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Intermolecular [2 + 2 + 2] Cycloaddition Reactions of Alkynes and Alkenes Mediated by Cobalt: X-ray Crystal Structures of Two Isomeric (η^5-Cyclopentadienyl)(η^4-1,3-cyclohexadiene)cobalt Complexes

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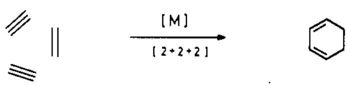
Treatment of bicyclic alkenes (norbornylene, *endo*-dicyclopentadiene) with alkynes (diphenylacetylene, dimethyl acetylenedicarboxylate) in the presence of $CpCo(CO)_2$ produced CpCo(η^4-1,3-cyclohexadiene) complexes (**1**, **2**, **6**, **7**, **10**, **11**) in good yields. Oxidation of complexes **1**, **2**, **6**, **7**, **10**, and **11** using $CuCl_2{\cdot}2H_2O$ afforded the free diene ligands **4**, **8**, and **13**. Further oxidation of **4** and **8** using ceric ammonium nitrate produced the aromatic derivatives **5** and **9**. The isomeric complexes **1** and **2**, which were obtained from *endo*-dicyclopentadiene and diphenylacetylene, were characterized by two-dimensional NMR spectroscopic techniques as well as X-ray crystallography. Complex **1** isomerized to **2** at 154 °C in a first-order process with an observed rate constant of $(1.5 \pm 0.1) \times 10^{-5}\ s^{-1}$. Treatment of norbornylene with diphenylacetylene in the presence of (η^5-$C_5H_4CH_3$)$Co(CO)_2$ produced two isomeric (η^5-$C_5H_4CH_3$)Co(η^4-1,3-cyclohexadiene) complexes (**14**, **15**). A 1:1 mixture of **1** and **14** isomerized intramolecularly to **2** and **15** in xylene-d_{10} at 155 °C. Both **1** and **2** are triclinic, $P\bar{1}$; **1** has unit cell parameters a = 10.943 (2) Å, b = 11.439 (1) Å, c = 14.954 (6) Å, α = 71.94 (3)°, β = 87.00 (3)°, γ = 62.27 (1)°, and D(calcd) = 1.30 g cm^{-3} for Z = 2. These values for **2** are a = 10.752 (1) Å, b = 12.640 (3) Å, c = 13.754 (3) Å, α = 69.89 (3)°, β = 66.83 (1)°, γ = 68.38 (1)°, and D(calcd) = 1.31 g cm^{-3} for Z = 2. Both were refined via least-squares, **1** to a conventional R value of 0.041 based on 4605 independent observed reflections ($[F_o \geq 5\sigma(F_o)]$ and **2** to 0.041 utilizing 3530 reflections. Each cobalt atom is η^5-coordinated to the cyclopentadienyl ligand (Co–Cp(av) = 2.09 (2) Å for **1** and 2.08 (3) Å for **2**) and η^4-bonded to the 1,3-cyclohexadiene ligand. The two exterior Co–C distances average 2.08 (3) Å in **1** and 2.07 (2) Å in **2**, whereas the two interior Co–C values average 1.97 (1) and 1.984 (8) Å, respectively.

Introduction

The cyclooligomerization of alkynes and alkenes in the presence of transition-metal complexes has a rich and varied history.[1] Among these reactions studied is the [2 + 2 + 2] cycloaddition of two alkynes and one alkene to yield cyclohexadienes or metal-complexed cyclohexadiene adducts (eq 1). The reaction has been carried out catalytically by using iron,[2] rhodium,[3] nickel,[4] palladium,[5] or cobalt[6a] catalysts to produce free cyclohexadienes. Moreover, the most extensively studied systems capable of promoting this cycloaddition reaction have been (η^5-cyclopentadienyl)cobalt (CpCo) complexes (eq 2). Vollhardt and co-workers have pioneered the use of such complexes in intramolecular cycloadditions of enediynes,[6,7] intermolecular cyclizations of enynes and alkynes,[7a,c,8] and



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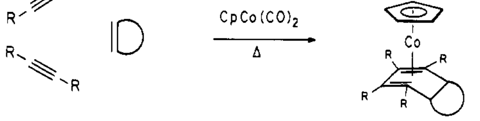

(2)

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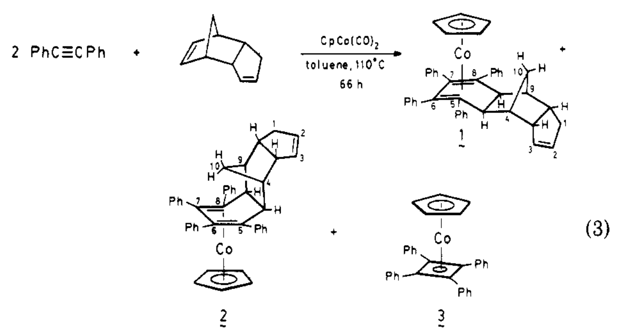
cycloadditions of alkynes with various indoles,[9] pyrroles,[10] and imidazoles.[11] Recently, $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ has been used to cyclo-cotrimerize two alkynes and one alkene (mainly ethylene) to produce $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-}1,3\text{-cyclohexadiene})$ complexes.[12] In addition to the above reports, the CpCo nucleus has been used as a template for the stepwise construction of $CpCo(\eta^4\text{-}1,3\text{-cyclohexadiene})$ adducts from alkynes and alkenes.[13] In this paper we report the synthesis, reactivity, and crystal structures of $CpCo(\eta^4\text{-}1,3\text{-cyclohexadiene})$ complexes formed from the $CpCoL_2$ (L = CO, C_2H_4) mediated intermolecular [2 + 2 + 2] cycloaddition of alkynes and alkenes.

Results and Discussion

1. Synthesis and NMR Characterization. Treatment of 2.2 equiv of diphenylacetylene with 5 equiv of *endo*-dicyclopentadiene in the presence of $CpCo(CO)_2$ in refluxing toluene for 66 h produced three organometallic compounds (eq 3). Removal of the solvent and chromatography of the reaction mixture on alumina produced a small amount of the cyclobutadiene compound 3 and a dark red residue containing 1, 2, and 3. Compounds 1 and 2 were formed in yields of 64% and 26%, respectively, as determined by ^1H NMR spectroscopy. Although compounds 1 and 2 could not be separated by column chromatography, it was found that 1 could be obtained in pure form by subjecting a portion of the dark red residue to preparative thin-layer chromatography on silica gel. Under these latter conditions, compound 2 was oxidatively converted to the organic compound 4, which had a larger R_f value than 1. It was subsequently discovered that upon heating the dark red residue containing 1, 2, and 3 in refluxing xylene for 48 h, it was converted to a mixture of compounds 2 and 3 (vide infra). Recrystallization of this mixture from hexane afforded compound 2 in pure form as dark red crystals.



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Having compounds 1 and 2 in hand as pure materials allowed for their characterization using NMR spectroscopy. The salient difference between the ^1H NMR spectrum of 1 as compared to the spectrum of 2 is the chemical shift of H_c (Figures 1 and 2). In compound 1, H_c appears as a doublet (J_{ci} = 9.7 Hz) at δ 4.28, whereas in 2 H_c appears as a doublet (J_{ci} = 9.7 Hz) at 1.63 ppm. Although the chemical shift assignments for H_c (δ 1.63) and H_i (δ 0.89) in compound 2 have not been rigorously established, their assignments are based on chemical shift comparisons to closely related compounds described in this paper and also the literature. The downfield shift of H_c in 1 is due to its close proximity to cobalt (2.96 Å), which can readily be seen in the ORTEP drawing of the crystal structure of 1 (Figure 5). This effect has also been observed in other organometallic complexes containing coordinated norbornylene systems.[14] This downfield shift of protons like H_c in 1, which are attached to the bridging methano carbon and are directed toward cobalt, proved helpful in assigning the correct stereochemistries to other $CpCo(\eta^4\text{-}1,3\text{-cyclohexadiene})$ complexes described in this study. The chemical shift anisotropy associated with the CpCo group can be used to establish the stereochemical assignment of the protons of the complexed ring (H_j and H_k). The exo protons experience greater shielding relative to the endo protons.[7d] Thus, for compound 1, in which H_j and H_k are exo to the CpCo group, both appear as a broad singlet at δ 1.17 ($CDCl_3$). In compound 2 H_j and H_k are endo to the CpCo group and appear as two doublets (AB pattern) at δ 2.55 (J = 9.5 Hz) and 2.68 (J = 9.6 Hz). The exact chemical shift assignments of H_j and H_k in compound 2 were, however, not determined.

To confirm the above chemical shift assignments and establish those of the remaining protons in the ^1H NMR spectra of 1 and 2 a ^1H–^1H correlated spectrum (COSY) for each compound was obtained (Figures 1 and 2). Shown in Figures 1 and 2 are contour plots resulting from COSY, the proton signals are plotted along the diagonal, and the cross peaks indicate two mutually coupled protons. Also shown in these figures are structural drawings for 1 and 2 along with the proton assignments. It can readily be seen in Figure 2 that H_c is coupled to H_i producing an AX pattern, whereas H_j is coupled to H_k producing an AB pattern. For compound 1 a somewhat different situation is observed (Figure 1); H_c is coupled to H_i, but the resonance for H_i is hidden beneath the single resonance for H_j and H_k. When the ^1H NMR spectrum of 1 in toluene-d_8 was measured, it was observed that H_i, H_j, and H_k no longer had the same chemical shift values. In this solvent H_i appeared as a doublet (J = 9.0 Hz) at δ 1.18; moreover, protons H_j and H_k appeared as a closely spaced AB pattern centered at δ 1.45 with a small value for $|\delta_j - \delta_k|/J_{jk}$. The chemical shift assignments for the homoallylic methine protons H_e (δ 2.45 for 1 and δ 2.35 for 2) and allylic methine protons H_d (δ 2.98 for 1 and δ 2.93 for 2) were made by comparisons to literature values for *endo*-dicyclopentadiene and its dihydro analogue.[15] With use of these assignments for H_e and H_d, the chemical shifts of the bridgehead protons H_f and H_g could be established by inspecting the COSY spectra and then observing the associated cross peaks. It can be seen from Figures 1 and 2 that H_g occurs at higher field than H_f in both compounds 1 and 2 and that H_f and H_h have similar chemical shift values in compound 2. It can also be seen that in both compounds H_d couples to H_e, whereas H_e couples to H_d and one or both of the H_h protons. Furthermore, there appears to be long-range coupling between H_d and one or both of the H_h protons in compound 1. Long-range coupling of this type has previously been observed in dicyclopentadiene systems and may be due to a "W" arrangement of the bonds or to homoallylic coupling.[15a] The chemical shift assignments for the vinylic protons H_a (δ 5.65 for 1 and δ 5.82 for 2) and H_b (δ 5.48 for 1 and 5.66 for 2) were made by comparison to literature values for

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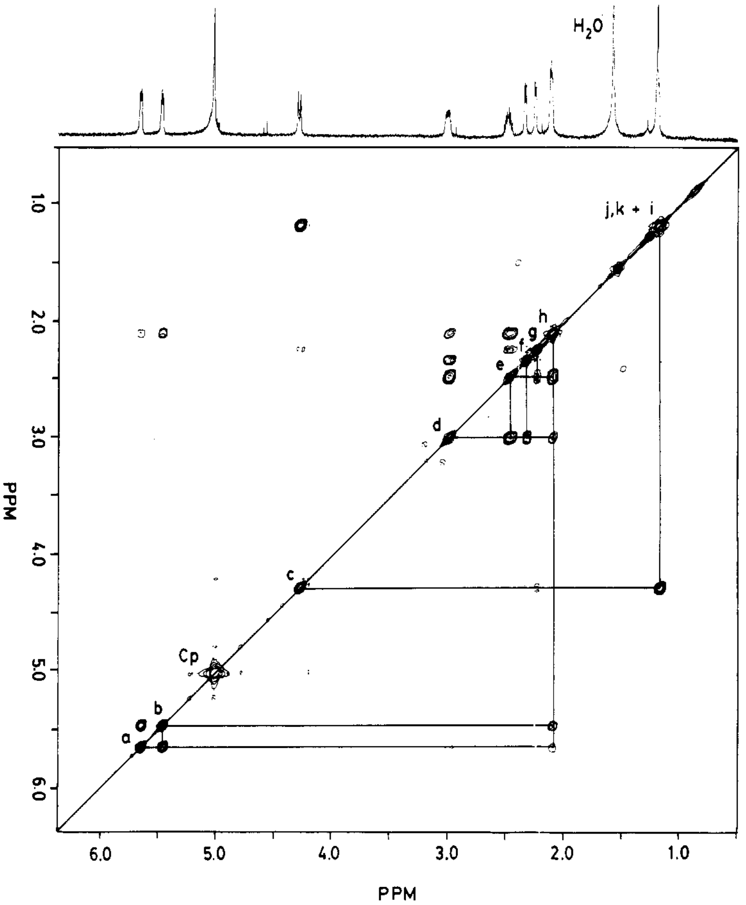

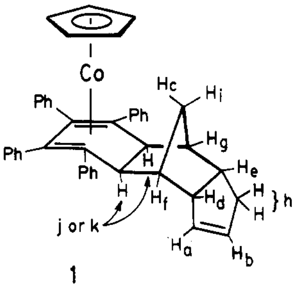

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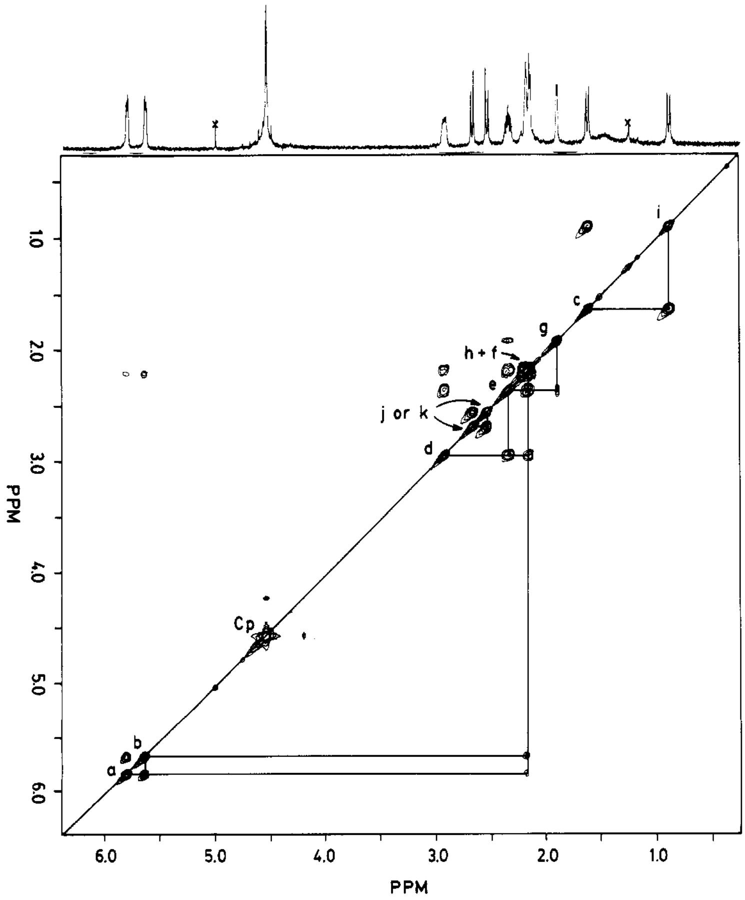
Figure 1. Four-contour plot of the two-dimensional ^{1}H–^{1}H J-correlated spectrum of **1** in CDCl$_3$.



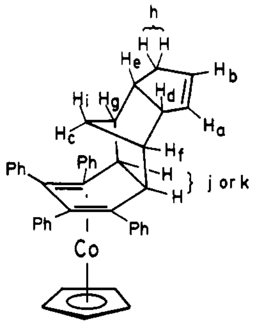


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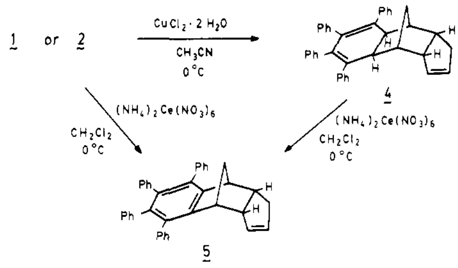
Figure 2. Four-contour plot of the two-dimensional ^{1}H–^{1}H J-correlated spectrum of **2** in CDCl$_3$ (X = impurity).

Scheme I



exo- and *endo*-dicyclopentadiene.[15] Inspection of Figures 1 and 2 reveals vicinal couplings for H_a–H_b and H_b–H_h, whereas allylic couplings are seen for H_a–H_h. The magnitudes of the vicinal coupling constants (J_{ab}) are 5.6 Hz for compound 1 and 5.7 Hz for 2 and fall within the 5–7 Hz range commonly observed for cyclopentene systems.[16]

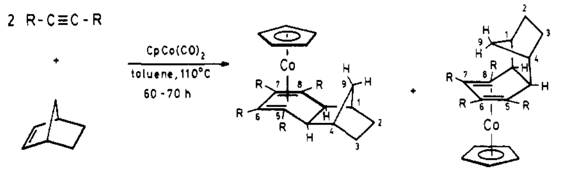
The $^{13}C\{^1H\}$ NMR spectra of compounds 1 and 2 each exhibit eight expected resonances in the upfield regions (δ 31–55) which correspond to the nonvinylic carbons of the dihydrodicyclopentadiene systems.[17] For compound 1, the resonances at δ 71.44 and 71.84 were assigned to the terminal quaternary diene carbons (C(5), C(8)), whereas the single peak at δ 95.15 corresponds to the two internal quaternary diene carbons (C(6), C(7)). Likewise for 2, the peaks at δ 67.19 and 68.56 correspond to either C(5) or C(8), while those at δ 96.44 and 96.70 correspond to either C(6) or C(7). The upfield shifts of these diene carbons in 1 and 2, relative to uncomplexed diene 4, are consistent with those observed in other CpCo–diene complexes.[6,7a,b,d] The $^{13}C\{^1H\}$ NMR spectra of 1 and 2 exhibit most of the 18 expected resonances for the remaining vinylic and aromatic carbons.

Besides spectroscopic (vide supra) and X-ray crystallographic (vide infra) information to establish the structures of compounds 1 and 2, it was also possible to support their structural assignments by using chemical evidence (Scheme I). Thus, both compounds 1 and 2 underwent oxidative demetalation to yield the same uncomplexed diene (4) upon treatment with $CuCl_2 \cdot 2H_2O$ in acetonitrile. This result clearly indicates that the isomeric compounds 1 and 2 differ only in the relative complexation of the CpCo groups to opposite sides of the diene ligand 4. Furthermore, compounds 1, 2, and 4 could be oxidized to the same aromatic compound 5 upon treatment with ceric ammonium nitrate.

The mass spectrum of compound 4 exhibits a parent molecular ion at *m/e* 488, whereas loss of two hydrogens is evident upon going from 4 to 5, which exhibits its parent molecular ion at *m/e* 486. The ^1H NMR spectra of compounds 1, 2, and 4 are all similar, except that H_c, H_i, H_j, and H_k are shifted downfield by ca. 0.5 ppm in 4 relative to 2. The multiplicities, however, remain the same. These chemical shift differences are probably due to electronic and stereochemical differences of the coordinated diene ligand in 2 (and 1) as compared to the uncomplexed diene ligand 4. As expected, the $^{13}C\{^1H\}$ NMR spectrum of 4 exhibited eight upfield resonances in the range δ 32–54. The quaternary diene carbons (C(5)–C(8)) are moved to their normal chemical shift range of δ 120–140 upon decomplexation of the CpCo group. These carbons could not, however, be distinguished from the other vinylic or aromatic carbons which appear in the same region.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of 5 complement the structural assignments already discussed for compounds 1, 2, and 4. The characteristic AB pattern for H_j and H_k (δ 3.05, 3.21) in compound 4 is no longer evident in the ^1H NMR spectrum of 5. The other noteworthy feature of these spectra are the chemical shift values of the bridgehead protons H_f and H_g, which change from homoallylic in 4 (δ 2.03, 2.33) to benzylic in 5 (δ 3.35, 3.45). As expected, the $^{13}C\{^1H\}$ NMR spectrum of 5 exhibits two fewer resonances in the upfield region (δ 34–55) as compared to 4.

We also found that norbornylene (bicyclo[2.2.1]-2-heptene) reacts, in an analogous manner to *endo*-dicyclopentadiene, with diphenylacetylene and $CpCo(CO)_2$ to afford two new compounds, 6 and 7 (eq 4). Compounds



(4)

6 R = Ph 7 R = Ph
10 R = CO₂Me 11 R = CO₂Me

6, 7, and 3 were formed in yields of 62%, 24%, and 12%, respectively, as determined by ^1H NMR spectroscopy. In another experiment, 2.2 equiv of diphenylacetylene and 5 equiv of norbornylene were treated with $CpCo(C_2H_4)_2$ at 0 °C in toluene. Under these conditions compounds 6 and 7 were produced in yields of 67% and 22%, respectively, along with a trace amount of 3. Compounds 6, 7, and 3 could be separated by preparative thin-layer chromatography and isolated in pure form by recrystallization. The structural assignments of compounds 6 and 7 were based on their mass spectra, NMR spectral comparisons with 1 and 2, and oxidative conversions to organic derivatives. The major peaks in the mass spectra, *m/e* 574 (M^+), 509 ($M^+ - Cp$), 450 ($M^+ - CpCo$), 441 ($M^+ - Cp - C_5H_8$), 124 ($CpCo^+$), for compounds 6 and 7 are typical of $CpCo(\eta^4\text{-}1,3\text{-cyclohexadiene})$ complexes.[6,7] The ^1H NMR spectrum of 6 exhibits the characteristic low field doublet at δ 3.98 (J = 9.0 Hz) for the C(9) proton directed at cobalt. Moreover, the C(4a) and C(8a) protons exo to the CpCo group in 6 are shielded (δ 1.12) relative to the same protons endo to the CpCo group in 7 (δ 2.59). The $^{13}C\{^1H\}$ NMR spectra of isomers 6 and 7 are similar and both can be easily interpreted. Each compound exhibits four upfield resonances between 29 and 55 ppm for the four types of inequivalent carbons of the norbornane system. The terminal quaternary diene carbons (C(5), C(8)) appear as single resonances at δ 70.89 for 6 and at δ 67.78 for 7. Likewise, the internal quaternary diene carbons (C(6), C(7)) appear as single resonances at δ 95.08 for 6 and at δ 96.25 for 7. Compound 6 exhibits only seven of the expected eight aromatic resonances (δ 123–146), whereas 7 exhibits ten resonances. The two extra aromatic resonances observed in the $^{13}C\{^1H\}$ NMR spectrum of 7 may be due to restricted rotation of one or more phenyl groups attached to the complexed ring.[18]

Further structural verification of 6 and 7 was obtained by oxidatively removing the CpCo groups from these compounds (Scheme II). Treatment of 6 or 7 with $CuCl_2 \cdot 2H_2O$ in acetonitrile at 0 °C produced the same organic

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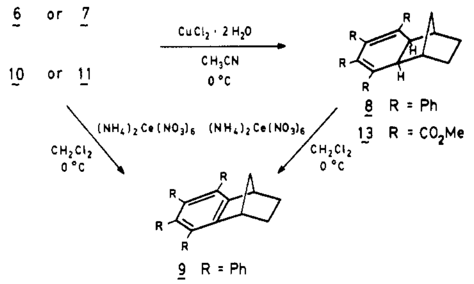
[18] Restricted rotation of aromatic groups attached to CpCo-complexed organic fragments has previously been observed. Rausch, M. D.; Westover, G. F.; Mintz, E.; Reisner, G. M.; Bernal, I.; Clearfield, A.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2605.

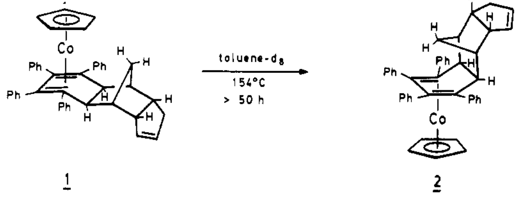
Scheme II



product **8**. It was also found that compounds **6**, **7**, and **8** could be transformed into the same aromatic compound **9** upon treatment with ceric ammonium nitrate. The mass spectrum of **8** exhibits a parent molecular ion at *m/e* 450, whereas **9** exhibits its parent molecular ion at *m/e* 448. The ^{1}H NMR spectrum of **8** shows the characteristic resonance for the protons attached to C(4a) and C(8a) at δ 3.10, whereas this resonance is absent in the spectrum of the oxidized compound **9**. The chemical shift values of the bridgehead protons (C(1), C(4)) appear at lower field in **9** (δ 3.35) than in **8** (δ 2.31); a similar trend observed earlier for compounds **4** and **5**. The ^{13}C{^{1}H} NMR spectrum of **8** exhibits all of the 14 expected resonances; four upfield (δ 30–50) for norbornane carbons and ten downfield (δ 125–143) for the vinylic and aromatic carbons. The aromatic compound **9** also exhibits the 14 requisite resonances in its ^{13}C{^{1}H} NMR spectrum. The three upfield resonances at δ 27.14, 43.18, and 48.64 correspond to those found in the parent aromatic compound benzonorbornane (δ 27.1, 43.8, and 49.4).[19]

It was also found that norbornylene reacted with dimethyl acetylenedicarboxylate in the presence of CpCo(CO)$_2$ to produce compounds **10**, **11**, and benzenecarboxylic acid hexamethyl ester (**12**) (eq 4). Compounds **10**–**12** were isolated in pure form by preparative thin-layer chromatography in the following percentages **10** (47%), **11** (7%), and **12** (20%). Presumably compound **12** arises by a CpCo-mediated cyclotrimerization of dimethyl acetylenedicarboxylate.[7c] The spectroscopic properties of **10** and **11** were consistent with their assigned structures and had comparable spectral features to **1**, **2**, **6** and **7**, described previously. Further structural evidence was provided by oxidizing compounds **10** or **11** with CuCl$_2$·2H$_2$O to a single organic compound **13** (Scheme II). Compound **13** prepared in this manner had an identical melting point (67–68 °C) and ^{1}H NMR spectral values as reported in the literature.[5] Furthermore, the ^{1}H NMR spectrum of **13** exhibited a single resonance at δ 2.97 for the protons attached to C(4a) and C(8a). This value is similar to those observed for compounds **4** (δ 3.05, 3.21) and **8** (δ 3.10). The mass spectrum of **13** exhibited a parent molecular ion at *m/e* 378.

It was discovered that compound **1** slowly, but completely, isomerized to **2** in xylene or toluene at 154 °C (eq 5). The process was followed by ^{1}H NMR spectroscopy and proceeded cleanly with only resonances for **1** or **2** observed. The disappearance of **1** (and appearance of **2**) followed first-order kinetics with an observed rate constant of (1.5 ± 0.1) × 10^{-5} s^{-1} at 154 °C (Figure 3). This information suggested that an intramolecular isomerization mechanism was occurring. Further evidence for such a process was corroborated by the results of a crossover experiment described below. It was also observed by using ^{1}H NMR spectroscopy that compound **6** isomerized cleanly to **7** (145 °C), whereas **10** isomerized to **11** (165 °C) in xylene-d_{10}. The rate constants for these two processes were, however, not measured.



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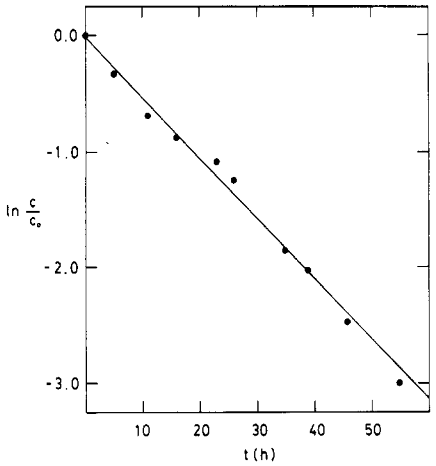
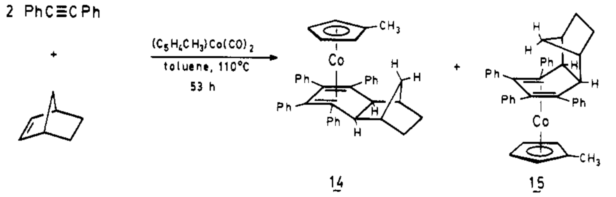


Figure 3. First-order kinetic plot for the thermal isomerization of **1** to **2** in toluene-d_8 at 154 °C.

For the crossover experiment it was necessary to synthesize two different CpCo(η^4-1,3-cyclohexadiene) complexes specifically labeled at the CpCo and diene groups. It was thought that compound **1** could serve as the diene labeled molecule because of the fused cyclopentene ring. A methylcyclopentadienyl ligand was chosen as the CpCo-labeled group because of synthetic simplicity. It was also felt that a methyl substituent attached to the cyclopentadienyl ligand would not significantly alter the mechanism of isomerization. Thus, treatment of 2.2 equiv of diphenylacetylene with 5 equiv of norbornylene in the presence of (η^5-C$_5$H$_4$CH$_3$)Co(CO)$_2$ in refluxing toluene for 53 h produced equal amounts of **14** and **15** in a combined yield of 51% (eq 6). Compound **15** could be obtained in pure form by subjecting the crude reaction mixture to preparative thin-layer chromatography followed by recrystallization. On the other hand, **14** could only be obtained ca. 95% pure (5% of isomer **15**) by repeated fractional crystallization of the reaction mixture from hexane. The spectral parameters of **14** and **15** were consistent with their assigned structures and correlated well with the other CpCo(η^4-1,3-cyclohexadiene) complexes described above.



(6)

The crossover experiment (Scheme III) was conducted in an NMR tube and the progress followed by ^{1}H NMR spectroscopy. Equimolar amounts of **1** and **14** (containing 5% of **15**) were dissolved in xylene-d_{10} and sealed under vacuum. The NMR tube was immersed in an oil bath at ca. 155 °C and removed periodically to record the ^{1}H NMR spectrum. After 112 h the intensities of the cyclo-

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[19] Levy, G. C.; Craik, D. J.; Norden, B.; Phan Viet, M. T.; Dekmezian, A. *J. Am. Chem. Soc.* **1982**, *104*, 25.

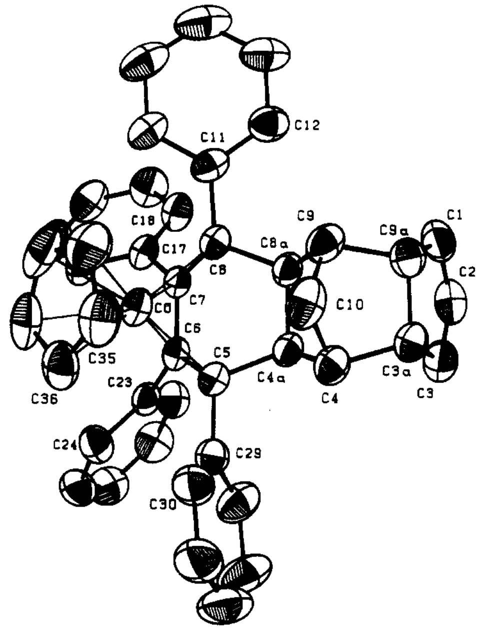
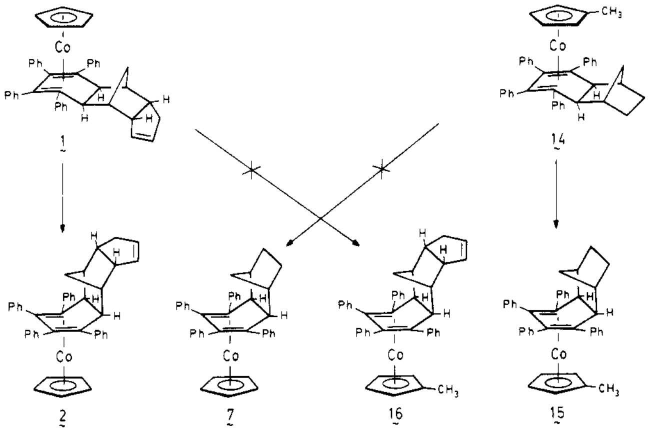


Figure 4. Molecular structure and atom-labeling scheme for complex 1 with the atoms represented by their 50% probability ellipsoids. Hydrogen atoms have been omitted.

Scheme III



pentadienyl resonances corresponding to 1 and 14 were negligible. Present in the ^{1}H NMR spectrum were resonances attributable only to compounds **2** and **15**. Moreover, the ^{13}C{^{1}H} NMR spectrum of this sample exhibited all 23 expected upfield (δ 11–101) resonances corresponding to the aliphatic, cyclopentadienyl, and quaternary diene carbons of **2** and **15**. The NMR tube was then opened, the xylene-d_{10} removed under vacuum, and the resulting solid residue subjected to mass spectral analysis. The mass spectrum of this residue exhibits peaks only for compounds **2** (m/e 612 (M^+)) and **15** (m/e 588 (M^+)). Furthermore, expanding the vertical scale of this spectrum 200 times revealed only a very small peak at m/e 626 which corresponds to the crossover product **16**. The remainder of the above residue was dissolved in $CDCl_3$, and the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded. Present in the ^{1}H NMR spectrum were resonances only for compounds **2** and **15** with no resonance at δ 4.59 which could be attributable to the cyclopentadienyl protons of crossover product **7**. The ^{13}C{^{1}H} NMR of this mixture also exhibited all 23 expected upfield resonances; moreover, the chemical shift values corresponded very well with those of compounds **2** and **15** obtained separately in $CDCl_3$.

2. Crystal Structure Description of 1 and 2. The structures of compounds **1** and **2** have been determined by X-ray diffraction methods and confirm the spectral assignments discussed earlier. The molecular structures and atom-labeling schemes for these compounds are shown in Figures 4–6; interatomic distances and bond angles are presented in Table I. The structural features of compounds **1** and **2** are almost identical except that the CpCo fragments are coordinated to nonequivalent stereochemical faces of the C_{14}-diene ligand. Isomer **1** has the CpCo fragment on the same side as the bridging methano group (C(10)) of the norbornane system, whereas isomer **2** has the CpCo fragment on the opposite side. The six-membered ring (C(4a), C(5), C(6), C(7), C(8), C(8a)) and the five-membered ring (C(1), C(2), C(3), C(3a), C(9a)) are both cis-fused to the norbornane system in compounds **1** and **2**. Moreover, the four-carbon group (C(5), C(6), C(7), C(8)), which comprises part of the six-membered ring, is on the same side (exo) as the bridging methano group (C(10)), whereas the three-carbon group (C(1), C(2), C(3)), which comprises part of the five-membered ring, is on the opposite side (endo).

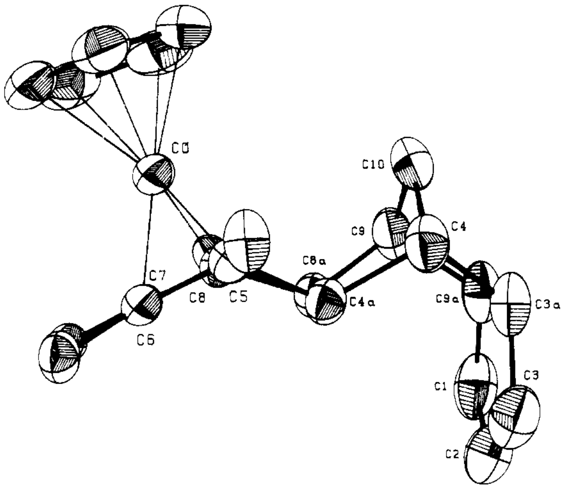


Figure 5. Another view of the molecular structure of 1 with the carbons of the phenyl groups not directly bonded to the diene ligand omitted for clarity.

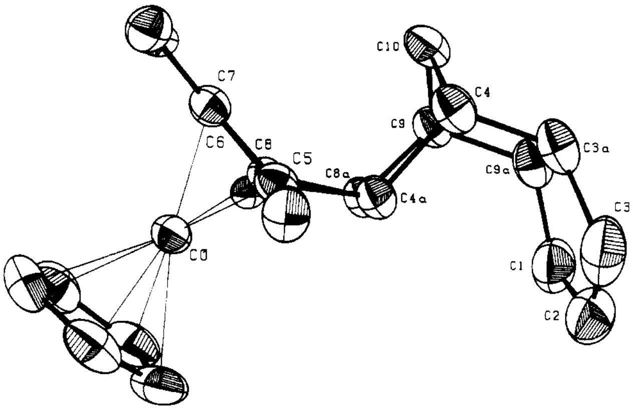


Figure 6. Molecular structure and atom-labeling scheme for complex 2 with the carbons of the phenyl groups not directly bonded to the diene ligand omitted for clarity.

The bond distances and angles associated with the CpCo fragments of **1** and **2** are unexceptional. Thus, the average Co–C(π) separations of 2.09 (2) and 2.08 (3) Å for **1** and **2**, respectively, are typical of CpCo complexes.[11,20-22] The

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(21) (a) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1982**, 89. (b) Gomes de Lima, M. B.; Guerchais, J. E.; Le Floch-Pérennou, F. J.; L'Haridon, P.; Pētillon, F. Y.; Talarmin, J. *Organometallics* **1987**, *6*, 1930.

Table I. Bond Distances (Å) and Angles (deg) for Compounds 1 and 2

	1	2		1	2
		Bond Distances			
Co–C(5)	2.055 (3)	2.052 (3)	C(4)–C(10)	1.522 (5)	1.528 (5)
Co–C(6)	1.957 (3)	1.976 (3)	C(5)–C(6)	1.445 (4)	1.439 (4)
Co–C(7)	1.986 (3)	1.992 (3)	C(5)–C(29)	1.499 (5)	1.516 (4)
Co–C(8)	2.109 (3)	2.083 (3)	C(6)–C(7)	1.440 (4)	1.454 (4)
Co–C(35)	2.062 (4)	2.055 (4)	C(6)–C(23)	1.501 (4)	1.487 (5)
Co–C(36)	2.074 (4)	2.058 (4)	C(7)–C(8)	1.447 (4)	1.456 (4)
Co–C(37)	2.117 (4)	2.115 (4)	C(7)–C(17)	1.495 (4)	1.494 (4)
Co–C(38)	2.105 (4)	2.107 (4)	C(8a)–C(8)	1.537 (4)	1.521 (4)
Co–C(39)	2.073 (4)	2.057 (4)	C(8a)–C(9)	1.553 (5)	1.552 (4)
C(1)–C(2)	1.389 (6)	1.389 (6)	C(8)–C(11)	1.496 (5)	1.507 (4)
C(1)–C(9a)	1.519 (6)	1.523 (5)	C(9a)–C(9)	1.562 (5)	1.556 (5)
C(2)–C(3)	1.388 (6)	1.422 (6)	C(9)–C(10)	1.530 (5)	1.530 (5)
C(3a)–C(3)	1.516 (6)	1.522 (5)	C–C(Ph)	1.38 (1)[a]	1.385 (9)[a]
C(3a)–C(4)	1.547 (5)	1.530 (5)	C–C(Cp)	1.40 (2)[a]	1.41 (1)[a]
C(3a)–C(9a)	1.556 (5)	1.564 (5)	Cent–Co[b]	1.71	1.70
C(4a)–C(5)	1.539 (4)	1.511 (4)	M(56)–Co	1.87	1.88
C(4a)–C(4)	1.547 (4)	1.563 (4)	M(78)–Co	1.92	1.90
C(4a)–C(8a)	1.539 (4)	1.538 (4)			
		Bond Angles			
C(2)–C(1)–C(9a)	109.3 (4)	109.6 (4)	C(8a)–C(8)–C(11)	114.2 (3)	115.1 (3)
C(1)–C(2)–C(3)	112.2 (4)	113.1 (4)	C(1)–C(9a)–C(3a)	104.3 (3)	103.9 (3)
C(3)–C(3a)–C(4)	117.8 (3)	117.8 (3)	C(1)–C(9a)–C(9)	119.8 (3)	119.4 (3)
C(3)–C(3a)–C(9a)	104.1 (3)	105.7 (3)	C(3a)–C(9a)–C(9)	101.6 (3)	103.4 (3)
C(4)–C(3a)–C(9a)	104.1 (3)	101.9 (3)	C(8a)–C(9)–C(9a)	107.4 (3)	109.9 (3)
C(2)–C(3)–C(3a)	109.7 (4)	107.4 (3)	C(8a)–C(9)–C(10)	103.1 (3)	101.8 (3)
C(4)–C(4a)–C(5)	116.2 (3)	113.5 (3)	C(9a)–C(9)–C(10)	100.9 (3)	100.5 (3)
C(4)–C(4a)–C(8a)	103.6 (3)	104.2 (3)	C(4)–C(10)–C(9)	94.8 (3)	94.4 (3)
C(5)–C(4a)–C(8a)	111.1 (3)	112.3 (3)	C(8)–C(11)–C(12)	120.9 (3)	120.6 (3)
C(3a)–C(4)–C(10)	100.8 (3)	109.2 (3)	C(8)–C(11)–C(16)	123.1 (3)	123.1 (3)
C(4a)–C(4)–C(10)	101.2 (3)	100.2 (3)	C(7)–C(17)–C(18)	119.6 (3)	118.8 (3)
C(3a)–C(4)–C(4a)	109.2 (3)	102.6 (3)	C(7)–C(17)–C(22)	122.4 (3)	122.7 (3)
C(4a)–C(5)–C(6)	114.3 (3)	119.8 (3)	C(6)–C(23)–C(24)	123.1 (3)	119.4 (3)
C(4a)–C(5)–C(29)	110.9 (3)	109.1 (3)	C(6)–C(23)–C(28)	118.4 (3)	122.3 (3)
C(6)–C(5)–C(29)	120.7 (3)	122.2 (3)	C(5)–C(29)–C(30)	122.7 (3)	123.1 (3)
C(5)–C(6)–C(7)	114.9 (3)	113.5 (3)	C(5)–C(29)–C(34)	119.2 (3)	118.2 (3)
C(5)–C(6)–C(23)	122.2 (3)	123.6 (3)	C–C–C(Ph)	120 (2)[a]	120 (1)[a]
C(7)–C(6)–C(23)	122.7 (3)	122.8 (3)	C–C–C(Cp)	108.0 (7)[a]	108.0 (8)[a]
C(6)–C(7)–C(8)	115.3 (3)	115.5 (3)	Cent–Co–C(5)[b]	136.5	136.0
C(6)–C(7)–C(17)	121.5 (3)	121.0 (3)	Cent–Co–C(6)	145.5	148.8
C(8)–C(7)–C(17)	123.2 (3)	123.5 (3)	Cent–Co–C(7)	146.4	149.2
C(4a)–C(8a)–C(8)	111.6 (3)	110.8 (3)	Cent–Co–C(8)	138.0	135.1
C(4a)–C(8a)–C(9)	102.7 (3)	101.8 (2)	Cent–Co–M(56)	146.0	147.3
C(8)–C(8a)–C(9)	118.5 (3)	115.8 (3)	Cent–Co–M(78)	147.2	146.8
C(7)–C(8)–C(8a)	116.6 (3)	120.5 (3)	M(56)–Co–M(78)	65.6	65.8
C(7)–C(8)–C(11)	118.9 (3)	120.0 (3)			

[a] average value. [b] Cent is the centroid of the cyclopentadienyl ring. M(56) and M(78) are the midpoints of the double bonds C(5)–C(6) and C(7)–C(8), respectively.

diene ligands of 1 and 2 are both coordinated in an η^4-fashion to the CpCo fragments. The average Co–C distances to the terminal carbon atoms (C(5), C(8)) are 2.08 (3) and 2.07 (2) Å, whereas those to the internal carbon atoms (C(6), C(7)) are 1.97 (1) and 1.984 (8) Å for compounds 1 and 2, respectively. The three bond lengths of the diene skeleton in 1, C(5)–C(6) (1.445 (4) Å), C(6)–C(7) (1.440 (4) Å), and C(7)–C(8) (1.447 (4) Å), are essentially equal within experimental error. In 2 a small variation in the lengths of the diene skeleton, C(5)–C(6) (1.439 (4) Å), C(6)–C(7) (1.454 (4) Å), and C(7)–C(8) (1.456 (4) Å), is observed. These Co–C(η^4-diene) and diene skeletal C–C bond distances found in compounds 1 and 2 are similar to those found in other CpCo(η^4-diene) complexes.[21]

Another important structural feature of transition-metal diene complexes is the bent angle, which for compounds 1 and 2, is defined by the angle between the C(5)–Co–C(8) and C(5)–C(6)–C(7)–C(8) planes. Generally, the bent angles for low-valent late-transition-metal (Fe, Co, Rh) η^4-diene complexes lie between 70 and 85°, whereas for high-valent early-transition-metal (Zr, Hf, Ta) η^4-diene complexes, they lie between 95 and 130°.[22-24] The bent angles for compounds 1 and 2 are 77.5° and 78.4°, respectively. The carbons of the phenyl substituents (C(17), C(23)), which are directly bonded to the internal carbons of the diene skeleton, lie in the diene plane (C(5)–C(6)–C(7)–C(8)) to within 0.12 Å for 1 and to within 0.07 Å for 2. On the other hand, the carbons of the phenyl substituents (C(11), C(29)), which are directly bonded to the terminal carbons of the diene skeleton (C(5), C(8)), bend out of the diene plane by 0.21 Å for 1 and 0.38 Å for 2 in the direction of the CpCo fragments. Similar deviations from planarity of the terminal substituents have been noted in other CpCo(η^4-diene) complexes, and several factors have been proposed to explain this observation.[21] With respect to the diene plane, the phenyl groups of the

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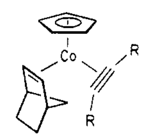
diene skeleton are twisted about their bonds to C(5), C(6), C(7), and C(8) at angles of 53°, 50°, 64°, 56°, respectively, for compound 1 and 41°, 48°, 66°, 36°, respectively, for compound 2, giving a "propeller" configuration (Figure 4). This is probably a consequence of intramolecular steric interactions and has been observed in other CpCo systems with π-coordinated ligands containing four aromatic groups.[18,25]

As previously mentioned, the carbons of the "outer" substituents (C(11), C(29)), which are directly bonded to the terminal carbons of the diene skeleton are bent toward the CpCo fragment in both compounds 1 and 2. This results in the carbons of the "inner" substituents (C(4a), C(8a)) being directed away from the CpCo fragments. As a consequence of this, two key structural differences arise between isomers 1 and 2 upon π-coordination of a CpCo fragment to the diene ligand 4. The most obvious difference between compounds 1 and 2 is that the CpCo fragment is coordinated to different sides of the diene ligand. Secondly, upon changing from isomer 1 to isomer 2, C(5) and C(8) invert their configurations. This results in a change in the angle between the C(5)–C(6)–C(7)–C(8) and C(4)–C(4a)–C(8a)–C(9) planes. For compound 1 this angle is 171° whereas in compound 2 the angle is 95.8°. The angles about these two "hingelike" carbons (C(5), C(8)) are smaller for 1 than for 2. For compound 1, C(4a)–C(5)–C(6) is 114.3 (3)° and C(7)–C(8)–C(8a) is 116.6 (3)° whereas for 2, C(4a)–C(5)–C(6) is 119.8 (3)° and C(7)–C(8)–C(8a) is 120.5 (3)°.

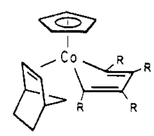
The norbornane systems in compounds 1 and 2 are as usual, very strained, bond angles being strongly distorted (94.3 (3)–118.5 (3)° at sp^3-hybridized carbons). The C(4a)–C(4) and C(8a)–C(9) bonds in 1 are longer by 0.012 and 0.018 Å (i.e. by 3σ and 4σ) than the standard C(sp^3)–C(sp^3) single bond distance of 1.535 Å.[26] Likewise, the C(4a)–C(4) and C(8a)–C(9) bonds in 2 are longer by 0.028 and 0.017 Å (i.e. by 7σ and 4σ).

3. Mechanistic Considerations. There are several possible intermediates that could account for the observed products **1–3**, **6**, **7**, **10**, **11**, **14**, and **15**. Among the proposed intermediates for the CpCo-mediated cyclization of two alkynes and one alkene are bis(alkyne) (CpCo(RC$\equiv$CR)$_2$) or alkyne–alkene (**17**) complexes which could lead to metallacyclopentadiene (**18**)[13c,27,28] or metallacyclopentene (**19**)[13d] complexes, respectively. Complexes **18** or **19** could in turn be transformed into metallacycloheptadiene intermediates (**20**).[7a,c,d,13c,d,27] Reductive elimination in **20** would then produce the observed CpCo(η^4-1,3-cyclohexadiene) complexes. The observed products **1**, **3**, **6**, **7**, **11**, **14**, and **15** could also form by a Diels–Alder type cycloaddition involving an alkene-coordinated metallacyclopentadiene complex **18**.[13c] The cyclobutadiene complex **3** most likely is formed in eq 3 and 4 by the reductive elimination of a tetraphenylmetallacyclopentadiene intermediate.[29]

A probable explanation for the formation of only the isomer that has the exo stereochemistry at the C(4a)–C(8a) ring juncture in **1**, **2**, **6**, **7**, **10**, **11**, **14**, and **15** is the stereospecific exo coordination of the bicyclic alkenes (norbornylene or dicyclopentadiene). If exo coordination is assumed favored on steric grounds, then either of two structures **17** or **18** could be possible intermediates. This same mode of bonding was observed in the solid-state structure of (η^5-C_5H_5)Mn(CO)$_2$(η^2-norbornadiene).[14] Oxidative coupling in **17** and coordination of another alkyne molecule would lead to metallacyclopentene complexes (**19**),[13d] whereas insertion into the Co–C(vinylic) bond of **18** would produce metallacycloheptadiene complexes **20**.



17



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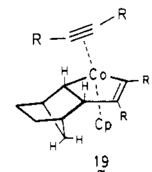

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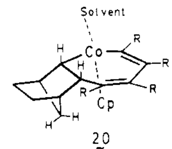

20

This latter transformation has been proposed to occur in a catalytic process involving a palladiacyclopentene complex, dimethyl acetylenedicarboxylate, and norbornylene.[5] It was reported[5] that this reaction led to the formation of **13** and is significant in that this compound possessed the same stereochemistry at the C(4a)–C(8a) bond as **13** isolated by us from the oxidation of **10** or **11**.

It is clear from the above spectroscopic and kinetic results that the isomerization of **1** to **2** (as well as **6** to **7**, **10** to **11**, and **14** to **15**) occurs by an intramolecular process. Two possible mechanisms include (1) oxidative addition[30] into the carbon–carbon single bonds of the coordinated 1,3-cyclohexadiene ligand or (2) a *retro*-Diels–Alder reaction. Oxidative addition into the C(4a)–C(5) or C(8)–C(8a) bonds in **1** would result in the formation of metallacycloheptadiene derivatives **20**, whereas oxidative addition into the C(6)–C(7) bond of **1** would yield an unconjugated metallacycloheptadiene isomer of **20**. Either metallacycloheptadiene complex could undergo inversion at cobalt[13d,31] followed by reductive elimination to produce complex **2**. The *retro*-Diels–Alder scheme would yield complexes having structures **18** in which the appended alkene could rotate and re-add to yield **1** or **2**. The driving force for the isomerization of **1** to **2** is not presently known, but, no doubt, intramolecular steric interactions in **1** are responsible.

Experimental Section

General Data. All reactions were carried out under an inert nitrogen atmosphere. Toluene, xylene, hexane, and methylene chloride were distilled from CaH_2 under nitrogen. Diphenylacetylene, dimethyl acetylenedicarboxylate, and norbornylene were purchased from Aldrich Chemical Co. and used without further purification. *endo*-Dicyclopentadiene was obtained from Wiley Organics and used without further purification. Literature procedures were employed to synthesize CpCo(CO)$_2$,[32] CpCo(C_2H_4)$_2$,[33] and (η^5-$C_5H_4CH_3$)Co(CO)$_2$.[34] Flash chromatography[35]

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Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	1	2
color/shape	red/parallelepiped	red/plate
mol wt	612.7	612.7
space group	$P\bar{1}$	$P\bar{1}$
temp, °C	20	20
cell const[a]		
a, Å	10.943 (2)	10.752 (1)
b, Å	11.439 (1)	12.640 (3)
c, Å	14.954 (6)	13.754 (3)
α, deg	71.94 (3)	69.89 (2)
β, deg	87.00 (3)	66.83 (1)
γ, deg	62.27 (1)	68.38 (1)
cell vol, Å^3	1563.5	1553.7
formula units/unit cell	2	2
D(calcd), g cm^{-3}	1.30	1.31
μ(calcd), cm^{-1}	6.03	5.35
diffractometer/scan	Enraf-Nonius CAD4/θ–2θ	
radiatn, graphite monochromator	Mo Kα (λ = 0.71073 Å)	
max cryst dimens, mm	0.38 × 0.80 × 0.80	0.10 × 0.25 × 0.35
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
std reflctns	500, 080, 007	200, 040, 006
decay of stds	±2%	±2%
reflcts measd	5840	5428
2θ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
range of h,k,l	+13,±13,±17	+12,±15,±16
reflctns obsd $[F_o \geq 5\sigma(F_o)]$[b]	4605	3530
computer programs[c]	SHELX[38]	
structure soln	heavy-atom techniques	
no. of parameters varied	397	397
weights	unit	$[\sigma(F_o)^2 + 0.000\,04F_o^2]^{-1}$
GOF	0.99	0.71
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.041	0.041
R_w	0.050	0.041
largest feature final diff map, e/Å^3	0.3	0.2

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 16°$ (1) and 20° (2). [b] Corrections: Lorentz and polarization. [c] Neutral atom scattering factors and anomalous dispersion corrections from ref 39.

was carried out by using activated alumina (neutral, 60 mesh) obtained from Alfa Products. Preparative thin-layer chromatography was carried out on 20 × 20 × (2.5 × 10^{-2}) cm precoated silica gel (pore diameter 60 Å) plates obtained from Aldrich Chemical Co.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-400 instrument at 400.1 and 100.6 MHz, respectively. ^{1}H NMR data are reported as follows: chemical shift in parts per million referenced to residual solvent proton resonance or TMS (multiplicity, coupling constant(s) in hertz, number of protons). ^{13}C NMR data are reported as follows: chemical shift in parts per million referenced to residual solvent carbon resonance. Low-resolution mass spectra were acquired on a Finnigan 4000 instrument, and spectral data are listed as m/e (intensity as percent of base peak). High-resolution mass spectra were obtained at the Midwest Center for Mass Spectroscopy, Department of Chemistry, University of Nebraska. Elemental analyses were performed by Microlytics, South Deerfield, MA. Two-dimensional proton J-correlated NMR experiments (COSY-90)[36] were performed in CDCl$_3$ solutions by using Bruker's software package and pulse sequence program. Quadrature detection was used in each case, and 16 1K transients were collected for each of the 256 incremental spectra.

Table III. Final Fractional Coordinates for Compound 1

atom	x/a	y/b	z/c
Co	0.26837 (5)	0.17779 (5)	0.17075 (3)
C(1)	0.8584 (4)	0.0390 (4)	0.2453 (4)
C(2)	0.8326 (4)	0.1152 (5)	0.3068 (3)
C(3a)	0.6880 (4)	0.2801 (4)	0.1646 (3)
C(3)	0.7408 (4)	0.2559 (5)	0.2639 (3)
C(4a)	0.4879 (3)	0.2389 (3)	0.2272 (2)
C(4)	0.5322 (4)	0.3265 (4)	0.1441 (3)
C(5)	0.3311 (3)	0.2867 (3)	0.2264 (2)
C(6)	0.2962 (3)	0.1892 (3)	0.2954 (2)
C(7)	0.3732 (3)	0.0467 (3)	0.2962 (2)
C(8a)	0.5680 (3)	0.0905 (3)	0.2209 (2)
C(8)	0.4732 (3)	0.0231 (3)	0.2280 (2)
C(9a)	0.7642 (4)	0.1329 (4)	0.1531 (3)
C(9)	0.6394 (4)	0.1128 (4)	0.1291 (3)
C(10)	0.5376 (4)	0.2617 (4)	0.0683 (3)
C(11)	0.5418 (4)	−0.1163 (4)	0.2134 (2)
C(12)	0.6864 (4)	−0.1909 (4)	0.2173 (3)
C(13)	0.7516 (5)	−0.3206 (4)	0.2070 (3)
C(14)	0.6770 (6)	−0.3847 (5)	0.1954 (3)
C(15)	0.5345 (6)	−0.3163 (5)	0.1944 (3)
C(16)	0.4689 (5)	−0.1855 (4)	0.2033 (3)
C(17)	0.3503 (4)	−0.0670 (4)	0.3639 (2)
C(18)	0.4623 (4)	−0.1873 (4)	0.4192 (3)
C(19)	0.4446 (5)	−0.2948 (4)	0.4832 (3)
C(20)	0.3130 (5)	−0.2818 (5)	0.4928 (3)
C(21)	0.2005 (5)	−0.1616 (5)	0.4394 (3)
C(22)	0.2176 (4)	−0.0551 (4)	0.3760 (3)
C(23)	0.1975 (3)	0.2310 (3)	0.3667 (2)
C(24)	0.0588 (4)	0.3306 (4)	0.3416 (3)
C(25)	−0.0238 (4)	0.3776 (5)	0.4092 (3)
C(26)	0.0305 (5)	0.3268 (5)	0.5019 (3)
C(27)	0.1678 (5)	0.2253 (5)	0.5276 (3)
C(28)	0.2499 (4)	0.1778 (4)	0.4609 (3)
C(29)	0.2507 (4)	0.4403 (4)	0.2115 (3)
C(30)	0.1886 (4)	0.5391 (4)	0.1234 (3)
C(31)	0.1265 (5)	0.6797 (5)	0.1095 (4)
C(32)	0.1277 (6)	0.7267 (5)	0.1832 (5)
C(33)	0.1907 (6)	0.6311 (6)	0.2709 (4)
C(34)	0.2525 (5)	0.4884 (5)	0.2858 (3)
C(35)	0.1906 (5)	0.2903 (5)	0.0305 (3)
C(36)	0.0829 (4)	0.3311 (5)	0.0887 (3)
C(37)	0.0658 (5)	0.2140 (5)	0.1364 (3)
C(38)	0.1612 (6)	0.1032 (6)	0.1108 (3)
C(39)	0.2411 (5)	0.1497 (6)	0.0443 (3)

X-ray Data Collection, Structure Determination, and Refinement for Compounds 1 and 2. Red single crystals of the title compounds were mounted on pins and transferred to the goniomenter. The space group for each was determined to be either the centric P$\bar{1}$ or acentric P1. Statistical tests indicated that the space groups were centric, and the subsequent solution and successful refinement of the structures in the space group P$\bar{1}$ confirmed this. A summary of data collection parameters is given in Table II.

After least-squares refinement with isotropic thermal parameters, most of the hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Hydrogen atom positions for C(1), C(2), and C(3) were located from a difference Fourier. Two hydrogen positions were located for both C(1) and C(3), and these were considered to be disordered as a result of a 50/50 mix of the two isomers in the centrosymmetric P$\bar{1}$. These positions refined satisfactorily for several cycles in 1 and were fixed for 2. The disorder model is supported by the equivalence of the C(1)–C(2) and C(2)–C(3) bond distances in 1 (1.389 (6) and 1.388 (6) Å, respectively) and near equivalence in 2 (1.389 (6) and 1.422 (6) Å). Refinement of the non-hydrogen atoms with anisotropic temperature factors led to the final values of R given in Table II. The final values of the positional parameters are given in Table III for 1 and Table IV for 2.

(5,6,7,8-η^4-5,6,7,8-Tetraphenyl-3a,4,4a,8a,9,9a-*exo*-hexahydro-4,9-methano-1*H*-benz[*f*]indene)(η^5-cyclopentadienyl)cobalt (1) and (5,6,7,8-η^4-5,6,7,8-Tetraphenyl-3a,4,4a,8a,9,9a-*endo*-hexahydro-4,9-methano-1*H*-benz[*f*]indene)(η^5-cyclopentadienyl)cobalt (2). In a 50-mL Schlenk tube under nitrogen atmosphere were placed a mixture of diphenylacetylene (310.0 mg, 1.74 mmol), CpCo(CO)$_2$ (144.0 mg,

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Table IV. Final Fractional Coordinates for Compound 2

atom	x/a	y/b	z/c
Co	0.19651 (5)	0.25771 (4)	0.11082 (4)
C(1)	−0.2977 (5)	0.5587 (4)	0.3287 (3)
C(2)	−0.2201 (5)	0.6270 (4)	0.3264 (4)
C(3a)	−0.1581 (4)	0.4486 (3)	0.4521 (3)
C(3)	−0.1398 (4)	0.5716 (4)	0.4002 (4)
C(4a)	0.0261 (3)	0.3720 (3)	0.2914 (3)
C(4)	−0.0333 (4)	0.3459 (3)	0.4182 (3)
C(5)	0.1743 (3)	0.2988 (3)	0.2498 (3)
C(6)	0.2005 (3)	0.1757 (3)	0.2609 (3)
C(7)	0.0987 (3)	0.1483 (3)	0.2350 (3)
C(8a)	−0.0792 (3)	0.3489 (3)	0.2565 (3)
C(8)	−0.0087 (3)	0.2485 (3)	0.1994 (3)
C(9a)	−0.2686 (4)	0.4413 (3)	0.4088 (3)
C(9)	−0.1961 (4)	0.3274 (3)	0.3662 (3)
C(10)	−0.1101 (4)	0.2543 (3)	0.4446 (3)
C(11)	−0.0927 (3)	0.2354 (3)	0.1406 (3)
C(12)	−0.2288 (4)	0.3047 (3)	0.1487 (3)
C(13)	−0.3077 (4)	0.2971 (4)	0.0936 (3)
C(14)	−0.2517 (4)	0.2192 (4)	0.0277 (3)
C(15)	−0.1155 (4)	0.1480 (3)	0.0178 (3)
C(16)	−0.0392 (4)	0.1559 (3)	0.0744 (3)
C(17)	0.1051 (4)	0.0245 (3)	0.2473 (3)
C(18)	−0.0171 (4)	−0.0125 (3)	0.3039 (3)
C(19)	−0.0135 (5)	−0.1277 (4)	0.3181 (3)
C(20)	0.1097 (5)	−0.2062 (4)	0.2778 (3)
C(21)	0.2322 (4)	−0.1714 (3)	0.2236 (3)
C(22)	0.2298 (4)	−0.0576 (3)	0.2076 (3)
C(23)	0.3161 (4)	0.0842 (3)	0.3000 (3)
C(24)	0.2839 (4)	0.0082 (3)	0.4009 (3)
C(25)	0.3886 (5)	−0.0717 (4)	0.4433 (4)
C(26)	0.5279 (5)	−0.0779 (4)	0.3865 (4)
C(27)	0.5613 (4)	−0.0036 (4)	0.2859 (4)
C(28)	0.4570 (4)	0.0770 (3)	0.2423 (3)
C(29)	0.2759 (3)	0.3479 (3)	0.2608 (3)
C(30)	0.3368 (4)	0.2290 (4)	0.3441 (3)
C(31)	0.4130 (4)	0.3574 (4)	0.3591 (4)
C(32)	0.4296 (4)	0.4637 (4)	0.2918 (4)
C(33)	0.3695 (4)	0.5138 (4)	0.2086 (4)
C(34)	0.2934 (4)	0.4568 (3)	0.1933 (3)
C(35)	0.2328 (5)	0.3958 (4)	−0.0200 (3)
C(36)	0.3617 (4)	0.3230 (4)	0.0007 (3)
C(37)	0.3852 (4)	0.2114 (4)	−0.0138 (3)
C(38)	0.2721 (5)	0.2142 (4)	−0.0408 (3)
C(39)	0.1774 (5)	0.3263 (4)	−0.0432 (3)

0.79 mmol), *endo*-dicyclopentadiene (0.48 mL, 3.95 mmol), and 3 mL of toluene. The solution was refluxed for 66 h, and the solvent was then removed under high vacuum. The resulting red solid residue was then chromatographed on alumina (30 g). Eluting the column with hexane produced a yellow band. Removal of the solvent from this band afforded 12.0 mg of complex **3** as a yellow solid. Further elution of the column with 10% CH$_2$Cl$_2$/hexane produced a red band that was collected, and the solvent was removed under vacuum to afford 0.46 g of a dark red solid. ^{1}H NMR spectroscopy showed this solid to be a mixture containing compounds **1** (67%), **2** (27%), and **3** (6%). Compound **3** exhibited a single resonance for the cyclopentadienyl protons at δ 4.64 in CDCl$_3$.[32] Preparative TLC (silica gel, 5% CH$_2$Cl$_2$/hexane, ten developments) using 20.0 mg of the above mixture gave 11.9 mg (60% recovery) of **1**. Crystallization from 5% methylene chloride/hexane gave **1**: dark red cubes; mp 232–233 °C; ^{1}H NMR (CDCl$_3$) δ 1.17 (br s, 3 H), 2.09 (m, 2 H), 2.23 (d, J = 4.0, 1 H), 2.32 (d, J = 4.5, 1 H), 2.45 (m, 1 H), 2.98 (m, 1 H), 4.28 (d, J = 9.7, 1 H), 5.02 (s, 5 H), 5.48 (dd, J = 5.6, 1.9, 1 H), 5.65 (dd, J = 5.6, 1.9, 1 H), 6.65–7.12 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ 31.52, 36.76, 43.00, 43.72, 44.20, 44.61, 46.59, 54.30, 71.44, 71.84, 85.22 (Cp), 95.15, 124.61, 125.39, 126.53, 126.57, 131.01, 131.12, 131.78, 131.87, 132.50, 139.57, 139.65, 145.84, 146.11; MS (35 eV), m/e 613 (M$^+$ + 1, 21%), 612 (M$^+$, 48), 548 (14), 547 (37), 546 (10), 545 (30), 480 (30), 479 (84), 442 (12), 441 (39), 306 (17), 202 (14), 124 (12), 84 (16), 75 (23), 67 (28), 58 (80), 57 (100); HRMS calcd for C$_{43}$H$_{37}$Co 612.2227, found 612.2206. Anal. Calcd for C$_{43}$H$_{37}$Co: C, 84.29; H, 6.08. Found: C, 84.16; H, 6.06. Besides **1**, 3.0 mg of compound **4** and 1.2 mg of compound **3** were isolated from this preparative TLC.

Compound **2** was obtained by a thermal isomerization of **1** in the following manner. A solution of 3 mL of xylene containing 0.30 g of the dark red solid, obtained after column chromatography on alumina, was refluxed for 48 h under a nitrogen atmosphere. The solvent was then removed under high vacuum to afford a dark red solid residue that was dissolved in 10 mL of hexane and filtered through a small layer of Celite. Cooling this solution to 0 °C produced **2**: dark red cubes; mp 229–230 °C; ^{1}H NMR (CDCl$_3$) δ 0.89 (d, J = 9.5, 1 H), 1.63 (d, J = 9.7, 1 H), 1.91 (d, J = 4.2, 1 H), 2.16 (m, 2 H), 2.21 (m, 1 H), 2.35 (m, 1 H), 2.55 (d, J = 9.5, 1 H), 2.68 (d, J = 9.6, 1 H), 2.93 (m, 1 H), 4.56 (s, 5 H), 5.66 (dd, J = 5.6, 1.9, 1 H), 5.82 (dd, J = 5.7, 1.9, 1 H), 6.86–7.48 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ 32.16, 35.29, 41.77, 43.69, 44.51, 47.32, 48.57, 53.17, 67.19, 68.56, 84.85 (Cp), 96.44, 96.70, 123.76, 123.98, 125.92, 126.65, 127.03, 129.70, 130.29, 131.07, 131.27, 131.56, 131.83, 133.96, 134.18, 139.92, 146.04, 146.50; MS (70 eV), m/e 613 (M$^+$ + 1, 18%), 612 (M$^+$, 35), 547 (13), 545 (10), 479 (19), 441 (10), 124 (9), 84 (10), 57 (13), 55 (15), 44 (100); HRMS calcd for C$_{43}$H$_{37}$Co 612.2227, found 612.2220. Anal. Calcd for C$_{43}$H$_{37}$Co: C, 84.29; H, 6.08. Found: C, 84.25; H, 6.11.

The above reaction was repeated on the same scale but with xylene as the solvent. The reaction mixture was refluxed under a nitrogen atmosphere for 48 h. The solvent was removed under vacuum and the resulting residue chromatographed on alumina to afford 0.45 g of a dark red solid. ^{1}H NMR analysis of this solid indicated the presence of the following compounds: **1** (11%), **2** (78%), **3** (11%).

5,6,7,8-Tetraphenyl-3a,4,4a,8a,9,9a-hexahydro-4,9-methano-1*H*-benz[*f*]indene (4). To a solution of either complex **1** or **2** (15.0 mg, 0.024 mmol) in 5 mL of acetonitrile cooled to 0 °C was added a solution of CuCl$_2$·2H$_2$O (41.0 mg, 0.24 mmol) and triethylamine (0.015 mL) in 1 mL of acetonitrile. After 30 min of stirring at 0 °C, 6 mL of water was added and the resulting solution extracted three times with 10-mL portions of hexane. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. Evaporation of the majority of the solvent was followed by filtration of the organic fraction through 5 g of alumina with methylene chloride/hexane (1:1) as eluent. Finally, removal of the solvent under vacuum gave white crystals of **4** (4.4 mg, 37% yield from **1**; 8.4 mg, 70% yield from **2**). The crystals obtained from the oxidation of **1** or **2** had identical melting points (225–227 °C) and ^{1}H NMR and ^{13}C NMR spectra: ^{1}H NMR (CDCl$_3$) δ 1.48 (d, J = 9.5, 1 H), 2.03–2.21 (m, 3 H), 2.33 (d, J = 4.6, 1 H), 2.39 (d, J = 9.4, 1 H), 2.45 (m, 1 H), 3.02 (m, 1 H), 3.05 (d, J = 12.4, 1 H), 3.21 (d, J = 12.5, 1 H), 5.50 (dd, J = 5.6, 2.1, 1 H), 5.74 (dd, J = 5.7, 2.1, 1 H), 6.39–7.12 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ 32.82, 37.01, 41.16, 43.31, 44.52, 47.48, 49.63, 53.48, 124.87, 125.56, 127.34, 129.16, 129.31, 130.97, 132.88, 135.68, 135.72, 136.10, 140.57, 140.62, 142.56, 142.92; MS (70 eV), m/e 489 (M$^+$ + 1, 22%), 488 (M$^+$, 100), 421 (45), 420 (100), 382 (19), 372 (17), 302 (17), 289 (20), 265 (15), 161 (15), 133 (20), 105 (34), 91 (31), 77 (26), 67 (53), 66 (13), 58 (17), 41 (16); HRMS calcd for C$_{38}$H$_{32}$ 488.2504, found 488.2504.

5,6,7,8-Tetraphenyl-3a,4,9,9a-tetrahydro-4,9-methano-1*H*-benz[*f*]indene (5). Complex **4** (30.0 mg, 0.061 mmol) was dissolved in methylene chloride (5 mL) and cooled to 0 °C. One portion of ceric ammonium nitrate (65.0 mg, 0.12 mmol) was added with stirring, followed by a second portion (19.0 mg, 0.035 mmol) 20 min later. The solution was stirred for an additional 30 min, the solvent removed under vacuum, and the residue chromatographed on silica gel. Eluting the column with 10% methylene chloride/hexane and removal of the solvent under vacuum gave 10.0 mg (33%) of **5**: mp 188–189 °C; ^{1}H NMR (CDCl$_3$) δ 1.67 (m, 1 H), 1.73 (d, J = 8.6, 1 H), 2.07 (m, 1 H), 2.12 (d, J = 8.6, 1 H), 2.88 (m, 1 H), 3.35 (dd, J = 4.6, 1.4, 1 H), 3.38 (m, 1 H), 3.45 (d, J = 4.4), 5.35 (dd, J = 5.7, 1.8, 1 H), 5.45 (dd, J = 5.6, 2.2, 1 H), 6.66–7.26 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ 34.11, 41.77, 47.10, 47.24, 50.83, 54.45, 124.94, 125.74, 126.20, 126.50, 127.14, 127.33, 130.40, 130.83, 131.30, 131.45, 131.69, 132.16, 132.24, 135.26, 135.88, 137.59, 137.79, 140.21, 140.35, 140.83, 142.90, 144.38; MS, m/e 487 (M$^+$ + 1, 6%), 486 (M$^+$, 15), 421 (44), 420 (100), 343 (17), 265 (22), 165 (13), 91 (10); HRMS calcd for C$_{38}$H$_{30}$ 486.2347, found 486.2339.

In another experiment a mixture of compounds **1** (ca. 70%) and **2** (ca. 30%) (0.05 g, 0.08 mmol), obtained as described above, was dissolved in acetone (5 mL) and cooled to 0 °C. One portion of ceric ammonium nitrate (80.0 mg, 0.15 mmol) was added with stirring followed by a second portion (32.4 mg, 0.06 mmol) 20 min later. The solution was stirred for an additional 30 min, the solvent removed under vacuum, and the resulting residue chromatographed on silica gel. Eluting the column with 10% methylene chloride/hexane produced 24.0 mg (60%) of **5** as white crystals.

(5,6,7,8-η^4-5,6,7,8-Tetraphenyl-1,2,3,4,4a,8a-*exo*-hexahydro-1,4-methanonaphthalene)(η^5-cyclopentadienyl)cobalt (6) and (5,6,7,8-η^4-5,6,7,8-Tetraphenyl-1,2,3,4,4a,8a-*endo*-hexahydro-1,4-methanonaphthalene)(η^5-cyclopentadienyl)cobalt (7). In a 50-mL Schlenk tube were placed diphenylacetylene (310.0 mg, 1.74 mmol), $CpCo(CO)_2$ (144.0 mg, 0.79 mmol), norbornylene (372.0 mg, 3.95 mmol), and 3 mL of toluene. The reaction mixture was then refluxed under a nitrogen atmosphere for 69 h. The solvent was removed under high vacuum and the resulting dark red residue chromatographed on alumina (30 g). Eluting the column with 10% methylene chloride/hexane produced a red band that was collected and the solvent removed under vacuum to afford 0.44 g of a dark red solid. ^{1}H NMR spectroscopy showed this solid to be a mixture containing compounds **6** (63%), **7** (25%), and **3** (12%). Preparative thin-layer chromatography (silica gel, 5% methylene chloride/hexane, ten developments) using 20.0 mg of the above mixture afforded 11.3 mg (56% recovery) of **6**. Crystallization from 5% methylene chloride/hexane gave **6**: dark red cubes; mp 296–298 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (d, J = 9.0, 1 H), 1.04 (d, J = 7.3, 1 H), 1.12 (s, 2 H), 1.42 (d, J = 7.6, 2 H), 2.18 (s, 2 H), 3.98 (d, J = 9.0, 1 H), 4.99 (s, 5 H), 6.67–7.11 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 30.08, 32.74, 40.50, 51.62, 70.89, 85.23 (Cp), 95.08, 124.56, 125.43, 126.47, 126.55, 131.01, 139.57, 145.92; MS (70 eV), *m/e* 575 (M^+ + 1, 41%), 574 (M^+, 100), 510 (15), 509 (41), 508 (38), 507 (92), 478 (13), 450 (5), 442 (30), 441 (93), 365 (18), 302 (20), 289 (15), 220 (16), 124 (62); HRMS calcd for $C_{40}H_{35}Co$ 574.2071, found 574.2080. Anal. Calcd for $C_{40}H_{35}Co$: C, 83.60; H, 6.14. Found: C, 83.54; H, 5.97. Besides **6**, 2.8 mg of the organic compound **8** and 1.1 mg of the cyclobutadiene compound **3** were isolated from this preparative TLC.

Compound **7** was obtained by a thermal isomerization of **6** in the following manner. A solution of 2 mL of xylene containing 0.20 g of the dark red solid, obtained after column chromatography on alumina, was refluxed for 48 h under a nitrogen atmosphere. The solvent was then removed under high vacuum to afford a dark red solid residue that was dissolved in 10 mL of hexane and filtered through a small layer of Celite. Cooling this solution to 0 °C produced **7**: dark red cubes; mp 289–290 °C; ^{1}H NMR ($CDCl_3$) δ 0.66 (d, J = 10.0, 1 H), 1.14 (d, J = 7.4, 2 H), 1.37 (d, J = 7.6, 2 H), 1.45 (d, J = 9.9, 1 H), 2.00 (s, 2 H), 2.59 (s, 2 H), 4.59 (s, 5 H), 6.68–7.42 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 29.15, 31.81, 40.42, 55.04, 67.78, 84.78 (Cp), 96.25, 123.95, 125.93, 126.68, 126.90, 127.05, 130.08, 131.23, 134.08, 139.78, 146.24; MS (70 eV), *m/e* 575 (M^+ + 1, 47%), 574 (M^+, 100) 510 (11), 509 (36), 508 (34), 507 (84), 479 (9), 450 (4), 442 (14), 441 (47), 253 (41), 220 (22), 124 (32), 86 (56), 49 (95), 44 (84). Anal. Calcd for $C_{40}H_{35}Co$: C, 83.60; H, 6.14. Found: C, 83.89; H, 6.24.

The above reaction was repeated on the same scale but using xylene as the solvent. The reaction mixture was refluxed for 72 h under a nitrogen atmosphere. The solvent was removed under vacuum and the resulting residue chromatographed on alumina to afford 0.38 g of a dark red solid. ^{1}H NMR analysis of this solid indicated the presence of the following compounds: **6** (29%), **7** (46%), **3** (25%).

Preparation of 6 and 7 Using $CpCo(C_2H_4)_2$. In a 50-mL Schlenk tube were placed $CpCo(C_2H_4)_2$ (88.0 mg, 0.49 mmol), norbornylene (230.7 mg, 2.45 mmol), and 2 mL of toluene. The solution was allowed to stir at 25 °C for 30 min and then cooled to 0 °C. To this solution was added diphenylacetylene (192.5 mg, 1.08 mmol) in 1 mL of toluene. The reaction mixture was stirred at 0 °C for 20 min and then at 25 °C for 30 min. The solvent was removed under high vacuum and the resulting residue chromatographed on alumina (30 g). Eluting the column with 10% methylene chloride/hexane produced a red band that was collected, and the solvent was removed under vacuum to afford 0.25 g of a dark red solid. ^{1}H NMR spectroscopy showed this solid to be a mixture containing compounds **6** (75%), **7** (25%), and a trace of **3**.

5,6,7,8-Tetraphenyl-1,2,3,4,4a,8a-hexahydro-1,4-methanonaphthalene (8). To a solution of either complex **6** or **7** (12.0 mg, 0.02 mmol) in 5 mL of acetonitrile cooled to 0 °C was added a solution of $CuCl_2\cdot 2H_2O$ (34.1 mg, 0.20 mmol) and triethylamine (0.015 mL) in 1 mL of acetonitrile. After 40 min of stirring at 0 °C, 6 mL of water was added and the resulting solution extracted three times with 10-mL portions of hexane. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. Evaporation of the majority of the solvent was followed by filtration of the organic fraction through 5 g of alumina with methylene chloride/hexane (1:1) as eluent. Finally, removal of the solvent under vacuum gave white crystals of **8** (5.0 mg, 53% yield from **6**; 6.6 mg, 70% yield from **7**). The crystals obtained from the oxidation of **6** or **7** had identical melting points (283–284 °C) and ^{1}H NMR and ^{13}C NMR spectra: ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 7.7, 2 or 3 H), 1.47 (br d, J = 8, 2 or 3 H), 2.27 (s, 1 H), 2.31 (br s, 2 H), 3.10 (s, 2 H), 6.48–7.25 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 30.25, 34.32, 44.43, 49.66, 124.88, 125.61, 126.55, 127.38, 129.31, 131.42, 135.14, 135.54, 140.47, 142.97; MS (35 eV), *m/e* 451 (M^+ + 1, 42%), 450 (M^+, 100), 420 (16), 393 (9), 383 (14), 382 (22), 373 (3), 317 (9), 289 (7), 167 (7), 149 (7), 91 (6), 57 (9); HRMS calcd for $C_{35}H_{30}$ 450.2347, found 450.2338.

5,6,7,8-Tetraphenyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene (9). Complex **8** (25.0 mg, 0.055 mmol) was dissolved in 5 mL of methylene chloride and cooled to 0 °C. One portion of ceric ammonium nitrate (60.0 mg, 0.109 mmol) was added, followed by a second portion (15.4 mg, 0.027 mmol) 20 min later. The solution was stirred for an additional 30 min, the solvent removed under vacuum, and the residue chromatographed on silica gel. Eluting the column with 10% methylene chloride/hexane and removal of the solvent under vacuum gave 8.0 mg (32%) of **9**: mp 251–253 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (d, J = 7.0, 2 H), 1.46 (d, J = 9.2, 1 H), 1.90 (br d, 3 H), 3.35 (s, 2 H), 6.75–7.26 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 27.14, 43.18, 48.64, 125.01, 125.82, 126.50, 127.28, 130.34, 131.72, 133.85, 137.81, 140.17, 140.71, 145.75; MS (35 eV), *m/e* 449 (M^+ + 1, 31%), 448 (M^+, 100), 421 (31), 420 (97), 383 (11), 382 (36), 343 (34), 341 (23), 289 (8), 265 (27), 197 (11), 165 (15), 149 (15), 91 (24), 57 (80); HRMS calcd for $C_{35}H_{28}$ 448.2191, found 448.2194.

In another experiment a mixture of compounds **6** (63%), **7** (25%), and **3** (12%) obtained as described above (0.05 g, 0.09 mmol) was dissolved in acetone (5 mL) and cooled to 0 °C. One portion of ceric ammonium nitrate (80.0 mg, 0.15 mmol) was added with stirring followed by a second portion (35.0 mg, 0.06 mmol) 20 min later. The solution was stirred for an additional 30 min, the solvent removed under vacuum, and the resulting residue chromatographed on silica gel. Eluting the column with 10% methylene chloride/hexane produced 8.3 mg (21%) of **9** as white crystals.

[5,6,7,8-η^4-5,6,7,8-Tetrakis(methoxycarbonyl)-1,2,3,4,4a,8-*exo*-hexahydro-1,4-methanonaphthalene](η^5-cyclopentadienyl)cobalt (10) and [5,6,7,8-η^4-5,6,7,8-Tetrakis(methoxycarbonyl)-1,2,3,4,4a,8-*endo*-hexahydro-1,4-methanonaphthalene](η^5-cyclopentadienyl)cobalt (11). In a 50 mL Schlenk tube were placed dimethyl acetylenedicarboxylate (247.3 mg, 1.74 mmol), $CpCo(CO)_2$ (144.0 mg, 0.79 mmol), norbornylene (372.0 mg, 3.95 mmol), and 3 mL of toluene. The reaction mixture was then refluxed under a nitrogen atmosphere for 63 h. The solvent was removed under high vacuum and the resulting dark red residue chromatographed on alumina (30 g). Eluting the column with 10% ethyl acetate/methylene chloride produced a red band that was collected and the solvent removed under vacuum to afford 0.31 g of a dark red solid. Preparative thin-layer chromatography (silica gel, 5% ethyl acetate/methylene chloride, eight developments) using 15.0 mg of the above mixture afforded 7.0 mg (47% recovery) of **10**.

Crystallization from methylene chloride at 0 °C gave **10**: orange-red crystals; mp 123–124 °C; ^{1}H NMR ($CDCl_3$) δ 0.91 (d, J = 9.4, 1 H), 0.96 (d, J = 7.5, 2 H), 1.08 (s, 2 H), 1.41 (d, J = 7.8, 2 H), 2.31 (s, 2 H), 3.11 (d, J = 9.9, 1 H), 3.69 (s, 6 H), 3.80 (s, 6 H), 5.05 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 29.57, 32.13, 40.17, 48.25, 51.81, 52.71, 65.00, 85.82, 86.66 (Cp), 169.22, 173.15; MS (70 eV), *m/e* 503 (M^+ + 1, 23%), 502 (M^+, 100), 436 (2), 378 (21), 345 (12), 287 (29), 279 (84), 275 (15), 221 (16), 124 (32), 115 (15), 86 (20), 67 (31), 59 (29). Anal. Calcd for $C_{24}H_{27}CoO_8$: C, 57.37; H, 5.42. Found: C, 57.16; H, 5.69. The more polar compound **11** (1.0 mg, 7% recovery) was also isolated from this preparative thin-layer chromatography. Crystallization from methylene chloride at 0 °C gave **11**: red-brown crystals; mp 116–117 °C; ^{1}H NMR ($CDCl_3$)

δ 0.54 (d, J = 10, 1 H), 0.99 (d, J = 7, 2 H), 1.03 (d, J = 10, 1 H), 1.26 (d, J = 8, 2 H), 1.82 (s, 2 H), 2.37 (s, 2 H), 3.71 (s, 6 H), 3.85 (s, 6 H), 4.80 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 28.58, 31.24, 41.56, 49.45, 51.84, 52.89, 57.27, 84.81 (Cp), 92.36, 168.23, 173.69; MS (70 eV), m/e 503 (M^+ + 1, 22%), 502 (M^+, 100), 443 (2), 378 (16), 345 (8), 287 (16), 279 (62), 221 (7), 124 (13), 86 (30), 84 (48), 59 (8). Anal. Calcd for $C_{24}H_{27}CoO_8$: C, 57.37, H; 5.42. Found: C, 57.28, H; 5.50. Besides **10** and **11**, 3.0 mg (20% recovery) of benzenecarboxylic acid hexamethyl ester (**12**) was isolated as a white solid: ^{1}H NMR ($CDCl_3$) δ 3.89(s);[37] MS m/e 426 (M^+).

The above reaction was repeated on the same scale but using xylene as the solvent. The reaction mixture was refluxed under a nitrogen atmosphere for 48 h. The solvent was removed under vacuum and the resulting residue chromatographed on alumina to afford 0.22 g of a dark red solid. Preparative thin-layer chromatography using 23.0 mg of this solid gave 12.0 mg (52% recovery) of **10**, 5.0 mg (22% recovery) of **11**, and 3.0 mg (13% recovery) of **12**.

5,6,7,8-Tetrakis(methoxycarbonyl)-1,2,3,4,4a,8a-hexahydro-1,4-methanonaphthalene (13). To a solution of either complex **10** or **11** (10.0 mg, 0.020 mmol) in 5 mL of acetonitrile cooled to 0 °C was added a solution of $CuCl_2·2H_2O$ (34.1 mg, 0.20 mmol) and triethylamine (0.015 mL) in 1 mL of acetonitrile. After 1.5 h of stirring at 0 °C, 6 mL of water was added and the resulting solution extracted three times with 10-mL portions of methylene chloride. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. Evaporation of the majority of the solvent was followed by filtration of the organic fraction through 5 g of alumina with methylene chloride/hexane (1:1) as eluent. Finally, removal of the solvent under vacuum gave white crystals of **13** (2.5 mg, 33% from **10**; 3.9 mg, 52% from **11**). Complex **13** prepared from **10** or **11** exhibited identical melting points of 67–68 °C as reported in the literature:[5] ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 10.3, 1 H), 1.49 (d, J = 7.7, 2 H), 1.66 (d, J = 8.2, 2 H), 1.71 (d, J = 10.3, 1 H), 2.39 (br s, 2 H), 2.97 (s, 2 H), 3.75 (s, 6 H), 3.77 (s, 6 H); MS (13 eV), m/e 379 (M^+ + 1, 10%), 378 (M^+, 51), 346 (12), 311 (22), 279 (100).

Thermal Isomerization Kinetics of 1. The thermal isomerization kinetics of **1** were followed in sealed, 507-PP, Wilmad, 5-mm NMR tubes. In a typical experiment, a 0.017 M solution of **1** was prepared by dissolving 10.1 mg (0.017 mmol) of **1** in 1.00 mL of toluene-d_8. Ferrocene (1.53 mg, 0.0082 mmol) was next added as the internal standard. This solution was divided equally (0.50 mL) and each part syringed into two separate NMR tubes. The two NMR tubes were connected to a vacuum line and the solutions subjected to six freeze–pump–thaw cycles. The NMR tubes were then flame-sealed under vacuum and immersed in a solvent–vapor bath of anisole (bp 154 °C). The NMR tubes were removed at regular time intervals and immediately immersed in water (25 °C) and the ^{1}H NMR spectra recorded. The rates of isomerization were determined by measuring the decrease in concentration of **1** with concomitant increase in concentration of **2**. The concentrations were determined by integrating the five-proton cyclopentadienyl signals of **1** and **2** as compared to the signal of the internal standard. Isomerizations were typically followed to about 90% completion. ^{1}H NMR of **1** (toluene-d_8): δ 1.18 (d, J = 9.0, 1 H), 1.45 (AB pattern, 2 H), 2.04 (m, 1 H), 2.21 (m, 1 H), 2.42 (m, 2 H), 2.52 (d, J = 4.8, 1 H), 2.99 (m, 1 H), 4.39 (d, J = 9.1, 1 H), 4.93 (s, 5 H), 5.49 (dd, J = 5.6, 2.2, 1 H), 5.59 (dd, J = 5.7, 2.0, 1 H), 6.73–7.27 (m, 20 H). ^{1}H NMR of **2** (toluene-d_8): δ 0.88 (d, J = 9.4, 1 H), 1.84 (d, J = 10.1, 1 H), 2.05 (br s, 2 H), 2.28 (m, 3 H), 2.77 (d, J = 9.4, 1 H), 2.90 (m, 1 H), 2.92 (d, J = 9.6, 1 H), 4.52 (s, 5 H), 5.65 (dd, J = 5.6, 2.1, 1 H), 5.74 (dd, J = 5.6, 2.1, 1 H), 6.85–7.56 (m, 20 H).

(5,6,7,8-η^4-5,6,7,8-Tetraphenyl-1,2,3,4,4a,8a-*exo*-hexahydro-1,4-methanonaphthalene)(η^5-methylcyclopentadienyl)cobalt (14) and (5,6,7,8-η^4-5,6,7,8-Tetraphenyl-1,2,3,4,4a,8a-*endo*-hexahydro-1,4-methanonaphthalene)(η^5-methylcyclopentadienyl)cobalt (15). In a 50-mL Schlenk tube were placed diphenylacetylene (1.02 g, 5.7 mmol), (η^5-$C_5H_4CH_3$)$Co(CO)_2$ (0.50 g, 2.6 mmol), norbornylene (1.22 g, 0.013 mol), and 3 mL of toluene. The reaction mixture was then refluxed under a nitrogen atmosphere for 53 h. The solvent was then removed under high vacuum and the resulting dark red residue chromatographed on alumina (30 g). Eluting the column with 10% methylene chloride/hexane produced a red band that was collected and the solvent removed under vacuum to afford 0.78 g of a dark red solid. ^{1}H NMR analysis indicated this solid to be a mixture containing **14** and **15** in approximately a 1:1 ratio. Also present in this mixture were small amounts of unidentifiable materials. Preparative thin-layer chromatography (silica gel, 5% methylene chloride/hexane, ten developments) using 12.0 mg of this mixture produced 3.1 mg (26% recovery) of isomer **15**. Crystallization from 5% methylene chloride/hexane gave **15**: dark red crystals; mp 252–253 °C; ^{1}H NMR ($CDCl_3$) δ 0.67 (d, J = 10.0, 1 H), 1.16 (d, J = 7.1, 2 H), 1.39 (d, J = 7.7, 2 H), 1.46 (br s, 2 H), 1.49 (s, 3 H), 2.02 (br s, 2 H), 2.51 (s, 2 H), 4.36 (s, 4 H), 6.90–7.47 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 16.58, 29.20, 31.82, 40.51, 54.20, 66.91, 82.48, 84.96, 96.27, 99.86, 123.88, 125.87, 126.65, 126.68, 127.08, 130.25, 131.27, 134.22, 140.14, 145.86; MS (70 eV), m/e 589 (M^+ + 1, 28%), 588 (M^+, 74), 510 (19), 509 (60), 508 (38), 507 (100), 479 (13), 450 (26), 442 (26), 441 (85), 365 (16), 302 (11), 260 (26), 220 (11), 138 (4), 83 (8), 67 (8). Anal. Calcd for $C_{41}H_{37}Co$: C, 83.65; H, 6.37. Found: C, 83.74; H, 6.40. Compound **14** was obtained in ca. 95% purity (5% of isomer **15**) by repeated fractional crystallization from hexane at 0 °C of the solid mixture obtained after column chromatography on alumina. ^{1}H NMR ($CDCl_3$) δ 0.97 (d, J = 9.0, 1 H), 1.06 (d, J = 7.1, 2 H), 1.11 (s, 2 H), 1.44 (d, J = 7.5, 2 H), 1.80 (s, 3 H), 2.16 (br s, 2 H), 4.09 (d, J = 8.9, 1 H), 4.68 (br s, 2 H), 4.91 (br s, 2 H), 6.87–7.17 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 16.48, 30.05, 32.55, 40.08, 51.45, 69.92, 83.30, 85.36, 95.28, 100.39, 124.41, 125.33, 126.49, 131.25, 140.00, 145.30; MS (70 eV), m/e 589 (M^+ + 1, 33%), 588 (M^+, 84), 510 (20), 509 (62), 508 (37), 507 (100), 479 (12), 450 (11), 449 (17), 448 (42), 441 (84), 421 (15), 420 (42), 365 (13), 138 (9); HRMS calcd for $C_{41}H_{37}Co$ 588.2227, found 588.2257.

Crossover Experiment between 1 and 14. In a 5-mm NMR tube were placed **1** (5.5 mg, 0.0089 mmol) and the mixture containing 95% **14** and 5% **15** (5.5 mg, 0.0093 mmol). This mixture was dissolved in 0.60 mL of xylene-d_{10} and the NMR tube attached to a vacuum line. The solution was subjected to five freeze–pump–thaw cycles and then flame-sealed under vacuum. ^{1}H NMR of **1** and **14** (xylene-d_{10}): δ 0.94 (d, J = 8.7), 1.06 (d, J = 7.3), 1.10 (s), 1.14 (d, J = 9.1), 1.39 (d, J = 2.0), 1.42 (d, J = 7.9), 2.04 (m), 2.17 (m), 2.38 (m), 2.45 (d, J = 4.4), 2.95 (m), 4.12 (d, J = 8.8), 4.35 (d, J = 9.1), 4.61 (t, J = 2.0), 4.76 (t, J = 1.9), 4.91 (s), 5.47 (dd, J = 5.7, 2.1), 5.56 (dd, J = 5.7, 2.0), 6.63–7.19 (m). The NMR tube was then placed in an oil bath maintained at 150–160 °C and removed at regular time intervals and the ^{1}H NMR spectra recorded. After 112 h the cyclopentadienyl resonances for **1** and **14** were negligible compared to those for **2** and **15**. ^{1}H NMR (xylene-d_{10}): δ 0.65 (d, J = 9.8), 0.86 (d, J = 9.7), 1.10 (d, J = 6.5), 1.32 (d, J = 8.3), 1.38 (s), 1.61 (d, J = 9.8), 1.79 (d, J = 9.8), 1.99 (m), 2.25 (m), 2.51 (s), 2.72 (d, J = 9.5), 2.87 (br d), 4.31 (br s), 4.47 (s), 5.63 (br d), 5.71 (br d), 6.76–7.50 (m). ^{13}C NMR (xylene-d_{10}): δ 11.79, 29.91, 32.60, 32.87, 36.18, 41.38, 42.78, 44.68, 45.43, 48.47, 49.68, 54.17, 55.33, 67.93, 68.14, 69.57, 83.75, 85.06, 85.69, 96.94, 97.09, 97.38, 101.01, and many resonances in the region δ 124–150. The NMR tube was opened and the solvent removed under vacuum to produce a dark red residue. Part of this residue was subjected to mass spectral analysis (20 eV): m/e 613 (28%), 612 (58), 589 (45), 588 (100), 547 (18), 545 (17), 510 (9), 509 (29), 508 (22), 507 (66), 488 (6), 451 (8), 450 (26), 448 (11), 420 (12), 281 (16), 116 (22), 98 (10). The remaining residue was dissolved in $CDCl_3$ for NMR analysis: ^{1}H NMR δ 0.67 (d, J = 9.9), 0.89 (d, J = 9.8), 1.16 (d, J = 6.9), 1.38 (d, J = 7.6), 1.49 (s), 1.63 (d, J = 9.8), 1.91 (d, J = 3.8), 2.01 (br s), 2.17 (m), 2.32 (m), 2.51 (s), 2.55 (d, J = 9.4), 2.68 (d, J = 9.5), 2.93 (m), 4.36 (s), 4.56 (s), 5.66 (br d), 5.83 (br d), 6.86–7.47 (m); ^{13}C NMR δ 16.53, 29.17, 31.82, 32.21, 35.31, 40.48, 41.79, 43.71, 44.53, 47.33, 48.59, 53.20, 54.16, 66.88, 67.20, 68.59, 82.49, 84.86, 84.91, 96.29, 96.46, 96.73, 99.86, and many resonances in the region δ 123–147.

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Registry No. **1**, 113567-74-1; **2**, 113626-31-6; **3**, 1278-02-0; **4**, 113567-78-5; **5**, 113567-79-6; **6**, 113666-00-5; **7**, 113567-75-2; **8**, 62117-01-5; **9**, 113567-80-9; **10**, 113567-76-3; **11**, 113666-01-6; **12**, 6237-59-8; **13**, 61165-96-6; **14**, 113666-02-7; **15**, 113567-77-4; $CpCo(CO)_2$, 12078-25-0; $CpCo(C_2H_4)_2$, 69393-67-5; $(\eta^5$-$C_5H_4HCH_3)Co(Co)_2$, 75297-02-8; diphenylacetylene, 501-65-5; *endo*-dicyclopentadiene, 1755-01-7; norbornylene, 498-66-8; dimethyl acetylenedicarboxylate, 762-42-5.

Supplementary Material Available: Tables A–H listing hydrogen atom coordinates, thermal parameters, and least-squares plane results (10 pages); listings of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Steric and Electronic Interactions between Cofacial Metallocene Rings

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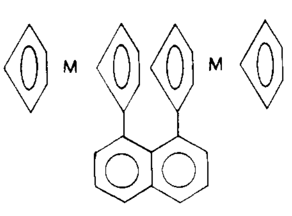
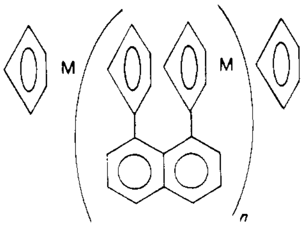
As part of a study of interactions between metallocenes, held so that two cyclopentadienyl rings are constrained to be proximate and facing one another, 1,8-diruthenocenylnaphthalene (**1b**) has been prepared and its crystal structure has been determined. This structure is shown to be close to that of 1,8-diferrocenylnaphthalene (**1a**) reported earlier, especially in respect to the dihedral angle between the substituted cyclopentadienyl and naphthalene ring planes and the splay angle between the two substituted cyclopentadienyl rings. Both of these distortions are significantly diminished in the monocation derived from **1a**, suggesting that there is a significant decrease in electron density on the cyclopentadienyl rings on oxidation of ferrocene to a ferricenium cation, consistent with theoretical analyses.

Introduction

We recently reported the synthesis of 1,8-diferrocenylnaphthalene (**1a**) through palladium-catalyzed coupling of ferrocenyl zinc chloride with 1,8-diiodonaphthalene.[1] This substance represents the first member of a family of "face to face" metallocenes designed to serve as monomeric model compounds for their polymeric analogues **2** whose mixed-valence state might be expected to have interesting physical properties.



1a, M = Fe
b, M = Ru



2

Since π-orbital interactions across the cofacial cyclopentadienyl rings in such a polymeric system would be important for valence band formation, the crystal structure of the model compound **1a** was determined. This showed a highly distorted structure in which the two opposed cyclopentadienyl rings were found to be rotated 45–47° from a conformation perpendicular to the naphthalene best plane. Such a rotation, together with a splaying of these rings, so that the dihedral angle between them is 29.1 (1)°, would be expected to lower their repulsive π-orbital interactions. We were, however, surprised to find that this ring rotational angle was significantly greater for **1a** than has been observed in analogous π-cofacial systems such as 1,8-diphenylnaphthalene[2] (**3**), 5,6-diphenylacenaphthene[3] (**4**), or 1,4,5,8-tetraphenylnaphthalene[4] (**5**) (Table VII) and suggested that nonbonding interactions between β-naphthalene hydrogen atoms and hydrogen atoms on the unsubstituted cyclopentadienyl ring in **1a** might be responsible for this difference. In order to test this hypothesis, we undertook the synthesis and crystal structure determination of the analogous 1,8-diruthenocenylnaphthalene (**1b**), since the distance separating the two cyclopentadienyl rings in ruthenocene is more than 0.3 Å larger than it is in ferrocene.[5] Consequently, steric interactions such as those described above would be expected to be significantly lowered. The crystal structure of the monocation **1a**$^+$, derived by one electron oxidation of **1a**, has also been determined in order to probe the effect of such

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