Facile Carbon−Carbon Bond Cleavage in an (η^3-Cyclooctenyl)cobalt Complex Exhibiting Agostic C···H···Co Bonding

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Received September 12, 1995[⊗]

Summary: The reaction of [(η^5-C_5Me_5)Co(η^4-1,5-cyclooctadiene)] with $HBF_4{\cdot}Me_2O$ affords, at room temperature, an agostic η^3-cyclooctenyl complex which undergoes a facile ring opening to afford anti-[(η^5-C_5Me_5)Co(η^5-1-propylpentadienyl)]BF_4.

Introduction

Interest in C−C bond cleavage by soluble transition metal complexes has recently been revived[1] and directed toward the challenge of designing selective homogeneous C−C activation catalysts.[2] Complexes that may be capable of insertion into C−C bonds tend to react preferentially with C−H bonds, due to the relatively lower kinetic barrier for C−H activation.[3] The thermodynamics of C−H bond cleavage may also be more favorable than for C−C bond cleavage.[4] Most examples of C−C activation tend to have a driving force such as relief of ring strain,[5] aromatization,[6] or the presence of a carbonyl group,[7] though β-alkyl transfer has been observed in highly Lewis-acidic complexes.[8]

Recently Milstein et al.[1d] have shown that preferential C−H activation can be made reversible by the use of H_2 pressure, thereby allowing C−C activation to occur in an unstrained sp^2−sp^3 bond. An alternative strategy for achieving C−C cleavage in hydrocarbon ligands is to utilize complexes which may exhibit an C···H···M (agostic)[9] ground state in preference to the alkene−hydride form.[1c] Brookhart et al.[10] have shown that complexes which have an agostic ground state have a lower energy barrier to C−C bond formation compared to those with an alkene−hydride ground state.[11] A corollary of this is that agostic systems should show a lower energy barrier to C−C bond cleavage. Factors which may influence the ground state observed include steric[12a] (the agostic form requires less space than the alkene−hydride form) and also electron density at the metal center.[12b,13]

The reaction of noncoordinating acids with d^8 [L_3M-(η^4-cyclooctadiene)]^n [n = 0 or −1; Fe,[13] Ru,[14−16] Os,[16b] Co,[17] Rh,[17−19] Ir[17,20,21]] complexes has been an extensively researched area of organometallic chemistry. Typi-

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[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

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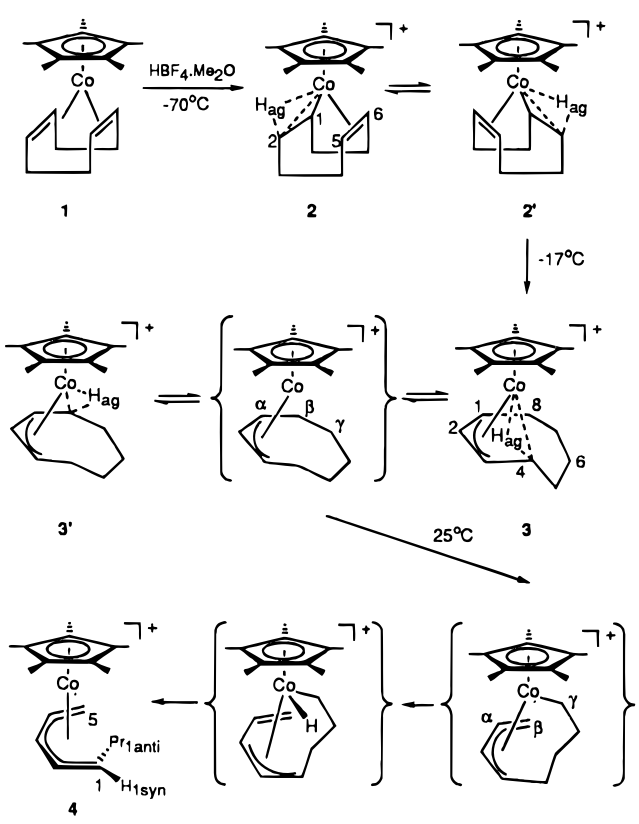
0276-7333/96/2315-0446$12.00/0

Scheme 1



cally[22] the reaction affords metal diene−hydride complexes [M = Ru,[14−16] Os,[16b] Ir[17,20]] and/or η^3-cyclooctenyl complexes exhibiting three-center, two-electron C···H···M interactions [M = Fe,[13] Ru,[14a,b] Rh[18]]. We report here the first example of C−C bond cleavage in a relatively unstrained C_8 ring.

Results and Discussion

The reaction of [(η^5-C_5Me_5)Co(η^4-1,5-cyclooctadiene)][23] (**1**) with $HBF_4{\cdot}Me_2O$ in CD_2Cl_2 at −70 °C affords, initially, the red complex [(η^5-C_5Me_5)Co((1:5,6-η)-C_8H_{13})]BF_4 (**2**) (Scheme 1) that exhibits an agostic interaction as part of the metal ring bond. At the observation temperature (−70 °C), the NMR spectra are consistent with **2** undergoing rapid 1,4-hydride shifts [^{13}C NMR δ 57.4 ppm (dd, $J_{C-H} = 156$ and 32 Hz, C2 and C5); ^{1}H NMR δ −10.29 (t, 1 H, $J_{H-H} = 12.0$ Hz, H_{ag})]. Similar hydride shifts have been observed in related cobalt agostic species.[24] In the product of protonation of [PPN][*closo*-3,3-(η^4-1,5-cyclooctadiene)-1,2-$(CH_3)_2$-3,1,2-$RhC_2B_9H_9$][18] 1,2-hydride shifts were observed as well as 1,4-hydride shifts. If 1,2-hydride shifts are occurring in the cobalt system, these are slow on the NMR time scale. The average $J_{C-H_{ag}}$ value of 32 Hz for **2** ⇌ **2′** equates with a static $^1J_{C2-H_{ag}}$ value of 64 Hz, assuming that $^2J_{C5-H_{ag}} = 0$ Hz. A low J_{C-H} value is indicative of an agostic M···H···C interaction.[9] At −17 °C the green crystalline agostic species [(η^5-C_5Me_5)Co((1−3-η)-C_8H_{13})]BF_4 (**3**) was isolated (Scheme 1). The NMR spectra at −30 °C are characteristic of **3** exhibiting rapid exchange of the agostic interaction between the endo C−H bonds adjacent to the allyl moiety [^{13}C NMR δ 21.8 (dd, $J_{C-H} = 135$ Hz and 106 Hz), C4 and C8]. Assuming $J_{CH_{methylene}} = 128$ Hz, a value of $J_{CH} = 84$ Hz is obtained for the agostic C−H bond [$(J_{CH_{methylene}} + J_{CH_{agostic}})/2 = 106$ Hz], and a value of $J_{CH} = 142$ Hz for the noninteracting bond [$(J_{CH_{methylene}} + J_{CH_{noninteracting}})/2 = 135$ Hz]. Cooling to −80 °C did not freeze out this process, indicating a barrier to agostic endo hydrogen exchange of $\Delta G < 25$ kJ mol^{-1}.

Spin saturation transfer experiments[25] at −30 °C show two sets of exchanging hydrogens, one set containing the five endo hydrogens; the other contains the allyl and exo hydrogens. This suggests that β-hydrogen elimination is occurring (slowly on the NMR time scale) which, coupled with endo-exchange, leads to 1,2-metal migration around the carbocyclic framework.[13,14a]

The conversion of **2** to **3** is analogous to those previously reported.[13,14a,b,18,19] On the basis of a study of a series of ruthenium complexes, Singleton et al.[14a] have suggested that the rearrangement occurs via successive β-hydrogen elimination/olefin insertion steps rather than by suprafacial shifts[26] as the rate of rearrangement is dependent on the size of the phosphine in the $[Ru(PR_3)_3H(COD)]^+$ complexes.

In dichloromethane solution at room temperature **3** undergoes a facile ($t_{1/2} = 6$ h) irreversible, intramolecular C−C bond cleavage to afford the red crystalline species *anti*-[(η^5-C_5Me_5)Co(η^5-1-propylpentadienyl)]BF_4 (**4**) in quantitative yield. The NMR parameters and homonuclear decoupling experiments allowed the determination of the geometry. The anti position of the propyl group was suggested by the size of the J_{HH} coupling of $H1_{syn}$ to H2 (9.0 Hz). In the closely related complex *syn*-[Co(η^5-C_5Me_5)(η^5-1-ethylpentadienyl)]$^+$,[1c] characterized by a single-crystal X-ray diffraction study, $J_{HH} = 11.7$ Hz for $H1_{anti}$ to H2. In addition, precedent would suggest that H_{syn} resonates at higher frequency than H_{anti} in pentadienyl complexes.[27] One possible mechanism for this rearrangement is outlined in Scheme 1. The decoordination of the agostic interaction (to give the 16-electron η^3-cyclooctenyl intermediate) followed by cleavage of the C_β−C_γ bond and a 1,4-hydride shift would afford **4**. We favor cleavage of the C_β−C_γ bond by analogy with the ring opening observed in [(η^5-C_5Me_5)Co((1−3-η)-4-ethylcyclopentenyl)]$^+$.[1c]

Bond cleavage is not observed in the agostic cyclooctenyl−Fe(II) and −Ru(II) complexes which are similar to **3**, and we attribute this contrasting behavior to the greater electrophilicity of the Co(III) center. A more electrophilic metal center may have a greater propensity to interact with the C−C bond. While β-hydrogen elimination in **3** is kinetically more facile, C−C bond

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[22] The transfer of hydride to "L_3" [15,19,21] and the isolation of 16-electron cyclooctenyl compounds[17,18] have also been observed. Reaction of [CpCoCOD] with H^+ led to decomposition or unassigned products.[17]

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cleavage affords the thermodynamic product, driven by relief of ring strain and an increase in delocalization.

The observation of facile C−C bond cleavage in agostic complexes suggests alternative strategies to the use of H_2[1a,d] for the homogeneous catalyzed C−C activation of hydrocarbons.

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 by prolonged reflux over the appropriate reagent: CH_2Cl_2 over CaH_2; toluene over Na/K alloy. Solvents for NMR were degassed by freeze/pump/thaw techniques. NMR spectra were recorded on JEOL GX 400 MHz and Bruker AC 300 MHz spectrometers. The ^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 (NMR notations: n = endo, e = exo, ag = agostic). The compound $[(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-1,5-cyclooctadiene})]$[23] was prepared by the literature method. $HBF_4{\cdot}Et_2O$ was purchased from Aldrich Chemical Co.

Reaction of $[(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-1,5-cyclooctadiene})]$ (1) with $HBF_4{\cdot}Et_2O$. An orange CH_2Cl_2 solution (10 mL) of **1** (210 mg, 0.70 mmol) at −78 °C was treated with $HBF_4{\cdot}Et_2O$ (97 μL, 0.70 mmol) causing an immediate color change to deep red (complex **2**; see below). The solution was allowed to warm slowly to ambient temperature. At ca. −20 °C the color of the solution changed to deep green. Reduction in the volume of the solution to ca. 2 mL and addition of toluene (ca. 5 mL) and cooling to −17 °C afforded green crystals of $[(\eta^5\text{-}C_5Me_5)Co((1,2,3\text{-}\eta)\text{-}C_8H_{13})]BF_4$ (**3**). Yield = 246 mg, 90%. ^1H NMR (−50 °C, CD_2Cl_2 400 MHz): δ −5.28 m, 2 H, H4n and H8n), 0.74 (m, 1 H, H6e), 1.20 (m, 3 H, H5n, H7n and H6n), 1.57 (m, 2 H, H4e and H8e or H5e and H7e), 1.73 (s, 15 H, C_5Me_5), 2.04 (m, 2 H, H5e and H7e or H4e and H8e), 4.78 (t, 1 H, J_{HH} = 7.4 Hz {1 and 3, 2}, H2), 5.27 ppm [ddd, 2 H, J_{HH} = 7.4 {2, 1 and 3}, 7.6 Hz {4e and 8e, 1 and 3} and {4n and 8n, 1 and 3}, H1 and H3). Fully coupled ^{13}C NMR (−80 °C, CD_2Cl_2, 50 MHz): δ 9.3 (q, $^1J_{CH}$ = 129 Hz, C_5Me_5), 19.5 (t, $^1J_{CH}$ = 122 Hz, C6), 21.8 (dd, $^1J_{CH}$ = 106, 135 Hz, C4 and C8), 24.7 (t, $^1J_{CH}$ = 128 Hz, C5 and C7), 77.7 (d, $^1J_{CH}$ = 163 Hz, C1 and C3), 95.5 (s, C_5Me_5), 98.2 ppm (d, $^1J_{CH}$ = 163 Hz, C2). Anal. Calcd for $C_{18}H_{28}CoBF_4$: C, 55.38; H, 7.18. Found: C, 55.05; H, 7.21.

The NMR spectra of the thermally unstable red complex **2** were obtained by protonation of a CD_2Cl_2 solution of **1** in a cooled (−78 °C) NMR tube. ^1H NMR (−70 °C, CD_2Cl_2, 300 MHz): δ −10.29 (t, 1 H, J_{HH} = 12.0 Hz {2e and 5, H_{ag}}, H_{ag}), 1.45 (dd, 2 H, J_{HH} = 9.5 {2e and 5, 3e and 4e} 2.9 Hz {3n and 4n, 3e and 4e}, H3e and H4e), 1.64 (s, 15 H, C_5Me_5) 1.86 (d, 2 H, J_{HH} = 9.6 Hz {7n and 8n, 7e and 8e}, H7e and H8e), 2.24 (m, 2 H, 3n and 4n), 2.65 (m, 2 H, H2e and H5), 2.88 (m, 2 H, 7n and 8n), 3.57 ppm (m, 2 H, H1 and H6). Fully coupled ^{13}C NMR (−70 °C, CD_2Cl_2, 75 MHz): δ 8.85 (q, $^1J_{CH}$ = 129 Hz, C_5Me_5), 29.43 (t, $^1J_{CH}$ = 129 Hz, C3 and C4 or C7 and C8), 32.81 (t, $^1J_{CH}$ = 128 Hz, C7 and C8 or C3 and C4), 57.45 (dd, $^1J_{CH}$ = 156 and 32 Hz, C2 and C5), 84.88 (d, $^1J_{CH}$ = 155 Hz, C1 and C6), 98.72 ppm (s, C_5Me_5).

Thermal Rearrangement of $[(\eta^5\text{-}C_5Me_5)Co((1\text{−}3\text{-}\eta)\text{-}C_8H_{13})]BF_4$ (3) to *anti*-$[(\eta^5\text{-}C_5Me_5)Co(\eta^5\text{-1-propylpentadienyl})]BF_4$ (4). A deep green dichloromethane solution of **3** (100 mg, 0.26 mmol) was left standing at 25 °C for ca. 24 h. The resultant red solution was concentrated in vacuo, and toluene was added. Red crystals of **4** were isolated. Yield = 92 mg, 92%. ^1H NMR (+25 °C, CD_2Cl_2, 400 MHz): δ 0.29 (dddd, 1 H, J_{HH} = 9.0 {7 or 7′, 6 or 6′}, 6.4 {7′ or 7, 6 or 6′}, 13.5 {6, 6′}, 9.0 Hz {$H1_{syn}$, 6 or 6′}, H6 or H6′), 0.82 (m, 1 H, H6 or H6′), 0.86 (t, 3 H, J_{HH} = 7.3 Hz {7 and 7′, 8} Me8), 1.45 (m, 2 H, H7 and H7′), 1.86 (s, 15 H, C_5Me_5), 1.98 (dd, 1 H, J_{HH} = 11.4 {H4, 5_{anti}}, 3.4 Hz {5_{syn}, 5_{anti}}; $H5_{anti}$), 3.23 (dd, 1 H, J_{HH} = 9.5 {4, 5_{syn}}, 3.4 Hz {5_{anti}, 5_{syn}} $H5_{syn}$), 3.62 (ddd, 1 H, J_{HH} = 9.0 {6 or 6′, 1_{syn}}, 5.6 {6′ or 6, 1_{syn}}, 9.0 {2, 1_{syn}}, $H1_{syn}$), 4.80 (dd, 1 H, J_{HH} = 9.0 {1_{syn}, 2}, 7.5 Hz {3, 2} H2), 5.04 (ddd, 1 H, J_{HH} = 7.5 {3, 4}, 9.5 {5_{syn}, 4} 11.4 Hz {5_{anti}, 4} H4), 6.47 ppm (dd, 1 H, J_{HH} = 7.5 {2, 3} 7.5 Hz {4,3}, H3). Fully coupled ^{13}C NMR (+25 °C, CD_2Cl_2 50 MHz): δ 9.6 (q, $^1J_{CH}$ = 129 Hz, C_5Me_5), 13.6 (q, $^1J_{CH}$ = 126 Hz, Me8), 24.1 (t, $^1J_{CH}$ = 126 Hz, C7), 35.0 (t, $^1J_{CH}$ = 128 Hz, C6), 60.8 (t, $^1J_{CH}$ = 161 Hz, C5), 78.8 (d, $^1J_{CH}$ = 150 Hz, C1), 93.9 (d, $^1J_{CH}$ = 167 Hz, {C2 or C3 or C4}, 98.8 (d, $^1J_{CH}$ = 167 Hz, {C4 or C2 or C3}, 99.4 (s, C_5Me_5), 103.9 ppm (d, $^1J_{CH}$ = 170 Hz, C3 or C2 or C4). Anal. Calcd for $C_{18}H_{28}CoBF_4$: C, 55.38; H, 7.18. Found: C, 54.54; H, 6.86.

Acknowledgment. The support of the Engineering and Physical Sciences Research Council, Grant H69793, is acknowledged.

OM950727+