# Carbon–Carbon Bond Cleavage in Organocobalt Complexes with Agostic C···H···Co Bonding

Julian C. Nicholls and John L. Spencer*

*Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.*

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The reaction of noncoordinating acid, for example $HBF_4{\cdot}OMe_2$, with the neutral (4-vinylcyclopentene)- and (4-vinylcyclohexene)cobalt(I) complexes $[Co(\eta\text{-}C_5R_5)((1,2{:}6,7\text{-}\eta)\text{-}CH_2{=}CHCHCH_2CH{=}CHCH_2)]$ [R = H (1), R = Me (2)] and $[Co(\eta\text{-}C_5Me_5)((1,2{:}7,8\text{-}\eta)\text{-}CH_2{=}CHCHCH_2CH{=}CHCH_2CH_2)]$ (13) affords the cationic ethylcyclopentenyl and ethylcyclohexenyl complexes $[Co(\eta\text{-}C_5Me_5)\{(1,2,3\text{-}\eta)\text{-}C_5H_6(endo\text{-Et-}4)\}]^+$ (7), $[Co(\eta\text{-}C_5Me_5)\{(1,2,3\text{-}\eta)\text{-}C_6H_8(endo\text{-Et-}4)\}]^+$ (16), and $[Co(\eta\text{-}C_5Me_5)\{(1,2,3\text{-}\eta)\text{-}C_6H_8(endo\text{-Et-}5)\}]^+$ (17) in which the otherwise electron-deficient metal centers are stabilized by a three-center, two-electron (agostic) interaction. The 4-ethylcyclopentenyl complex readily undergoes disrotatory "inwards" ring opening to afford $[Co(\eta\text{-}C_5Me_5)\{\eta\text{-}C_5H_6(syn\text{-Et-}5)\}]^+$ (12) containing an acyclic 5-ethylpentadienyl ligand.

## Introduction

The cleavage of carbon–carbon bonds in hydrocarbons is frequently observed in reactions involving heterogeneous catalysts, particularly those recognized as having acid sites.[1] In contrast, the direct intermolecular insertion of a soluble transition metal complex into an unstrained alkane C–C bond is yet to be observed. There are, however, numerous examples of C–C activation of highly strained hydrocarbons by transition metal complexes[2] and also a number of intramolecular C–C bond cleavage reactions reported.[3–7] These were initially of interest because of observations of thermally forbidden pericyclic reactions occurring in the coordination sphere of transition metals, such as the conversion of quadricyclane to norbornadiene by Rh(I) catalysts.[8] However, most of these reactions were later shown to occur in a stepwise, nonconcerted manner.[9] More recently, C–C activation reactions of transitions metals with various strained small ring organic compounds (and subsequent reaction with unsaturated substrates) have been applied toward the development of a general strategy for the synthesis of ring-expanded products.[10]

The breaking of C–C bonds by soluble transition metal complexes is relatively rarely observed compared to that of C–H bonds, although C–H bonds are stronger. A higher kinetic barrier to C–C bond cleavage and formation relative to the corresponding C–H reactions has also been suggested by theoretical studies,[11] as well as the observation of the rarity of alkyl hydride complexes compared with polyalkyl complexes.[3a,12] Bergman[4] has shown that cyclopropane reacts with "$Rh(\eta^5\text{-}C_5Me_5)PMe_3$" firstly by C–H activation affording a $\sigma$-cyclopropyl ligand, before undergoing an intramolecular C–C bond cleavage, forming the thermodynamically favored rhodacyclobutane product. This result supports the suggestion by Suggs et al.[5] that C–H activation is, for bulky transition metal complexes (of this type), the kinetically favored product. Thermodynamics may also be unfavorable for the oxidative addition of C–C bonds[13] in the absence of a driving force such as relief of ring strain or aromatization.

Highly electrophilic metal centers[6,7] have been reported to facilitate C–C bond cleavage reactions such as intramolecular $\beta$-alkyl cleavage, and skeletal rearrangements, and also C–C bond formation reactions such as alkene insertion into the metal–alkyl bond. Electrophilic metal centers are able to satisfy their electronic requirements by forming an intramolecular three-center, two-electron interaction (agostic) with the $\sigma$-electrons of an adjacent C–H bond.[14] The agostic cations $[Co(\eta^5\text{-}C_5Me_5)(PR_3)C_2H_5]^+$ have been shown to be active ethene polymerization[15,16] catalysts. Brookhart and Schmidt[16] have demonstrated the sequential insertion of ethene and have provided an explanation

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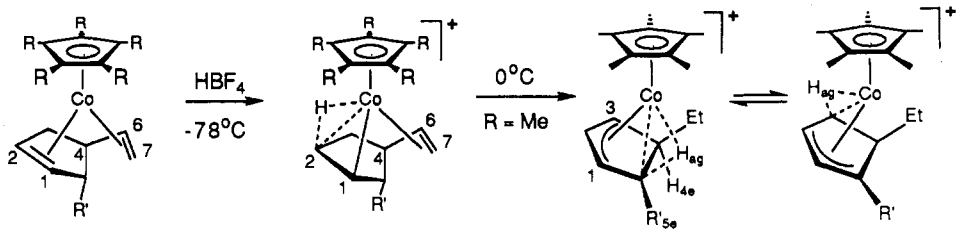
**Scheme 1**



1: R = H, R' = H
2: R = Me, R' = H
3: R = Me, R' = D

4: R = H, R' = H
5: R = Me, R' = H
6: R = Me, R' = D

7: R' = H
8: R' = D
9: R' = D

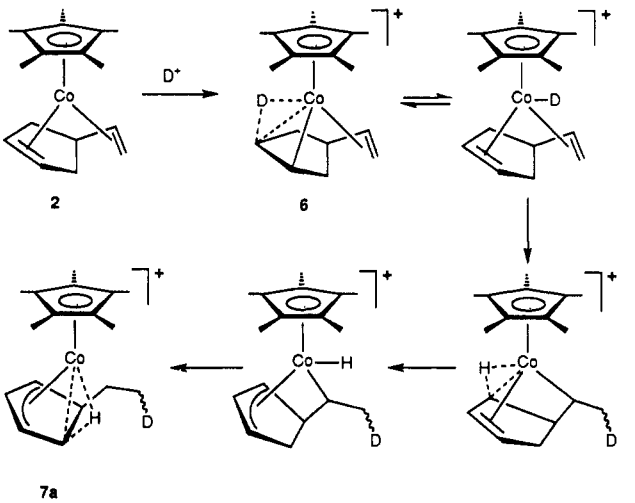
for the relationship between an M···H···C ground state and a low activation barrier to C–C bond formation.[17] From their experimental studies on $[Cp^*RhP(OMe)_3(C_2H_4)R]^+$ (R = H, Me), Brookhart et al. have calculated a difference in free energy of activation of 10.2 kcal mol$^{-1}$ for alkyl migration (22.4 kcal mol$^{-1}$) versus hydride migration (12.2 kcal mol$^{-1}$) and estimated a difference of 6–8 kcal mol$^{-1}$ for the corresponding cobalt system in which $[Cp^*CoP(OMe)_3(CH_2CH_2\text{-}\mu\text{-}H)]^+$ has an agostic ground state. This suggests that the kinetic barrier to C–C cleavage will be lower in complexes in which agostic bonding is favored. It is known that compounds of the type $[Co(\eta^5\text{-}C_5R_5)(L_2)]$ (R = H, Me; $L_2$ = cyclic diene) upon protonation afford complexes with agostic ground states.[18] We have demonstrated that strained bicyclic diene compounds of this type afford, on protonation, agostic complexes that undergo facile C–C bond cleavage.[19] We report here our attempts to observe C–C bond cleavage in less strained diene complexes. A preliminary account of this work has been reported.[19]

## Results and Discussion

The complexes $[Co(\eta^5\text{-}C_5R_5)((1,2{:}6,7\text{-}\eta)\text{-}CH_2CHCHCH_2(CH)_2CH_2)]$ [R = H (**1**), R = Me (**2**)] are obtained[19] from the respective norbornadiene complexes $[Co(\eta^5\text{-}C_5R_5)(\eta^4\text{-bicyclo[2.2.1]hepta-2,5-diene})]$ by, firstly, protonation with $HBF_4{\cdot}Et_2O$ (affording $[Co(\eta^5\text{-}C_5R_5)((1,2,3{:}6,7\text{-}\eta)\text{-5-vinylcyclopentenyl})]BF_4$), followed by hydride addition with $LiEt_3BH$.

The reaction of $[Co(\eta^5\text{-}C_5H_5)((1,2{:}6,7\text{-}\eta)\text{-}CH_2CHCHCH_2(CH)_2CH_2)]$ (**1**) with $HBF_4{\cdot}Et_2O$ at −78 °C affords the red complex $[Co(\eta^5\text{-}C_5H_5)((1{:}6,7\text{-}\eta)\text{-}CH_2CHCH(CH_2)_2CHCH_2)]BF_4$ (**4**) (Scheme 1), which includes an agostic interaction as part of the metal–ring bond. The $^1$H NMR at −68 °C showed a high field resonance at $\delta$ −14.4 ppm (d, $J_{HH}$ = 25 Hz), and the $^{13}$C NMR spectrum at −65 °C exhibited a peak at $\delta$ 5.9 ppm (dd, $^1J_{CH}$ = 74 and 157 Hz). The low value of $^1J_{CH}$ is regarded as being characteristic of an agostic M···H···C bond.[14] On warming to room temperature, decomposition occurs, affording $[Co(\eta^5\text{-}C_5H_5)_2]BF_4$ in ~40% yield based on cobalt. Reactions involving the transfer of cyclopentadienyl ligands between metals are known.

**Scheme 2**



**7a**

The protonation reaction with the pentamethylcyclopentadienyl analogue **2** at −78 °C also affords an agostic complex $[Co(\eta^5\text{-}C_5Me_5)((1{:}6,7\text{-}\eta)\text{-}CH_2CHCH(CH_2)_2CHCH_2)]BF_4$ (**5**). The position of the agostic interaction was determined by $^1$H NMR decoupling experiments. In contrast to the cyclopentadienyl analogue, warming **5** to room temperature affords a green salt, $[Co(\eta^5\text{-}C_5Me_5)((1,2,3\text{-}\eta)\text{-4-Et}CH(CH)_3CH_2)]BF_4$ (**7**) (Scheme 1). The $^1$H NMR of **7** at −85 °C showed a resonance at $\delta$ −12.46 ppm [dd, $J_{HH}$ = 20.5 {H5 exo}, 10.9 Hz {H4 exo}, Hag]. The $^{13}$C NMR at −85 °C was consistent with the structure proposed [$\delta$ 9.9 ppm, dd, $^1J_{CH}$ = 90 and 160 Hz, C5]. The $^1$H NMR spectrum at +25 °C is characteristic of **7** undergoing rapid 1,4-hydride shifts (Scheme 1), the agostic signal appearing as a doublet of triplets [$\delta$ −12.27 ppm (dt, 1 H, $J_{HH}$ = 10.8 Hz {H4 exo}, 10.2 Hz {H3 and H5 exo} Hag)]. Reaction of **2** with $CF_3SO_3D$ gave **7a**, the analogue of **7** in which the deuterium was shown to be on the methyl group by $^2$H NMR. The proposed mechanism for the formation of **7a** from **2**, involving a double hydride shift, is outlined in Scheme 2. The ethyl group of **7** would therefore be endo to the metal center. Complex **7** undergoes deprotonation upon reaction with lithium diisopropylamide, affording the red complex $[Co(\eta^5\text{-}C_5Me_5)((1,2,3,4\text{-}\eta)\text{-5-Et}C_5H_5)]$ (**10**) (Scheme 3). The $^1$H and $^{13}$C NMR spectra are consistent with a 5-ethylcyclopentadiene ligand. The IR spectrum exhibited a strong C–H stretch at 2732 cm$^{-1}$, assigned to H5 exo, also suggesting that the ethyl group is endo to the

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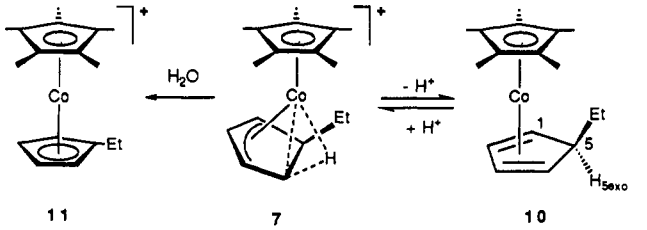
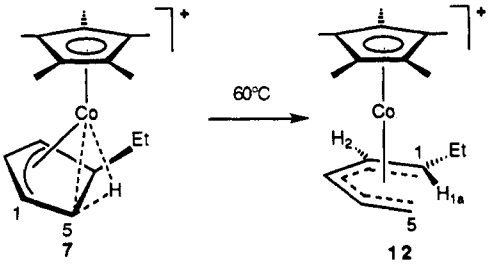
**Scheme 3**



**Scheme 4**



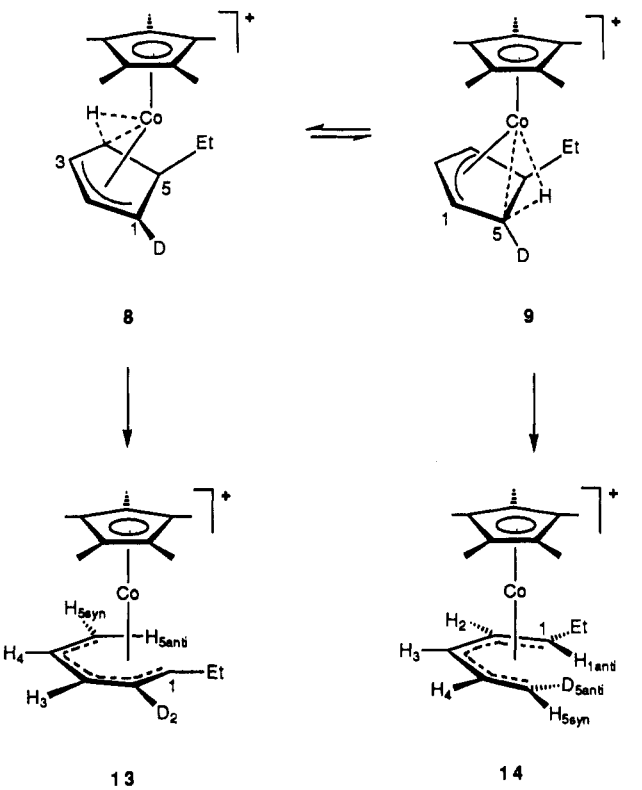
metal center.[20] The reaction of **10** with $HBF_4 \cdot Et_2O$ at −78 °C results in the reformation of **7**. We have observed, however, that the reaction of **10** with $HBF_4 \cdot Et_2O$ in the presence of $H_2O$ affords the yellow salt $[Co(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}EtC_5H_4)]BF_4$ (**11**) (Scheme 3). We have also observed that the heating of **7** in a $CH_2Cl_2/H_2O$ mixture affords **11**.

The heating of complex **7** to 60 °C for 8 h in the solid state (or in a *dry* $CH_2Cl_2$ solution) affords the complex *syn*-$[Co(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}1\text{-}EtC_5H_6)]BF_4$ (**12**) (Scheme 4).

The ring opened product *syn*-$[Co(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}1\text{-}EtC_5H_6)]BF_4$ (**12**) was characterized by $^1H$ NMR, by $^{13}C$ NMR, and also by a single crystal X-ray diffraction study by Redhouse of the $NaBPh_4$ metathesis product.[19] The crystal structure confirmed the syn position of the ethyl group, which was suggested from the $^1H$ NMR spectrum, with H2 having a coupling constant of 11.7 Hz to H1 anti. The carbon–carbon bond cleavage in the ring opening of $[Co(\eta^5\text{-}C_5Me_5)((1,2,3\text{-}\eta)\text{-}4\text{-}CH_3CH_2\overline{CH(CH)_3CH_2})]BF_4$ would presumably occur via the decoordination of the agostic C···H···Co interaction, forming a 16-electron intermediate, thereby allowing interaction between the C4–C5 bond electrons and the metal center, leading to cleavage of this bond. A possible intermediate in this pathway could therefore incorporate a three-centered, two-electron C···C···Co agostic interaction. It is also possible to speculate that a 16-electron intermediate is not involved, if the shift from the C···H···Co interaction to a C···C···Co interaction is concerted.

The ring opening of cyclopentenyl ions, to our knowledge, has not previously been observed other than for strained[21] or heterocyclic anions,[22] though it is expected to be exothermic for cyclopentenyl anions.[23] The reverse reactions, ring closures, have been reported for pentadienyl

**Scheme 5**



cations[24] and for strained pentadienyl anions.[23,25,26] More recently, transition metal assisted ring closures of pentadienyl ligands have been observed.[27] The gas pyrolysis of $[(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2Ru]$ at 450 °C afforded the mixed sandwich compound $[(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)Ru(\eta^5\text{-}1,3\text{-}Me_2\text{-}C_5H_3)]$. This reaction was postulated to occur via disrotatory ring closure and subsequent dehydrogenation, though C–H activation prior to ring closure was not ruled out.[27b]

The motion of the ring opening in **7** was determined by the protonation of $[Co(\eta^5\text{-}C_5Me_5)((1,2:6,7\text{-}\eta)\text{-}CH_2CH\text{-}\overline{CHCHD(CH)_2CH_2})]$ (**3**) with $HBF_4 \cdot Et_2O$ which at room temperature afforded the complexes $[Co(\eta^5\text{-}C_5Me_5)((1,2,3\text{-}\eta)\text{-}5\text{-}Et\overline{CHCD(CH)_2CH_2})]BF_4$ (**8**) and $[Co(\eta^5\text{-}C_5Me_5)\text{-}((1,2,3\text{-}\eta)\text{-}4\text{-}Et\overline{CH(CH)_3CHD})]BF_4$ (**9**) (Scheme 5), which are in equilibrium. The $^2H$ NMR of **8** ⇌ **9** exhibited, at 25 °C, one peak at δ 2.5 ppm. Heating **8** and **9** overnight at 60 °C afforded the ring opened complexes *syn*-$[Co(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}1\text{-}EtCHCD(CH)_2CH_2)]BF_4$ (**13**) and *syn*-$[Co(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}1\text{-}Et(CH)_4CHD)]BF_4$ (**14**) in a 1:1 ratio (Scheme 5). The $^2H$ NMR spectrum of the mixture exhibited peaks at δ 1.7 [D5 anti, **14**] and 5.0 ppm [D2, **13**]. The anti assignment of the D in **14** is given on the

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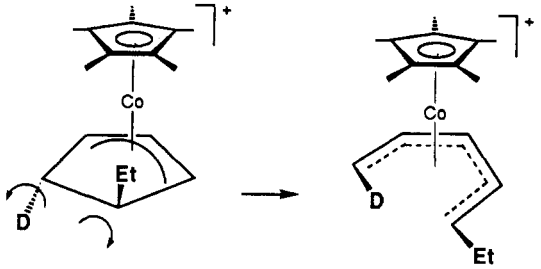
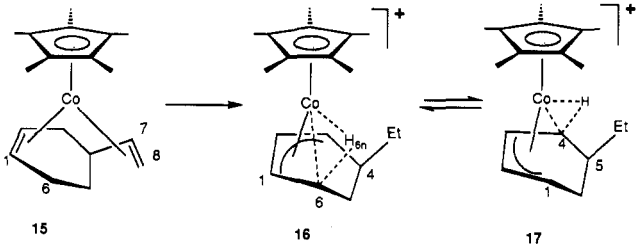
**Scheme 6**



**Scheme 7**



basis of the larger coupling of H5 anti ($\delta$ 1.73 ppm) to H4 (11.7 Hz) than of H5 syn ($\delta$ 3.19 ppm) to H4 (9.6 Hz) in **13**. For comparison the coupling of H1 anti ($\delta$ 1.52 ppm) to H2 is 11.7 Hz: the ethyl group is known to be syn to H2 from the X-ray diffraction study. In addition, precedent would suggest that H syn resonates at higher frequency than H anti in pentadienyl complexes.[28]

The position of deuterium in **14** shows that ring opening has occurred via disrotatory "inward" motion in **9** (Scheme 6). (The corresponding scheme in ref 19 is incorrectly drawn.)

The Woodward–Hoffmann rules[29] state that thermal ring opening of a $4n + 2$ $\pi$-electron system occurs by conrotatory motion, while ring opening of a $4n$ system occurs by disrotatory motion. Conventionally, [Co($\eta^5$-$C_5Me_5$)(1,2,3-$\eta$)-4-EtCH(CH)$_3$CHD)]$BF_4$ (**9**) is considered to be a Co(III) complex with the ethylpentenyl ligand acting as a four-electron donor (formal ligand charge −1) and we would therefore expect to observe disrotatory motion, assuming a concerted mechanism. Examples of metal assisted ring opening occurring by allowed[30] and disallowed[31] motion have been reported in the literature.

In an attempt to observe C–C cleavage in a six-membered ring, the complex [Co($\eta^5$-$C_5Me_5$)((1,2:7,8-$\eta$)-$CH_2$CHCH-($CH_2$)$_2$($CH$)$_2$$CH_2$)] (**15**) was protonated. The reaction of **15** with $HBF_4$·$Et_2O$ afforded deep red-brown crystals of **16** and **17** (Scheme 7). The $^{13}$C NMR at −85 °C showed the presence of two species in a ca. 1:1 ratio. Of the nineteen peaks observed only one showed couplings consistent with an agostic interaction [$\delta$ −13.4 ppm, dd, $J_{CH}$ = 87 and 160 Hz]. Ten of the peaks and the high field $^1$H NMR signal [$\delta$−13.14 ppm] could be considered consistent with [Co($\eta^5$-$C_5Me_5$)((1,2,3-$\eta$)-4-EtCH(CH)$_3$-

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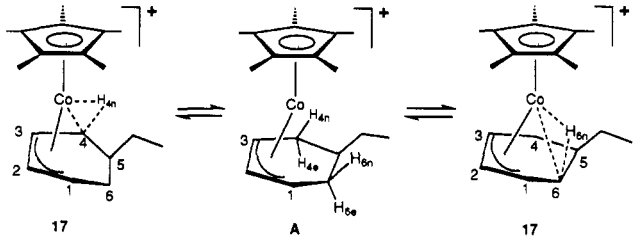
**Scheme 8**



CH$_2$CH$_2$)]$BF_4$ (**16**), exhibiting an agostic interaction involving the C6–H6n bond. The seven remaining carbon peaks are consistent with [Co($\eta^5$-$C_5Me_5$)((1,2,3-$\eta$)-5-EtCHCH$_2$(CH)$_3$CH$_2$)]$BF_4$ (**17**) exhibiting an agostic interaction between C4–H4n and the metal center. The complex **17** at the observation temperature, −85 °C (75 MHz), is postulated to undergo a rapid "flipping" of the agostic interaction between C4–H4n and C6–H6n. This "flipping" would impart averaged mirror symmetry through C2 and C5 on the NMR time scale at this temperature (Scheme 8) and hence explain the presence of only five peaks due to this ligand in the $^{13}$C NMR spectrum at −85 °C. The peak due to C4 and C6 might be expected to be very broad and therefore not observed. The double intensity of the peak at $\delta$ 79.5 ppm (d, $^1J_{CH}$ = 174 Hz) suggests that it be assigned to C1 and C3. This endo-hydrogen exchange process may take place via the 16-electron species (A) (Scheme 8) or possibly by a concerted mechanism, as has been proposed in similar compounds.[32]

The room temperature NMR spectra of **16** and **17** exhibit signals for only one species. The $^{13}$C NMR showed two broad peaks [$\delta$ 37.7 and 71.4 ppm] and sharp peaks for C1, C4, −$CH_2CH_3$, and $C_5Me_5$. The data are consistent with the flipping of the agostic interaction in **17** and the interchange of **16** and **17** presumably via 1,4-hydride shifts (Scheme 9).

The $\beta$-hydrogen elimination step involved in the interconversion of **16** and **17** has been reported[18] to occur at above −30 °C (400 MHz, $^1$H NMR time scale) in the closely related complex [Co($\eta^5$-$C_5Me_5$)((1,2,3-$\eta$)-cyclohexenyl)]$BF_4$. The "freezing out" of $\beta$-hydrogen elimination at low temperature would be consistent with the observation of the two species **16** and **17** at −85 °C. The initial agostic complex was not observed, presumably **16** and **17** are formed via hydride shifts similar to that suggested for conversion of **6** to **7a**, Scheme 2.

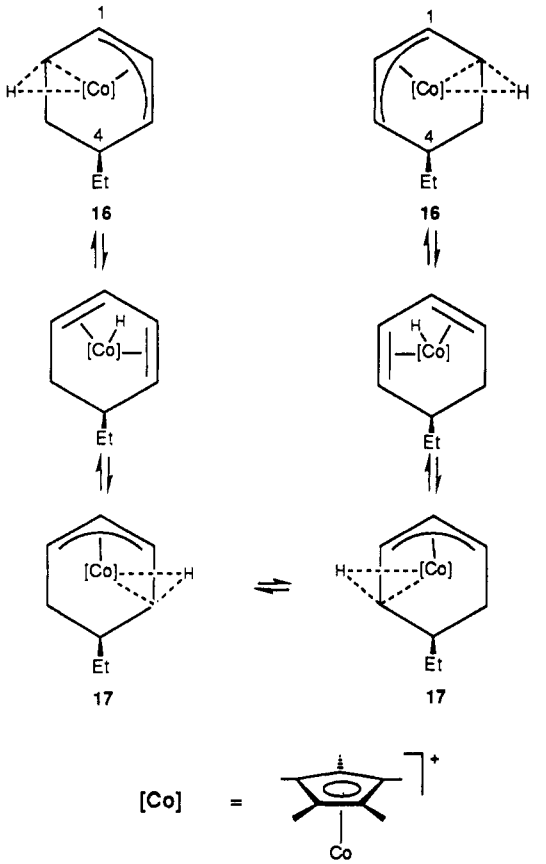
The complexes **16** and **17** were not observed to undergo carbon–carbon bond cleavage, even on heating to 70 °C for 7 days. This may be due to thermodynamic factors associated with the stability of the $C_6$ ring. Alternatively, the effect may be kinetic, arising from the poor accessibility of the C–C bonds to the metal orbitals.

## Conclusion

For intramolecular carbon–carbon bond cleavage to occur in soluble organometallic complexes the presence of a vacant or easily accessible coordination site is a necessity.

(32) (a) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (b) Ittel, S. D.; Van Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905. (c) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Dalton Trans.* **1984**, 1171. (d) Bennett, M. A.; McMahon, I. J.; Pelling, S.; Brookhart, M.; Lincoln, D. M. *Organometallics* **1992**, *11*, 127 and references therein.

**Scheme 9**




In the cobalt complexes studied, this is provided by the displacement of the agostic interaction.

Whereas C–H cleavage may be kinetically more favorable, carbon–carbon bond cleavage can occur if the C–H activation product is not thermodynamically stable, as seen in other systems such as the reaction of cyclopropane with "[Rh($\eta^5$-$C_5Me_5$)$PMe_3$]", which initially afforded the C–H cleavage product, before rearranging to the C–C cleavage product.[4] This would suggest why carbon–carbon bond cleavage is favorable in agostic complexes, where the diene–hydride form is known to be of higher energy. It is also implied by considering in reverse the proposal of Brookhart and Schmidt,[16] that carbon–carbon bond formation is more facile in complexes with an agostic ground state rather than a diene-hydride ground state.

In addition to the above, the accessibility of the C–C bond to the metal orbitals is presumably another factor since the ethylcyclopentenyl ring of [Co($\eta^5$-$C_5Me_5$)((1,2,3-$\eta$)-4-EtCH(CH)$_3$$CH_2$)]$BF_4$ (7) undergoes facile C–C bond cleavage, whereas we have not observed the ethylcyclohexenyl ring of [Co($\eta^5$-$C_5Me_5$)((1,2,3-$\eta$)-4-EtCH(CH)$_3$$CH_2CH_2$)]$BF_4$ (16) to undergo C–C bond cleavage. However, it is difficult to estimate the difference in the strain energy of the coordinated rings. In the cobalt carbon–carbon bond cleavages we have studied here and elsewhere,[19] a thermodynamic driving force such as relief of ring strain and/or aromatization has been present.

Carbon–carbon bond cleavage in agostic cobalt complexes can be facile, if the above conditions are favorable.

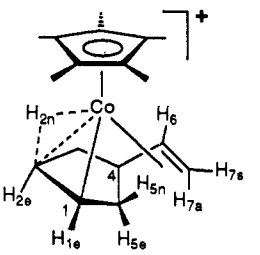
## Experimental Section

All manipulations of compounds and solvents were carried out on a vacuum/nitrogen line using conventional Schlenk type vessels and techniques. Solvents were dried immediately prior to use by prolonged reflux over the appropriate reagent: hexane and $CH_2Cl_2$ over $CaH_2$, THF and $Et_2O$ over Na/benzophenone. Solvents for NMR were degassed by freeze/pump/thaw techniques. NMR spectra were recorded on a Bruker AC 300-MHz spectrometer. $^1H$ and $^{13}C$ chemical shifts are reported relative to TMS at $\delta = 0$ and were determined by reference to the residual $^1H$ and $^{13}C$ solvent peaks. $^2H$ NMR chemical shifts were assigned with the use of $CD_2Cl_2$ or $C_6D_6$ as an internal reference. Notations used in the description of NMR spectra are e = exo, n = endo, a = anti, s = syn, ag = agostic.

[(Co($\eta^5$-$C_5H_5$)((1,2:6,7-$\eta$)-$CH_2CHCHCH_2(CH)_2CH_2$)] (1), [Co($\eta^5$-$C_5Me_5$)((1,2:6,7-$\eta$)-$CH_2CHCHCH_2(CH)_2CH_2$)] (2), [Co($\eta^5$-$C_5Me_5$)((1,2:6,7-$\eta$)-$CH_2CHCHCHD(CH)_2CH_2$)] (3), and [{Co($\eta^5$-$C_5Me_5$)$I_2$}$_2$], were prepared according to the literature.[19,33] Microanalyses were carried out by Butterworth Laboratories Ltd.

**[Co($\eta^5$-$C_5H_5$)((1:6,7-$\eta$)-$CH_2CHCHCH_2CH_2CHCH_2$)]$BF_4$ (4).** To a stirred solution of 1 (194 mg, 0.89 mmol) in $CH_2Cl_2$ (ca. 10 mL) a ca. 10% molar excess of $HBF_4$·$Et_2O$ (78 $\mu$L) was added, causing a color change to deep red (complex 4). The solution was allowed to warm to room temperature, and stirring was continued for 20 min, during which time the solution turned yellow. The product was precipitated and washed with $Et_2O$ (3 × 20 mL). Recrystallization from $CH_2Cl_2$/$Et_2O$ (ca. 1:1) afforded the yellow crystalline species [Co($\eta^5$-$C_5H_5$)$_2$]$BF_4$. Yield: 90 mg, 36%. NMR spectra of [Co($\eta^5$-$C_5H_5$)((1:6,7-$\eta$)-$CH_2CHCHCH_2$-$CH_2CHCH_2$)]$BF_4$ (4) were obtained by carrying out the protonation reaction in an NMR tube at −78 °C. $^1H$ NMR (−63 °C, $CD_2Cl_2$): broad and unassignable apart from $\delta$ −14.4 ppm (d, $J_{HH} \simeq 25$ Hz {2e, 2n}, H2n). Gated decoupled $^{13}C$ NMR (−63 °C, $CD_2Cl_2$): $\delta$ 5.9 (dd, $^1J_{CH}$ = 74 and 157 Hz, C2), 24.0 (t, $^1J_{CH}$ = 134 Hz, C5), 33.5 (d, $^1J_{CH}$ = 141 Hz, C4), 48.2 (t, $^1J_{CH}$ = 134 Hz, C3), 57.4 (t, $^1J_{CH}$ = 162 Hz, C7), 63.1 (d, $^1J_{CH}$ = 175 Hz, C6 or C1), 87.7 (d, $^1J_{CH}$ = 194 Hz, $C_5H_5$), 93.2 ppm (d, $^1J_{CH}$ = 153 Hz, C6 or C1).

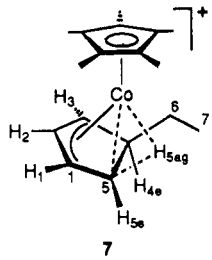
**[Co($\eta^5$-$C_5Me_5$)((1:6,7-$\eta$)-$CH_2CHCH(CH_2)_2CHCH_2$)]$BF_4$ (5) and [Co($\eta^5$-$C_5Me_5$)((1,2,3-$\eta$)-4-Et$C_5H_6$)]$BF_4$ (7).** To a stirred solution of 2 (291 mg, 1 mmol) in $CH_2Cl_2$ (ca. 10 mL) at −78 °C, a ca. 10% molar excess of $HBF_4$·$Me_2O$ (88 $\mu$L) was added causing an immediate color change to deep red (complex 5). The solution was allowed to warm to room temperature, during which time it gradually turned green in color. The product was precipitated and washed with $Et_2O$ (3 × 20 mL). Recrystallization from $CH_2Cl_2$/$Et_2O$ (ca. 1:2) at −20 °C afforded deep green crystals of [Co($\eta^5$-$C_5Me_5$)((1,2,3-$\eta$)-4-Et$C_5H_6$)]$BF_4$ (7). Yield: 345 mg, 91%. NMR spectra of [Co($\eta^5$-$C_5Me_5$)((1:6–7-$\eta$)-$CH_2CHCH(CH_2)_2CHCH_2CH_2$)]-$BF_4$ (5) were obtained by protonation of 2 in an NMR tube.




5

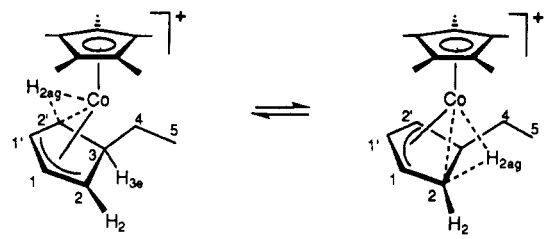
**NMR Data for 5.** $^1H$ NMR (−68 °C, $CD_2Cl_2$): $\delta$ −14.05 (dd, 1 H, $J_{HH}$ = 21.4 {2e, 2n}, 4.1 Hz {3n, 2n}, H2n), 0.14 (d, 1 H, $J_{HH}$ = 21.4 Hz {2n, 2e}, H2e), 0.75 (d, 1 H, $J_{HH}$ = 14.0 Hz {3n, 3e}, H3e), 0.82 (dd, 1 H, $J_{HH}$ = 14.0 Hz {3e, 3n}, 4.2 Hz {2n, 3n}, H3n), 1.63 (s, 15 Hz, $C_5Me_5$), 1.75 (m, 1 H, H4), 1.95 (d, 1 H, $J_{HH}$ = 14.1 Hz {5n, 5e}, H5e), 2.64 (d, 1 H, $J_{HH}$ = 14.1 Hz, {5e, 5n}, H5n), 3.06 (d, 1 H, $J_{HH}$ = 8.3 Hz {6, 7s}, H7s), 3.23 (dd, 1 H, $J_{HH}$ = 14.3 {7a,

6}, 8.3 Hz {7s, 6}, H6), 3.56 (d, 1 H, $J_{HH}$ = 14.3 Hz {6, 7a}, H7a), 3.79 ppm (s, 1 H, H1). Gated decoupled $^{13}C$ NMR (−68 °C, $CD_2Cl_2$): δ 5.6 (dd, $^1J_{CH}$ = 63 and 157 Hz, C2), 9.0 (q, $^1J_{CH}$ = 129 Hz, $C_5Me_5$) 24.6 (t, $^1J_{CH}$ = 134 Hz, C3 or C5), 34.2 (d, $^1J_{CH}$ = 142 Hz, C4), 47.4 (t, $^1J_{CH}$ = 132 Hz, C3 or C5), 64.3 (t, $^1J_{CH}$ = 158 Hz, C7), 65.9 (d, $^1J_{CH}$ = 158 Hz, C1 or C6), 96.4 (d, $^1J_{CH}$ = 154 Hz, C1 or C6), 98.2 ppm (s, $C_5Me_5$).




7

**NMR Data for 7 at −85 °C.** $^1H$ NMR (−85 °C, $CD_2Cl_2$): δ −12.46 (dd, 1 H, $J_{HH}$ = 20.5 {5e, 5ag}, 10.9 Hz {4e, 5ag}, H5ag), 0.72 (dd, 3 H, $J_{HH}$ = 7.1 {6, Me7}, 7.1 Hz {6′, Me7}, Me7), 1.42 (m, 1 H, H5e), 1.56 (m, 2 H, H6 and H6′), 1.74 (s, 15 H, $C_5Me_5$), 2.25 (m, 1 H, H4e), 3.85 (s, 1 H, H3), 5.71 (s, 1 H, H1), 6.50 ppm (s, 1 H, H2). Gated decoupled $^{13}C$ NMR (−85 °C, $CD_2Cl_2$): δ 9.9 (dd, $^1J_{CH}$ = 90 and 160 Hz, C5), 10.0 (q, $^1J_{CH}$ = 129 Hz, $C_5Me_5$), 12.0 (q, $^1J_{CH}$ = 127 Hz, C7), 25.9 (t, $^1J_{CH}$ = 126 Hz, C6), 58.2 (d, $^1J_{CH}$ = 136 Hz, C4), 75.5 (d, $^1J_{CH}$ = 174 Hz, C3), 79.6 (d, $^1J_{CH}$ = 182 Hz, C1), 96.6 (s, $C_5Me_5$), 102.0 ppm (d, $^1J_{CH}$ = 176 Hz, C2).



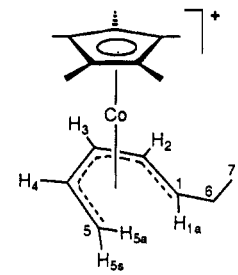

7 7′

**NMR Data for 7 at Room Temperature.** $^1H$ NMR (+25 °C, $CD_2Cl_2$): δ −12.27 (dt, 1 H, $J_{HH}$ = 10.0 {3, 2ag}, 10.2 Hz {2 and 2′, 2ag}, H2ag), 0.83 (t, 3 H, $J_{HH}$ = 7.4 Hz {4 and 4′, Me5}, Me5), 1.61 (dq, 2 H, $J_{HH}$ = 6.9 {3e, 4), 7.4 Hz {Me5, 4}, H4 and H4′), 2.29 (dt, 1 H, $J_{HH}$ = 10.8 {2ag, 3e}, 6.8 Hz {4 and 4′, 3}, H3e), 2.74 (d, 2 H, $J_{HH}$ = 10.2 Hz {2ag, 2 and 2′}, H2 and H2′), 6.23 ppm (s, 2 H, H1 and H1′). $^{13}C$ NMR (+25 °C, $CD_2Cl_2$, 75 MHz): δ 10.3 ($C_5Me_5$), 12.4 (C5), 26.6 (C4), 43.2 (br, C2 and C2′) 56.6 (C3), 92.5 (C1 and C1′), 97.8 ppm ($C_5Me_5$).

**[Co(η⁵-$C_5Me_5$)(1-4-η-5*endo*-Et$C_5H_4$)] (10).** To a stirred green solution of **7** (226 mg, 0.6 mmol) in $CH_2Cl_2$ (ca. 10 mL) at room temperature was added $LiN(^iPr)_2$ (53 mg, 0.5 mmol), causing an immediate color change to red in the solution. The solvent was removed in vacuo and the product extracted with hexane (ca. 15 mL). The red solution was filtered on ca. 1-mL plug of neutral alumina. Removal of the solvent in vacuo and cooling to −20 °C afforded red crystals of [Co(η⁵-$C_5Me_5$)((1,2,3,4-η)-5-*endo*-Et$C_5H_5$)] (**10**). Yield: 104 mg, 72%. $^1H$ NMR (+25 °C, $C_6D_6$): δ 1.04 (t, 3 H, $J_{HH}$ = 7.5 Hz {6 and 6′, Me7}, Me7), 1.73 (s, 2 H, H1 and H4), 1.78 (s, 15 H, $C_5Me_5$), 2.25 (dq, 2 H, $J_{HH}$ = 7.4 {5, 6 and 6′}, 7.4 Hz {Me7, 6 and 6′}, H6 and H6′), 2.41 (t, 1 H, $J_{HH}$ = 7.4 Hz {6 and 6′, 5}, H5), 4.66 ppm (s, 2 H, H2 and H3). Gated decoupled $^{13}C$ NMR (+25 °C, $C_6D_6$): δ 10.9 (q, $^1J_{CH}$ = 128 Hz, $C_5Me_5$), 13.4 (q, $^1J_{CH}$ = 128 Hz, C7), 27.9 (t, $^1J_{CH}$ = 125 Hz, C6), 45.5 (d, $^1J_{CH}$ = 165 Hz, C1 and C4), 55.7 (d, $^1J_{CH}$ = 125 Hz, C5), 78.3 (d, $^1J_{CH}$ = 153 Hz, C2 and C3), 89.0 ppm (s, $C_5Me_5$).

**[Co(η⁵-$C_5Me_5$)(η-Et$C_5H_4$)]$BF_4$ (11).** (i) To a stirred solution of **10** (172 mg, 0.43 mmol) in (wet) $CH_2Cl_2$ (ca. 10 mL) at −78 °C was added a ca. 10% molar excess of $HBF_4$·$Et_2O$ (39 μL), causing an immediate color change to green. The solution was allowed to warm to room temperature and the product precipitated and washed with $Et_2O$ (3 × 20 mL). Recrystallization from $CH_2Cl_2/Et_2O$ (ca. 2:1) afforded yellow crystals of [Co(η⁵-$C_5Me_5$)(η⁵-Et$C_5H_4$)]$BF_4$ (**11**). Yield: 148 mg, 93%. (ii) A $CH_2Cl_2$ solution of **7** saturated with $H_2O$ in a sealed tube with a PTFE vacuum tap was heated to 60 °C for 8 h. The solvent was removed in vacuo. Recrystallization from $CH_2Cl_2/Et_2O$ afforded yellow crystals of **11**. Yield: 74%. $^1H$ NMR (+25 °C, $CD_2Cl_2$): δ 1.17 (t, 3 H, $J_{HH}$ = 7.5 Hz {4 and 4′, Me5}, Me5), 1.67 (s, 15 H, $C_5Me_5$), 2.26 (q, 2 H, $J_{HH}$ = 75 Hz {Me5, 4 and 4′}, H4 and H4′), 4.96 (m, 2 H, H2 and H2′), 5.17 ppm (m, 2 H, H3 and H3′). Gated decoupled $^{13}C$ NMR (+25 °C, $CD_2Cl_2$, 75 MHz): δ 10.1 (q, $^1J_{CH}$ = 129 Hz, $C_5Me_5$), 14.4 (q, $^1J_{CH}$ = 124 Hz, C5), 19.4 (t, $^1J_{CH}$ = 129 Hz, C4) 84.6 (d, $^1J_{CH}$ = 181 Hz, C2 and C2′), 86.5 (d, $^1J_{CH}$ = 183 Hz, C3 and C3′), 97.2 (s, $C_5Me_5$) 105.1 ppm (s, C1). Anal. Calcd for $C_{17}H_{24}CoBF_4$: C, 54.58; H, 6.46. Found: C, 54.66; H, 6.35.

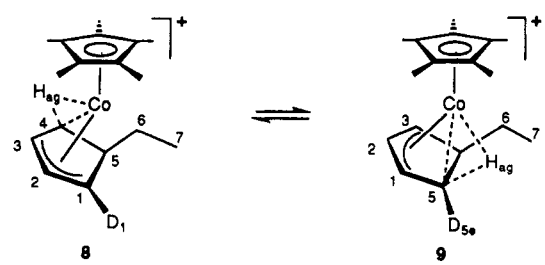
**[Co(η⁵-$C_5Me_5$)(η⁵-1-Et-$C_5H_6$)]$BF_4$ (12).** Solid **7** (286 mg) was heated at 60 °C overnight in a tube sealed with a PTFE vacuum tap. The red solid **18** was recrystallized from $CH_2Cl_2/Et_2O$ ca. 1:2. Yield: 249 mg, 88%.




12

$^1H$ NMR (+25 °C, $CD_2Cl_2$): δ 1.10 (dd, 3 H, $J_{HH}$ = 7.2 {6, Me7}, 7.2 Hz {6′, Me7}, Me7), 1.52 (m, 1 H, H6 or H6′), 1.73 (dd, 1 H, $J_{HH}$ = 11.7 (4, 5a}, 3.4 Hz {5s, 5a}, H5a), 1.99 (s, 15 H, $C_5Me_5$), 2.03 (m, 2 H, H1a and H6′ or H6), 3.19 (dd, 1 H, $J_{HH}$ = 9.6 {4, 5s}, 3.5 Hz {5a, 5s}, H5s), 4.93 (ddd, 1 H, $J_{HH}$ = 11.7 {5a, 4}, 9.6 {5s, 4}, 7.0 Hz {3, 4}, H4), 5.02 (dd, 1 H, $J_{HH}$ = 11.7 {1a, 2}, 7.1 Hz {3, 2}, H2), 6.28 ppm (dd, 1 H, $J_{HH}$ = 7.1 {2, 3}, 7.0 Hz {4, 3}, H3). Gated decoupled $^{13}C$ NMR (+25 °C, $CD_2Cl_2$): δ 10.0 (q, $^1J_{CH}$ = 127 Hz, $C_5Me_5$), 15.9 (q, $^1J_{CH}$ = 126 Hz, C7), 27.1 (t, $^1J_{CH}$ = 127 Hz, C6), 64.1 (t, $^1J_{CH}$ = 158 Hz, C5), 90.3 (d, $^1J_{CH}$ = 164 Hz), 95.5 (d, $^1J_{CH}$ = 164 Hz), 98.7 (d, $^1J_{CH}$ = 168 Hz, C4), 98.8 (s, $C_5Me_5$), 99.6 ppm (d, $^1J_{CH}$ = 170 Hz). Anal. Calcd for $C_{17}H_{26}CoBF_4$: C, 54.29; H, 6.96. Found: C, 53.93; H, 6.67.

**[Co(η⁵-$C_5Me_5$)((1,2,3-η)-4-Et$\overline{CHCDCHCHCH_2}$)]$BF_4$ (8) and [Co(η⁵-$C_5Me_5$)((1,2,3-η)-4-Et$CH\overline{(CH)_3CHD}$)]$BF_4$ (9).** Complex **3** was reacted with $HBF_4$·$Et_2O$ as for the nondeuterated analogue **2**.




8 9

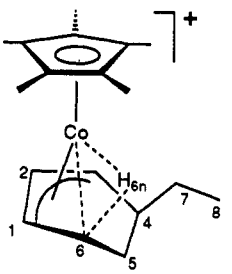
$^1H$ NMR (+25 °C, $CD_2Cl_2$, 300 MHz): as for **7** except δ 2.74 [1 H, H4e 8 ↔ H3 9]. $^2H$ NMR (+25 °C, $CH_2Cl_2$, 46 MHz, ref $C_6D_6$ at 7.34): one peak at ~δ 2.8 ppm [D1 8 ↔ D5e 9].

***syn*-[Co(η⁵-$C_5Me_5$)(η⁵-1-EtCHCD$(CH)_2CH_2$)]$BF_4$ (13) and *syn*-[Co(η⁵-$C_5Me_5$)(η⁵-1-Et$(CH)_4$CHD)]$BF_4$ (14).** The experimental procedure was identical to the thermal rearrangement of the nondeuterated analogue. **13** and **14** were isolated in a 1:1 ratio. $^2H$ NMR (+25 °C, $CH_2Cl_2$, ref $C_6D_6$, 46 MHz): δ 1.7 [D5a **14**], 5.0 [D2, **13**], in 1:1 ratio.

**[Co($^5$-$C_5Me_5$)((1,2:7,8-η)-$CH_2CHCH(CH_2)_2(CH)_2CH_2$)] (15).** To a rapidly stirred Hg/Zn amalgam[33] (8 g) in THF (ca. 40 mL) were added [{Co($\eta^5$-$C_5Me_5$)$I_2$}$_2$] (2.2 g, 2.5 mmol) and 4-vinylcyclohexene (0.75 g, 6.9 mmol). Stirring was continued for ca. 1 h until the solution was orange/red. The solution was decanted and the solvent removed in vacuo. The hexane extracts (2 × 20 mL) were filtered on a ca. 3-cm plug of neutral alumina. The volume of the solution was reduced in vacuo to ca. 2 cm$^3$. Cooling to −17 °C afforded red crystals of **15**. Yield: 1.03 g, 77%. Anal. Calcd for $C_{18}H_{27}Co$: C, 71.51; H, 9.00. Found: C, 71.44; H, 9.25. $^1$H NMR (25 °C, $C_6D_6$): δ 1.18–1.23 (m, 2 H), 1.44 (15 H, $C_5Me_5$), 1.53–1.68 (m, 2 H), 1.75–1.82 (m, 2 H) (H1, H5e, H5n, H6e, H6n, and H8a), 1.99 (m, 1 H, H4), 2.16 (d, 1 H, $J_{HH}$ = 12.3 Hz {3n, 3e}, H3e), 2.35 (d, 1 H, $J_{HH}$ = 8.2 Hz {7, 8s}, H8s), 2.75 (ddd, 1 H, $J_{HH}$ = 12.3 {3e, 3n}, 3.0 {2, 3n}, 3.0 Hz {4, 3n}, H3n), 3.00 (dd, 1 H, $J_{HH}$ = 5.1 {1, 2}, 3.0 {3n, 2}, H2), 3.10 ppm (dd, 1 H, $J_{HH}$ = 11.0 {8a, 7}, 8.1 Hz {8s, 7}, H7n). Gated decoupled $^{13}$C NMR (+25 °C, $C_6D_6$): δ 9.1 (q, $^1J_{CH}$ = 126 Hz, $C_5Me_5$), 22.8 (t, $^1J_{CH}$ = 125 Hz), 24.4 (t, $^1J_{CH}$ = 126 Hz), 35.2 (d, $^1J_{CH}$ = 130 Hz), 40.8 (t, $^1J_{CH}$ = 128 Hz) (C3, C4, C5, C6), 48.7 (t, $^1J_{CH}$ = 153 Hz, C8), 49.7 (d, $^1J_{CH}$ = 153 Hz), 67.0 (d, $^1J_{CH}$ = 165 Hz), 74.7 (d, $^1J_{CH}$ = 151 Hz) (C1, C2, or C7), 91.7 ppm (s, $C_5Me_5$).

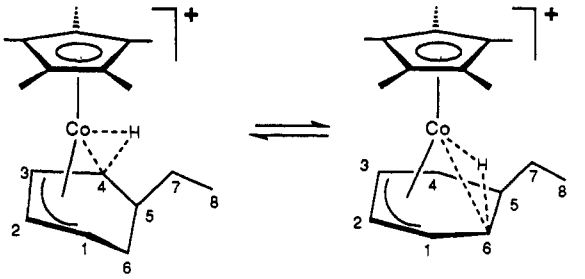
**[Co($\eta^5$-$C_5Me_5$)((1,2,3-η)-4-$EtCH(CH)_3CH_2CH_2$)] (16) and [Co($\eta^5$-$C_5Me_5$)((1,2,3-η)-5-$EtCHCH_2(CH)_3CH_2$)] (17).** To a stirred solution of **15** (186 mg, 0.6 mmol) in $CH_2Cl_2$ (ca. 10 mL) at −78 °C was added a ca. 10% molar excess of $HBF_4$·$Et_2O$ (54 μL), causing an immediate color change to deep brown. The solution was allowed to warm to room temperature and the product was precipitated and washed with $Et_2O$ (3 × 20 mL).

Recrystallization from $CH_2Cl_2/Et_2O$ (ca. 1:2) afforded deep red/brown crystals of [Co($\eta^5$-$C_5Me_5$)((1,2,3-η)-4-$EtCH(CH)_3CH_2CH_2$)]$BF_4$ (**16**) and [Co($\eta^5$-$C_5Me_5$)((1,2,3-η)-5-$EtCHCH_2(CH)_3CH_2$)]$BF_4$ (**17**). Yield: 211 mg, 88%. Anal. Calcd for $C_{18}H_{28}CoBF_4$: C, 55.41; H, 7.23. Found: C, 55.71; H, 7.06.



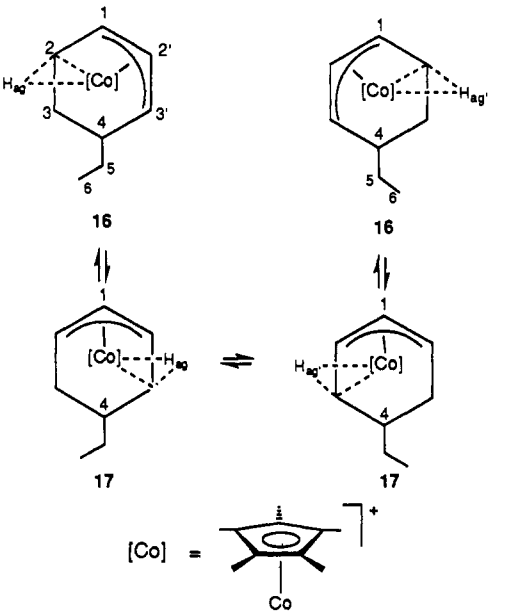

**16**

**NMR Data for 16 at −85 °C.** $^1$H NMR (−85 °C, $CD_2Cl_2$): δ −13.16 ppm (1 H, H6n). Other peaks were unassignable due to slight broadness and the presence of peaks due to **17**. Gated decoupled $^{13}$C NMR (−85 °C, $CD_2Cl_2$): δ 8.8 (q, $^1J_{CH}$ = 129 Hz, $C_5Me_5$), 10.6 (q, $^1J_{CH}$ = 126 Hz, Me8), 13.4 (dd, $^1J_{CH}$ = 87 and 160 Hz, C6), 22.3 (t, $^1J_{CH}$ = 132 Hz, C5), 27.7 (t, $^1J_{CH}$ = 123 Hz, C7), 39.8 (d, $^1J_{CH}$ = 130 Hz, C4), 81.2 (d, $^1J_{CH}$ = 182 Hz, C1), 86.1 (d, $^1J_{CH}$ = 159 Hz, C3), 94.7 (d, $^1J_{CH}$ = 172 Hz, C2), 95.8 ppm (s, $C_5Me_5$).




**17**

**NMR Data for 17 at −85 °C.** Gated decoupled $^{13}$C NMR (−85 °C, $CD_2Cl_2$): δ 8.9 (q, $^1J_{CH}$ = 129 Hz, $C_5Me_5$) 11.2 (q, $^1J_{CH}$ = 128 Hz, Me8), 28.1 (t, $^1J_{CH}$ = 126 Hz, C7), 30.5 (d, $^1J_{CH}$ = 131 Hz, C5), 79.5 (d, $^1J_{CH}$ = 174 Hz, C1 and C3), 94.5 (d, $^1J_{CH}$ = 171 Hz, C2), 95.8 ppm (s, $C_5Me_5$). The signals for C4/C6 are presumably very broad and in the baseline. The peak at δ 79.5 was twice the intensity of that at 94.5 ppm. The assignments of the carbon signals other than C6 of **16** and C1/C3 of **17** are not definitive.




**Data at Room Temperature for Interconverting Complexes 16 and 17.** $^1$H NMR (+25 °C, $CD_2Cl_2$): δ −6.07 (vbrs, Hag and Hag'), 0.75 (m, 1 H, H4), 0.83 (t, 3 H, $J_{HH}$ = 5.8 Hz {5 and 5', Me6}, Me6), 1.15 (dq, 2 H, $J_{HH}$ = 5.8 {4, 5 and 5'}, 7.3 Hz (Me6, 5 and 5'}, H5 and H5'), 1.84 (s, 15 H, $C_5Me_5$), 4.67 (br, s, H2, H2', H3 and H3'), 5.43 ppm (m, 1 H, H1). Gated decoupled $^{13}$C NMR (+25 °C, $CD_2Cl_2$): δ 10.3 (q, $^1J_{CH}$ = 129 Hz, $C_5Me_5$), 11.1 (q, $^1J_{CH}$ = 127 Hz, C6), 26.1 (t, $^1J_{CH}$ = 124 Hz, C5), 34.7 (d, $^1J_{CH}$ = 130 Hz, C4), 37.7 (v br, C3 and C3'), 71.4 (v br, C2 and C2'), 91.2 (d, $^1J_{CH}$ = 177 Hz, C1), 97.8 ppm (s, $C_5Me_5$).

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