Toward an Understanding of the Mechanism of Metal Exchange in (Propargyl Alcohol)$Co_2(CO)_6$ Clusters: Syntheses and Structures of [η^5-$C_5Ph_2R_2$−C≡C−TMS)(Fe(CO)$_2$(μ-H)]$Co_2(CO)_6$, R = Ph or Et

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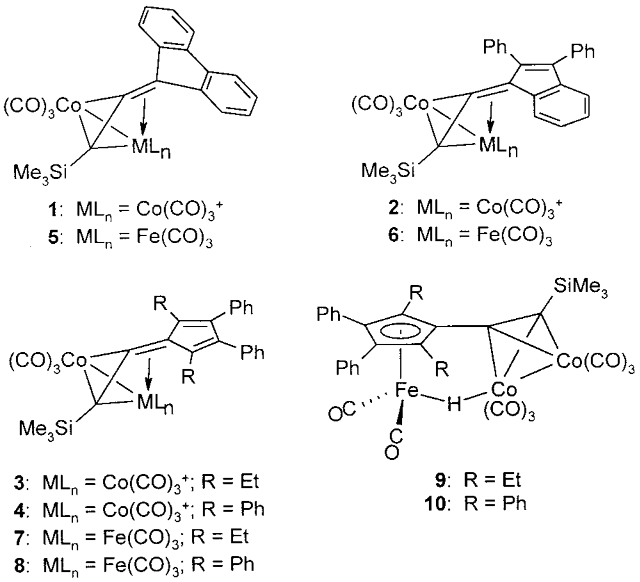
The reaction of (5-alkynylcyclopentadienol)$Co_2(CO)_6$ clusters with iron pentacarbonyl in acetone does not yield the expected product in which the hydroxyl substituent is lost and a tricarbonylcobalt vertex is replaced by an $Fe(CO)_3$ group. Instead, the product contains an (η^5-$C_5Ph_2R_2$)$Fe(CO)_2H$ moiety that is bridged to one of the cobalt vertexes of the intact dicobalt-alkyne cluster. The process is rationalized in terms of a *decarboxylation* rather than a *dehydroxylation* process, and the relevance to the mechanism of substitution of one metal vertex by another is discussed.

Introduction

In continuation of our studies on metal-stabilized short-lived species,[1] we have recently described the syntheses and molecular dynamics of a series of antiaromatic cations.[2] The fluorenyl, indenyl, and cyclopentadienyl cations possess 12π, 8π, and 4π electron counts, respectively, which do not conform to the Hückel rule for planar aromatic systems.[3] Nevertheless, these cations have been prepared as their alkynyl-dicobalt clusters **1**−**4**.[2] The structures of such dicobalt species, whereby the electron deficiency at the cationic site is alleviated by direct overlap with a filled metal orbital, are supported by NMR data,[4] molecular orbital calculations,[5] and the X-ray crystal structures of numerous dimolybdenum or molybdenum−cobalt analogues.[6] However, until very recently,[7] no X-ray crystal structure of a cobalt-stabilized carbocation had been reported, and the most closely analogous systems that had been structurally characterized were the neutral cobalt−iron clusters in which a $Co(CO)_3^+$ vertex had been replaced by the isolobal $Fe(CO)_3$ moiety.[8] Indeed, molecular orbital calculations indicated that these neutral iron−

Chart 1



1: ML$_n$ = $Co(CO)_3^+$
5: ML$_n$ = $Fe(CO)_3$
2: ML$_n$ = $Co(CO)_3^+$
6: ML$_n$ = $Fe(CO)_3$
3: ML$_n$ = $Co(CO)_3^+$; R = Et
4: ML$_n$ = $Co(CO)_3^+$; R = Ph
7: ML$_n$ = $Fe(CO)_3$; R = Et
8: ML$_n$ = $Fe(CO)_3$; R = Ph
9: R = Et
10: R = Ph

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(1) (a) Girard, L.; Decken, A.; Blecking, A.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1994**, *116*, 6427. (b) Gruselle, M.; El Hafa, H.; Nikolski, M.; Jaouen, G.; Vaissermann, J.; Li, L.; McGlinchey, M. J. *Organometallics* **1993**, *12*, 4917. (c) Kondratenko, M.; El Hafa, H.; Gruselle, M.; Vaissermann, J.; Jaouen, G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6907. (d) Downton, P. A.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1992**, *11*, 3281.

(2) Dunn, J. A.; Hunks, W. J.; Ruffolo, R.; Rigby, S. S.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **1999**, *18*, 3372.

(3) For a listing of the laser flash photolysis, mass spectrometric, and reactivity studies on fluorenyl, indenyl, and cyclopentadienyl cations, see ref 2.

(4) (a) Schreiber, S. L.; Klimas, M. T.; Sammakia, S. *J. Am. Chem. Soc.* **1987**, *109*, 5749. (b) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, C23. (c) Edidin, R. T.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561. (d) D'Agostino, M. F.; McGlinchey, M. J. *Polyhedron* **1988**, *7*, 807.

(5) (a) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (b) D'Agostino, M. F.; Mlekuz, M.; Kolis, J. W.; Sayer, B. G.; Rodger, C. A.; Halet, J.-F.; Saillard, J.-Y.; McGlinchey, M. J. *Organometallics* **1986**, *5*, 2345. (c) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *J. Organomet. Chem.* **1990**, *394*, 145.

(6) Girard, L.; Lock, P. E.; El Amouri, H.; McGlinchey, M. J. *J. Organomet. Chem.* **1994**, *478*, 189, and references therein.

(7) Melikyan, G. G.; Bright, S.; Monroe, T.; Hardcastle, K. I.; Ciurash, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 161.

(8) Victor, R. *J. Organomet. Chem.* **1977**, *127*, C25.

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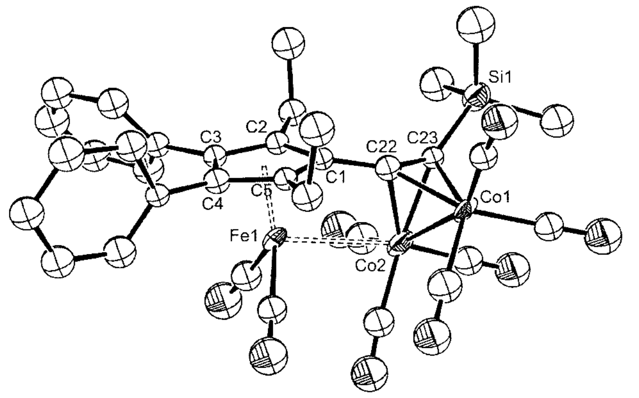

Figure 1. Molecular structure of [η^5-$C_5Ph_2Et_2$−C≡C−$SiMe_3$]($Fe(CO)_2$){μ-H}$Co_2(CO)_6$, **9** (50% probability).

cobalt clusters were excellent structural models for the cationic dicobalt systems.[9] The mixed metal clusters are conveniently prepared by treatment of the corresponding (propargyl alcohol)$Co_2(CO)_6$ precursor with iron pentacarbonyl in refluxing acetone.[2,8,9]

The fluorenyl and indenyl Fe/Co clusters, **5** and **6**, exhibit Fe···CR_2 distances of 2.626(11) and 2.347(7) Å, respectively,[2] and one might anticipate that, since the 4π cyclopentadienyl cation has an even greater need for electronic assistance from the metal center, the corresponding cyclopentadienyl complexes, **7** and **8**, would possess even shorter Fe···C bond lengths. Thus the syntheses of the cyclopentadienyl Fe/Co cluster complexes **7** and **8** were attempted. However, these experiments yielded instead the trimetallic clusters [η^5-$C_5Ph_2R_2$−C≡C−$SiMe_3$]($Fe(CO)_2$){μ-H}$Co_2(CO)_6$, where R = Et, **9**, or Ph, **10**, and serendipitously may have led toward an understanding of the mechanism of the $Co(CO)_3$/$Fe(CO)_3$ vertex replacement process.

Results and Discussion

Synthetic and Structural Aspects. With the intent of preparing the iron−cobalt clusters **7** and **8** as structural models of the [(alkynylcyclopentadienyl)$Co_2(CO)_6$]$^+$ cations **3** and **4**, respectively, the precursor (alkynyl-cyclopentadienol)$Co_2(CO)_6$ complexes were treated with iron pentacarbonyl and heated under reflux in acetone for 2−3 days, and the products repeatedly purified through multiple chromatographic separations. Final yields of pure products ranged from 7 to 14%. The ^{13}C NMR spectra of the products of both reactions revealed the presence of iron carbonyls (δ 215−218) and cobalt carbonyls (δ 200−202), but the appearance of extra resonances in the region δ 80−95 suggested the possibility of an η^5-bonded cyclopentadienyliron carbonyl moiety. The products, **9** and **10**, were finally identified by means of X-ray crystallography, and the structures appear as Figures 1 and 2.

There are two molecules of **9** in the asymmetric unit, but their structures are very similar, and only one is depicted in Figure 1. It reveals that in **9** both $Co(CO)_3$ vertexes have been retained, the hydroxyl group has been lost, and an $Fe(CO)_2$ moiety is π-complexed to the cyclopentadienyl ring. The iron is apparently linked to one of the cobalt atoms, but the observed distance of 2.833(4) Å [2.866(4) Å in the other independent molecule] is too long to be considered a bond, and the presence of a bridging metal hydride (which would also account for the diamagnetism of the complex) is the most probable explanation. Attempts to confirm this assumption through treatment with CCl_4 to give $CHCl_3$[10] were inconclusive. It is known that this process sometimes requires elevated temperatures; however, **9** decomposes rapidly upon heating.

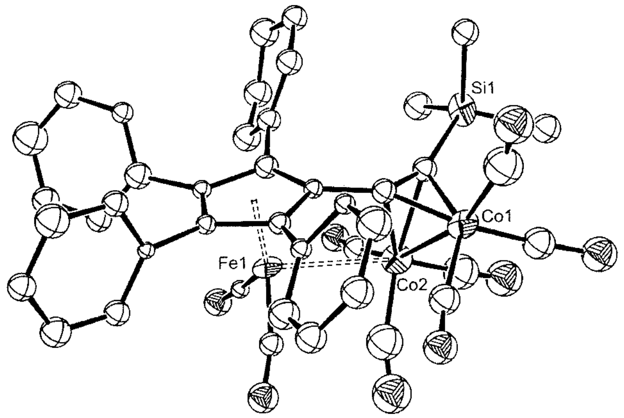

Figure 2. Molecular structure of [η^5-C_5Ph_4−C≡C−$SiMe_3$]-($Fe(CO)_2$){μ-H}-$Co_2(CO)_6$, **10** (30% probability).

Since there is an interaction between the iron and only one of the cobalt vertexes, the molecule does not possess a mirror plane in the solid state, and this asymmetry is maintained in solution such that the ^1H and ^{13}C NMR spectra reveal the presence of two nonequivalent ethyl groups, as well as two different iron carbonyl resonances, even at room temperature. Attempts to determine the barrier to migration of the Fe−H bond between cobalt vertexes (which would have equilibrated the ethyl environments, and Fe−CO's) were thwarted by the thermal instability of complex **9** in solution. Nevertheless, the observation of these doubled signals at room temperature reveals that the barrier must exceed 15 kcal mol^{-1}.

The structure of **10** is shown in Figure 2, but because of the relatively poor quality of the data,[11] we merely report the atom connectivity. As with **9**, the iron−cobalt vector in **10** is too long, 2.87 Å (mean value), to be considered a bond, and the presence of a bridging hydride is again invoked.

In each of these reactions, a further product, **11** or **12**, respectively, was obtained and identified by NMR and mass spectrometry as the $Fe(CO)_3$ derivative of the original 5-alkynylcyclopentadien-5-ol ligand. One can readily visualize these complexes arising via reaction of $Fe(CO)_5$ with starting material that had lost its $Co_2(CO)_6$ group during the thermolysis.

Mechanistic Considerations. The reaction of (propargyl alcohol)$Co_2(CO)_6$ clusters, **13**, or their corresponding diols ($HOCR_2C≡CCR_2OH$)$Co_2(CO)_6$, **14**, with

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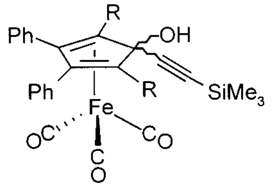
[9] (a) Aime, S.; Osella, D.; Milone, L.; Tiripicchio, A. *Polyhedron* **1983**, *2*, 77. (b) Osella, D.; Dutto, G.; Jaouen, G.; Vessières, A.; Raithby, P. R.; De Benedetto, L.; McGlinchey, M. J. *Organometallics* **1993**, *12*, 4545. (c) Ruffolo, R.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **1998**, *17*, 4992.

[10] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley-Interscience: New York, 1993; p 62.

[11] Unit cell parameters for **10**: a = 17.173 Å, b = 24.228 Å, c = 28.174 Å, α = 104.69°, β = 102.58°, γ = 100.52°, V = 10710 Å^3, Z = 10. The only available crystals were of rather poor quality and apparently exhibited multiple rotamers attributable to five different orientations of the peripheral phenyl substituents.



11: R = Et
12: R = Ph

$Fe(CO)_5$ in refluxing acetone to yield iron−cobalt or di-iron clusters, **15** or **16**, respectively, was originally reported by Victor in 1977.[8] It was described as a "dehydroxylation process", and several such iron/cobalt[9] or di-iron[12] products have now been crystallographically characterized.

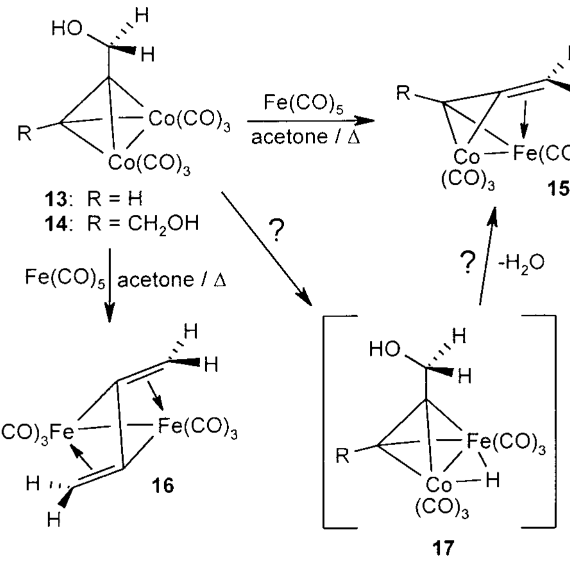
Although the mechanism of this "dehydroxylation" procedure remains unclear, speculation has focused on the possible role of metal hydrides.[13] For example, Chini demonstrated that $Co_2(CO)_8$ and $Fe(CO)_5$ in acetone react to form $HFeCo_3(CO)_{12}$.[14] Moreover, Geoffroy has reported that $MeCCo_3(CO)_9$ and $[Fe(CO)_4]^{2-}$ yield, upon protonation, the hydride cluster $MeCCo_2FeH(CO)_9$.[15] Thus the transformation of $(HC{\equiv}C{-}CH_2OH)Co_2(CO)_6$ into $(HC{=}C{=}CH_2)FeCo(CO)_6$ may involve the formation of an intermediate metal hydride, **17**; as depicted in Scheme 1, subsequent elimination of water could give the neutral iron−cobalt cluster **15**.

However, the isolation of the trimetallic species **9** and **10** suggests another possibility: nucleophilic attack by the hydroxyl group on a carbonyl ligand of $Fe(CO)_5$ could yield the hydrido metal carboxylate **18**. It is, of course, well known that the formation of the $[HFe(CO)_4]^-$ anion from $Fe(CO)_5$ and KOH proceeds through an intermediate carboxylate species.[16] It is relevant to note that Osella has obtained the carboxylate-containing cluster $Fe_2(CO)_6[(EtC{=}CEt)C({=}O)^{18}O]$ from hex-3-yne, $Fe_2(CO)_9$, and $^{18}OH_2$.[17] Moreover, Sappa has convincingly demonstrated that "deoxygenation" of the propargylic alcohol $HC{\equiv}CC(Me)(Ph)OH$ by $Fe_3(CO)_{12}$ is really a decarboxylation and proceeds with elimination of carbon dioxide.[18] It was tentatively suggested that the hydroxyl substituent from the alkyne attacks a carbonyl ligand on iron, and the current observations provide strong support for such a proposal.

As depicted in Schemes 2 and 3, one can envision two competing pathways. In the case of a cyclopentadiene ligand, decarbonylation and η^4-coordination to the five-membered ring could precede decarboxylation to yield **19**, which possesses an $(\eta^5\text{-}C_5R_4)Fe(CO)_2H$ moiety and corresponds to the observed product **9** or **10**.

In contrast, coordination to the five-membered ring of an indenyl or fluorenyl ligand is disfavored because of the resulting loss of aromaticity in the six-membered rings. Instead, one might invoke expansion of the tetrahedral cluster to a square-based pyramidal structure **20**. While the apical and basal plane cobalts in **20** would formally be assigned 19 and 17 electrons, respectively, the overall skeletal electron count is appropriate for a *nido* octahedral cluster,[19] and numerous examples of such cluster expansion[20] or vertex replacement[21] reactions are known. Finally, decarboxylation could yield the observed mixed metal cluster **21**, as typified by **5** and **6**.

Scheme 1



Future work in this area will look at examining the role of the solvent in these reactions to gain further understanding of these fascinating processes.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. Silica gel (particle size: 20−45 μm) was employed for flash column chromatography. ^1H and ^{13}C NMR spectra were acquired on a Bruker DRX 500 spectrometer and were referenced to the residual proton or ^{13}C solvent signal. Mass spectra were obtained using a Finnigan 4500 spectrometer by direct electron impact (DEI) or direct chemical ionization (DCI) with NH_3. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario.

The alkynylcyclopentadienol)$Co_2(CO)_6$ complexes **22** and **23** were prepared as previously described.[2]

Reaction of {5-(Trimethylsilyl)ethynyl)-1,4-diethyl-2,3-diphenylcyclopentadien-5-ol}$Co_2(CO)_6$, 22, with Iron Pentacarbonyl. Over a 25 min period, $Fe(CO)_5$ (9.90 mL, 75.3 mmol) was added to **22** (5.0 g, 7.44 mmol) dissolved in acetone (125 mL). The solution was heated to reflux and monitored by TLC approximately every 5 h. Samples of the effluent gases were shown by IR and mass spectrometry to contain traces of CO_2. After 60 h, the solution was allowed to cool and, after removal of solvent, yielded a brown oil. The residue was subjected to flash chromatography on silica gel with CH_2Cl_2 as eluent to remove inorganic salts arising from decomposed metal carbonyls. A second purification (flash chromatography)

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(12) (a) Gerlach, J, N.; Wing, R. M.; Ellgen, P. C. *Inorg. Chem.* **1976**, *15*, 2959. (b) Eigemann, S.-E.; Förtsch, W.; Hampel, F.; Schobert, R. *Organometallics* **1996**, *15*, 1511. (c) Bright, D.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2465.

(13) McGlinchey, M. J.; Girard, L.; Ruffolo, R. *Coord. Chem. Rev.* **1995**, *143*, 331.

(14) Chini, P.; Colli, L.; Peraldo, M. *Gazz. Chim. Ital.* **1960**, *90*, 1005.

(15) Epstein, R. A.; Withers, H. W.; Geoffroy, G. L. *Inorg. Chem.* **1979**, *18*, 942.

(16) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 403.

(17) Milone, L.; Osella, D.; Ravera, M.; Stanghellini, P. L.; Stein, E. *Gazz. Chim. Ital.* **1992**, *122*, 451.

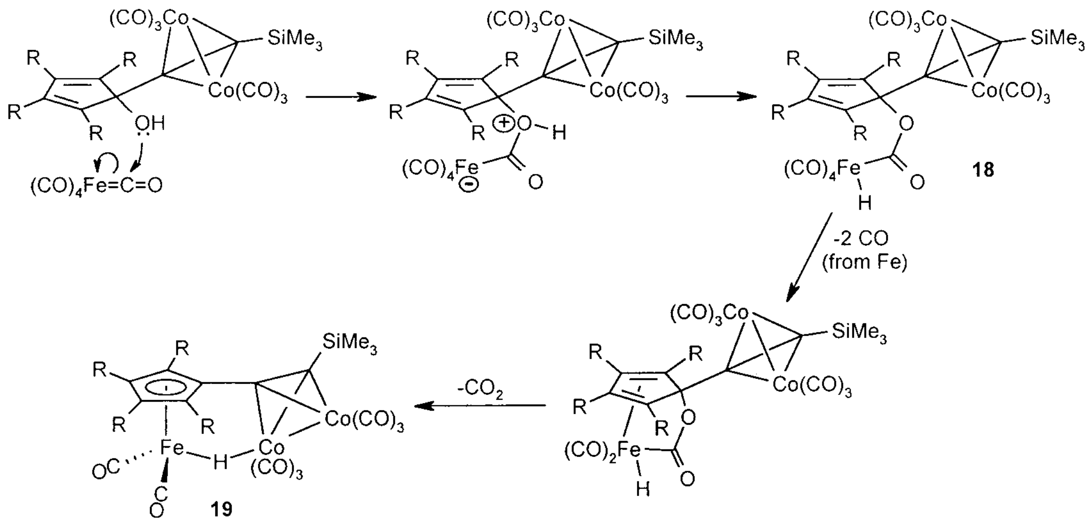
(18) Gervasio, G.; Sappa, E. *Organometallics* **1993**, *12*, 1458.

(19) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

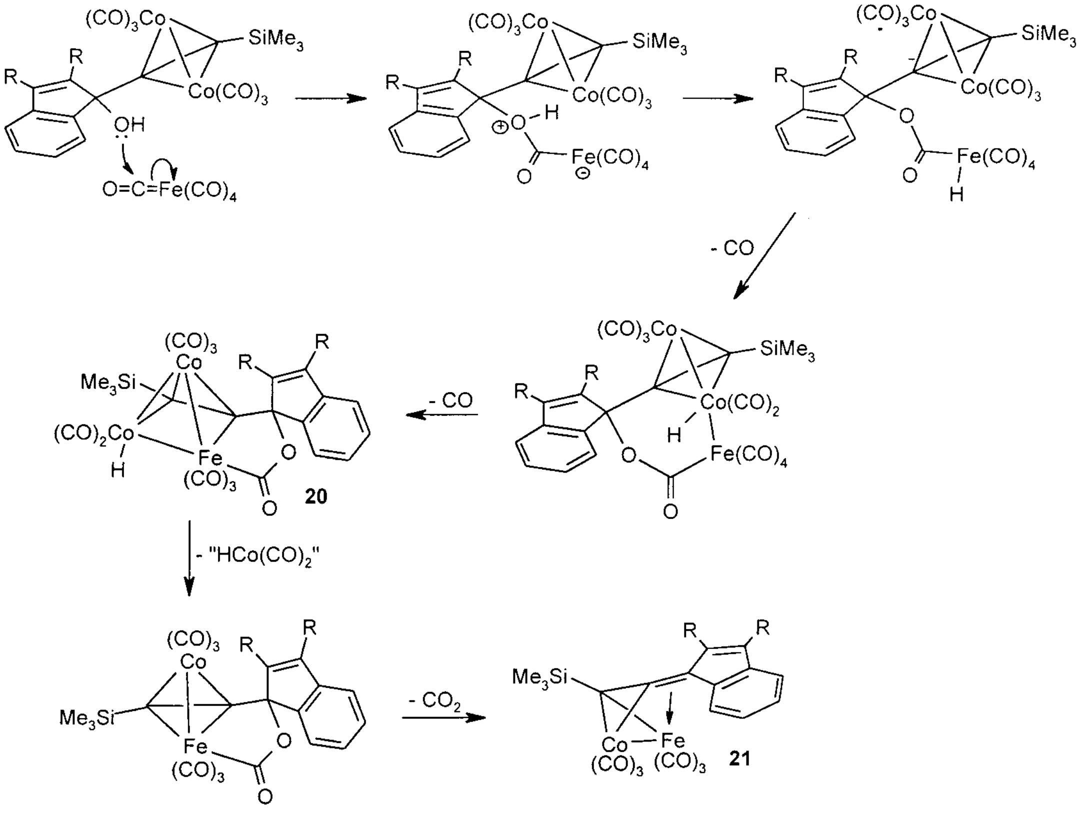
(20) Adams, R. D. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1989; Chapter 3, pp 121−170.

(21) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

Scheme 2



Scheme 3



using hexanes yielded recovered **22** (730 mg, 1.09 mmol, 15%) and the iron-dicobalt cluster **9**, as well as **11** and other unidentified decomposition products. The mixed metal cluster **9** was flash chromatographed a third time, with hexanes as eluent, to yield brown microcrystals (338 mg, 0.44 mmol, 6.9%), mp 110−113 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.40, 7.31, 7.21 (m, 10 H, 2 phenyls); 2.47 (m, 1H) and 2.04 (m, 1H), (CH$_2$); 1.57 (m, 1H) and 1.26 (m, 1H) (CH$_2$′); 1.26 (t, 3H, CH$_3$), 0.88 (t, 3H, CH$_3$′), 0.51 (s, 9 H, Me$_3$Si). ^{13}C NMR (CD$_2$Cl$_2$): δ 218.4, 215.6, 214.2, 202.2 (Fe−CO's and Co−CO's), 131.9, 131.3, 130.8, 128.8, 128.6, 128.5, 109.8, 109.7, 106.2, 100.1, 95.9, 81.4, 56.3, 18.6, 18.2, 17.2, 16.4, 2.4. IR (CH$_2$Cl$_2$): ν_{CO} at 2067, 2025, 1991, 1965 cm^{-1}. MS (DCI) *m*/*z* (%): 624 (6) ([M − HCo(CO)$_3$]$^+$), 540 (11) ([M − Co(CO)$_3$ − 3CO]$^+$), 481 (9) ([M − HCo$_2$(CO)$_6$]$^+$), 426 (14) ([M − FeCo(CO)$_6$]$^+$), 73 (100) ([Me$_3$Si]$^+$). Anal. Calcd for C$_{34}$H$_{30}$FeCo$_2$SiO$_8$: C, 53.15; H, 3.94. Found: C, 52.97; H, 4.13.

Crude **11** was also flash chromatographed a third time, using hexanes on alumina, to yield an orange-red oil (26 mg, 0.05 mmol; 0.8%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.31, 7.26 (m, 10 H, 2 phenyls), 6.56 (s, 1H, OH), 2.31 (m, 2H), 2.26 (m, 2H), 0.85 (t, 6H, CH$_3$'s), 0.13 (s, 9H, Me$_3$Si). ^{13}C NMR (CD$_2$Cl$_2$): δ 215.7 (Fe−CO's), 153.1, 151.3 (C$_{2,3}$), 132.4, 131.5, 128.4, 108.2 (*C*C-TMS), 96.5 (C$_1$), 86.7 (C*C*-TMS), 19.3 (CH$_2$), 14.1 (CH$_3$), 0.1 (Me$_3$Si); IR (CH$_2$Cl$_2$) ν_{CO} 1997, 1921 cm^{-1}. MS (DEI) *m*/*z* (%): 426 (11), ([M − Me − 3CO]$^+$), 370 (9) ([M − Me − Fe(CO)$_3$]$^+$), 154 (16), 73 (100) ([Me$_3$Si]$^+$).

Reaction of {5-(Trimethylsilylethynyl)-1,2,3,4-tetraphenylcyclopentadien-5-ol}Co$_2$(CO)$_6$, 23, with Iron Pentacarbonyl. Over a 25 min period, Fe(CO)$_5$ (17.0 mL, 131 mmol) was added to **23** (7.00 g, 9.11 mmol) dissolved in acetone (125 mL). The solution was heated to reflux and monitored by TLC approximately every 5 h. After 48 h, the solution was allowed to cool and, after removal of solvent, yielded a brown oil. The residue was subjected to flash chromatography on silica gel with CH_2Cl_2 as eluent to remove inorganic salts arising from decomposed metal carbonyls. A second purification (flash chromatography) using hexanes yielded recovered **23** (1.566 g, 2.04 mmol, 22%) and the iron-dicobalt cluster **10**, as well as **12** and other unidentified decomposition products. The mixed metal cluster **10** was flash chromatographed a third time, with CH_2Cl_2/hexanes (1:1) as eluent, to yield brown microcrystals (847 mg, 0.98 mmol, 13.9%), mp 107−108 °C. ^1H NMR (CD_2Cl_2): δ 7.32−6.89 (m, 20 H, 4 phenyls), 0.11 (s, 9 H, Me_3Si). ^{13}C NMR: (CD_2Cl_2) δ 218.4, 217.7 (Fe−CO's), 200.1 (Co−CO's), 135.7, 132.6−127.9 (∼17 overlapped peaks), 109.9, 109.2, 106.3, 101.5, 82.4, 59.7, 2.2 (Me_3Si). IR (CH_2Cl_2): ν_{CO} at 2066, 2018, 1987, 1965 cm^{-1}. MS (DCI) *m*/*z* (%): 636 (11) ($[M - HCo(CO)_3 - 3CO]^+$), 577 (14) ($[M - HCo_2(CO)_6]^+$), 521 (9) ($[M - HCo_2(CO)_8]^+$), 466 (15) ($[M - FeCo_2(CO)_8]^+$), 267 (56) ($[C_3Ph_3]^+$), 73 (100) ($[Me_3Si]^+$). Anal. Calcd for $C_{42}H_{30}FeCo_2SiO_8$: C, 58.35; H, 3.50. Found: C, 58.47; H, 3.72. Crude **12** was also flash chromatographed a third time, using hexanes on alumina, to yield an orange solid (287 mg, 0.46 mmol; 7%), mp 162−164 °C. ^1H NMR (CD_2Cl_2): δ 7.49−7.17 (m, 20H, 4 phenyls), 2.50 (s, 1H, OH), 0.58 (s, 9H, Me_3Si). ^{13}C NMR (CD_2Cl_2): δ 211.1 (Fe−CO's), 155.0, 154.3 ($C_{2,3}$), 132.6−126.8 (phenyls), 109.5 (*C*C-TMS), 90.2 (C_1), 83.7 (C*C*-TMS), −0.3 (Me_3Si). IR (CH_2Cl_2) ν_{CO} at 1997, 1965, 1925 cm^{-1}. MS (DCI) *m*/*z* (%): 606 (5) ($[M + H - OH]^+$), 550 (8) ($[M + H - OH - 2CO]^+$), 522 (11) ($[M + H - OH - 3CO]^+$), 466 (15) ($[M + H - OH - Fe(CO)_3]^+$), 450 (12), 436 (7), 380 (15), 315 (8), 289 (9), 73 (100) ($[Me_3Si]^+$). Anal. Calcd for $C_{37}H_{30}FeSiO_4$: C, 71.38; H, 4.86. Found: C, 71.66; H, 5.02.

Crystallographic Data for 9 and 10. X-ray crystallographic data for **9** and **10** were each collected from a suitable sample mounted with epoxy on the end of a thin glass fiber. Data were collected on a P4 Siemens diffractometer equipped with a Siemens SMART 1K CCD area detector (employing the program SMART[22]) and a rotating anode utilizing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was carried out by use of the program SAINT,[23] while the program SADABS[24] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct methods procedure in the Siemens SHELXTL[25] program library and refined by full-matrix least-squares methods on F^2.

Despite numerous attempts to obtain better crystals, the structure of **9** could only be refined to a reasonable, though high, *R* value of 0.137. However, there are high residual electron densities in the vicinity of metal or carbons that could not be attributed to solvent or water molecules. In **10**, only the heavy atoms Co, Fe, and Si were refined using anisotropic thermal parameters. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded.

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Supporting Information Available: Tables of crystal data, atomic parameters, bond lengths and angles, and anisotropic displacement parameters for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010494O

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[23] Sheldrick, G. M. *SAINT*, *Release 4.05*; Siemens Energy and Automation Inc.: Madison, WI 53719, 1996.

[24] Sheldrick, G. M. *SADABS* (*Siemens Area Detector Absorption Corrections*); Siemens Energy and Automation Inc.: Madison, WI 53719, 1996.

[25] Sheldrick, G. M. *SHELXTL*, *Version 5.03*; Siemens Crystallographic Research Systems: Madison, WI, 1994.