Metal Cluster Stabilized Fluorenyl, Indenyl, and Cyclopentadienyl Antiaromatic Cations: An NMR and X-ray Crystallographic Study

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Treatment of fluorenone, 2,3-diphenylindenone, tetraphenylcyclopentadienone, or 2,5-diethyl-3,4-diphenylcyclopentadienone with ((trimethylsilyl)ethynyl)lithium gives, after hydrolysis, the analogous alkynol; subsequent addition of dicobalt carbonyl and then fluoroboric acid yields the corresponding fluorenyl, indenyl, or cyclopentadienyl cation stabilized by complexation to a tricarbonylcobalt moiety. Variable-temperature NMR data on these cluster cations, and on their bis(diphenylphosphino)methane derivatives, reveal that the barrier to migration of the cationic center between cobalt cluster vertices increases in the order fluorenyl < indenyl < cyclopentadienyl and suggest that the cations with more antiaromatic character have the greatest need for charge delocalization onto the metal center. Replacement of a $Co(CO)_3$ cationic fragment by an $Fe(CO)_3$ unit yields the mixed-metal species $[((\text{fluorenyl}){=}C{=}CSiMe_3)FeCo(CO)_6]$ (**22**) and $[((2,3\text{-diphenylindenyl}){=}C{=}CSiMe_3)FeCo(CO)_6]$ (**27**). In these structural models for the cationic complexes, the Fe−C(9) distance in **22** is 2.626(11) Å, while in the indenyl system **27** the Fe−C(1) distance is 2.347(7) Å, again indicating that the 8π indenyl cation interacts more strongly with the metal center than does the 12π fluorenyl cation.

Introduction

The aromatic character and ready availability of cyclopentadienyl, indenyl, and fluorenyl anions contrasts with the relative inaccessibility of the corresponding cations, which have been the subject of an extensive series of laser flash photolysis studies[1] and also numerous mass spectrometric investigations.[2] Moreover, kinetic measurements have revealed that hydrolyses of 9-fluorenyl esters are retarded by a factor of approximately 10^7 relative to those of closely analogous benzhydryl systems which do not involve destabilizing effects.[3] Nevertheless, the debate concerning the antiaromatic/nonaromatic character of fluorenyl and indenyl cations continues to attract attention.[4] Very recently, however, Tidwell has provided clear experimental evidence for the transient intermediacy of the 1-methyl-2,4-bis(*tert*-butyl)cyclopentadienyl cation and has calculated that the relative rates of solvolysis of fluorenyl, indenyl, and cyclopentadienyl trifluoroacetates are approximately 3×10^4, 3.5×10^2, and 1, respectively.[5]

A different approach invokes the stabilization of such short-lived species as organometallic complexes;[6,7] one can then take advantage of a variety of structural and spectroscopic techniques to probe their electronic requirements. Recent examples include our X-ray crystallographic characterizations of the $[(endo\text{-}2\text{-propynylbornyl})Mo_2(CO)_4(C_5H_5)_2]^+$ and (*exo*-2-propynylfenchyl)-

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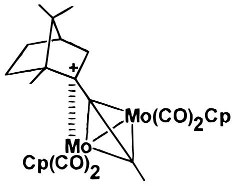
10.1021/om990292g CCC: $18.00

$Co(CO)_3Mo(CO)_2(C_5H_5)_2]^+$ cations (**1** and **2**, respectively).[8,9] In a related study, Olah and de Meijere have presented compelling NMR evidence that, unlike most cyclopropyl cations, the ferrocenyl-substituted system **3** does not ring-open to the corresponding allyl cation **4**.[10]



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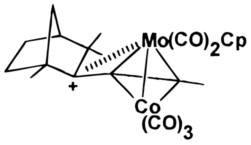

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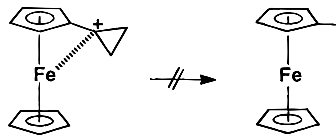
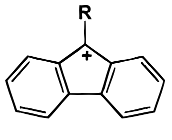


3 **4**



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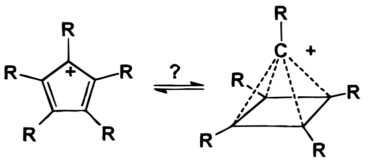
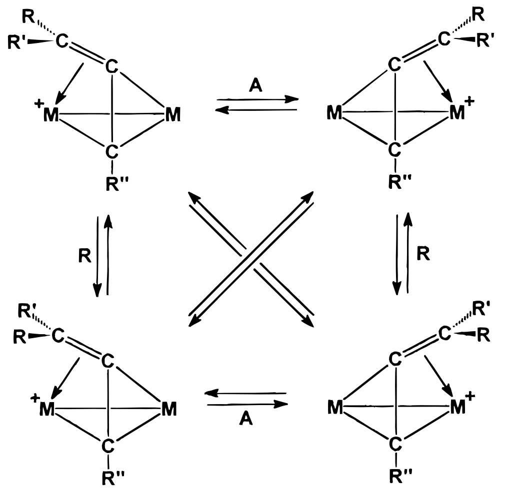


6

We are unaware of any reports of the isolation of the parent fluorenyl cation, $C_{13}H_9^+$; treatment of 9-fluorenol, 9-chlorofluorene, or 9-bromofluorene with FSO_3H, FSO_3H/SbF_5, or SbF_5 in SO_2ClF at −120 °C immediately yields dark, unidentifiable polymeric materials.[11] Nevertheless, fluorenyl cations **5**, bearing an alkyl, phenyl, chloro, ester, or hydroxy substituent at the C(9) position, are preparable in FSO_3H/SbF_5 or SbF_5/SO_2ClF solution at −78 °C, and their ^1H and ^{13}C NMR spectra have been reported.[11−13] It has been suggested that the corresponding cyclopentadienyl cations, $C_5R_5^+$ (**6**),[14] might rearrange through the square-pyramidal (C_{4v}) geometry, that could be categorized as a *nido*-octahedral cluster analogous to B_5H_9.[15] However, attempts to detect degenerate rearrangements of fluorenyl cations via such pyramidal intermediates were unsuccessful.[11]

We here describe the preparation of a series of fluorenyl, indenyl, and cyclopentadienyl cations stabilized as (alkynyl)$Co_2(CO)_6$ complexes. Although these dicobalt hexacarbonyl clusters are not isolable as X-ray-quality crystals, it is shown that isolobal replacement of a $[Co(CO)_3]^+$ vertex by an $Fe(CO)_3$ moiety yields stable fluorenyl and indenyl complexes that can be conveniently crystallographically characterized. These iron−cobalt systems may be viewed as models for their corresponding dicobalt cluster cations.

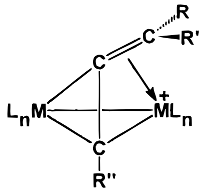
Scheme 1. Fluxional Processes in [Propargyl−$Co_2(CO)_6]^+$ Cluster Cations[a]



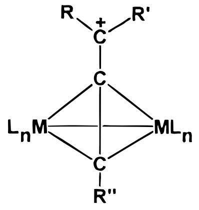
[a] **A** signifies an antarafacial migration; **R** represents rotation about the C=CR_2 bond.

Results and Discussion

Propargyl−$Co_2(CO)_6$ Cations. The stabilization of propargyl cations as dicobalt clusters, as in **7a**, is well-established;[16] analogous dimolybdenum complexes (**7b**)- are also known.[17]



7a : $ML_n = Co(CO)_3$
7b : $ML_n = Mo(CO)_2(C_5H_5)$



7c

Moreover, as shown in Scheme 1, such molecules exhibit two fluxional processes: antarafacial migration

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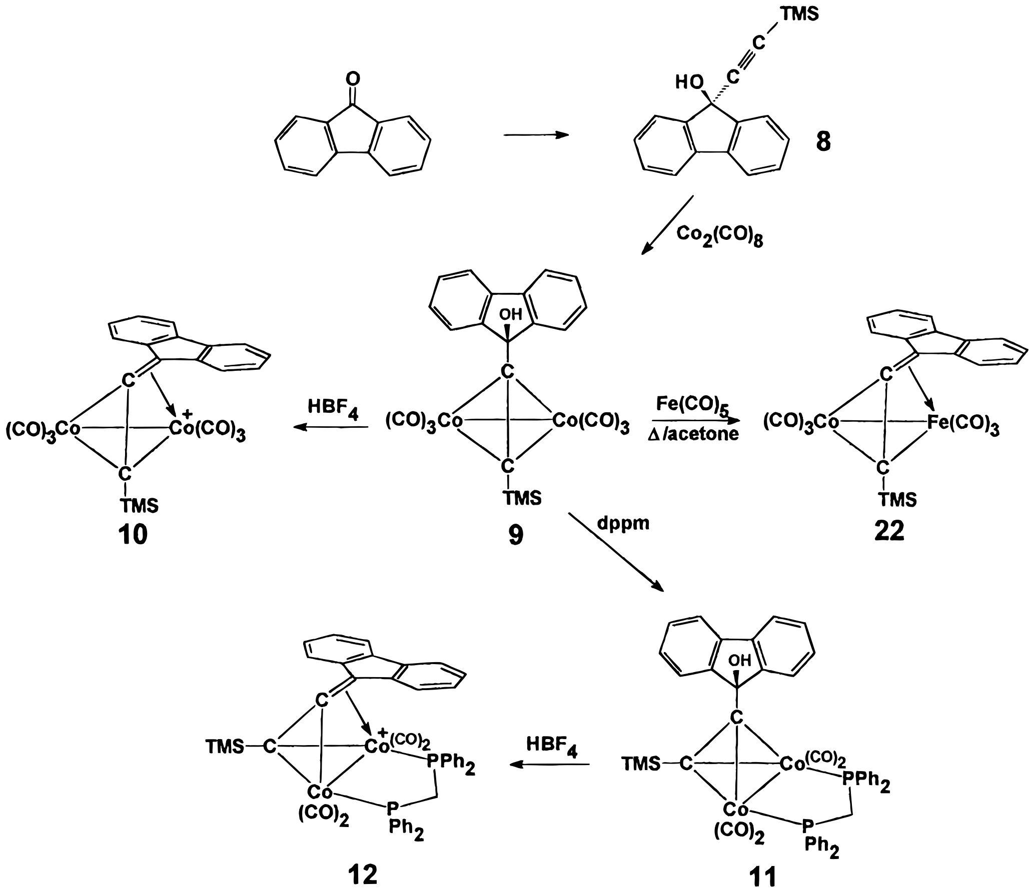
Scheme 2. Syntheses of Alkynyl−Fluorenyl Cluster Complexes



of the cationic carbon between the two metal vertices equilibrates the ML*n* moieties but maintains the difference between the *exo* and *endo* environments (defined relative to the metal−metal bond). A second, higher energy, process allows rotation about the C−CR′R″ bond and so interconverts the *exo* and *endo* substituents.[18] The activation energy for the antarafacial migration process falls from approximately 18 kcal mol^{-1} for primary cations to about 11 kcal mol^{-1} for tertiary cations, indicating that the more stable tertiary centers have less need for electronic assistance from the metal than do secondary or primary cations. Indeed, for the tertiary cations, the barriers for the antarafacial migration process and for the *exo*/*endo* interconversion are normally identical within experimental error.[6,17]

Fluorenyl− and Indenyl−Co$_2$(CO)$_6$ Cations. With the aim of isolating a metal-stabilized fluorenyl cation, fluorenone was converted to 9-((trimethylsilyl)ethynyl)-9-fluorenol (**8**) and then treated with Co$_2$(CO)$_8$ to give the tetrahedral dicobalt cluster **9**. Protonation of **9** with HBF$_4$ in CD$_2$Cl$_2$ at −78 °C resulted in the immediate development of a deep red coloration, indicating the formation of the cation **10**, whose ^{13}C NMR spectrum at −78 °C exhibits 13 resonances for the fluorenyl skeleton. Eight of these peaks represent proton-bearing carbons, and the ^{1}H and ^{13}C spectra reveal that these are grouped into two independent sets, each made up of four CH units. It is evident from these data that the two six-membered rings are nonequivalent at low temperature, as anticipated for the unsymmetrical structure **10**, shown in Scheme 2. Selected variable-temperature ^{13}C NMR spectra of the cobalt-stabilized fluorenyl cation **10** are shown in Figure 1, and they reveal peak coalescences between symmetry-related resonances. The Gutowsky−Holm approximation[19] yields a $\Delta G^\ddagger$ value of 12.2 ± 0.5 kcal mol^{-1} for the fluxional process that equilibrates the *exo* and *endo* six-membered-ring environments; this activation energy is in the normal range for cobalt-stabilized tertiary carbocations.[18] Interestingly, the resonance attributable to C(9), the formally cationic carbon, exhibits a noticeable temperature-dependent chemical shift.

In this particular system, there is no probe (such as diastereotopic isopropyl methyl groups) for the simple antarafacial migration between the metal centers, and it was necessary to incorporate a chelating bis(diphenylphosphino)methane (dppm) ligand to label the cobalt vertices, as in **11.** The variable-temperature NMR data on the corresponding cation [(C$_{13}$H$_8$C≡CSiMe$_3$)Co$_2$(CO)$_4$(dppm)]$^+$ (**12**) yield $\Delta G^\ddagger$ values of 11.4 ± 0.5 kcal mol^{-1} and 12.0 ± 0.5 kcal mol^{-1} for the antarafacial migration and *exo*/*endo* interconversion processes, respectively. The former was obtained from the temperature-dependent equilibration (see Figure 2) of the phosphorus environments (^{31}P NMR at 203 K shows peaks at 24.4 and 21.3 ppm, with ^2J(P−P) = 69.7 Hz), while the latter was derived from the coalescence behavior of the fluorenyl ring carbon resonances. As is commonly the case

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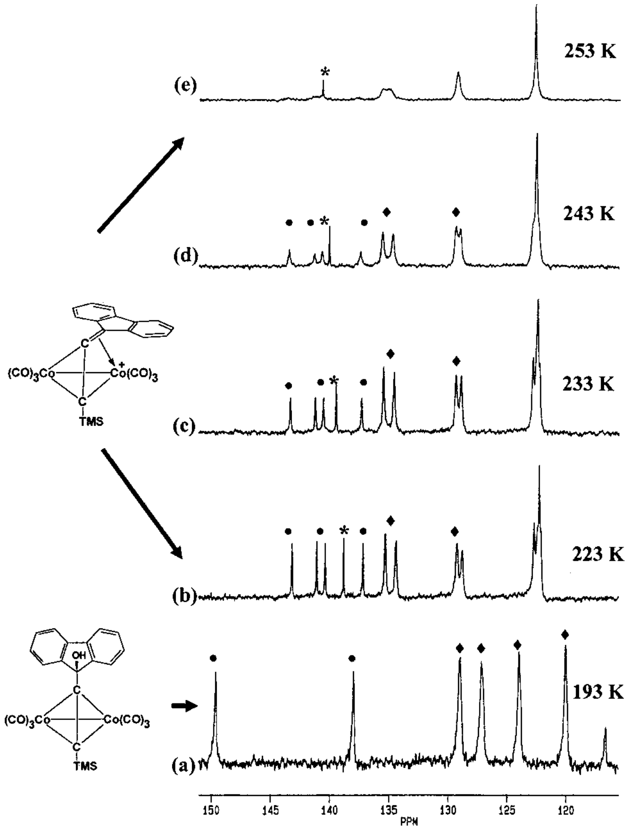


Figure 1. 75 MHz variable-temperature ^{13}C NMR spectra showing coalescence of the fluorenyl resonances in **10**: (♦) aromatic CH's; (●) aromatic C's; (*) C(9). Spectrum a is for the fluorenol **9**, spectra b−e are spectra of the cation.

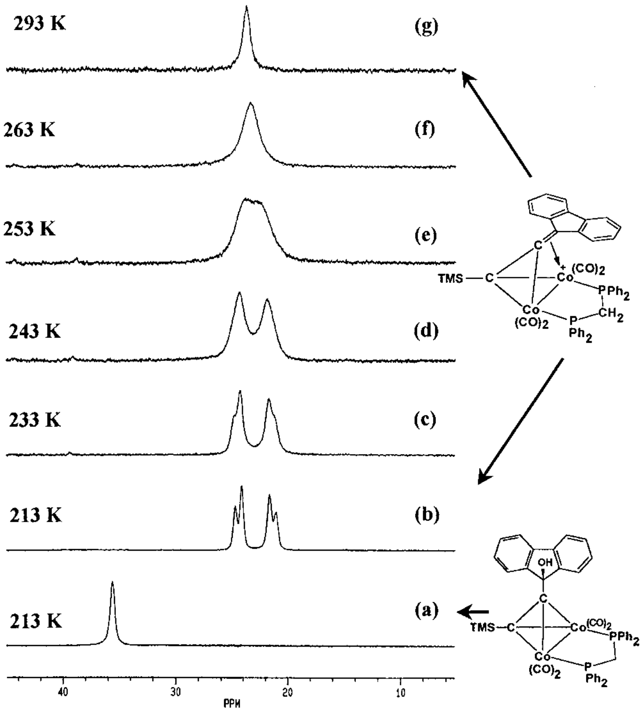
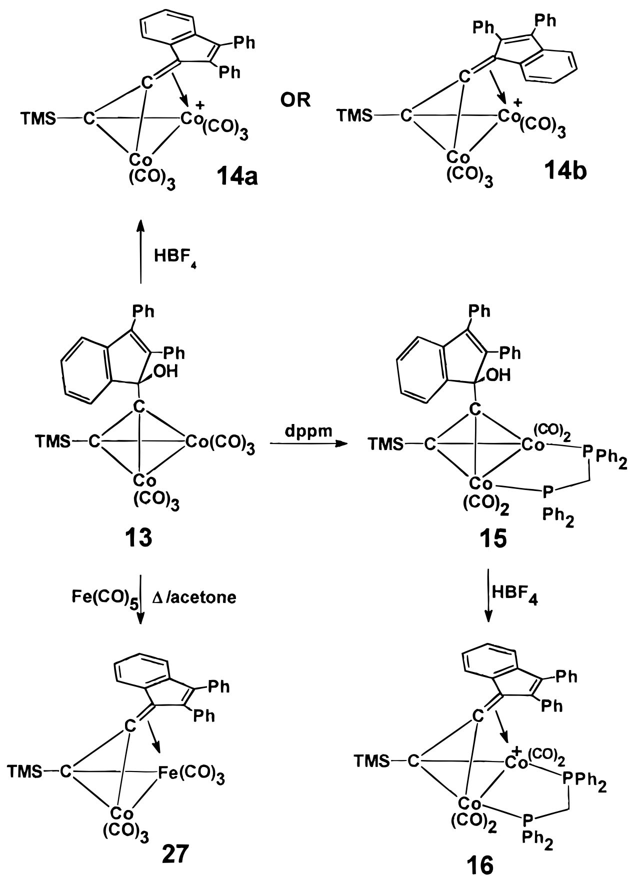


Figure 2. 121 MHz variable-temperature ^{31}P NMR spectra of **12.** Spectrum a is for the fluorenol **11**; spectra b−e are spectra of the cation.

with tertiary cations, within experimental error these two barriers do not differ significantly.

Although indenone itself is not stable except at very low temperatures,[20] the 2,3-diphenyl derivative is readily available. In an analogous fashion to the generation of the cluster-stabilized fluorenyl cation **10**, the 1-((trimethylsilyl)ethynyl)-2,3-diphenylindenol−Co$_2$(CO)$_6$ complex (**13**) was protonated to yield the indenyl cationic cluster **14,** as shown in Scheme 3. The variable-temperature ^{13}C NMR spectra of **14** exhibit only four CH resonances assignable to the indenyl moiety; furthermore, the spectra do not change with temperature until the onset of decomposition as one approaches 273 K. Thus, the cation appears to exist as a single isomer, but it is not possible to differentiate between structures **14a** and **14b** in which the six-membered ring is oriented *endo* or *exo*, respectively, relative to the cobalt−cobalt bond; we shall return to this point presently. In an attempt to detect fluxional behavior in an indenyl cluster cation, the bis(diphenylphosphino)methane complex **15** was prepared. The stereogenic center at C(1) renders diastereotopic the two cobalt vertices, and their attached phosphorus atoms (^{31}P NMR peaks at 34.6 and 30.4 ppm, with ^{2}J(P−P) = 114.6 Hz). Subsequent protonation to form the cation **16** gives rise to a ^{31}P NMR spectrum exhibiting only two equally intense doublet resonances (at 38.8 and 15.2 ppm, with ^{2}J(P−P) = 57.2 Hz). Once again, there is no change over the range 213−268 K, suggesting that a single isomer (with the benzo ring either *exo* or *endo*) is formed. Above this temperature, there is gradual peak broadening and loss of the phosphorus−phosphorus coupling constant; from these observations, one can estimate the barrier for indenyl migration between cobalt vertices to be at least 13.5 kcal mol^{-1}, and probably somewhat higher.

Scheme 3. Syntheses of Alkynyl−Indenyl Cluster Complexes



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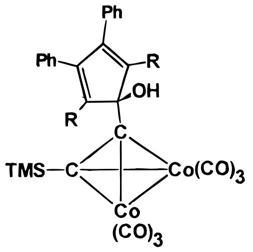
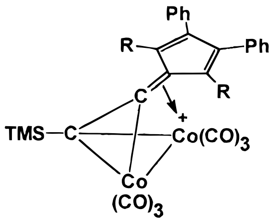
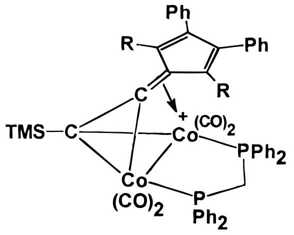
Cyclopentadienyl−$Co_2(CO)_6$ Cations. The preparation of cyclopentadienyl analogues of the fluorenyl cation **10** and the indenyl cation **14** require the availability of cyclopentadienones, and such molecules only resist Diels−Alder dimerization when bulky substituents are present.[21] Thus far, we have prepared the cyclopentadienyl clusters **18a**,**b** and the corresponding cations **19a**,**b** derived from tetraphenylcyclopentadienone and from 2,5-diethyl-3,4-diphenylcyclopentadienone, respectively. The ^{13}C NMR spectra of **19a** are complicated by the presence of many overlapping phenyl resonances, but the diethyl cation **19b** provides a more tractable system. In this latter case, the carbon resonances of the two ethyl groups are distinct (CH_3's at 14.8 and 16.8 ppm, CH_2's at 18.2 and 18.5 ppm) over the range 188−263 K, at which temperature decomposition becomes evident. That is, there is no rotation about the C−C_5R_4 bond that would equilibrate the *exo* and *endo* ethyl environments on the ^{13}C NMR time scale; however, this provides no indication as to whether there is antarafacial migration of the cation between cobalt vertices.



18a : R = Ph
18b : R = Et



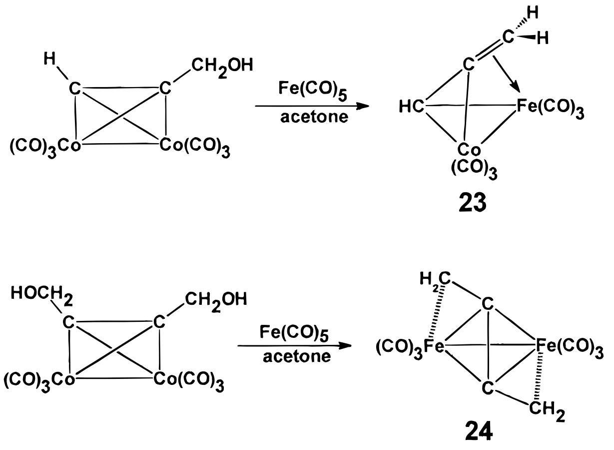
19a : R = Ph
19b : R = Et



21a : R = Ph
21b : R = Et

As was done for the fluorenyl and indenyl analogues, the dppm-substituted cyclopentadienyl clusters **20a**,**b** and cations **21a**,**b** were examined; the ^{31}P NMR spectra of the cations at 193 K showed in each case the expected two doublets with ^2J(P−P) values of 60.5 Hz and 58.9 Hz, respectively. In the diethyl cation **21b**, these resonances remain distinct until 248 K, at which temperature the onset of decomposition is evident. These data can only indicate a minimum $\Delta G^{\ddagger}$ value of ~12 kcal mol^{-1}, but the true barrier toward migration of the cyclopentadienyl ligand between cobalt vertices is presumably considerably higher. In contrast, the ^{31}P resonances of the tetraphenylcyclopentadienyl cationic complex **21a** coalesce at 233 K, indicating a barrier to antarafacial migration of ~10 kcal mol^{-1}. This surprisingly low barrier is perhaps attributable to steric interactions between the peripheral phenyls of the five-membered ring and the PPh_2 substituents of the dppm ligand.

Scheme 4. Isolobal Replacement of $Co(CO)_3$ Vertices by $Fe(CO)_3$ Fragments



Fe−Co Complexes as Models of Cluster Cations. Cobalt-stabilized cations **7a** have long been thought to adopt a molecular geometry such that the vinylidene capping group leans towards one of the metal vertices, as in **7a**, rather than the vertical orientation **7c**. This ground-state structure in which the cationic center is bonded to a single cobalt vertex gains strong support from variable-temperature NMR studies[22] and from molecular orbital calculations;[23] in addition, crystallographic data are available for numerous molybdenum-stabilized cluster cations **7b**.[17] Moreover, in a very recent and important study, Melikyan has obtained the X-ray crystal structure of the doubly complexed propargyl cation $[(t\text{-BuC}{\equiv}C)_3C(Co_2(CO)_6)_2]^+$, in which there is preferential coordination of the cationic center with one of the metal atoms in each cluster.[24]

We have previously suggested that isolobal substitution of a $Co(CO)_3^+$ vertex in $[Co_2(CO)_6(HC{\equiv}CCR_2)]^+$ by an $Fe(CO)_3$ unit to give $[CoFe(CO)_6(HC{=}C{=}CR_2)]$ should serve as an excellent model for the structure of the cluster cation.[25,26] Indeed, molecular orbital calculations yield almost identical energy-minimized geometries for such pairs of clusters. For this reason, we chose to synthesize and structurally characterize the neutral cluster $[(Me_3SiC{=}C{=}(\text{fluorenyl}))FeCo(CO)_6]$ (**22**). The neutral $Fe(CO)_3$ analogues of the $Co(CO)_3^+$ cationic clusters can be prepared directly from cobalt precursors. Thus, as depicted in Scheme 4, treatment of (propargyl alcohol)$Co_2(CO)_6$ with $Fe(CO)_5$ in refluxing acetone yields $(HC{=}C{=}CH_2)FeCo(CO)_6$ (**23**); this same reaction

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

(25) (a) Osella, D.; Dutto, G.; Jaouen, G.; Vessieres, A.; Raithby, P. R.; De Benedetto, L.; McGlinchey, M. J. *Organometallics* **1993**, *12,* 4545. (b) Ruffolo, R.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **1998,** *17,* 4992.

(26) One cannot claim a similar correspondence in susceptibility to nucleophilic attack, since the dicobalt cluster bears a positive charge, whereas the iron−cobalt complex is neutral.

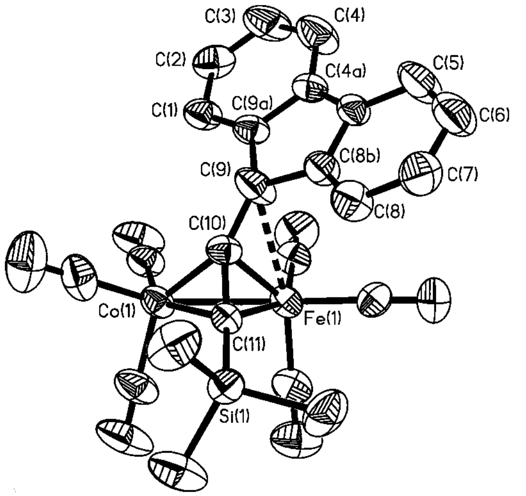
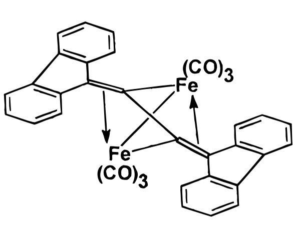


Figure 3. Molecular structure of **22** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Fe(1)−C(9) = 2.626(11), C(9)−C(10) = 1.351(8), C(10)−C(11) = 1.348(9); Fe(1)−C(10)−C(9) = 102.4(3).

is also applicable to the diol ($HOCH_2C{\equiv}CCH_2OH$)$Co_2(CO)_6$, which, upon treatment with $Fe(CO)_5$ in acetone, gives ($CH_2{=}C{=}C{=}CH_2$)$Fe_2(CO)_6$ (**24**).[27]

One might suggest that these (butatriene)$Fe_2(CO)_6$ complexes[28] may be regarded as models for the corresponding dicationic dicobalt clusters. In particular, [bis(biphenylene)butatriene]$Fe_2(CO)_6$ (**25**),[29] which has been prepared directly from the cumulene, may be regarded as a model for the dication **26**.



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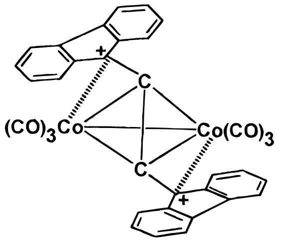

26

The reaction of (9-((trimethylsilyl)ethynyl)-9-fluorenol)-$Co_2(CO)_6$ (**9**) with $Fe(CO)_5$ in refluxing acetone gave, after chromatographic separation, crystals of [$FeCo(CO)_6$(TMS−C=C=(fluorenyl))] (**22**), whose structure appears in Figure 3; the bending of the fluorenyl unit toward the iron atom is evident. The Fe(1)−C(9) distance is 2.626(11) Å, and the Fe(1)−C(10)−C(9) angle is 102.4°; these may be compared with the EHMO-calculated values of 2.73 Å and 108° (see below). The C(11)−C(10) and C(10)−C(9) distances are 1.351(8) and 1.348(9) Å, respectively, and these values appear to be more indicative of an allenyl $C{=}C{=}C_{13}H_8$ system than of an acetylenic $C{\equiv}CC_{13}H_8$ linkage. It is also noteworthy that the peripheral six-membered rings are each bent away from the central five-membered ring through approximately 5°.

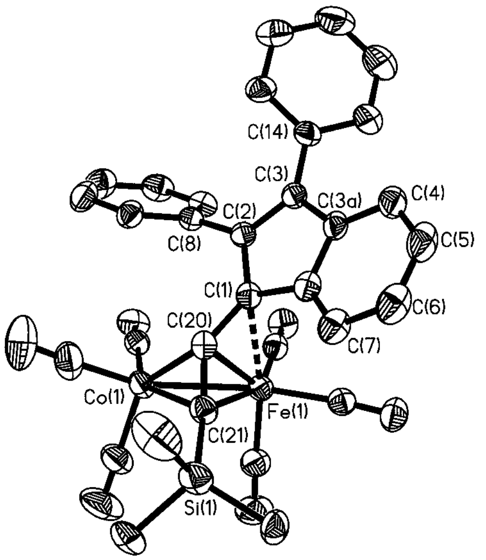

Figure 4. Molecular structure of **27** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Fe(1)−C(1) = 2.346(2), C(1)−C(20) = 1.387(4), C(20)−C(21) = 1.355(4); Fe(1)−C(20)−C(1) = 85.4(2).

Buoyed by this result, we chose to attempt the synthesis of the analogous 2,3-diphenylindenyl analogue. Indeed, treatment of the 2,3-diphenylindenol−dicobalt cluster **13** with $Fe(CO)_5$ in acetone yielded X-ray-quality crystals of the mixed-metal cluster **27**, and the structure appears in Figure 4. The orientation of the six-membered ring in the *endo* position is readily apparent (suggesting that the corresponding dicobalt cationic cluster exists as the *endo* isomer **14a),** but the most important observation is the Fe−C(1) distance in **27**, which is now only 2.347(7) Å, markedly shorter than the corresponding Fe−C(9) value in the fluorenyl analogue **22.** Furthermore, the Fe(1)−C(20)−C(1) angle is 85.4(2)°, considerably smaller than the corresponding angle in **22,** implying that the indenyl ligand has more need for electronic assistance from the neighboring metal center. As with **22**, the alkyne-derived unit exhibits allene-like character; the C(1)−C(20) and C(20)−C(21) distances are 1.387(4) and 1.355(4) Å, respectively.

Attempted syntheses of the analogous iron−cobalt clusters bearing cyclopentadienyl moieties, *i.e.* neutral analogues of cations **19a**,**b,** yield instead complexes of the type ($Co_2(CO)_6[TMS{-}C{\equiv}CC_5R_4]Fe(CO)_2H$, in which the incoming iron carbonyl moiety binds in an η^5 fashion to the cyclopentadienyl ring. The X-ray structures of these trimetallic systems and their mechanistic implications are deferred to another paper.

It is clearly relevant to compare the structures of the iron−cobalt fluorenyl cluster **22** and the diiron fluorenylidene complex **25.** The latter determination dates back more than 25 years and was obtained from film data; moreover, no absorption correction was applied.[29] Nevertheless, the essential features of the molecular geometry are clear. The triene backbone in **25** is no longer linear, and the fluorenyl moieties lean toward the iron atoms. The quoted $Fe{\cdots}CR_2$ distances are approximately 2.40 Å.

When we compare the structures of the known vinylidene clusters in which the capping group leans towards an $Fe(CO)_3$ vertex, it is clear that the $Fe{\cdots}CR_2$ distance is a sensitive probe of the strength of this interaction. To put this in perspective, we note that a comprehensive survey of the $Mo{\cdots}C^+$ distances in

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[27] Victor, R. *J. Organomet. Chem.* **1977,** *127,* C25.

[28] (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.

[29] Bright, D.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972,** 2465.

clusters of the type $[Cp_2Mo_2(CO)_4(RC\equiv CCR'R'')]^+$ reveals that the molybdenum-to-carbocation distance is in the range 2.44–2.55 Å for primary cations but increases to 2.61–2.63 Å for secondary cations and can reach 2.74–2.92 Å for tertiary carbocations.[17] Moreover, there is a very clear inverse relationship between this distance parameter and the NMR-derived activation energies for antarafacial migration between molybdenum centers: the longer the $Mo\cdots C^+$ bond, the lower the barrier! It has also been shown that one can apply the Bürgi–Dunitz structure correlation method,[30] whereby these structures can be mapped onto a calculated trajectory and, in effect, provide a series of snapshots of the migration pathway.[31]

We are aware of three relevant X-ray crystal structures in which $(OC)_3Fe\cdots CH_2$ distances have been reported.[32] In $Cp_2W_2(CO)_4Fe(CO)_3(C{=}CH_2)$,[33] $(MeC{=}C{=}CH_2)Fe(CO)_3Co(CO)_2PPh_3$,[25a] and $(CH_2{=}C{=}C{=}CH_2)Fe_2(CO)_5PPh_3$,[28a] the iron–carbon distances are 2.21, 2.195, and 2.208 Å, respectively. Taking an extreme view, these relatively short bonds can be considered as arising from the interaction of CH_2^+ (*i.e.* primary) cations with $[Fe(CO)_3]^-$ vertices. In contrast, in $(Me_3SiC{=}C{=}CMe_2)FeCo(CO)_6$,[25b] $(Me_2C{=}C{=}C{=}CMe_2)Fe_2(CO)_6$,[28b] and $(Me_3SiC{=}C{=}(\text{fluorenyl}))FeCo(CO)_6$ (**22**), the Fe–C distances of 2.335, 2.401 and 2.633 Å, respectively, are a manifestation of the weaker bonding between a tertiary cation and the formally anionic $Fe(CO)_3$ moiety. The relatively short (2.347 Å) Fe–C(1) bond in the indenyl cluster **27** supports the hypothesis that the less stable "indenyl cation" has more need of electronic assistance from the "$[Fe(CO)_3^-]$" unit than does a "fluorenyl cation". We plan to synthesize an extended series of such iron–cobalt clusters to probe the effect of changing the character of the vinylidene moiety.

Extended Hückel Molecular Orbital Calculations. Molecular orbital calculations at the extended Hückel level have allowed us to gain some understanding of the factors controlling the geometry of metal-stabilized cluster cations.[22] When the formally sp^2-hybridized carbocationic center is allowed to lean toward a metal vertex, the enhanced overlap between the vacant p orbital on the CR_2^+ moiety and a filled metal d orbital of suitable symmetry leads to marked stabilization of the system. Figure 5 shows the result of bending a cyclopentadienyl cation toward one of the cobalt vertices in $[(C_5H_4C\equiv CR)Co_2(CO)_6]^+$; the total electronic energy is minimized at a bend angle, θ, of approximately 35°, after which point unfavorable steric interactions with the carbonyl ligands begin to dominate. Concomitantly, the LUMO (which arises from out-of-phase overlap between the aforementioned carbon p orbital and metal d orbital) rises sharply in energy, thus markedly increasing the HOMO–LUMO gap.

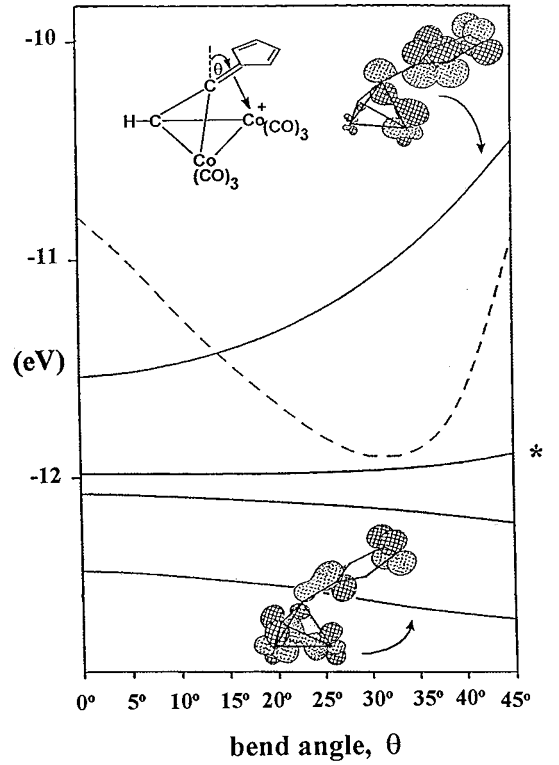
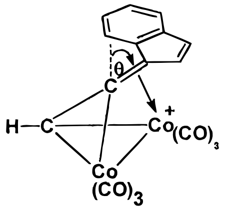


Figure 5. Orbital energy diagram showing the effect of bending a cyclopentadienyl cation toward a cobalt vertex in **29**. The HOMO is marked with an asterisk (*). The dashed line represents the change in total electronic energy and is drawn to a different scale.

For the fluorenyl cluster cation **10**, EHMO calculations predict a θ value of 25° and a $Co\cdots C^+$ distance of 2.71 Å for the energy-minimized geometry. Calculations for the analogous indenyl and cyclopentadienyl clusters **28** and **29** suggest somewhat larger θ values (**28**, θ = 30°, $Co\cdots C^+ = 2.62$ Å; **29**: θ = 35°, $Co\cdots C^+ = 2.53$ Å), as anticipated for the enhanced antiaromatic character of these ring systems. Doubtless, computations at a higher level of theory would lead to better calculated geometries, and we defer to our more knowledgeable colleagues for further exegesis.



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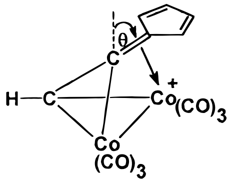

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It is noteworthy that cationic fragments in which the charge can be readily delocalized may have no need of assistance from neighboring organometallic units. For example, the pyrylium salts **30** and **31**,[34] and also the ferrocenyl–tropylium salt **32**,[35] have been characterized crystallographically; the cationic units retain their planarity and there is no intimation of a $metal\cdots C^+$ interaction.

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

(32) Another closely related molecule is $Co_2Ru(CO)_9C{=}CH^tBu$: Bernhardt, W.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1994,** *23,* 141.

(33) Delgado, E.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986,** 2105.

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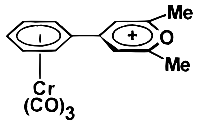
(35) Brownstein, S. K.; Gabe, E. J.; Hynes, R. C. *Can. J. Chem.* **1992,** *70,* 1011.



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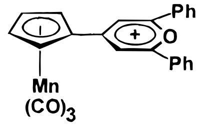

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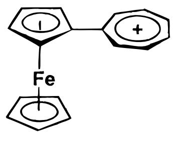

32

To conclude, we report the synthesis and NMR characterization of alkynyl−fluorenyl, −indenyl, and −cyclopentadienyl cations stabilized by coordination to a $Co_2(CO)_6$ moiety. In the first two instances, isolobal replacement of one tricarbonylcobalt vertex by an $Fe(CO)_3$ moiety yields stable iron−cobalt clusters whose X-ray crystal structures correspond reasonably well with the energy-minimized geometry predicted from extended Hückel molecular orbital calculations. The experimental extension of these concepts to the unsubstituted indenyl and cyclopentadienyl cluster cations $[(C_9H_7C{\equiv}CR)Co_2(CO)_6]^+$ and $[(C_5H_4C{\equiv}CR)Co_2(CO)_6]^+$ (**28** and **29,** respectively) is presently under investigation and will be the subject of a future report.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[36] Silica gel (particle size 20-45 μm) was employed for flash column chromatography. ^1H and ^{13}C solution NMR spectra were acquired on Bruker DRX 500, AM 300, and AM 200 spectrometers and were referenced to the residual proton signal, or the ^{13}C solvent signal. ^{31}P solution NMR spectra were acquired on a Bruker AM-300 spectrometer (^{31}P at 121.5 MHz) and referenced to an external 85% H_3PO_4 sample. Mass spectra were determined using a VG Analytical ZAB-E spectrometer by direct electron impact (EI) or positive electrospray (ES+) methods. Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer. Melting points (uncorrected) were determined on a Thomas-Hoover melting point apparatus. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada.

9-((Trimethylsilyl)ethynyl)fluoren-9-ol (8). *n*-BuLi (11.67 mL of a 1.44 M hexane solution, 16.80 mmol) was added dropwise to a solution of (trimethylsilyl)acetylene (1.65 g, 16.80 mmol) in ether at −78 °C *via* cannula over a 60 min period, and the solution was warmed to room temperature. After it was stirred for 1.5 h, the solution was then cooled to −78 °C and fluorenone (3.024 g, 16.80 mmol) in ether (40 mL) was added dropwise. The solution was warmed to room temperature, stirred for 24 h, and washed with distilled water, and the organic layer was collected. Removal of ether yielded 9-((trimethylsilyl)ethynyl)fluorenol (**8**; 4.077 g, 14.67 mmol, 87%) as a light yellow powder, mp 120-121 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.69 (d, 2H, $H_{1,8}$, $^3J(^1H-^1H) = 7.4$ Hz), 7.65 (d, 2H, $H_{4,5}$, $^3J(^1H-^1H) = 7.4$), 7.43 (t, 2H, $H_{3,6}$ $^3J(^1H-^1H) = 7.2$), 7.38 (t, 2H, $H_{2,7}$, $^3J(^1H-^1H) = 7.2$), 2.74 (s, OH), 0.19 (s, 9H, Me_3Si). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 147.5 ($C_{8a,9a}$), 139.5 ($C_{4a,4b}$), 130.1 ($C_{3,6}$), 129.0 ($C_{2,7}$), 124.6 ($C_{1,8}$), 120.6 ($C_{4,5}$), 105.6 (*C*≡C−TMS), 88.5 (C≡*C*−TMS), 75.3 (C_9), −0.13 (Me_3Si). IR (CH_2Cl_2): $\nu_{C\equiv C}$ at 2304 cm^{-1}; MS (EI) *m/z* (%): 278 $[M]^+$ (30), 263 $[M - CH_3]^+$ (100), 202 (25), 165 $[C_{13}H_9]^+$ (15), 73 $[Me_3Si]^+$ (20). HRMS (EI): calcd for $C_{18}H_{18}OSi$, 278.1127; found, 278.1132.

$(Me_3SiC{\equiv}CC_9H_8OH)Co_2(CO)_6$ (9). 9-((Trimethylsilyl)ethynyl)fluoren-9-ol (0.969 g, 3.49 mmol) dissolved in THF (50 mL) was added dropwise over a 45 min period to dicobalt octacarbonyl (1.26 g, 3.68 mmol) dissolved in THF (30 mL). The solution was then stirred for 24 h at room temperature. After removal of solvent, the product was recrystallized from a hexane/CH_2Cl_2 (9:1) mixture to give dark brown-red crystals of **9** in quantitative yield, mp 118 °C. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.66 (d, 2H, $H_{1,8}$, $^3J(^1H-^1H) = 7.4$ Hz), 7.60 (d, 2H, $H_{4,5}$, $^3J(^1H-^1H) = 7.5$), 7.39 (td, 2H, $H_{3,6}$, $^3J(^1H-^1H) = 7.4$, $^4J(^1H-^1H) = 1.3$), 7.29 (td, $H_{2,7}$, $^3J(^1H-^1H) = 7.4$, $^4J(^1H-^1H) = 1.3$), 2.74 (s, OH), 0.43 (s, 9H, Me_3Si). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 200.6 (Co−CO's); 150.9 ($C_{8a,9a}$), 139.3 ($C_{4a,4b}$), 129.9 ($C_{3,6}$), 128.0 ($C_{2,7}$), 124.7 ($C_{1,8}$), 120.6 ($C_{4,5}$), 118.2 (*C*≡C−TMS), 83.7 (C_9), 80.4 (C≡*C*−TMS), 0.60 (Me_3Si). IR (CH_2Cl_2): ν_{CO} at 2089, 2053, 2027 cm^{-1}. MS (EI) *m/z* (%): 536 $[M - CO]^+$ (10), 480 $[M - 3CO]^+$ (40), 452 $[M - 4CO]^+$ (10), 424 $[M - 5CO]^+$ (25), 396 $[M - 6CO]^+$ (40), 278 $[M - Co_2(CO)_6]^+$, 263 $[M - Co_2(CO)_6 - CH_3]^+$ (100), 180 $[C_{13}H_8OH]^+$ (60), 73 $[Me_3Si]^+$ (70). Anal. Calcd for $C_{24}H_{18}Co_2SiO_7$: C, 51.08; H, 3.21. Found: C, 51.28; H, 3.40.

$[(Me_3SiC{=}C{=}C_9H_8)Co_2(CO)_6]BF_4$ (10). Two drops of HBF_4/Et_2O were added to **9** in CD_2Cl_2 at −78 °C in an NMR tube, and the sample immediately turned deep red in colour, indicating the formation of **10**. ^{13}C NMR (75 MHz, CD_2Cl_2, 223 K): δ 192.7 (br, Co−CO's), 142.8, 140.7, 140.0, 138.5 (C_9), 136.8, 135.0, 134.1, 129.0, 128.5, 122.4, 122.0 (br), 121.9, 111.8 (*C*≡C−TMS), 88.7 (C≡*C*−TMS), 1.2 (Me_3Si).

$(Me_3SiC{\equiv}CC_9H_8OH)Co_2(CO)_4dppm$ (11). $(Me_3SiC{\equiv}CC_9H_8OH)Co_2(CO)_6$ (**9**; 0.356 g, 0.631 mmol) and bis(diphenylphosphino)methane (0.376 g, 0.979 mmol) were dissolved in hexanes (60 mL), and the mixture was heated under reflux for 2 h. After removal of the solvent, the residue was subjected to flash chromatography. Elution with a 2:1 hexanes/CH_2Cl_2 solvent mixture yielded **11** (0.365 g, 0.409 mmol, 65%) as a brownish red powder, mp 208−209 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.80−6.65 (m, 28H), 3.52 (br, 2H, CH_2), 2.45 (s, 1H, OH), −0.37 (s, 9H, Me_3Si). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 208.2, 204.4 (CO's), 152.3 ($C_{9a,9b}$), 139.2 ($C_{4a,4b}$), 140.1 (*ipso*, br), 136.7 (*ipso*, br), 132.7, 131.3 (*meta*), 129.8, 129.4 (*para*), 128.9, 128.8 (*ortho*), 128.3, 127.5, 126.0, 119.9 (C−H's), 114.5 (*C*≡C−TMS), 89.7 (C≡*C*−TMS), 86.9 (C_9), 36.8 (CH_2, t, $^1J(^{31}P-^{13}C) = 19.9$ Hz), 0.1 (Me_3Si). ^{31}P NMR (CD_2Cl_2): δ 35.54 (s). IR (CH_2Cl_2) ν_{CO} at 2018, 1990, 1963 cm^{-1}. MS (ES+) *m/z* (%): 892 $[M]^+$ (25), 875 $[M - OH]^+$ (100). Anal. Calcd for $C_{47}H_{40}Co_2P_2SiO_5$: C, 63.23; H, 4.52. Found: C, 63.56; H, 4.50.

$[(Me_3SiC{=}C{=}C_9H_8)Co_2(CO)_4dppm]BF_4$ (12). Protonation of **11** with HBF_4/Et_2O at −78 °C resulted in an immediate deep brown-red solution, indicating the formation of the cation **12**. ^{13}C NMR (75 MHz, CD_2Cl_2, 213 K): δ 203.6, 201.8, 197.3, 193.2 (Co−CO's), 149.5, 143.1, 140.1, 139.0, 137.3 ($C_{4a,4b,8a,9,9a}$), 134.1, 132.7, 131.6−128.2 (broad), 122.9, 122.0, 121.9, 114.3 (*C*≡C−TMS), 86.6 (C≡*C*−TMS), 31.8 (br, CH_2), 1.6 (Me_3Si). ^{31}P NMR (CD_2Cl_2, 213 K): δ 24.37 (d, 1P), 21.31 (d, 1P), $^2J(^{31}P-^{31}P) = 69.7$ Hz.

2,3-Diphenyl-l-((trimethylsilyl)ethynyl)inden-l-ol. By analogy to the procedure described for **8**, 2,3-diphenylindenone (2.00 g, 7.10 mmol) in THF (20 mL) was added to a 3-fold excess of the lithium salt of (trimethylsilyl)ethyne. The solution was quenched with water and extracted with ether, and the solvent was removed to yield the product (2.102 g, 5.53 mmol, 78%) as a light yellow powder, mp 102.5−104 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.70−7.69 (m, 1H), 7.61−7.59 (m, 2H), 7.42−7.39 (br, 4H), 7.36−7.34 (m, 3H), 7.30−7.29 (m, 3H), 7.24−7.23 (m, 1H), 2.69 (s, OH), 0.21 (s, 9H, Me_3Si). ^{13}C NMR (125 MHz, $CDC1_3$): δ 146.3, 144.0, 142.7, 140.2 ($C_{2,3,4,9}$), 134.1, 133.6 (*ipso*), 129.8, 129.2 (*meta, ortho*), 129.1 (*para*), 128.5,

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(36) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

127.91 (*meta, ortho*), 127.86 (*para*), 127.6, 127.2, 123.1, 121.1 ($C_{5,6,7,8}$), 104.9 (*C*≡C−TMS), 89.7 (C≡*C*−TMS), 78.3 (C_1), −0.3 (Me_3Si). IR (CH_2Cl_2) $\nu_{C\equiv C}$ at 2309 cm^{-1}. MS (EI) *m/z* (%): 380 $[M]^+$ (80), 365 $[M - CH_3]^+$ (22), 303 $[M - C_6H_5]^+$ (35), 291 (51), 252 (10), 73 $[Me_3Si]^+$ (100). HRMS (El): calcd for $C_{26}H_{24}OSi$, 380.1596; found, 380.1547.

{2,3-Diphenyl-(1-(trimethylsilyl)ethynyl)inden-l-ol}$Co_2(CO)_6$ (13). 2,3-Diphenyl-1-((trimethylsilyl)ethynyl)inden-l-ol (0.511 g, 1.34 mmol) dissolved in THF (20 mL) was added to a solution of $Co_2(CO)_8$ (0.803 g, 2.34 mmol) in THF (20 mL). The solution was stirred for 24 h, the solvent was removed on a rotary evaporator, and the product was purified by flash chromatography using a solvent mixture of 1:1 hexanes/CH_2Cl_2, yielding **13** (0.761 g, 1.14 mmol, 85%) as a brown-red powder, mp 153−154 °C. ^1H NMR (500 MHz, CD_2Cl_2): *δ* 7.67−7.60 (br, 3H), 7.39−7.08 (br, 11 H), 2.86 (s, 1H, OH), 0.17 (s, 9H, Me_3Si). ^{13}C NMR (125 MHz, CD_2Cl_2): *δ* 200.6, 200.2 (Co−CO's), 151.4, 146.4, 142.9, 141.1 ($C_{2,3,4,9}$), 135.5, 134.6 (*ipso*), 130.9, 129.5 (2C), 129.2, 128.3, 128.2 (*o, m, p*), 128.1, 126.7, 123.3, 21.4 ($C_{5,6,7,8}$), 114.3 (*C*≡C−TMS), 88.2 (C_1), 80.8 (C≡*C*−TMS), 1.1 (Me_3Si). IR (CH_2Cl_2): ν_{CO} at 2087, 2051, 2022 cm^{-1}. MS (El) *m/z* (%): 582 $[M - 3CO]^+$ (45), 498 $[M - 6CO]^+$ (70), 422 $[M - Co(CO)_6 - OH]^+$ (50), 380 $[M - Co_2(CO)_6]^+$ (65), 365 (40), 291 (35), 282 (70), 252 (20), 73 $[Me_3Si]^+$ (100). Anal. Calcd for $C_{32}H_{24}Co_2SiO_7$: C, 57.66; H, 3.63. Found: C, 57.34; H, 3.42.

[{2,3-Diphenyl-l-((trimethylsilyl)ethynyl)indenyl}$Co_2(CO)_6$]BF_4 (14). Protonation of **13** in CD_2Cl_2 with 2 drops of HBF_4/Et_2O at −78 °C resulted in an immediate deep brown-red solution, indicating the formation of the cation **14**. ^1H NMR (300 MHz, CD_2Cl_2, 233 K): 7.41−7.29 (m, 10H), 7.20−7.13 (m, 4H), 0.69 (s, 9H, Me_3Si). ^{13}C NMR (75 MHz, CD_2Cl_2, 233 K): *δ* 192.7 (br., Co−CO's), 156.5, 142.1, 140.7, 140.4, 138.5, 132.6, 132.4, 131.8, 130.2, 130.0, 129.7, 129.2, 128.7 (2C's), 128.5, 124.1, 121.2, 117.6 (*C*≡C−TMS), 89.2 (C≡*C*−TMS), 1.8 (Me_3Si).

{2,3-Diphenyl-l-((trimethylsilyl)ethynyl)indenol}$Co_2(CO)_4$dppm (15). **13** (0.491 g, 0.737 mmol) and bis(diphenylphosphino)methane (0.432 g, 1.13 mmol) were heated under reflux in hexanes (60 mL) for 2 h. Removal of the solvent, and flash chromatography of the residue using 3:1 hexanes/CH_2Cl_2 as eluent, yielded **15** (0.412 g, 0.414 mmol, 56%) as a brown-red powder, mp 215−216 °C. ^1H NMR (300 MHz, CD_2Cl_2): *δ* 7.67−7.00 (m, 30H), 4.97 (br, 1H, methylene−H), 3.55 (br, 1H, methylene−H), 2.78 (s, OH), 0.03 (s, 9H, Me_3Si). ^{13}C NMR (75 MHz, CD_2Cl_2): *δ* 208.2, 206.1, 205.6, 201.6 (Co−CO's), 152.4, 148.3, 143.1, 139.6 ($C_{2,3,4,9}$), 139.0, 137.3, 136.1, 134.9 (*ipso* C's), 132.6, 132.5, 132.0, 131.9, 131.6, 130.6, 129.8, 129.5, 128.8, 128.3, 128.2, 127.5, 127.3, 125.9, 125.1, 120.5, 114.3 (*C*≡C−TMS), 91.0 (C_1), 84.7 (C≡*C*−TMS), 36.8 (t, CH2, $^1J(^{13}C-^{31}P) = 20.9$ Hz), 1.3 (Me_3Si). ^{31}P NMR (CD_2Cl_2): *δ* 34.56 (d), 30.41 (d), $^2J(^{31}P-^{31}P) = 114.6$ Hz). IR (CH_2Cl_2): ν_{CO} at 2018, 1991, 1963 cm^{-1}. MS (ES+) *m/z* (%): 994 $[M]^+$ (30), 977 $[M - OH]^+$. Anal. Calcd for $C_{55}H_{46}Co_2P_2SiO_5$: C, 66.39; H, 4.66. Found: C, 66.33; H, 4.62.

[{2,3-Diphenyl-l-((trimethylsilyl)ethynyl)indenyl}$Co_2(CO)_4$dppm]BF_4 (16). Protonation of **15** in CD_2Cl_2 at 195 K with HBF_4/Et_2O at −78 °C resulted in an immediate deep brown-red solution, indicating the formation of the cation **16**. ^{13}C NMR (75 MHz, CD_2Cl_2, 213 K): *δ* 202.3, 200.7, 197.3, 193.7 (Co−CO's), 90.5 (C≡*C*−TMS), 35.7 (br, CH_2), 2.5 (Me_3Si). ^{31}P NMR (CD_2Cl_2, 213 K): *δ* 38.78 (d), 15.16 (d), $^2J(^{31}P-^{31}P) = 57.2$ Hz. A marked increase in complexity of the aromatic region in the ^{13}C NMR spectrum with respect to **15** was observed.

5-((Trimethylsilyl)ethynyl)-1,2,3,4-tetraphenylcyclopentadien-5-ol (17a). By the procedure described for **8**, 2,3,4,5-tetraphenylcyclopentadienone (6.630 g, 17.3 mmol) dissolved in THF (30 mL) was added to ((trimethylsilyl)ethynyl)lithium (2 equiv) to yield **17a** (7.594 g, 15.8 mmol, 91%) as a yellow powder, mp 179−181 °C. ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.55 (dd, *ortho*, 4H, $^3J(^1H_o-^1H_m) = 7.9$ Hz, $^4J(^1H_o-^1H_p) = 1.7$ Hz), 7.23−7.19 (m, *meta, para*, 6H), 7.13−7.07 (m, *meta, para*, 6H), 6.97 (dd, *ortho*, 4H, $^3J(^1H_o-^1H_m) = 7.6$ Hz, $^4J(^1H_o-^1H_p) = 1.5$ Hz), 2.56 (s, OH), 0.12 (9H, Me_3Si). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 143.0, 142.6 ($C_{1,2}$), 134.7, 133.8 (*ipso*), 129.82, 129.79 (*meta*), 127.81, 127.76 (*ortho*), 127.2, 127.1 (*para*), 104.9 (*C*≡C−TMS), 91.3 (C≡*C*−TMS), 81.4 (C_5), −0.4 (Me_3Si). IR (CH_2Cl_2): $\nu_{C\equiv C}$ at 2306 cm^{-1}. MS (EI) *m/z* (%): 482 $[M]^+$ (100), 467 $[M - CH_3]^+$ (10), 405 $[M - Ph]^+$ (50), 381 (30), 315 (15), 289 (10), 178 $[C_2Ph_2]^+$ (20), 73 $[Me_3Si]^+$ (40). HRMS (EI): calcd for $C_{34}H_{30}OSi$, 482.2065; found, 482.2027.

{5-((Trimethylsilyl)ethynyl)-1,2,3,4-tetraphenylcyclopentadien-5-ol}$Co_2(CO)_6$ (18a). Compound **17a** (1.207 g, 2.50 mmol) dissolved in THF (20 mL) was added dropwise over a 30 min period to dicobalt octacarbonyl (1.084 g, 3.17 mmol) dissolved in THF (15 mL) and the solution stirred for 24 h at room temperature. The product was recrystallized from hexane/CH_2Cl_2 (1:1) to give dark red crystals of **18a** in quantitative yield, mp 169−171 °C. ^1H NMR (300 MHz, CD_2Cl_2): *δ* 7.66 (br, 4H), 7.12 (br, 12H), 7.04 (br, 4H), 2.95 (s, 1H, OH), 0.11 (s, 9H, Me_3Si). ^{13}C NMR (75 MHz, CD_2Cl_2): *δ* 200.3 (Co−CO's), 147.0, 144.9 ($C_{1,2}$), 136.7, 134.8 (*ipso*), 130.7, 130.2 (*meta*), 128.2 (br, *ortho*), 128.0, 127.2 (*para*), 110.8 (*C*≡C−TMS), 92.9 (C_5), 81.5 (C≡*C*−TMS), 1.3 (Me_3Si). IR (CH_2Cl_2): ν_{CO} at 2086, 2050, 2020 cm^{-1}. MS (EI) *m/z (%)*: 580 $[M - Co(CO)_4 - OH]^+$ (5), 524 $[M - Co(CO)_6 - OH]^+$ (15), 178 $[C_2Ph_2]^+$ (20), 73 $[Me_3Si]^+$ (100). Anal. Calcd for $C_{40}H_{30}Co_2SiO_7$: C, 62.50; H, 3.94. Found: C, 62.74; H, 3.84.

[{5-((Trimethylsilyl)ethynyl)-1,2,3,4-tetraphenylcyclopentadienyl}$Co_2(CO)_6$]BF_4 (19a). Protonation of **18a** in CD_2Cl_2 with HBF_4/Et_2O at −78 °C resulted in an immediate deepening in color, indicating formation of the cation **19a.** ^{13}C NMR (75 MHz, CD_2Cl_2, 233 K): *δ* 198.4 (br, Co−CO's), 151.9, 147.8, 141.6, 137.4 ($C_{1,2,3,4}$), 94.1 (*C*≡C−TMS), 83.6 (C≡*C*−TMS), 0.2 (Me_3Si). The ^{13}C NMR spectrum of **19a** exhibited a marked increase of complexity in the aromatic region with respect to **18a.**

{5-((Trimethylsilyl)ethynyl)-1,2,3,4-tetraphenylcyclopentadien-5-ol}$Co_2(CO)_4$dppm (20a). **18a** (0.250 g, 0.326 mmol) and dppm (0.188 g, 0.490 mmol) were dissolved in THF (50 mL), and the mixture was stirred at room temperature for 40 h. Removal of the solvent and flash chromatography of the residue with 2:1 hexanes/CH_2Cl_2 as eluent yielded **20a** (0.126 g, 0.115 mmol, 35%) as a brown-red powder, mp 193−194 °C. ^1H NMR (500 MHz, CD_2Cl_2): *δ* 7.70−6.98 (m, 40H), 3.57 (q, 1H, methylene−H), 3.43 (q, 1H, methylene−H), 3.30 (s, OH), 0.38 (s, 9H, Me_3Si). ^{13}C NMR (125 MHz, CD_2Cl_2): *δ* 208.7, 202.4 (Co−CO's), 148.3, 144.4 ($C_{1,2}$), 138.5 (t, *ipso*, $^1J(^{31}P-^{13}C)$ $^3J(^{31}P-^{13}C) = 24.0$ Hz), 137.2, 135.9 (*ipso* C's), 134.4 (t, *ipso*, $J(^{31}P-^{13}C) \equiv {}^3J(^{31}P-^{13}C) = 17.6$ Hz), 132.9, 131.3, 131.2, 130.6, 130.0, 129.5, 128.6, 128.2, 127.8, 127.6, 127.2, 126.8 *(o, m, p* C−H's), 120.1 (*C*≡C−TMS), 94.8 (C_5), 73.1 (C≡*C*−TMS), 40.1 (t, CH_2, $^1J(^{31}P-^{13}C) = 18.1$ Hz), 3.1 (Me_3Si). ^{31}P NMR (CD_2Cl_2): *δ* 31.78 (s). IR (CH_2Cl_2): ν_{CO} at 2019, 1994, 1964 cm^{-1}. MS (ES+) *m/z* (%): 1096 $[M]^+$ (100). Anal. Calcd for $C_{63}H_{52}Co_2P_2SiO_5$: C, 68.97; H, 4.78. Found: C, 69.06; H, 4.80.

[{5-((Trimethylsilyl)ethynyl)-1,2,3,4-tetraphenylcyclopentadienyl}$Co_2(CO)_4$dppm]BF_4 (21a). Protonation of **20a** in CD_2Cl_2 with HBF_4/Et_2O at −78 °C in an NMR tube resulted in an immediate deepening in color of the solution, indicating formation of the cation **21a**. Upon protonation, the ^{13}C NMR spectrum exhibited a marked increase in complexity in the aromatic region relative to **20a**. ^{31}P NMR (CD_2Cl_2, 193 K): *δ* 39.00 (d), 18.14 (d), $^2J(^{31}P-^{31}P) = 60.5$ Hz.

5-((Trimethylsilyl)ethynyl)-1,4-diethyl-2,3-diphenylcyclopentadien-5-ol (17b). By analogy to the procedure described for **8**, diethyldiphenylcyclopentadienone (4.987 g, 17.31 mmol) in THF (50 mL) was added to a 2-fold excess of the lithium salt of (trimethylsilyl)ethyne. The solution was quenched with water and extracted with ether and the solvent removed to yield **17b** (5.709 g, 14.79 mmol, 85%) as a yellow oil. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.25−7.22 (m, 6H, *m* and *p* H's), 7.06 (d, 4H, *ortho*, $^3J(^1H_o{-}^1H_m) = 7.7$ Hz), 2.58−2.46 (m, 4H, CH_2), 2.37 (s, OH), 1.31 (t, 6H, CH_3, $^3J(^1H{-}^1H) = 7.6$ Hz), 0.28 (s, 9H, Me_3Si). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 145.8 ($C_{1,4}$), 141.4 ($C_{2,3}$), 135.8 (*ipso*), 129.5 (*ortho*), 128.2 (*meta*), 127.3 (*para*), 105.5 (*C*≡C−TMS), 89.5 (C≡*C*−TMS), 81.9 (C_5), 19.6 (CH_2), 14.8 (CH_3), 0.2 (Me_3Si). IR (CH_2Cl_2): $\nu_{C\equiv C}$ at 2305 cm^{-1}. MS (EI) *m/z* (%): 386 [M]$^+$ (10), 371 (12) [M − CH_3]$^+$, 357 (8) [M − CH_2CH_3]$^+$, 343 (5), 327 (5), 73 (100) [Me_3Si]$^+$.

{5-((Trimethylsilyl)ethynyl)-1,4-diethyl-2,3-diphenylcyclopentadien-5-ol}$Co_2(CO)_6$ (18b). Compound **17b** (0.900 g, 2.33 mmol) dissolved in THF (15 mL) was added dropwise over a 15 min period to dicobalt octacarbonyl (1.114 g, 3.34 mmol) dissolved in THF (40 mL). The solution was stirred for 24 h at room temperature. The residue was purified by flash chromatography using 3:1 petroleum ether/CH_2Cl_2 eluent and recrystallized from a hexane/CH_2Cl_2 (9:1) mixture to give dark red crystals of **18b** (1.311 g, 1.95 mmol, 84%), mp 123−125 °C. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.20−7.16 (m, 6H), 7.03−6.99 (m, 4H), 2.61−2.39 (m, 4H, CH_2), 2.00 (s, 1H, OH), 1.13 (t, 6H, CH_3, $^3J(^1H{-}^1H) = 7.4$ Hz), 0.41 (s, 9H, Me_3Si). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 200.6 (Co−CO's) 149.9 ($C_{1,4}$), 141.5 ($C_{2,3}$), 136.0 (*ipso*), 129.3, 128.1 (*ortho, meta* C's), 127.1 (*para*), 112.0 (*C*≡C−TMS), 91.6 (C_5), 83.1 (C≡*C*−TMS), 20.7 (CH_2), 14.9 (CH_3), 2.0 (Me_3Si). IR (CH_2Cl_2): ν_{CO} at 2087, 2050, 2020 cm^{-1}. MS (EI) *m/z* (%): 588 [M − 3CO]$^+$ (5), 532 [M − 5CO]$^+$ (30), 504 [M − 6CO]$^+$ (55), 428 [M − $Co(CO)_6$ − OH]$^+$ (12), 386 [M − $Co_2(CO)_6$]$^+$ (10), 371 [M − $Co_2(CO)_6$ − CH_3]$^+$ (15), 348 (25), 73 [Me_3Si]$^+$ (100). Anal. Calcd for $C_{32}H_{30}Co_2SiO_7$: C, 57.14; H, 4.50. Found: C, 56.81; H, 4.37.

[{5-((Trimethylsilyl)ethynyl)-1,4-diethyl-2,3-diphenylcyclopentadienyl}$Co_2(CO)_6$]BF_4 (19b). Protonation of **18b** in CD_2Cl_2 with HBF_4/Et_2O at −78 °C in an NMR tube resulted in an immediate deepening in color, indicating formation of the cation **19b**. ^{13}C NMR (75 MHz, CD_2Cl_2, 223 K): δ 192.4 (br, Co−CO's), 152.8, 145.7, 141.3, 135.3 ($C_{1,2,3,4}$), 134.1 (C_5), 133.4, 133.1 (*ipso*), 128.8, 128.6 (2C's), 128.2, 128.0, 127.8 (*o, m, p*), 126.4, 93.3 (*C*≡C−TMS), 83.5 (C≡*C*−TMS), 18.5 (CH_2), 18.2 (CH_2), 16.8 (CH_3), 14.8 (CH_3), 1.6 (Me_3Si).

{5-((Trimethylsilyl)ethynyl)-1,4-diethyl-2,3-diphenylcyclopentadien-5-ol}$Co_2(CO)_4$dppm (20b). Cluster **18b** (0.495 g, 0.737 mmol) and bis(diphenylphosphino)methane (0.385 g, 1.00 mmol) were dissolved in THF (45 mL), and the solution was stirred for 18 h. The residue was purified by flash chromatography using a 2:1 hexanes/CH_2Cl_2 solvent mixture to yield **20b** (73 mg, 0.073 mmol, 10%) as a brownish red powder, mp 197−198 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.72 (br, 4H), 7.41−7.30 (m, 10H), 7.11−6.88 (m, 16H), 4.55 (q, 1H, methylene−H), 3.71 (q, 1H, methylene−H, {$^1J(^1H{-}^1H) \cong {}^2J(^{31}P{-}^1H) = 11.2$ Hz}), 2.06 (q, 4H, CH_2), 1.64 (s, OH), 0.57 (t, 6H, CH_3, $^3J(^1H{-}^1H) = 7.3$ Hz), 0.23 (s, 9H, Me_3Si). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 208.2, 204.9 (Co−CO's), 151.9, 139.5 ($C_{1,2}$), 139.6 (t, *ipso*, $^1J(^{31}P{-}^{13}C) = {}^3J(^{31}P{-}^{13}C) = 23.9$ Hz), 136.7 (t, *ipso*, $^1J(^{31}P{-}^{13}C) \cong {}^3J(^{31}P{-}^{13}C) = 16.7$ Hz), 136.4 (*ipso*), 132.4, 131.2, 129.7, 129.5 (2C's), 128.9, 128.3, 127.9, 126.6 (*o, m, p*), 110.4 (*C*≡C−TMS), 93.4 (C_1), 86.3 (C≡*C*−TMS), 35.8 (t, CH_2, $^1J(^{31}P{-}^{13}C) = 21.4$ Hz), 21.2 (CH_2), 14.6 (CH_3), 1.3 (Me_3Si). ^{31}P NMR (CD_2Cl_2): δ 32.65 (s). IR (CH_2Cl_2) ν_{CO} at 2015, 1985, 1959 cm^{-1}. MS (ES) *m/z* (%): 1000 [M]$^+$ (40), 983 [M − OH]$^+$. Anal. Calcd for $C_{55}H_{52}Co_2P_2SiO_5$: C, 65.99; H, 5.24. Found: C, 66.02; H, 5.40.

[{5-((Trimethylsilyl)ethynyl)-1,4-diethyl-2,3-diphenylcyclopentadienyl}$Co_2(CO)_4$dppm]BF_4 (21b). The addition of HBF_4/Et_2O to **20b** in CD_2Cl_2 at −78 °C in an NMR tube resulted in an immediate darkening of the solution, indicating the formation of the cation **21b**. ^{31}P NMR (CD_2Cl_2, 193 K): δ 41.07 (d), 23.74 (d), $^2J(^{31}P{-}^{31}P) = 58.9$ Hz.

($Me_3SiC{=}C{=}C_9H_8$)$FeCo(CO)_6$ (22). By analogy to the procedure previously described for ($MeC{=}C{=}CH_2$)$FeCo(CO)_6$,[27] freshly distilled $Fe(CO)_5$ (2.19 g, 11.18 mmol) was added to a solution of **9** (0.784 g, 1.39 mmol) dissolved in acetone (35 mL), and the mixture was heated under reflux for 24 h. After removal of solvent, the residue was subjected to flash chromatography on silica gel. Elution with hexanes gave light red crystals of **22** (96 mg, 0.018 mmol, 13%), mp 300 °C dec. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.98 (H_5)§, 7.81 (H_8)§, 7.75 (H_4)$^♦$, 7.69 (H_1)$^♦$, 7.48 (H_7)§, 7.37 (H_2)$^♦$, 7.32 (H_6)§, 7.24 (H_3)$^♦$. ^{13}C NMR (125.72 MHz, CD_2Cl_2): δ 209.7 (CO's), 145.3 (C_{4a}), 141.4 (C_{4b})§, 141.1 (C_{9a})$^♦$, 140.6 (C_{8a})§, 129.6 (C7)§, 129.0 (C_2)$^♦$, 127.4 (C_6)§, 127.1 (C_3)$^♦$, 121.3 (C_1)$^♦$, 120.9 (C_8)§, 120.6 (C_5)§, 120.5 (C_4)$^♦$, 106.7 (*C*≡C−TMS), 70.0 (C≡*C*−TMS), 2.8 (Me_3Si). ♦ and § denote environments shown by the ^{1}H−^{13}C shift-correlated and ^{1}H−^{1}H COSY spectra to be in the same ring; assignment of the *exo and endo* rings is arbitrary. IR (CH_2Cl_2): ν_{CO} at 2078, 2039, 2019 cm^{-1}. MS (EI) *m/z* (%): 460 [M − 3CO]$^+$ (5), 432 [M − 4CO]$^+$ (5), 404 [M − 5CO]$^+$ (10), 376 [M − 6CO]$^+$ (10), 261 [$Me_3SiC{\equiv}CC_9H_8$]$^+$ (100), 73 [Me_3Si]$^+$ (66). Anal. Calcd for $C_{24}H_{17}CoFeSiO_6$: C, 52.96; H, 3.15. Found: C, 53.26; H, 3.39. X-ray-quality crystals of **22** were grown from a 5:1 hexanes/CH_2Cl_2 solvent mixture.

{2,3-Diphenyl-1-((trimethylsilyl)ethynyl)indenyl}FeCo(CO)$_6$ (27). **13** (0.484 g, 0.73 mmol) dissolved in acetone (20 mL) was added to freshly distilled $Fe(CO)_5$ (1.480 g, 6.61 mmol) in acetone (20 mL). The solution was heated under reflux for 12 h while being monitored by TLC (1:1 hexanes/CH_2Cl_2). After removal of the solvent the residue was purified by flash chromatography using 1:1 hexanes/CH_2Cl_2 as the eluent. A dark red band was collected and chromatographed twice using hexanes solvent. X-ray-quality crystals of the dark red band, **27,** were grown from a 9:1 CH_2Cl_2/hexanes solution (26 mg, 0.04 mmol, 6%): mp 123−124 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.14−6.82 (m, 14H), 0.59 (s, 9H, Me_3Si). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 210.1 (Fe−CO's), 200.6 (Co−CO's), 144.7, 141.3, 140.5, 133.8, 130.7, 129.8, 129.6, 129.1, 128.6, 128.4, 128.0, 127.8, 125.8, 125.6, 125.0, 121.2, 120.8, 110.2, 70.4, 2.9 (Me_3Si). IR (CH_2Cl_2) ν_{CO} at 2079, 2036, 2020 cm^{-1}. MS (EI) *m/z* (%): 419 [M − $Co(CO)_6$]$^+$ (40), 364 [M − $FeCo(CO)_6$]$^+$ (18), 289 (20), 207 (25), 73 [Me_3Si]$^+$ (100). Anal. Calcd for $C_{32}H_{23}CoFeSiO_6$: C, 59.46; H, 3.59. Found: C, 59.74; H, 3.28.

X-ray Crystallographic Structure Determinations for 22 and 27. Crystal data and refinement parameters are collected in Table 1. All crystals were grown using vapor

Table 1. Summary of Crystal Data and Structure Refinement

	22	**27**
empirical formula	$C_{24}H_{17}CoFeO_6Si$	$C_{32}H_{23}CoFeO_6Si$
M_r	544.25	646.40
T (K)	293(2)	300(2)
λ (Å)	0.710 73	0.710 73
descripn	red plate	red plate
cryst size (mm)	0.14 × 0.22 × 0.41	0.06 × 0.25 × 0.50
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.293(2)	11.58980(10)
b (Å)	15.865(2)	12.57340(10)
c (Å)	18.697(3)	12.63060(10)
α (deg)	106.462(10)	65.97(10)
β (deg)	104.059(14)	73.21(10)
γ (deg)	102.17(2)	75.940(10)
V (Å^3), Z	2445.7(7), 4	1592.74(2), 2
ρ_{calcd} (g cm^{-3})	1.478	1.496
abs coeff (mm^{-1})	1.356	1.223
θ range/index ranges (deg)	2.14−22.50	1.79−26.35
limiting indices	$0 < h < +9$, $-15 < k < +15$, $-20 < 1 < +19$	$-14 < h < +14$, $-15 < k < +14$, $-15 < 1 < +14$
no. of rflns collected	6684	12 901
no. of indep rflns	6220	6000
R(int)	0.0304	0.0243
goodness of fit on F^2	0.893	1.045
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0500 wR2 = 0.1022	R1 = 0.0444 wR2 = 0.1171
R indices (all data)[a]	R1 = 0.0961 wR2 = 0.1165	R1 = 0.0631 wR2 = 0.1308

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

diffusion techniques[37] and were mounted on fine glass fibers with epoxy cement. X-ray crystallographic data for **22** were collected on a Siemens P4 diffractometer fitted with a rotating anode using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystallographic data for **27** were obtained using a P4 Siemens diffractometer, equipped with a rotating anode utilizing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and a Siemens SMART 1K charge-coupled device (CCD) area detector, employing the program SMART.[38] The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, employing 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 using three 4.5° scans (15 frames each) over three different parts of reciprocal space (45 frames total). All structures were solved by using the direct methods routine contained outlined in the Siemens SHELXTL-PLUS program library[39] followed by full-matrix least-squares refinement on F^2 with anisotropic thermal parameters and include idealized hydrogen-atom contributions. In **27**, the final refined structure was based on a rotational disorder in which the carbon atoms of the $Si(CH_3)_3$ substituent could exist in a minimum of five different conformations which were refined assuming an equal occupancy of 0.2. Refinement of the data revealed electron density in the second coordination sphere, and the exact molecular formula could not be determined. The solvent molecule was assumed to be CH_2Cl_2 and was refined as a free variable, yielding a final occupancy of 0.64. The unit cell for **22** contains two independent molecules whose structures differ only slightly, and only one is shown.

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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 structures of **22** and **27**. This material is available free of charge via the Internet at http://pubs.acs.org.

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