ($[M - 6CO]^+$), 123 (100) ($[CH_2{=}CHCH_2SiMe_2C{\equiv}C]^+$); (CI, *m/z* (%)) 451 (30) ($[M + 1]^+$). Anal. Calcd for $C_{16}H_{16}SiCo_2O_6$: C, 42.68; H, 3.58. Found: C, 42.98; H, 3.80.

Reaction of $[(CH_2{=}CHCH_2)SiMe_2C{\equiv}CC(CH_3){=}CH_2]Co_2(CO)_6$, (10) with HBF_4. A 100 mL round-bottom flask was charged with **10** (0.254 g, 0.56 mmol) in 50 mL of CH_2Cl_2 and cooled to −78 °C. HBF_4 in ether (0.083 mL, 0.56 mmol) was next added and allowed to stir at −78 °C for 2 h. The reaction mixture was allowed to warm slowly to 10 °C and was stirred for an additional 24 h. The reaction mixture was quenched with 5 mL of a 0.1 M solution of sodium bicarbonate and then extracted with three 15 mL portions of pentane. The organic layers were combined and dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The resulting solid was subjected to flash silica gel chromatography with hexane as the solvent to give **8** as a brown solid (0.15 g, 0.31 mmol, 55%). ^1H NMR ($CDCl_3$, 500.13 MHz): δ 5.90 (m, 1H, $CH_2{=}C\mathit{H}CH_2C(CH_3)_2$), 5.12 (m, 2H, $C\mathit{H}_2{=}CHCH_2C(CH_3)_2$), 2.29 (m, 2H, $CH_2{=}CHC\mathit{H}_2C(CH_3)_2$), 1.26 (m, 6H, $C(C\mathit{H}_3)_2$), 0.53 (s, 6H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 200.6 ($\mathit{C}{\equiv}O$), 134.8 ($CH_2{=}\mathit{C}HCH_2C(CH_3)_2$), 118.6 ($\mathit{C}H_2{=}CHCH_2C(CH_3)_2$), 50.4 ($CH_2{=}CH\mathit{C}H_2C(CH_3)_2$), 39.9 ($CH_2{=}CHCH_2\mathit{C}(CH_3)_2$), 30.8 ($C(\mathit{C}H_3)_2$), 0.7 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 99.36 MHz): δ 19.4 (d, $^1J_{Si-F} = 251$ Hz). IR (hexane): ν_{CO} at 2091, 2051, and 2025 cm^{-1}. Mass spectrum (DEI, *m/z* (%)): 442 (5) ($[M - CO]^+$), 414 (45) ($[M - 2CO]^+$), 386 (65) ($[M - 3CO]^+$), 358 (70) ($[M - 4CO]^+$), 330 (100) ($[M - 5CO]^+$). Anal. Calcd for $C_{16}H_{17}SiFCo_2O_6$: C, 40.87; H, 3.64. Found: C, 41.04; H, 3.73.

Reaction of $[(CH_2{=}CHCH_2)SiMe_2C{\equiv}CCMe_2OH]Co_2(CO)_6$, (5) with HBF_4 or $BF_3{\cdot}$etherate. Analogous to the synthesis described above, **5** (0.212 g, 0.45 mmol) and HBF_4 in ether (0.067 mL, 0.45 mmol) yielded **8** as a dark red oil (0.10 g, 0.22 mmol; 49%) with spectroscopic data as above. Likewise, in the presence of activated 4 Å molecular sieve, **5** (0.265 g, 0.57 mmol) and $BF_3{\cdot}$etherate (0.070 mL, 0.57 mmol) yielded **8** as a dark red oil (0.14 g, 0.29 mmol; 52%). In both cases, flash chromatography on silica gel with hexane as solvent gave **8** as a red-brown solid that, despite repeated attempts, could not be induced to yield X-ray-quality crystals.

Preparation of $[(CH_2{=}CHCH_2)SiMe_2C{=}C{=}CMe_2]CoFe(CO)_6$, (13). A one-neck 250 mL round-bottom flask fitted with a reflux condenser was charged with **5** (5.0 g, 10.29 mmol), freshly distilled iron pentacarbonyl (10.15 mL, 15.12 g, 77.16 mmol), and acetone (75 mL) and allowed to reflux for 48 h. Subsequently the solvent was removed from the mixture under vacuum. The mixture was subjected to flash silica gel chromatography with petroleum ether/hexanes solvent (5:1). The first orange band was collected, and the solvent removed by rotary evaporation, yielding **13** as a orange oil (1.05 g, 2.26 mol, 22%). ^1H NMR ($CDCl_3$, 500.13 MHz): δ 5.86 (m, 1H, $CH_2{=}C\mathit{H}CH_2$), 4.94 (m, 2H, $C\mathit{H}_2{=}CHCH_2$), 2.02 and 1.88 (each s, 3H) diastereotopic methyls $C(CH_3)_2$), 1.81 (m, 2H, $CH_2{=}CHC\mathit{H}_2$), 0.37 and 0.32 (each s) diastereotopic methyls, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 211.0 ($\mathit{C}{\equiv}O$), 134.3 ($CH_2{=}\mathit{C}HCH_2$), 114.3 ($\mathit{C}H_2{=}CHCH_2$), 109.4 (cluster carbons), 34.3 ($\mathit{C}(CH_3)_2OH$), 30.1 ($C(\mathit{C}H_3)_2OH$), 25.5 ($CH_2{=}CH\mathit{C}H_2$), −0.8 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 99.36 MHz): δ 1.3. IR (hexane): ν_{CO} at 2088, 2086, 2049, 2020, and 1973 cm^{-1}. Mass spectrum: (DEI, *m/z* (%)) 392 (20) ($[M - 2CO]^+$), 364 (15) ($[M - 3CO]^+$), 336 (20) ($[M - 4CO]^+$), 308 (10) ($[M - 5CO]^+$), 280 (100), ($[M - 6CO]^+$), 123 (35) ($[CH_2{=}CHCH_2Si(CH_3)_2C{\equiv}C]^+$); (CI, *m/z* (%)) 449 (80) ($[M - H]^+$), 420 (70) ($[M - CO]^+$); (high resolution, DEI) calculated for mass $^{12}C_{14}H_{17}SiCoFeO_4$ ($[M - 2CO]^+$), 391.9578 amu; observed, 391.9588 amu. Anal. Calcd for $C_{16}H_{17}SiFeCoO_6$: C, 42.88; H, 3.82. Found: C, 43.14; H, 3.52.

Preparation of $[Me_2C{=}C{=}CSiMe_2F]CoFe(CO)_6$, (14). To a cooled (−80 °C) solution of **13** in CD_2Cl_2 (1.5 mL of a 0.05 M solution) in a 10 mm NMR tube was added HBF_4 (0.9 equiv) in diethyl ether, and the 59.6 MHz ^{29}Si NMR spectrum was acquired at this temperature. Under these conditions, **13** gave **14**: δ 20.7 (d, $^1J_{Si-F} = 276$ Hz). Crystals of **14** suitable for X-ray diffraction were grown by slow evaporation of CD_2Cl_2 in the NMR tube.

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Supporting Information Available: Tables of atomic parameters including fractional atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, and anisotropic displacement parameters for the crystal structure of **14** (6 pages). Ordering information is given on any current masthead page.

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