Intramolecular Cobalt-Mediated [2 + 2 + 2] Cycloaddition of Linear Enediynes. A Useful Synthetic Entry into Cobalt-Protected Tricyclic Dienes and Their Synthetic Elaboration

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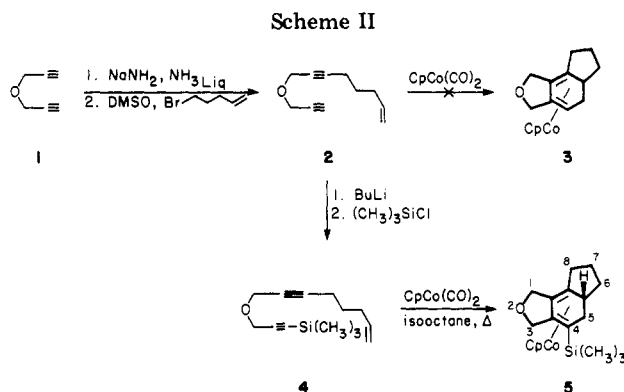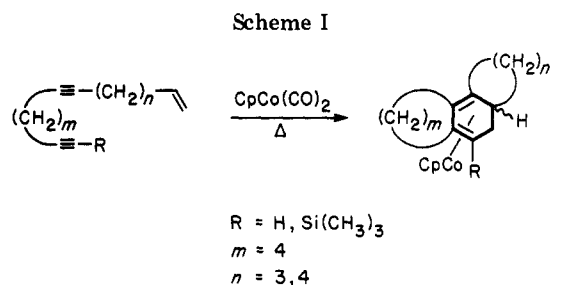
CpCo(CO)$_2$ undergoes reaction with the linear α,δ,ω-enediynes 4, 10, 18, 22, and 25 to give the CpCo-complexed tricyclic dienes 5, 11, 19, 20, 23, 24, 26, and possibly 27. The free ligands may be obtained in good yield by oxidative demetalation. Treatment of the dienylsilane 12 with bromine gave the desilylated aromatic 13, whereas reaction with *m*-chloroperbenzoic acid furnished the dienol 14 and α-trimethylsilyl β,γ-enone 15. The latter rearranged to the desilylated α,β-enone 17 with acid. Some mechanistic discussion is presented concerned with the course of the cobalt-mediated cyclization reaction. Hydride abstraction from 11 resulted in the cation 28 which underwent unexpected nucleophilic addition to both ligands, in addition to deprotonation to benzene complex 32 and the free aromatic ligand 31.

Carbon–carbon bond formation is the most important process in organic chemistry. When such a transformation can be executed in a multiple manner with chemo-, regio-, and stereoselectivity the rapid construction of complex molecules can usually be attained, significantly reducing the number of steps normally required to achieve access to structures of equivalent complexity. One such process is the Diels–Alder reaction in which a diene and a dienophile react with simultaneous generation of two new bonds to give 6-membered rings with extensive specificity. Within the framework of the concept of changes in topology and molecular complexity in a given reaction[1] it is immediately apparent that an even more useful variant would be a [2 + 2 + 2] cycloaddition of three unsaturated moieties in which a six-membered ring would be derived by 3-fold bond formation. Although symmetry allowed, this reaction is rare, particularly when involving carbocycle formation.[2] Thus, the clean conversion of three ethylene molecules to cyclohexane is unknown.

Reasoning that entropy and, perhaps to a certain degree, enthalpy problems may be the cause of this failure we have felt that transition metals may provide a suitable matrix on which such cyclizations might occur, concerted or otherwise. Indeed, there are examples, albeit few, in the literature in which strained alkenes were induced to enter into transformations of this type.[3] There are also a number of reports, mainly of organometallic nature, describing the cocyclization of alkynes with alkenes to give complexed and uncomplexed cyclohexadienes.[4]

In order to develop synthetic applications of these processes, we found among the systems investigated those based on stoichiometric (η-cyclopentadienyl)cobalt (CpCo)[5] particularly attractive because of the commercial availa-

bility of CpCo(CO)$_2$, its easy handling, the stability of the Cp–Co bond, the potential use of the metal as a protecting as well as electronically activating group, and our previous experience with this system as a catalyst in alkyne cyclizations.[6] These attributes suggested that it might be possible to use the system in attempts to develop useful synthetic methodology en route to polycyclic systems and ultimately natural and/or medicinally important products. In this paper we disclose the full details of a series of model reactions in which α,δ,ω-enediynes were induced to undergo cobalt-mediated intramolecular [2 + 2 + 2] cycloadditions to furnish complexed tricyclic dienes (Scheme I).[7] The chemistry of one of the products, 11, was explored with a view to further functional group manipulation and carbon–carbon bond formation. An accompanying paper describes the application of the method to a novel construction of the steroid nucleus.[8]

Scheme I

R = H, Si(CH$_3$)$_3$
m = 4
n = 3, 4

Scheme II

(1) Bertz, S. H. *J. Am. Chem. Soc.* 1982, *104*, 5801.
(2) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970; p 23.
(3) See: Binger, P.; Büch, H. M.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 62; *Angew. Chem., Suppl.* 1982, 153. Binger, P.; Schuchardt, U. *Chem. Ber.* 1981, *114*, 1649. Spee, T.; Mackor, A. *J. Am. Chem. Soc.* 1981, *103*, 6901. Lyons, J. E.; Meyers H. K.; Schneider, A. *Ann. N.Y. Acad. Sci.* 1980, *333*, 273 and the references therein.
(4) For a brief review, see: Chang, C-A.; Francisco, C. G.; Gadek, T. R.; King, Jr., J. A.; Sternberg, E. D.; Vollhardt, K. P. C. In "Organic Synthesis Today and Tomorrow"; Trost, B. W., Hutchinson, C. R., Eds.; Pergamon Press: New York, 1981; p 71.
(5) (a) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* 1974, 4549. (b) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* 1977, *139*, 169. (c) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* 1979, *101*, 1123.

(6) Vollhardt, K. P. C. *Ann. N.Y. Acad. Sci.* 1980, *333*, 241; *Pure Appl. Chem.* 1980, *52*, 1645.
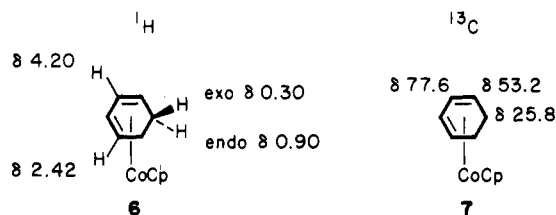(7) A preliminary report has appeared: Sternberg, E. D.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* 1980, *102*, 4839.

Results and Discussion

Cobalt-Mediated Cyclization of Enediynes. Alkylation of the sodium salt of bis(2-propynyl) ether (1)[9] [NaNH$_2$/NH$_3$ (liquid)] with the commercially available 5-bromopentene in an NH$_3$ (liquid)/Me$_2$SO mixture proceeded to give 2 in 38% yield (Scheme II).

When 2 was exposed to ∼1.1 equiv of CpCo(CO)$_2$ in boiling toluene a brown intractable tar formed. The known ability of dipropargyl ethers to undego retroene reactions to thermally unstable allenes and α,β-unsaturated alkynals might account for these results.[10]

Treatment of 2 with butyllithium in ethyl ether followed by trimethylsilyl chloride afforded the trimethylsilyl enediyne 4 in good yield (83%). Gratifyingly, cyclization with excess CpCo(CO)$_2$ in boiling isooctane produced the red crystalline complex 5 in 34% yield. The structure of 5 was in accordance with its spectral and analytical characteristics, in particular the 180 MHz ^{1}H and the ^{13}C NMR spectra and the mass spectrum. The anisotropy due to cobalt is especially helpful in the stereochemical assignments of the protons of the complexed ring.[11] As observed in the proton spectrum of the parent (η^4-cyclohexadiene)(η^5-cyclopentadienyl)cobalt (6), there is com-

paratively greater shielding of the exo protons relative to the endo protons of the cyclohexadiene ring. The anisotropy due to cobalt also causes a shielding of the carbons directly bound to the metal as in 7.[12]

With these data in hand, the ^{1}H NMR spectra assignments of 5 were made as follows. Two sharp singlets at δ 0.12 and 4.46 in a ratio of 9:5, assigned respectively to the trimethylsilyl and the cyclopentadienyl groups, suggested that the product consisted of only one isomer. Four doublets with geminal couplings of 11.5 Hz in the region of δ 4.57 to 4.97 were assigned to the diastereotopic protons on carbons 1 (C-1) and 3 (C-3). The rather low geminal coupling can be explained by the tendency of electronegative groups to reduce the coupling constants of adjacent protons.[13] Three unusually high-field signals at δ 1.23 (dd, J = 14.9, 3.9 Hz), 0.95 (dd, J = 14.9, 7.8 Hz), and 0.45 (m) were assigned to the exo methylene (H-5), endo methylene (H-5), and exo methyne (H-5a) protons, respectively. Finally, irradiation of the exo methyne (H-5a) signal simplified the absorption of H-5 exo, endo to two doublets due to the remaining geminal coupling (14.9 Hz), whereas irradiation of either H-5 exo or H-5 endo caused a narrowing of the multiplet at δ 0.45.

(8) Sternberg, E. D.; Vollhardt, K. P. C. *J. Org. Chem.*, the following paper in this issue.

(9) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier Publishing Co.: New York, 1971.

(10) For a review of the subject, see: Cookson, R. C.; Wallis, S. R. *J. Chem. Soc. B* **1966**, 1245.

(11) "Gmelin's Handbuch der anorganischen Chemie", Supplement to the 8th ed.; 1973; Vol. 5, Part I, p 340. King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3593. Herberich, G. E.; Schwarzer, J. *Chem. Ber.* **1970**, *103*, 2016.

(12) (a) Stone, F. G. A.; West, R. *Adv. Organometal. Chem.* **1974**, *12*, 135. (b) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

(13) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; p 276.

Scheme III
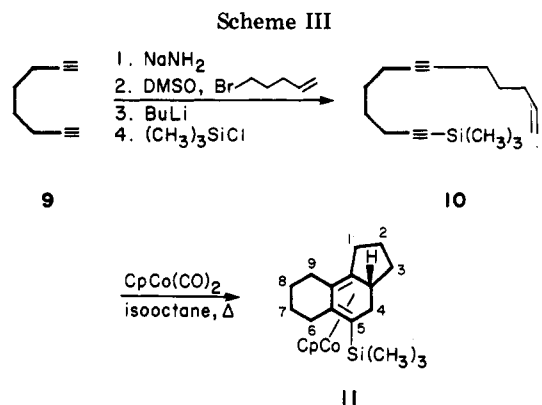
As expected, 13 carbon resonances were found in the ^{13}C NMR spectrum of 5. The peaks at δ 42.3 and 68.6 were assigned to the terminal quaternary diene carbons (C-8a, C-4), while the two remaining quaternary peaks at δ 89.5 and 95.8 corresponded to the internal carbons (C-3a, C-8b) of the complexed diene. The large difference between the shifts of the two terminal carbons may be explained by invoking d orbital interactions of the metal with the d orbitals of the silicon, thereby causing a shielding of the carbon (C-4) substituted by the trimethylsilyl group. This type of interaction has been proposed by Haiduc and Popa to explain some of the unusual chemistry of metal-complexed vinylsilanes.[14]

The major peaks in the mass spectrum at m/e 358 (M$^+$, 26%), 356 (15%), 234 (13%), and 232 (21%) are typical for (η^4-cyclohexadiene)cobalt complexes. Yamazaki has shown that such compounds lose either m/e 2 (H$_2$) on electron impact to form a complexed aromatic fragment, or m/e 124 (CpCo) yielding the charged ligand.[15]

In order to further clarify the structure of 5 by chemical methods and to explore some of its chemistry, attempts were made to free the ligand. Of the various oxidizing agents used in the literature to accomplish similar transformations[5,16] we chose the mildest,[17] cupric chloride, because of the anticipated sensitivity of the product.[18] Treatment of 5 with CuCl$_2$·H$_2$O and triethylamine in acetonitrile gave the intact ligand 8 in 93% yield. The presence of the base was necessary to prevent protodesilylation of 8. The structure of 8 was in accordance with its spectral characteristics. The only distinctive resonance in the 270-MHz ^{1}H NMR spectrum was a single trimethylsilyl peak which indicated the presence of only one isomer. In the ^{13}C NMR spectrum the two most deshielded carbons (δ 145.0 and 134.7) were assigned to the two "vinylsilane" carbons (C-3a and C-4, respectively). This judgment was based on the known tendency of a trimethylsilyl group to deshield an alkene α-carbon to a greater extent than the β-carbon.[19] Finally, the mass spectral fragmentation pattern of 8 resembled that of 5 below, m/e M$^+$ − CoCp (124).

The cobalt-mediated cyclization of enediyne 10 was expected to provide access to a hydrobenz[e]indene upon decomplexation. Such carbocyclic systems are often en-

(14) Haiduc, I.; Popa, V. *Adv. Organometal. Chem.* **1977**, *15*, 137.

(15) Yasofuku, K.; Yamazaki, H. *Org. Mass Spectrom.* **1970**, *3*, 23.

(16) Thompson, D. J. *J. Organomet. Chem.* **1976**, *108*, 381. Birch, A. J.; Liepa, A. J.; Stephenson, G. R. *Tetrahedron Lett.* **1979**, 3565. Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253.

(17) Skook, D. A.; West, D. M. "Fundamentals of Analytical Chemistry", 2nd ed.; Holt, Rinehart and Winston: New York, 1969.

(18) Brook, A. G.; Duff, J. M.; Reynolds, W. F. *J. Organomet. Chem.* **1976**, *121*, 293. Jarvie, A. W. P.; Halt, A.; Thompson, J. *J. Chem. Soc. B* **1969**, 852.

(19) Rybinskaya, M. I.; Rybin, L. V.; Pogrebnyak, A. A.; Nurtdinova, G. V.; Yurev, V. P. *J. Organomet. Chem.* **1981**, *217*, 373.

countered in di- and triterpene natural products. Furthermore, it provided an opportunity to circumvent the problem of the thermal instability of the starting material. Similar to the synthesis of 4, construction of 10 starting from 9 proceeded as in Scheme III in 40% overall yield. Cyclization took place smoothly to give 11 as red crystals in 84% yield. The 180-MHz ^{1}H NMR spectrum of 11 had the same pattern of resonances between δ 0–1 as the spectrum of 5: δ 0.25 (s, 9 H), 0.53 (m, 1 H), 1.01 (dd, J = 16, 8 Hz, 1 H), and 1.31 (dd, J = 16, 4 Hz, 1 H). As in the case of 5, irradiation at δ 0.53 (H-3a) led to the simplification of the peak pattern for the methylene protons (H-4) to two doublets (J_{gem} = 16 Hz). Conversely, irradiation at either of the H-4 proton peaks led to a narrowing of the absorption for H-3a. The distinctive quaternary ^{13}C NMR resonances at δ 46.3 (C-5), 72.0 (C-9b), 86.7, and 91.5 were assigned to the complexed diene carbons. The ^{1}H coupled spectrum revealed only one doublet at δ 37.0. This was assigned to C-3a. Oxidative demetalation as above gave the free ligand 12 in 85% yield.

Dienylsilanes of the type represented by 12 appeared to be promising substrates for further functionalization.
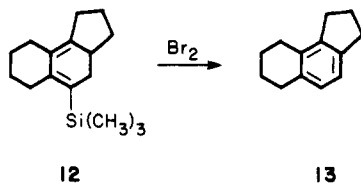

Although such conversions are well-known for vinylsilanes[20] we were not aware of any work of a similar nature for dienylsilanes. It was hoped that regioselective oxidation of 12 would possibly unmask an α,β-unsaturated ketone. Preferential oxidation of the silyl-bearing double bond when using electrophilic reagents was anticipated, because of the known ability of trimethylsilyl groups to stabilize β-carbonium ions.[20] In the event, treatment of 12 with bromine resulted in its clean conversion to the known hexahydrobenz[e]indene 13.[21] Presumably 13 arises by initial bromodesilylation, followed by acid-promoted isomerization of the resulting bromodiene and dehydrobromination.

Attempted epoxidation of 12 with *m*-chloroperbenzoic acid led to the unexpected formation of two isomeric compounds, the crystalline alcohol 14 (13%) and the liquid ketone 15 (52%). The structural assignments were based on IR, ^{1}H NMR, ^{13}C NMR, and UV spectra. Compound 14 exhibited an OH stretching absorption in the IR spectrum, and single vinyl and trimethylsilyl resonances at δ 6.03 (dd, J = 4.0, 4.0 Hz) and 0.17 (s) in the ^{1}H NMR spectrum. The λ_{max} (CH$_3$OH) at 256 nm (ϵ 21 000), along with the resonances of the vinyl carbons in the ^{13}C NMR specrum (δ 123.8, 129.5, 139.6, 140.6) confirmed the presence and the location of the transoid diene bond.[12b]

The ketonic absorption at 1695 cm^{-1} in the IR and the single trimethylsilyl group resonance (δ 0.08) in the ^{1}H NMR spectrum were the important spectral data on which the assignment for structure 15 was based. The ^{13}C NMR spectrum showed only 14 lines, indicating the presence of only one isomer.

Compounds 14 and 15 could arise as in Scheme IV through the common intermediate cation 16 derived by ring opening of the expected epoxide. Loss of a proton would generate the minor product 14, while [1,2]-silyl
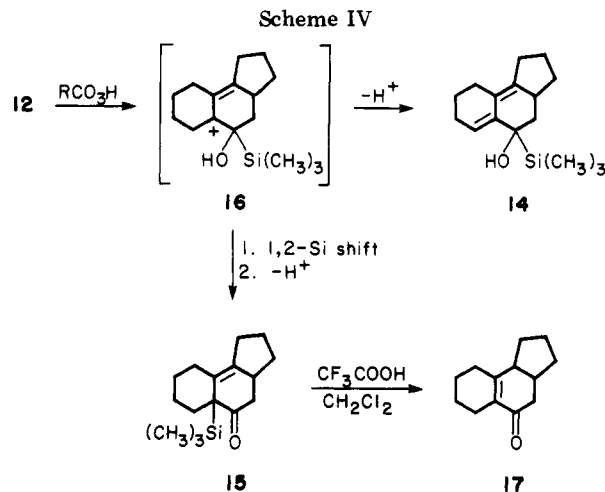
Scheme IV

Scheme V
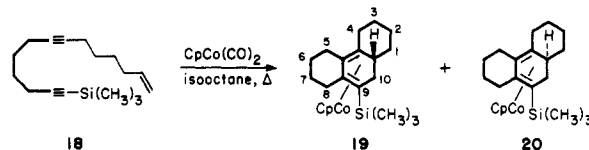
migration[22] followed by deprotonation would account for the formation of ketone 15.

The potential utility of a terminal dienylsilane as a masked α,β-unsaturated ketone was confirmed by treatment of 15 with acid which resulted in the known 17 (69%).[23] The 270-MHz ^{1}H NMR spectrum of 17 showed no diagnostic peaks. Therefore, the structural assignment was based upon the IR absorption at 1660 cm^{-1}, as compared to published data,[23] the UV maximum at 247 nm, and the mass spectrum. The stereochemistry of the ring junction is, however, uncertain. The structure of the literature compound, which had been formed under equilibrating conditions, was assigned as cis, based on degradation to a known fused ring compound. Since compound 17 was also formed under equilibrating conditions, its stereochemistry was deemed to be cis by inference.

Interestingly, both cyclizations leading to 5 and 11, respectively, proceeded in a stereospecific manner. In order to further explore the scope of the reaction and its associated stereospecificity, its potential in hydrophenanthrene synthesis, another carbopolycycle of synthetic interest, was probed. For this purpose 14-(trimethylsilyl)-1-tetradecene-7,13-diyne (18) was synthesized in a scheme analogous to that used in the preparation of 10 (but using commercial 6-bromohexene) in 40% overall yield. Cyclization afforded an excellent yield (92%) of a mixture of 19 and 20 (1:1) as a red oil (Scheme V). Mass spectral analysis gave the typical fragmentation pattern expected for the products, m/e 384 (27%), 382 (5%), and 260 (11%), while ^{1}H NMR spectroscopy revealed two resonances of equal intensity for the Cp ligands at δ 4.56 and 4.63. Crystallization of one isomer [δ 4.56 (Cp)] was accomplished from aqueous methanol. The relatively shielded protons at δ 0.56 (m, 1 H), 0.60 (m, 1 H), and 0.74 (m, 1 H) were assigned to H-10a, H-10 exo, and H-10 endo, respectively, of 19. The ^{13}C NMR resonances were positioned similarly to those of 11, with the diene carbon resonances at δ 94.1, 88.6, 67.4

(20) Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

(21) Barbalescu, N.; Leca, M. *Rev. Roum. Chim.* 1974, *19*, 443.

(22) For similar silyl migrations, see: Hillard, III, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* 1977, *99*, 4058. Brook, A. G.; Limburg, W. W.; MacRae, D. M.; Fieldhouse, S. A. *Ibid.* 1967, *89*, 704.

(23) Christol, H.; Pietrasanta, F.; Pietrasanta, Y.; Vernet, J. L. *Bull. Soc. Chim. Fr.* 1971, 4518.

Scheme VI

22   **23**   **24**

Scheme VII

25   **26**

+ other isomer

27
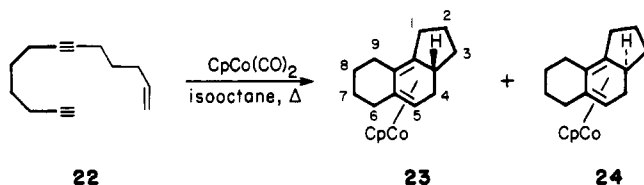
(C-4a), and 46.8 (C-9) and the methyne carbon peak (C-10a) at 36.9. These assignments were made by comparison to the ^{13}C spectra of **5** and **11** and by applying standard ^{13}C NMR decoupling techniques. Finally, an X-ray structural analysis[24] of **19** confirmed the stereochemical features strongly implied by the spectral data, and also further corroborated the structural assignments for **5** and **11**.

Decomplexation of the mixture of isomers **19** and **20** in acetonitrile with $CuCl_2 \cdot 2H_2O$ and triethylamine gave only one crystalline compound, the free ligand **21** (80%). A single trimethylsilyl peak at δ 0.16 indicated the isomeric purity of **21**. The ^{13}C NMR spectrum was similar to that of **11**, exhibiting fifteen lines with the diene carbons absorbing at δ 124.8, 125.6, 133.8, and 143.4 (C-9). Since only one compound was formed in the decomplexation, the second cobalt complex obtained in the cyclization of **18** was assigned the endo structure **20**.

The lack of stereospecificity in the cyclization of **18** was puzzling. In order to explore the possible role of the trimethylsilyl substituent in these reactions, it was of interest to expose the terminal enediynes **22** and **25** to the same conditions. Cyclization of **22** with $CpCo(CO)_2$ in boiling isooctane yielded a somewhat volatile red oil (66%) (Scheme VI). The mass spectrum of this substance showed the expected parent ion for a product at m/e 298. However, the ^1H NMR spectrum revealed two distinct Cp resonances at δ 4.59 and 4.42. After several attempts at separating this mixture by standard purification techniques (crystallization, column chromatography), it was found that the compound associated with the Cp resonance at δ 4.59 eluted more quickly on reverse-phase high-performance liquid chromatography[25] than the compound associated with the Cp resonance at δ 4.42.

On the basis of spectral data the compound which eluted first and was obtained in crystalline form was assigned the structure with the exo stereochemistry **23**. Irradiation of the vinyl proton multiplet (H-5) at δ 2.72 caused a narrowing of the multiplet at δ 1.33 assigned to the exo and endo methylene protons (H-4 endo, H-4 exo). Furthermore, irradiation at δ 1.33 effected simplification of the exo methyne multiplet (H-3a exo) to a double doublet (J = 10, 7 Hz) along with a narrowing of the vinyl absorption (H-5) to a broad singlet. Finally, irradiation at δ 0.67 resulted in simplification of the multiplet at δ 1.33. The ^{13}C resonance at δ 34.3 assigned to the methyne carbon (C-3a) is in the approximate range of the other methyne carbons containing an exo hydrogen, such as **5** (δ 37.5), **11** (37.0), and **19** (36.9).

The structural assignment of **24** relied on similar spectral interpretation. The ^1H NMR spectrum showed a multiplet for the endo and exo methylene protons (H-4 endo, H-4 exo) at δ 0.94, along with two multiplets at δ 2.99 and 2.89, which were assigned to the endo methyne (H-3a endo) and the vinyl proton (H-5). Interestingly, the ^{13}C resonance of the endo methyne carbon (C-3a) at δ 47.1 occurred 12.8
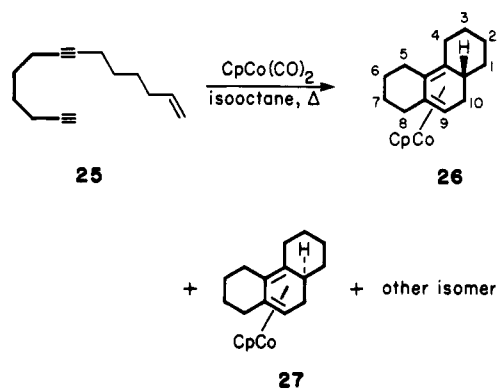
ppm downfield from the analogous exo methyne carbon (C-3a) of **23**. Additional chemical structure proof for the identity of compounds **23** and **24** was provided by decomplexation with excess ceric ammonium nitrate to yield **13** identical with the product of the bromination of **12** (vide supra).

The lack of stereospecificity in the cyclization of **22** was somewhat unexpected. Why would the presence or absence of a trimethylsilyl substituent positioned relatively remote from the prochiral center have such a profound influence? To check further on this question, we were curious to establish the stereochemical fate of enediyne **25**. Reaction with $CpCo(CO)_2$ in boiling isooctane yielded a red oil of crude material (76%) (Scheme VII). Examination of its spectral characteristics, specifically the mass spectrum (m/e 312, M^+) and the ^1H NMR spectrum (three Cp resonances, δ 4.56, 4.48, and 4.39, ratio, 2:1:1.5) revealed that a product of the correct composition had apparently been formed, but possibly in the form of three isomers. Fractional crystallization from aqueous methanol resulted in the isolation of the major isomer **26**. Four distinct proton resonances at δ 0.58 (m, 1 H), 0.78 (m, 1 H), 1.05 (ddd, J = 14.7, 7.6, 2.2 Hz, 1 H), and 2.78 (dd, J = 4.0, 2.2 Hz, 1 H) were assigned to the exo methyne (H-10a), the exo methylene (H-10 exo), the endo methylene (H-10 endo), and the vinyl (H-9) hydrogens of the complexed cyclohexadiene, respectively. Irradiation at δ 2.78 caused a change of the absorption at δ 0.78 to a double doublet (J = 14, 4 Hz) and at δ 1.05 to another double doublet (J = 14, 7.5 Hz). On the other hand, irradiation at δ 1.05 produced a doublet (J = 3.3 Hz) at δ 2.78 and a sharpening of the peak at δ 0.58. Again, the ^{13}C NMR spectrum showed a typical pattern for a complexed diene [δ 89.4, 88.4, 66.0 (C-4a), and 46.0 (C-9)] and a characteristic resonance for the exo methyne carbon [(C-10a) δ 35.6].[26]

The structures of the two compounds giving rise to the additional two Cp peaks in the ^1H NMR spectrum of the crude product are uncertain. The 270-MHz ^1H NMR spectrum of the original reaction mixture showed one isolated proton resonance at δ 0.32 (ddd, J = 14.9, 7.1, 1.4 Hz, 1 H) assignable to H-10 exo of **27** and hence taken as evidence for its presence. A third and more isomers could possibly be the result of double bond isomerization of the complexed diene. These types of isomerizations have been observed previously for metal-complexed dienes,[27] although it is not clear why in the case of CpCo they should be restricted to the cyclization of **25**. Degradation of the above mixture with ceric ammonium nitrate yielded the

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(24) We thank Prof. S. D. Darling, University of Akron, for undertaking this study.

(25) Huggins, J. M.; King, Jr., J. A.; Vollhardt, K. P. C.; Winter, M. J. *J. Organomet. Chem.* **1981**, *216*, 97.

(26) Gadek, T. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 802.

(27) For recent work, see: Karel, K. J.; Brookhart, M.; Aumann, R. *J. Am. Chem. Soc.* **1981**, *103*, 2697. Drew, M. G. B.; Regan, C. M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1034.
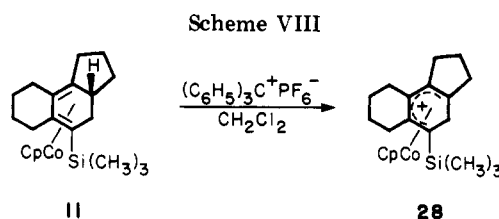
Chart I

A

B

C

Scheme VIII

II

28
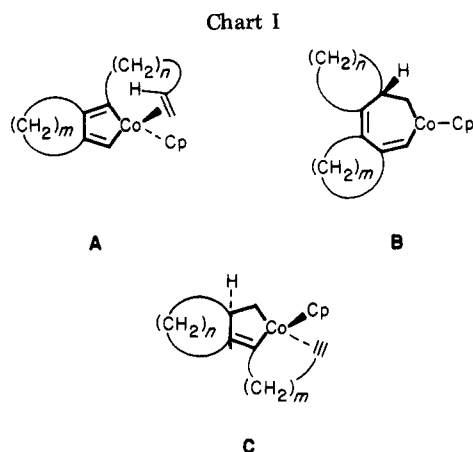
known 1,2,3,4,5,6,7,8-octahydrophenanthrene (67%).[28]

Mechanistic Considerations. On the basis of work in the literature a number of mechanisms may be considered in an effort to account for the stereochemistry of the above cyclizations. Among the crucial proposed intermediates are metallacyclopentenes, -pentadienes, and -heptadienes.[3-6,29]

If one assumes that the metal initially preferentially binds to the alkyne units of the substrate, subsequent oxidative coupling to a metallacyclopentadiene[5b] of the type A (Chart I) might be facilitated by concomitant complexation of the attached alkene moiety, thus avoiding coordinative unsaturation around the metal. Should this compound proceed to product via a Diels–Alder type cycloaddition step, then the stereochemical outcome of the reaction might be expected to be governed by electronic as well as steric factors, particularly those associated with the conformational stability of the appended alkene in A. The stereochemistry is set either already in the formation of A (exo complexation prior to cycloaddition) or, if alkene addition is reversible, possibly in the actual Diels–Alder step (exo transition state). It is interesting to note in this connection that the reaction of various cobaltacyclopentadienes with dimethyl maleate proceeds in a fairly stereorandom manner.[5b] However, it is not clear to what extent the presence of an appended and unactivated potential dienophile as in A controls the stereochemistry of the reaction.

A second mechanism in which the alkene unit in A stereospecifically inserts into the cobalt–vinyl bond[5c] would lead to the formation of either one of two metallacycloheptadienes B (Chart I) in which the cobalt likely constitutes a chiral center.[5c,30] The relevance of the relative stereochemistry in these intermediates with respect to the stereochemistry in the products will depend upon whether the chiral cobalt center is configurationally stable. The rearrangement of B to the final products may also be envisaged to proceed with inversion or with retention of configuration at cobalt.

A third mechanism may be considered in which the stereochemistry at the metal center relative to the methyne carbon is set during the formation of an initial metallacyclopentene C (Chart I), as seen by Yamazaki.[5c] Subse-

quent insertion of the second alkyne unit would furnish B which in turn would rearrange to product. Stereocontrol could occur in several of these steps. Yamazaki has found[5c] that a stereochemically defined metallacyclopentene underwent reaction with an added alkyne to give a CpCo–cyclohexadiene with retention.

It is clear that a more detailed understanding of the kinetic and thermodynamic features of the above cyclizations is required in order to be able to account for the observed results. None of the above alternatives provides a satisfactory clue for the effect of trimethylsilyl substitution and relative chain length on the stereochemistry of the reaction. Nevertheless, since the stereochemistry around cobalt is irrelevant once the metal is removed, the reaction still constitutes a powerful addition to the armamentarium of the synthetic organic chemist interested in carbocycle construction. Moreover, in those cases where only one complex is formed, the metal might be utilizable as a sterically protecting and electronically activating group.

Nucleophilic Additions to CpCo–Cyclohexadienyl Cation 28. Having developed a method for the construction of tricyclic diene complexes we became interested in exploring the chemistry of these systems, particularly with a view to the introduction of additional substituents. This was deemed possible by nucleophilic additions to metal-complexed cyclohexadienyl cations, in turn thought available by hydride abstractions from the neutral diene complexes. Although there are only few such CpCo–cyclohexadienyl systems in the literature,[31] nucleophilic additions have been shown to occur stereospecifically exo and to the 6-membered ring in accord with the Davies, Green, Mingos rules.[32] The extensive studies carried out on the isoelectronic iron tricarbonyl cations[33] served as a further incentive to explore the chemistry to be described. In these systems it had been shown that steric as well as electronic factors strongly influence the regioselectivity of both initial hydride removal and subsequent nucleophilic addition.[33] Consideration of the available precedence suggested that hydride abstraction from the complex 11 should be controlled by the bulk of the trimethylsilyl group. To what extent this substituent would exert electronic influence was uncertain.[34]

Treatment of 11 with trityl hexafluorophosphate resulted in the deep red crystalline salt 28 (70%) (Scheme VIII). A single trimethylsilyl resonance at δ 0.29 and a single cyclopentadienyl resonance at δ 5.16 in the ^{1}H NMR spectrum indicated that only one isomer had been formed. A doublet at δ 2.87 (d, $J = 17$ Hz, 1 H) was assigned to the H-4 endo proton, while the H-4 exo signal was obscured

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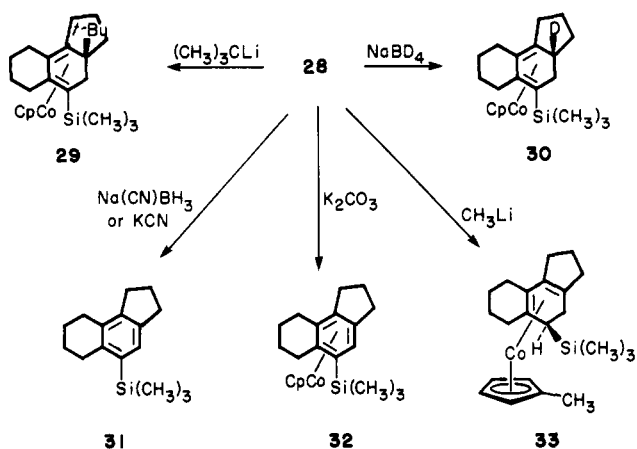
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Scheme IX

29   (CH₃)₃CLi ⟵   28   ⟶ NaBD₄   30

29

Na(CN)BH₃ or KCN   K₂CO₃   CH₃Li

Si(CH₃)₃   CpCo Si(CH₃)₃   Co H Si(CH₃)₃ — CH₃

31   32   33

by the multiplet due to the remaining protons (δ 1.0–2.75). The field-desorption mass spectrum showed major fragments at m/e 883 and 369. These indicated the presence of the cluster ion $[(LCoCp)_2PF_6]^+$ and cation $[LCoCp]^+$.[35]

There are several possible sites for nucleophilic addition on cation **28**, involving both ligands and the metal. Although in the parent CpCo–cyclohexadienyl cation[31] and in many substituted iron tricarbonyl analogues nucleophilic attack had been observed to occur at the terminal position of the cyclohexadienyl ligand,[32,33] the highly substituted and different electronic nature[36] of **28** made such a prediction tenuous.

When *tert*-butyllithium was added to complex **28** at –78 °C the red crystalline compound **29** was formed (77%) (Scheme IX). Three singlets in the proton NMR spectrum at δ 0.24, 0.74, and 4.44 were assigned to the trimethylsilyl, the *tert*-butyl, and the cyclopentadienyl group, respectively. Two doublets at δ 1.55 and 1.60 (J = 16 Hz) were assigned to the methylene protons (H-4 exo, H-4 endo) on C-4. Steric compression by the *tert*-butyl group may account for the relatively deshielded positions of H-4 exo.[37] Of the fifteen carbon resonances in the ^{13}C NMR spectrum, six were assigned to be quaternary (δ 92.4, 87.9, 73.4, 49.4, 44.1, 42.6) based on their relatively diminished peak heights. The chemical shifts of four of these agreed favorably with those of the analogous tricyclic diene complexes obtained by cyclization (vide supra). The other two were assigned to C-3a and the *tert*-butyl carbon. Thus, despite its bulk, *tert*-butyllithium attacks **28** according to literature precedence to give angular substitution.

The outcome of this experiment suggested that other nucleophiles of lesser size might undergo similar regioselective reactions. However, surprisingly, this proved not to be the case. Thus, in an attempt to regenerate **11** from **28** with LiAlH₄ only decomposition was observed. Reduction with NaBH₄ gave some **11**, but in addition a second very air-sensitive organometallic compound which decomposed on attempted column chromatography (vide infra). Treatment with NaBD₄ allowed the isolation of **30** (Scheme IX).

In an attempt to increase the yield of hydride reduction and eliminate the unknown side product, an interesting decomplexation was discovered. Treatment of **28** with

excess $Na(CN)BH_3$ in the two-phase system CH_3OH/petroleum ether resulted in formation of the colorless crystalline compound **31** (87%) (Scheme IX). The progress of the reaction was marked by several color changes, suspected to be due to initial cyanide attack followed by decomplexation. To test this hypothesis, **28** was exposed to KCN in the same solvent system with similar results.

These experiments suggested that potential nucleophiles might also be acting as bases, surprisingly deprotonating the relatively hindered endocyclic complexed pentadienyl system (i.e., H-4) rather than an exocyclic position (i.e., H-3) as observed in certain systems for the iron carbonyl analogues.[38] The origin of this regioselectivity is obscure.[39] The observed results also led to the suspicion that the air-sensitive organometallic observed in the reaction of **28** with NaBH₄ might in fact be the intermediate benzene complex **32** en route to **31**.

Indeed, treatment of **28** with K₂CO₃ gave the same product in high yield (87%). The ^1H NMR spectrum displayed three singlets at δ 0.23, 4.47, and 5.15 which were assigned to the trimethylsilyl, the cyclopentadienyl, and the complexed vinyl protons, respectively. The hapticity of the aromatic ligand was indicated by the ^{13}C NMR spectrum. Four quaternary resonances at δ 42.1, 76.4, 86.0, and 91.0 exhibited chemical shifts in close agreement with the position of the carbon absorptions in the ^{13}C NMR spectra of the other analogues diene complexes discussed. Two additional resonances at δ 145.0 and 111.2 were assigned to C-3a (based on its relatively diminished peak height) and C-4 (based on its relatively enhanced peak height).

There have been few reports of aromatic rings complexed to the CpCo moiety.[40] None of these complexes were formed by base-promoted deprotonations of a cationic complex. Compound **32** is the hitherto spectrally bst characterized system of this type. Reaction of **32** with trifluoroacetic acid followed by addition of NaPF₆ yielded **28** (86%).

Several other nucleophiles [$(CH_3)_2Cd$, $Al(CH_3)_3$, $Li(CH_3)_2Cu$, and CH_3MgBr] were added to **28**. None of these formed any characterizable products. Addition of phenyllithium or dimethyl lithiomalonate resulted in the generation of only the aromatic complex **32**.

Treatment of **28** with excess methyllithium at –78 °C in THF produced two compounds in a 4:1 ratio, as determined by the ^1H NMR spectrum of the crude reaction mixture. The minor component was assigned to be the aromatic complex **32**. The major component in the mixture exhibited four separate broad singlet signals in the ^1H NMR spectrum at δ 3.94 (1 H), 4.03 (1 H), 4.26 (1 H), and 4.30 (1 H), a three proton singlet at δ 2.13, and a nine proton singlet at δ –0.06. This spectrum indicated that an unexpected and mechanistically complex addition of the methyl group had occurred to give a methylcyclopentadienyl ring. Purification of the methyl adduct was accomplished by column chromatography. The unusually shielded trimethylsilyl group (δ –0.06), along with the resonances assigned to the two protons on C-4 at δ 0.92 (dd, J = 17, 11.5 Hz, 1 H, H-4 endo) and 0.23 (dd, J = 17, 3.5 Hz, 1 H, H-4 exo), and the absence of any other

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high-field absorptions suggested the presence of the substitution pattern shown for the cyclohexadiene ligand in compound **33**.

A possible mechanism for the formation of this product might involve initial methyllithium attack at the Cp ring, a process at odds with the rules governing such additions.[32] This process would generate a complex containing an η^4-methylcyclopentadiene and an η^5-cyclohexadienyl ligand. If methyl came in exo, the resulting endo hydrogen at the same carbon could subsequently be envisioned to migrate (via a cobalt hydride?) to the other ring such as to furnish **33**.

Precedence for these individual steps exists. Thus, a similarly unexpected preferential addition of metyllithium to the cyclopentadienyl ring of hexamethylbenzene cyclopentadienyl iron has been observed.[41] Hydride transfers, possibly related to the one postulated in the **28** → **33** conversion, were seen by Wilkinson in the reduction of ruthenium bisbenzene dication.[42] The mechanistic details by which these transformations proceed are obscure. The complex behavior of **28** in nucleophilic additions clearly indicates that much work remains to be done in order to understand the chemistry of systems of this type and in order to exploit them synthetically.

Experimental Section

General Data. ^{1}H NMR spectra were recorded on a Varian T-60, a Hitachi Perkin-Elmer R-24B (60 MHz) instrument, a UCB-180 MHz instrument consisting of a Bruker magnet and Nicolet computer and software, UCB-200 MHz and UCB-250 MHz instruments consisting of a Cryomagnet Systems magnet and Nicolet computer and software, a UC-Biodynamics 220-MHz instrument consisting of a Varian magnet and Nicolet computer and software, a UC-Biodynamics 270-MHz instrument consisting of a Bruker magnet and Nicolet computer and software, and an NIH (Pittsburg) 600-MHz instrument consisting of a Bruker magnet and in house computer and software. Data are reported as follows: chemical shift in parts per million downfield of an internal standard (Me$_4$Si), in the case of air-stable compounds, or in parts per million as compared to the D$_5$HC$_6$ peak at 7.20 ppm downfield of Me$_4$Si for air-sensitive compounds. The ^{13}C NMR spectra were obtained on a 25.4-MHz instrument consisting of a Varian magnet, Bruker electronics, and Nicolet computer and software, and a UCB-50.5 MHz instrument consisting of a Bruker magnet and Nicolet computer and software. Chemical shifts are reported in parts per million downfield from Me$_4$Si, referenced to the central peak of the deuteriochloroform triplet (77.0 ppm downfield from Me$_4$Si) or to the central peak of the benzene triplet of deuteriobenzene (126.0 ppm downfield from Me$_4$Si).

Infrared spectra were obtained on one of Perkin-Elmer Models 710A, 137, 283, 337, or 681 and were referenced to polystyrene (1601 cm^{-1}). Electronic spectra were recorded on a Cary 219 spectrometer in MeOH. Mass spectra [reported as m/e (rel intensity) at 70eV unless mentioned otherwise] and elemental analyses were provided by the Mass Spectral Service and Microanalytical Laboratory, respectively, at the University of California, Berkeley. Field-desorption mass spectra were provided by the Biomedical and Environmental Mass Spectrometry Resource, Space Sciences Laboratory, University of California, Berkeley. Melting points were determined in open Pyrex capillary tubes on a Thomas-Hoover Unimelt apparatus or on a Kofler micro-hotstage. Melting points and boiling points are uncorrected. Gas chromatography was performed on a Varian Aerograph Model 920 instrument with a 10 × $^1/_4$ in. glass column on SE-30 on Chromosorb.

All column chromatography was executed with E.M. Reagents silica gel (70-230 mesh ASTM) or Woelm neutral alumina. Thin-layer chromatography was carried out on Analabs analytical

silica gel plates. Rotary chromatography was made possible by a Harrison Research Model 7924 chromatotron with either silica gel-PF 254 with CaSO$_4$ as binder and fluorescent indicator, or alumina GF-254 with CaSO$_4$ as binder and fluorescent indicator. High-pressure liquid chromatography (HPLC) was carried out with an Altex system consisting of a Model 110A pump, a Model 153 UV detector at 254 nm, and an Ultrasphere ODS, 1 cm × 25 cm column.

Unless otherwise noted, all starting materials were obtained from commercial suppliers without further purification. When necessary, non-ether solvents were dried over molecular sieves (4 Å). Ether solvents were dried over boiling sodium benzophenone. All reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen. Solvents were degassed by either boiling for 15 min under a nitrogen stream or freeze/thaw under high vacuum. Vacuum line operations were carried out with multiple line apparatus. Either spectral grade isooctane or toluene washed with sulfuric acid and distilled from CaCO$_3$ (anhydrous) onto molecular sieves (4 Å) was utilized for any cobalt-promoted cyclizations.

9-Oxa-1-dodecene-6,11-diyne (2). To sodium amide (1.07 g, 27.4 mmol) in liquid NH$_3$ (150 mL) was added bis(2-propynyl) ether 1 (2.40 g, 25.5 mmol) followed by Me$_2$SO (50 mL). After stirring the solution for 1 h to generate the anion, 5-bromo-1-pentene (3.75 g, 25.2 mmol) was added to the mixture. The liquid NH$_3$ solution was stirred for 5 h, after which the NH$_3$ was allowed to evaporate. In a standard workup, to the reaction residue were added ethyl ether/petroleum ether (200 mL, 3:7) and H$_2$O (50 mL). The reaction mixture was washed with 6 × 100 mL of H$_2$O to remove the residual Me$_2$SO. The organic layer was dried over Na$_2$SO$_4$ (anhydrous) and the solvent was then evaporated to yield a colorless oil. Distillation of the product at 55-60 °C (0.01 mm) using a Kugelrohr apparatus yielded the product 2 (1.55 g, 38%): colorless oil; R_f 0.46, ethyl ether/petroleum ether (4:96) as eluent; IR (thin film) 3330, 3115, 2955, 2240, 2120, 1645, 1435, 1060 cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$) δ 1.43 (br pentet, J = 7, 2 H), 1.54-2.17 (m, 4 H), 2.43 (t, J = 2.2, 1 H), 4.23 (m, 4 H), 4.8-6.1 (m, 3 H); MS, m/e 162 (2%), 131 (9), 117 (19), 105 (19), 91 (66), 39 (100).

9-Oxa-12-(trimethylsilyl)-1-dodecene-6,11-diyne (4). To compound 2 (0.60 g, 3.7 mmol) in diethyl ether (20 mL) cooled in a dry ice/acetone bath was added butyllithium in hexane (2.5 mL, 4.05 mmol). After warming the mixture to 0 °C, trimethylsilyl chloride (0.50 g, 4.63 mmol) was added to the reaction flask. The reaction mixture was allowed to warm to room temperature and was stirred for 12 h. Standard workup and distillation at 95-105 °C (0.01 mm) yielded 4 (0.720 g, 83%): colorless oil; R_f 0.54, ethyl ether/petroleum ether (4:96) as eluent; IR (thin film) 3110, 2960, 2245, 2195, 1665, 1445, 1245, 860 cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$) δ 0.16 (s, 9 H), 1.45 (m, 2 H), 1.55-2.50 (m, 4 H), 4.10 (br s, 4 H), 4.8-6.1 (m, 3 H); MS (30 eV), m/e 234 (1%), 219 (1), 147 (14), 91 (15), 73 (100); HRMS (M$^+$ − CH$_3$) calcd for C$_{14}$H$_{22}$OSi, 219.1210; found, 19.1218.

(4,4a,8a,8b-η^4-4-(Trimethylsilyl)-1,3,5,5a-*exo*,6,7-hexahydro-8*H*-indeno[4,5-*c*]furan)(η^5-cyclopentadienyl)cobalt (5). To a degassed solution of compound 4 (0.140 g, 0.6 mmol) in isooctane (20 mL) was added CpCo(CO)$_2$ (0.100 mL, 0.80 mmol). The solution was heated to reflux for 97 h under a slow N$_2$ stream (∼3 mL/min). After cooling to room temperature, the solvent and excess CpCo(CO)$_2$ were vacuum transferred from the deep red reaction mixture resulting in a reddish-brown residue. The residue was dissolved in ethyl ether/petroleum ether (5 mL, 5:95) and passed through alumina (10 g, activity 2.5) with the above solvent mixture as eluent. A slow moving red band was isolated and the solvent was removed by evaporation leaving complex 5 (0.073 g, 34%). Crystallization occurred upon prolonged cooling (∼−30 °C). Recrystallization from MeOH/H$_2$O resulted in the formation of 5: red prisms, mp 78-79 °C; IR (thin film) 2970, 2832, 1440, 1260, 1065, 910 cm^{-1}; ^{1}H NMR (180 MHz, C$_6$D$_6$) δ 0.12 (s, 9 H), 0.45 (m, 1 H), 0.95 (dd, J = 14.9, 7.8, 1 H), 1.23 (dd, J = 14.9, 3.9, 1 H), 1.55 (m, 4 H), 1.92 (m, 2 H), 4.46 (s, 5 H), 4.57 (d, J = 11.5, 1 H), 4.68 (d, J = 11.5 1 H), 4.83 (d, J = 11.5, 1 H), 4.97 (d, J = 11.5, 1 H); ^{13}C NMR (25.4 MHz, C$_6$D$_6$) δ −2.7, 20.9, 29.5, 32.0, 33.1, 37.5, 42.3, 68.6, 69.3, 70.7, 79.0 (Cp), 89.6, 95.8; MS (30 eV), m/e 358 (26%), 356 (15), 234 (13), 232 (21), 73 (100). Anal. Calcd for C$_{19}$H$_{27}$OSiCo: C, 63.67; H, 7.58. Found: C, 63.78; H, 7.49.

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4-(Trimethylsilyl)-1,3,5,5a,6,7-hexahydro-8*H*-indeno[4,5-*c*]furan (8). To a stirring, degassed solution of complex **5** (0.038 g, 0.106 mmol) in CH_3CN (5 mL) cooled to 0 °C was added a solution of $CuCl_2 \cdot 2 H_2O$ (0.54 g, 0.32 mmol) and Et_3N (0.019 mL) in CH_3CN (3 mL). After 10 min of stirring the reaction mixture at 0 °C, petroleum ether (15 mL) was added to the reaction flask. The colorless top organic layer was removed and to it was added H_2O (1 mL). The resulting organic fraction was then extracted twice with aqueous CH_3CN (5 mL, 30:70). The organic fraction was dried over Na_2SO_4 (anhydrous). Evaporation of the majority of the solvent was followed by filtration of the organic fraction through 1 g of alumina (activity 2.5) with ethyl ether/petroleum ether (20:80) as eluent. Finally, removal of the solvent yielded a colorless oil (0.023 g, 93%). The oil crystallized upon prolonged cooling at -5 °C. Recrystallization from $MeOH/H_2O$ yielded **8**: colorless needles, mp 24.5–26.0 °C; IR (thin film) 2950, 1660, 1440, 1245, 1048, 970 cm^{-1}; ^1H NMR (220 MHz, CCl_4) δ 0.11 (s, 9 H), 1.11 (m, 2 H), 1.40 (m, 1 H), 1.63 (m, 1 H), 1.72 (m, 1 H), 1.87 (ddd, J = 9.5, 6, 5, 1 H), 2.05 (m, 2 H), 2.21 (m, 1 H), 4.38 (m, 2 H), 4.47 (m, 2 H); ^{13}C NMR (25.4 MHz, C_6D_6) δ -3.2, 22.7, 26.1, 30.9, 32.0, 38.7, 66.7, 69.1, 118.7, 134.7, 145.0, one carbon appears masked by a solvent resonance; MS (30 eV), m/e 234 (23%), 145 (13), 73 (100); HRMS calcd for $C_{14}H_{22}OSi$, 234.1440; found, 234.1450.

1-Tridecene-6,12-diyne (22). To sodium amide (1.86 g, 47.7 mmol) in liquid NH_3 (150 mL) was added first 1,7-octadiyne (5.0 g, 47.2 mmol) and then Me_2SO (30 mL). After stirring for 1 h, 5-bromo-1-pentene (7.02 g, 47.1 mmol) was added to the reaction flask. The mixture was stirred for 4.5 h, after which the NH_3 was allowed to evaporate. The product was isolated in the usual manner (see the synthesis of **2**). Kugelrohr distillation of the product at 50 °C (0.01 mm) yielded **22** (3.41 g, 41%): colorless oil; R_f 0.20, petroleum ether as eluent; IR (thin film) 3340, 3100, 2945, 2150, 1620, 1420 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 1.1–1.7 (m, 6 H), 1.83 (t, J = 2, 1 H), 1.9–2.4 (m, 8 H), 4.8–6.1 (m, 3 H); MS (30 eV), m/e 174 (2%), 145 (14), 131 (43), 117 (32), 105 (35), 91 (100). Anal. Calcd for $C_{13}H_{18}$: C, 89.67; H, 10.35. Found: C, 89.46; H, 10.41.

13-(Trimethylsilyl)-1-tridecene-6,12-diyne (10). To a solution of **22** (1.74 g, 10 mmol) in ethyl ether (35 mL), which was cooled to dry ice/acetone temperature, was added butyllithium in hexane (7.10 mL, 11 mmol). After warming the flask to 0 °C and then cooling it back to -78 °C, trimethylsilyl chloride (1.25 g, 11.5 mmol) was added. The reaction mixture was allowed to warm to room temperature and then stirred for 12 h. Standard work up followed by Kugelrohr distillation of the resulting oil at 105 °C (0.01 mm) yielded **10** (2.36 g, 96%): colorless oil; R_f 0.24, petroleum ether as eluent; IR (thin film) 3120, 2935, 2180, 1640, 1440, 1250 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 0.16 (s, 9 H), 1.0–1.6 (m, 6 H), 1.7–2.5 (m, 8 H), 4.8–6.1 (m, 3 H); MS (30 eV), m/e 231 (2%, M$^+$ – 15), 173 (17), 144 (17), 131 (30), 109 (12), 73 (100). Anal. Calcd for $C_{16}H_{26}Si$: C, 77.83; H, 10.05. Found: C, 77.54; H, 10.54.

(5,5a,9a,9b-η^4-5-(Trimethylsilyl)-2,3,3a-*exo*,4,6,7,8,9-octahydro-1*H*-benz[*e*]indene)(η^5-cyclopentadienyl)cobalt (11). To a degassed solution of **10** (0.200 g, 0.813 mmol) in isooctane (20 mL) was added CpCo(CO)$_2$ (0.111 mL, 0.089 mmol). The stirred mixture was brought to boil under a slow N_2 stream (~3 mL/min) and was allowed to react for 99 h. Vacuum transfer of the solvent and residual CpCo(CO)$_2$ left a reddish-brown oil. This oil was dissolved in petroleum ether (5 mL) and was filtered through an alumina column (15 g, activity 2.5) with petroleum ether as eluent. A fast moving red band was collected. The solvent was initially removed on a rotary evaporator and then by pumping on the residual red oil under high vacuum. The oil, upon prolonged cooling (~-30 °C), crystallized to a solid (0.257 g, 85%). Recrystallization from $MeOH/H_2O$ yielded **11**: red-orange needles, mp 72–74 °C; IR (thin film) 2975, 2890, 2870, 1445, 1240, 920, 795 cm^{-1}; ^1H NMR (180 MHz, C_6D_6) δ 0.25 (s, 9 H), 0.53 (m, 1 H), 1.01 (dd, J = 16, 8, 1 H), 1.31 (dd, J = 16, 4, 1 H), 1.42–2.97 (m, 14 H), 4.45 (s, 5 H); ^{13}C NMR (25.4 MHz, C_6D_6) δ -2.05, 20.3, 20.6, 21.5, 25.4, 27.1, 30.1, 31.8, 33.3, 37.0, 46.3, 72.0, 78.7 (Cp), 86.7, 91.5; MS (30 eV), m/e 370 (23%), 368 (3), 297 (77), 73 (100). Anal. Calcd for $C_{21}H_{31}SiCo$: C, 68.08; H, 8.36. Found: C, 68.09; H, 8.15.

5-(Trimethylsilyl)-2,3,3a,4,6,7,8,9-octahydro-1*H*-benz[*e*]indene (12). To a stirred solution of the complex **11** (0.240 g,

0.65 mmol) in CH_3CN (5 mL) cooled to 0 °C was added a solution of $CuCl_2 \cdot 2H_2O$ (0.270 g, 1.6 mmol) and Et_3N (0.1 mL) in CH_3CN (10 mL). Aqueous work using added petroleum ether, followed by filtration through alumina (3 g, activity 2.5) with ethyl ether/petroleum ether (5:95) gave a colorless oil (0.136 g, 85%). Crystallization from $MeOH/H_2O$ gave **12**: colorless needles, mp 44–46 °C; IR (thin film) 2945, 1610, 1540, 1435, 1245, 890, 833 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 0.16 (s, 9 H), 1.0–3.0 (m, 17 H); ^{13}C NMR (25.4 MHz, C_6D_6) δ -1.65, 22.1, 22.7, 23.0, 25.7, 26.7 (2 carbons), 30.9, 32.4, 37.8, 123.7, 124.2, 139.9, 143.9; MS, m/e 246 (23%), 231 (13), 172 (46), 73 (100); HRMS calcd for $C_{16}H_{26}Si$, 246.1804; found, 246.1809.

2,3,6,7,8,9-Hexahydro-1*H*-benz[*e*]indene (13).[21] To the mixture of complexes **23** and **24** (0.058 g, 0.195 mmol) in acetone (5 mL) was added ceric ammonium nitrate (1.00 g, 1.82 mmol) in acetone (15 mL) cooled to 0 °C. The reaction mixture was stirred for 4 h at 10 °C and worked up as in the synthesis of **8** to give a light yellow oil (0.031 g). Chromatography on silica gel with petroleum ether as eluent resulted in product **13** as a clear oil (0.020 g, 60%): colorless oil; R_f 0.67, petroleum ether as eluent; IR (thin film) 3025 (vinyl C–H), 2955, 1650, 1475, 1435, 1240, 830, 790 cm^{-1}; ^1H NMR (180 MHz, CDCl$_3$) δ 1.77 (m, 4 H), 2.05 (pentet, J = 8.5, 2 H), 2.61 (br t, J = 8.1, 2 H), 2.77 (br t, J = 8.4, 4 H), 2.88 (t, J = 8.7, 2 H), 6.88 (d, J = 8.5, 1 H), 6.98 (d, J = 8.5, 1 H); MS, m/e 172 (87%), 144 (100), 129 (83), 128 (64), 115 (52), 91 (23).

In a second experiment, to diene **12** (0.0447 g, 0.182 mmol) dissolved in CH_2Cl_2 (2 mL) cooled to dry ice/acetone bath temperature was added bromine (0.029 g, 0.181 mmol) dissolved in CH_2Cl_2 (0.85 mL). Discoloration occurred almost immediately even at that temperature. Standard workup gave a clear oil of **13** (0.030 g, 96%).

5a-(Trimethylsilyl)-2,3,3a,4,5,5a,6,7,8,9-decahydro-1*H*-benz[*e*]inden-5-one (15) and 5-(Trimethylsilyl)-2,3,3a,4,5,7,8,9-octahydro-1*H*-benz[*e*]inden-5-ol (14). To a stirred solution of diene **12** (0.26 g, 1.05 mmol) in CH_2Cl_2 (25 mL) cooled to 0 °C was added over 5 min a solution of purified *m*-chloroperbenzoic acid (0.20 g, 1.16 mmol) in CH_2Cl_2 (25 mL). The mixture turned light purple and then colorless. After 0.5 h of stirring at 0 °C the solution was worked up using petroleum ether (50 mL) and 5% KHCO$_3$ solution (15 mL). After removal of the aqueous layer, the organic layer was washed with 5% KHCO$_3$ solution (15 mL) followed by H_2O (15 mL). After drying over Na_2SO_4 (anhydrous), evaporation of the solvent yielded a colorless oil (200 mg). Thin-layer chromatography on silica gel eluting with ethyl ether/petroleum ether (15:85) showed two products (R_f 0.53, a non-UV active spot that stained with I_2, and R_f 0.32, a UV active spot). Column chromatography was performed on silica gel (20 g) eluting first with petroleum ether (100 mL) and then ethyl ether/petroleum ether (100 mL, 1:99). The ketone **15** eluted with a gradient of ethyl ether/petroleum ether (300 mL), 5:95 to 15:85 (0.143 g, 52%): colorless oil; R_f 0.36, ethyl ether/petroleum ether (3:7) as eluent; IR (thin film) 2930, 1695, 1437, 1245, 1105, 840 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 0.08 (s, 9 H), 1.0–2.6 (m, 17 H); ^{13}C NMR (50.5 MHz, CDCl$_3$) δ -0.30, 23.2, 24.3, 26.6, 27.2, 29.7, 29.9, 34.7, 43.4, 45.1, 50.8, 130.5, 133.3, 212.4; MS, m/e 262 (100%), 233 (28), 190 (32), 148 (61), 73 (74); HRMS calcd for $C_{16}H_{26}OSi$, 262.1753; found, 262.1740.

The alcohol **14** eluted with additional ethyl ether/petroleum ether/methanol (100 mL, 30:69:1) yielding 0.035 mg (13%) of a white amorphous solid which was recrystallized from $MeOH/H_2O$ to give **14**: white solid, mp 99–102 °C; R_f 0.12, ethyl ether/petroleum ether (3:7) as eluent; IR (thin film) 3350 (O–H), 1660, 1560, 1445, 1248, 1020, 835, cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 0.17 (s, 9 H), 1.0–2.6 (m, 15 H), 6.03 (dd, J = 4, 4, 1 H); ^{13}C NMR (50.5 MHz, CDCl$_3$) δ 0.0, 20.2, 22.9, 25.9, 29.5, 31.3, 33.7, 37.7, 45.0, 80.8, 123.8, 129.5, 139.6, 140.6; UV λ_{max} (CH$_3$OH) 256 nm (ϵ 21 000); MS, m/e 262 (11%), 244 (7), 73 (100); HRMS calcd for $C_{16}H_{26}OSi$, 262.1753; found, 262.1752.

2,3,3a,4,5,6,7,8,9,9b-Decahydro-1*H*-benz[*e*]inden-5-one (17).[23] To a stirred solution of ketone **15** (0.020 g, 0.76 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added trifluoroacetic acid (0.009 g, 0.82 mmol) in CH_2Cl_2 (0.5 mL). After 10 min all of the starting material was consumed, as shown by thin-layer chromatography on silica gel. Aqueous workup resulted in a colorless oil which was dissolved in ethyl ether/petroleum ether (30:70) and then

filtered through silica gel (2 g). Evaporation of the solvent left the ketone 17 (10.1 mg, 69%): colorless oil; R_f 0.27, ethyl ether/petroleum ether (3:7) as eluent; IR (thin film) 2935, 1660 (ν_{CO}), 1438, 1360, 1270, cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1–3 (m); UV λ_{max} (CH$_3$OH) 247 nm; MS, m/e 190 (100%), 175 (14), 162 (15), 161 (17), 109 (88), 91 (55), 79 (49), 67 (22).

1-Tetradecene-7,13-diyne (25). To sodium amide (1.84 g, 47.2 mmol) in liquid NH$_3$ (150 mL) was added 1,7-octadiyne (3.25 g, 30.6 mmol) followed by Me$_2$SO (50 mL). After stirring the solution for 1 h, 6-bromohexene (5.0 g, 30.6 mmol) was added. After 24 h, the mixture was worked up in the usual manner (see the synthesis of 2). Distillation of the product using a Kugelrohr apparatus at 70–80 °C (0.01 mm) yielded 25 (2.47 g, 43%): colorless oil; R_f 0.20, petroleum ether as eluent; IR (thin film) 3340, 3115, 2950, 2135, 1655, 1440, 925 cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$) δ 1.0–1.7 (m, 8 H), 1.81 (t, J = 2, 1 H), 2.0–2.5 (m, 8 H), 4.8–6.1 (m, 3 H); MS, m/e 188 (0.2%), 174 (14), 145 (61), 117 (53), 105 (55), 89 (100), 77 (60), 41 (100).

14-(Trimethylsilyl)-1-tetradecene-7,13-diyne (18). To a solution of 25 (1.00 g, 5.32 mmol) in ethyl ether (25 mL) cooled with a dry ice/acetone bath was added n-butyllithium in hexane (2.75 mL, 5.9 mmol). After warming to 0 °C and cooling back to −78 °C, trimethylsilyl chloride (0.74 mL, 6.05 mmol) was added. After stirring at ambient temperature for 12 h standard work up and distillation of the resulting clear oil using a Kugelrohr apparatus at 105 °C (0.02 mm) yielded the product 18 (1.24 g, 89%): colorless oil; R_f 0.27, petroleum ether as eluent; IR (thin film) 3115, 2945, 2190, 1640, 1435, 1250 cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$) δ 0.16 (s, 9 H), 1.1–1.6 (m, 8 H), 1.6–2.5 (m, 8 H), 4.8–6.1 (m, 3 H); MS (30 eV), m/e 245 (6%, M$^+$ − 15), 187 (27), 171 (14), 158 (22), 131 (40), 117 (27), 73 (100). Anal. Calcd for C$_{17}$H$_{28}$Si: C, 78.45; H, 10.77. Found: C, 78.52; H, 10.57.

(5a,5b,9,9a-η⁴-9-(Trimethylsilyl)-1,2,3,4,5,6,7,8,10,10a-*exo*-decahydrophenanthrene)(η⁵-cyclopentadienyl)cobalt (19). To a degassed solution of 18 (0.150 g, 0.577 mmol) in isooctane (30 mL) was added CpCo(CO)$_2$ (0.085 mL, 0.68 mmol). The solution was heated to reflux under a slow N$_2$ stream (~3 mL/h) for 96 h and then worked up as in the synthesis of 5 leaving 19 (0.204 g, 92%) as a red oil. ^{1}H NMR spectroscopy revealed a mixture of two complexes [δ 4.63 (Cp) and 4.56 (Cp)] in a ratio of 45:55 endo to exo. Crystallization of the major isomer was accomplished from MeOH/H$_2$O or CH$_3$CN/H$_2$O. 19: red needles, mp 101–102.5 °C; IR (thin film) 2930, 1452, 1250, 1110, 1013, 805 cm^{-1}; ^{1}H NMR (270 MHz, C$_6$D$_6$) δ 0.25 (s, 9 H), 0.56 (m, 1 H), 0.60 (m, 1 H), 0.74 (m, 1 H), 1.17 (m, 1 H), 1.33 (m, 1 H), 1.5–2.0 (m, 10 H), 2.13 (ddd, J = 16.0, 5, 5, 1 H), 2.27 (m, 2 H), 2.52 (ddd, J = 16, 6, 6, 1 H), 4.56 (s, 5 H); ^{13}C NMR (50.5 MHz, C$_6$D$_6$) δ −1.3, 21.7 (2 carbons), 24.4 (2 carbons), 25.4, 28.0, 31.9 (2 carbons), 34.6, 36.9, 46.8, 67.4, 78.9 (Cp), 88.6, 94.1; MS (30 eV), m/e 384 (27%), 382 (5), 311 (41), 260 (11), 73 (100). Anal. Calcd for C$_{22}$H$_{33}$SiCo: C, 68.66; H, 8.57. Found: C, 68.37; H, 8.55.

9-(Trimethylsilyl)-1,2,3,4,5,6,7,8,10,10a-decahydrophenanthrene (21). To a solution, cooled to 0 °C, of the complexes 19 and 20 (0.200 g, 0.521 mmol) in CH$_3$CN (5 mL) was added a solution of CuCl$_2$·2H$_2$O (0.265 g, 1.55 mmol) and Et$_3$N (0.069 mL) in CH$_3$CN (10 mL). The mixture was stirred for 15 min at 0 °C and worked up as in the synthesis of 8 to give a colorless oil (0.108 g, 80%). Crystallization from MeOH/H$_2$O gave 21: colorless crystals, mp 34–35.5 °C; R_f 0.67, petroleum ether as eluent; IR (thin film) 2944, 1645, 1448, 1248, 805 cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$) δ 0.16 (s, 9 H), 1.0–3.0 (m, 19 H); ^{13}C NMR (25.4 MHz, C$_6$D$_6$) δ −1.3, 21.3, 21.4, 23.5, 23.6, 24.2, 26.0, 29.2, 32.4, 33.6, 34.3, 124.8, 125.6, 133.8, 143.4; MS, m/e 260 (19%), 245 (11), 186 (44), 73 (100); HRMS Calcd for C$_{17}$H$_{28}$Si, 260.1960; found, 260.1965.

(5,5a,9a,9b-η⁴-2,3,3a-*exo*,4,6,7,8,9-Octahydro-1H-benz[e]indene)(η⁵-cyclopentadienyl)cobalt (23) and (5,5a,9a,9b-η⁴-2,3,3a-*endo*,4,6,7,8,9-Octahydro-1H-benz[e]indene)(η⁵-cyclopentadienyl)cobalt (24). To a degassed solution of 22 (0.120 g, 0.689 mmol) in isooctane (30 mL) was added CpCo(CO)$_2$ (0.093 mL, 0.74 mmol). The solution was heated to reflux for 95 h and then worked up as in the synthesis of 5 to give 0.135 g (66%) of a red oil. The ^{1}H NMR spectrum revealed a mixture of two complexes. Reverse-phase HPLC separation with dioxane/CH$_3$CN (5:95) produced two fractions in the ratio of 1:1. Fraction 1 eluted off the column to give 23 (H exo, recrystallized from

MeOH/H$_2$O): red crystals, mp 48–52 °C; IR (thin film) 3096, 2931, 1445, 1111, 803 cm^{-1}; ^{1}H NMR (180 MHz, C$_6$D$_6$) δ 0.67 (m, 1 H, H-3a exo), 1.33 (m, 2 H, H-4 exo–endo), 1.65 (m, 6 H), 2.02 (m, 5 H), 2.35 (m, 3 H), 2.72 (dd, J = 2.3, 2.3, 1 H), 4.59 (s, 5 H); irradiation at δ 2.72 caused the multiplet at δ 1.33 to sharpen; irradiation at δ 1.33 changed the multiplet at δ 0.67 to a dd (J = 10, 7) and the peaks at δ 2.72 to a singlet; irradiation at δ 0.67 effected no change at δ 2.72 but a simplification at δ 1.33; ^{13}C NMR (50.5 MHz, C$_6$D$_6$) δ 21.7, 22.1 (2 carbons), 25.2, 27.6, 30.3, 32.3, 34.3 (C-3a), 38.0 (C-5 vinyl), 47.4, 79.6 (Cp), 87.1, 88.2; MS (30 eV), m/e 298 (100%), 228 (34), 224 (84), 124 (14); HRMS calcd for C$_{18}$H$_{23}$Co, 298.1131; found, 298.1134.

Fraction 2 gave 24 (Hendo): red oil; IR (thin film) 3094, 2936, 1448, 1110, 805 cm^{-1}; ^{1}H NMR (180 MHz, C$_6$D$_6$) δ 0.94 (m, 2 H, H-4 exo–endo), 1.20–2.67 (m, 14 H), 2.89 (m, 1 H, H-3a endo or H-5 vinyl), 2.99 (m, 1 H, H-3a endo or H-5 vinyl), 4.42 (s, 5 H); ^{13}C NMR (180 MHz, C$_6$D$_6$) δ 23.4, 24.1, 24.3, 24.6 (2 carbons), 29.2, 34.5, 35.8, 40.8 (C-5), 47.1 (C-3a), 49.3, 78.4 (Cp), 92.0, 94.6; MS (30 eV), m/e 298 (57%), 228 (39), 224 (100), 124 (14); HRMS calcd for C$_{18}$H$_{23}$Co, 298.1131; found, 298.1134.

(4a,4b,10,10a-η⁴-1,2,3,4,5,6,7,8,10,10a-*exo*-Decahydrophenanthrene)(η⁵-cyclopentadienyl)cobalt (26). To a degassed solution of 25 (0.130 g, 0.691 mmol) in isooctane (50 mL) was added CpCo(CO)$_2$ (0.100 mL, 0.80 mmol). The mixture was heated to reflux for 91 h and then worked up as in the synthesis of 5 leaving a red oil (0.164 g, 76%). A proton NMR spectrum revealed three isomers in the ratio of 2:1.5:1, as determined by the Cp resonances at δ 4.56, 4.48, and 4.39. The major isomer was crystallized from CH$_3$CH/H$_2$O to give 26: red crystals, mp 48–51 °C; IR (thin film) 2935, 1442, 1105, 1010, 800 cm^{-1}; ^{1}H NMR (180 MHz, C$_6$D$_6$) δ 0.58 (m, 1 H, H-3a), 0.78 (m, 1 H, H-4 exo), 1.05 (ddd, J = 14.7, 7.6, 2.2, 1 H, H-4 endo), 1.1–2.5 (m, 16 H), 2.78 (dd, J = 4.0, 2.2, 1 H), 4.56 (s, 5 H); irradiation at δ 2.78 caused a change of the absorption at δ 0.78 to a dd (J = 14, 4) and that at δ 1.05 to another dd (J = 14, 7.5), whereas irradiation at δ 1.05 gave a d (J = 3.3) at δ 2.78 and a narrowing of the absorption at δ 0.58; irradiation at δ 0.58 resulted in broad doublets at δ 0.78 and 1.05; ^{13}C NMR (50.5 MHz, C$_6$D$_6$) δ 20.7, 21.9, 23.6, 24.2, 24.4, 27.9, 31.1, 31.2, 34.5, 35.6, 46.0, 66.0, 78.3 (Cp), 88.4, 89.4; MS (30 eV), m/e 312 (84%), 310 (43), 238 (100); HRMS calcd for C$_{19}$H$_{25}$Co, 312.1288; found, 312.1291.

1,2,3,4,5,6,7,8-Octahydrophenanthrene. To a solution of complexes obtained as the crude product from the cyclization of 25 (0.100 g, 0.32 mmol) in CH$_3$CN (2 mL) at ambient temperature was added ceric ammonium nitrate (1.00 g, 1.82 mmol) in CH$_3$CN (8 mL). The reaction mixture was allowed to stir for 1 h, petroleum ether (10 mL) was added, and the mixture subjected to aqueous workup. Subsequently the solution was filtered through silica gel (1 g) and the solvent removed leaving a clear oil of octahydrophenanthrene (0.40 g, 67%): colorless oil; R_f 0.70, petroleum ether as eluent; IR (thin film) 2945, 1465, 1448, 800 cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$) δ 1.3–2.1 (m, 8 H), 2.2–3.0 (m, 8 H), 6.58 (s, 2 H); MS m/e 186 (100%), 158 (66), 145 (31), 143 (31), 141 (35), 129 (3), 115 (23), 91 (11); HRMS calcd for C$_{14}$H$_{18}$, 186.1408; found, 186.1412.

(3a,5,5a,9a,9b-η⁴-5-(Trimethylsilyl)-2,3,3a,4,6,7,8,9-octahydro-1H-benz[e]indenylium)(η⁵-cyclopentadienyl)cobalt Hexafluorophosphate (28). To a degassed solution of 11 (2.40 g, 6.49 mmol) in CH$_2$Cl$_2$ (100 mL) at −78 °C was added via cannula triphenylmethyl hexafluorophosphate (2.50 g, 6.44 mmol) in degassed CH$_2$Cl$_2$ (50 mL). The dark red mixture was stirred at −78 °C for 0.25 h and then allowed to warm to room temperature. Wet ether (50 mL) was added to destroy any excess (C$_6$H$_5$)$_3$C$^+$PF$_6^-$. The product 28 was separated as an oil by addition of petroleum ether (400 mL). Crystallization was accomplished by using CH$_2$Cl$_2$/ethyl ether/petroleum ether in a ratio of 1:1:1 to give 28 (2.34 g, 70%): reddish-black lustrous crystals, mp 219–224 °C dec; IR (thin film) 3100, 2950, 1430, 1250, 1025, 940 cm^{-1}; ^{1}H NMR (220 MHz, CDCl$_3$) δ 0.29 (s, 9 H), 1.0–2.75 (m, 14 H), 2.87 (d, J = 17, 1 H), 3.29 (ddd, J = 18.6, 6.9, 6.9, 1 H), 5.16 (s, 5 H); field-desorption MS, m/e 883 (M$_2^+$PF$_6^-$), 369 (M$^+$). Anal. Calcd for C$_{21}$H$_{30}$SiF$_6$PCo: C, 49.03; H, 5.88; P, 6.02. Found: C, 48.92; H, 5.89; P, 6.03.

(5,5a,9a,9b-η⁴-5-(Trimethylsilyl)-3a-deuterio-2,3,3a,4,6,7,8,9-octahydro-1H-benz[e]indene)(η⁵-cyclopentadienyl)cobalt (30). To a degassed stirred solution of the

cation **28** (0.100 g, 0.195 mmol) dissolved in MeOH (10 mL) cooled to −78 °C was added petroleum ether (10 mL) and solid NaBD$_4$ (0.0254 g, 0.605 mmol). The reaction mixture was slowly allowed to warm to room temperature. During this process the red color began to disappear from the methanol layer to reappear in the petroleum ether layer. After stirring for 1 h the petroleum ether layer was removed, washed with two portions (10 mL) of H$_2$O, dried over Na$_2$SO$_4$ (anhydrous), and filtered through alumina (1.0 g, activity 3) with petroleum ether as eluent. The ^{1}H NMR spectrum showed the presence of two compounds in the ratio of 3:2 by integration of the cyclopentadienyl protons. The minor compound associated with the downfield Cp absorption was assigned aromatic complex structure **32** based upon the ^{1}H NMR resonances at δ 0.23 (Me$_3$Si), 4.47 (Cp), and 5.15 (complexed aromatic). The other compound was assigned the diene complex structure **30** on the basis of the ^{1}H NMR resonances at δ 0.22 (s, 9 H, Me$_3$Si), 1.01 (d, J = 14.8, 1 H, exo methylene), 1.30 (d, J = 14.8, 1 H, endo methylene), 4.45 (s, 5 H, Cp) and the MS (30 eV), m/e 371 (38), 229 (40), 298 (100), 229 (31), 173 (19), 73 (67) in comparison with those of compound **11**.

(5,5a,9a,9b-η⁴-5-(Trimethylsilyl)-3a-*tert*-butyl-2,3,3a,4,6,7,8,9-octahydro-1*H*-benz[*e*]indene)(η⁵-cyclopentadienyl)cobalt (29). To a degassed solution of **28** (0.300 g, 0.580 mmol) in dry THF (30 mL) was added via cannula a solution of *tert*-butyllithium in pentane (1.93 ml, 2.32 mmol) and THF (50 mL) at −78 °C. The reaction mixture was stirred for 15 min at −78 °C and then allowed to warm to room temperature. Aqueous petroleum ether (50 mL) workup, followed by filtration of the resulting dark red oil through alumina (30 g, activity 2.5) with petroleum ether as eluent gave **29** (0.190 g, 77%), as a red oil, pure by ^{1}H NMR spectroscopy. Crystallization from MeOH/H$_2$O afforded red crystals: mp 95–97 °C; IR (thin film) 2940, 1560, 1435, 1245, 834 cm^{-1}; ^{1}H NMR (180 MHz, C$_6$D$_6$) δ 0.24 (s, 9 H), 0.74 (s, 9 H), 1.55 (d, J = 16, 1 H), 1.60 (d, J = 16, 1 H), 1.28–2.33 (m, 12 H), 2.47 (m, 2 H), 4.44 (s, 5 H); ^{13}C NMR (50.5 MHz, C$_6$D$_6$) δ −1.9, 20.9, 21.8, 22.0, 25.9, 26.3, 27.3, 33.8, 35.0, 37.6, 42.6, 44.1, 49.4, 73.4, 79.5 (Cp), 87.9, 92.4; MS (30 eV), m/e 426 (15%), 369 [100, M⁺ − C(CH$_3$)$_3$], 303 (89), 296 (81), 73 (29); HRMS calcd for C$_{25}$H$_{39}$SiCo, 426.2153; found, 426.2151. Anal. Calcd for C$_{25}$H$_{39}$SiCo: C, 70.39; H, 9.22. Found: C, 70.14; H, 9.27.

5-(Trimethylsilyl)-2,3,6,7,8,9-hexahydro-1*H*-benz[*e*]indene (31). To a stirred solution of the cation **28** (0.100 g, 0.195 mmol) in methanol (10 mL), H$_2$O (2 mL), and petroleum ether (10 mL) at 0 °C was added KCN (powdered) (0.050 g, 0.77 mmol). The red color moved from the aqueous methanol to the petroleum ether phase, then faded to a light yellow. After 0.5 h the petroleum ether was washed with H$_2$O (2 × 5 mL), and the solvent was evaporated leaving a light yellow oil. The oil was dissolved in ethyl ether/petroleum ether (1:9) and filtered through alumina (1 g, activity 2.5) using ethyl ether/petroleum ether (1:9). Evaporation of the solvent resulted in crystalline material (0.042 g, 88%). Recrystallization from MeOH/H$_2$O gave pure **31**: colorless needles, mp 44–46 °C; R_f 0.65, petroleum ether as eluent; IR (thin film) 2955, 1660, 1435, 1248, 950 cm^{-1}; ^{1}H NMR (180 MHz, CDCl$_3$) δ 0.40 (s, 9 H), 1.70 (m, 4 H), 1.94 (pentet, J = 7.5, 2 H), 2.53 (t, J = 5.8, 2 H), 2.65 (t, J = 7.4, 2 H), 2.87 (t, J = 7.5, 2 H), 2.91 (t, J = 7.0, 2 H), 7.43 (s, 1 H); ^{13}C NMR (25.4 MHz, CDCl$_3$) δ 0.30, 22.9, 23.5, 24.7, 27.4, 30.6, 31.4, 32.8, 127.7, 132.7,

136.3, 140.4 (2 carbons), 144.6; MS (30 eV), m/e 244 (31%), 243 (100), 165 (16), 106 (7); HRMS calcd for C$_{16}$H$_{24}$Si, 244.1639; found, 244.1643.

(5,5a,9a,9b-η⁴-5-(Trimethylsilyl)-2,3,6,7,8,9-hexahydro-1*H*-benz[*e*]indene)(η⁵-cyclopentadienyl)cobalt (32). To a stirred degassed solution of **28** (0.050 g, 0.097 mmol) in MeOH/H$_2$O (5:1, 10 mL) and petroleum ether (10 mL) at 0 °C was added crushed K$_2$CO$_3$ (0.150 g, 1.08 mmol). The reaction mixture was stirred for 45 min and then allowed to warm to room temperature. The red organic layer was removed from the aqueous methanol layer and washed with MeOH/H$_2$O (3:1, 2 × 5 mL). The solvent was vacuum transferred leaving a red, thermally and oxygen sensitive oil of **32** (0.031 g, 87%): IR (thin film) 3075, 3050, 2950, 1645, 1460, 1250, 1105, 1020, 805 cm^{-1}; ^{1}H NMR (270 MHz, C$_6$D$_6$) δ 0.23 (s, 9 H), 1.4–2.8 (m, 14 H), 4.47 (s, 5 H), 5.15 (br s, 1 H); ^{13}C NMR (50.5 MHz, C$_6$D$_6$) δ −1.9, 21.5, 22.2, 24.1, 25.8, 28.0, 28.3, 29.6, 42.1, 76.4, 78.9 (Cp), 86.0, 91.1, 111.2, 145.0; MS (30 eV), m/e 368 (100%), 244 (32), 229 (89), 169 (37), 73 (69); HRMS calcd for C$_{21}$H$_{24}$SiCo, 368.1370; found, 368.1364.

(3a,5a,9a,9b-η⁴-5-*exo*-(Trimethylsilyl)-2,3,4,5,6,7,8,9-octahydro-1*H*-benz[*e*]indene)(η⁵-methylcyclopentadienyl)cobalt (33). To a stirred degassed solution of **28** (0.300 g, 0.58 mmol) in THF (60 mL) cooled to dry ice/acetone bath temperature was added methyllithium in ethyl ether (1.68 mL, 9.28 mmol). The reaction mixture was allowed to warm to 0 °C, worked up with H$_2$O, and dried over Na$_2$SO$_4$ (anhydrous). Evaporation of the solvent yielded a red oil (0.230 g). Filtration through alumina (1 g, activity 3) with petroleum ether as eluent was followed by evaporation of the solvent under a stream of N$_2$. The ^{1}H NMR spectrum revealed the presence of both the benzene complex **32** and the methyl adduct **33** in a ratio of 1:4. Column chromatography on alumina (15 g, activity 3) with undegassed petroleum ether effected preferential decomposition of **32** and allowed the isolation of **33** (0.127 g, 59%): air sensitive red oil; ^{1}H NMR (180 MHz, C$_6$D$_6$) δ −0.06 (s, 9 H), 0.23 (dd, J = 17, 3.5, 1 H, H-4 exo), 0.92 (dd, J = 17, 11.5, 1 H, H-4endo), 1.2–2.1 (m, 6 H), 2.13 (s, 3 H), 2.20–3.0 (m, 9 H), 3.94 (br s, 1 H, Cp), 4.03 (br s, 1 H, Cp), 4.26 (br s, 1 H, Cp), 4.30 (br s, 1 H, Cp); ^{13}C NMR (50.5 MHz, C$_6$D$_6$) δ −3.0, 20.7, 21.4, 21.6, 21.9, 25.4, 26.7, 29.1, 32.7, 33.5, 35.4, 59.9, 65.3, 79.0 (Cp), 79.5 (Cp), 79.8 (Cp), 80.3 (Cp) 82.8 (Cp), 93.0, 93.3; MS (30 eV), m/e 384 (100%), 382 (30), 311 (87), 172 (53), 79 (42, CpMe), 73 (91); HRMS calcd for C$_{22}$H$_{33}$SiCo, 384.1683; found, 384.1679.