Articles

Stereoelectronic Constraints in Metal-Assisted β-Elimination Reactions

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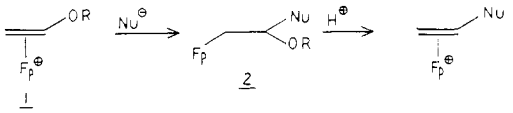
The stereochemical requirements for metal-assisted ring opening in Fp-substituted 1,4-dioxanes (Fp = [η^5-$C_5H_5(CO)_2Fe$]) have been examined. It has been found that trans-fused perhydrobenzodioxins (**11a + b**) in which the Fp group is locked in the axial position resist rearrangement on treatment with BF_3. By contrast, the corresponding cis-fused isomers (**12a + b**) and the phenyl-substituted trans-fused perhydrobenzodioxin **11c** are readily converted to the corresponding dioxolanes **13**, **15**, and **18**, respectively, under these conditions. These differences in reactivity suggest that in the absence of an electron-donor group capable of stabilizing a developing cationic center Fp-assisted ring opening requires an antiperiplaner conformation between the leaving group and the Fp.

Introduction

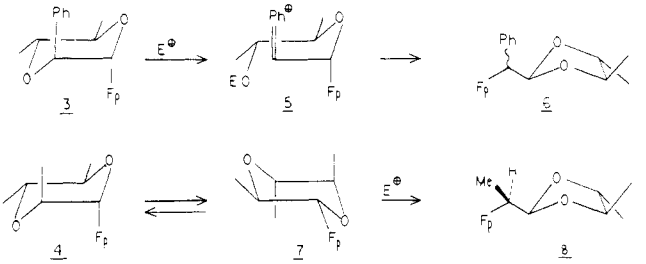
The addition of nucleophiles to Fp-vinyl ether salts **1** (Fp = [η^5-$C_5H_5(CO)_2Fe$]) followed by electrophile-induced elimination of the alkoxy substituent has been shown to be a useful synthetic sequence.[1]



There is now considerable evidence that the stereochemistry of the first step in these reactions involves a trans addition of the nucleophile to the Fp–ligand bond.[2] The stereochemistry of the second step has also been shown to involve preferential trans elimination of alkoxide from the adduct **2**,[3] in close analogy to the trans elimination of hydroxide from β-(hydroxyalkyl)-Fp complexes.[4] However, the stereoelectronic boundaries of these processes have not been examined, since these reactions were applied only to acyclic systems. The present paper provides the results of such an examination.

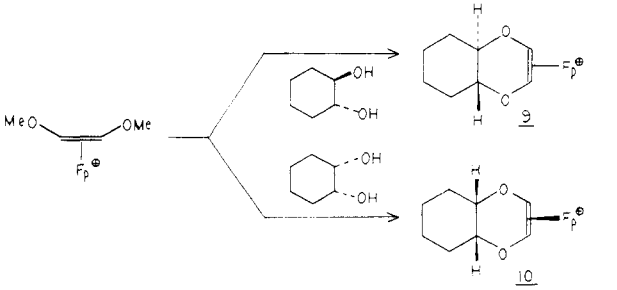
Results and Discussion

The disparate behavior of the phenyl- and methyl-substituted dioxane complexes **3** and **4** were the first observations that could be interpreted as providing evidence for preferred antiperiplaner elimination of alcohol from these compounds.[5] Optically active **3** was observed to rearrange to the racemic dioxolane complex **6** on treatment with various electrophiles, while **4** underwent the same transformation to give **8** without significant racemization. We interpreted these observations in terms of phenyl-assisted opening of **3** through the phenonium ion **5** and Fp-assisted opening of **4** through its less stable conformer **7**.



These results led us to examine the dependence of the ring-opening process on conformational effects and the nature of the substituent at the β-carbon in these dioxane complexes. To this end, we prepared a number of Fp-substituted cis- and trans-fused perhydrobenzodioxins and examined their reactivities toward electrophile-induced ring opening.

Transetherification of Fp(η^2-*cis*-1,2-dimethoxyethene)-BF_4 with *trans*- and *cis*-cyclohexanediol gave the hexahydrobenzodioxin complexes **9** and **10**, respectively. Only one isomer is possible for **9**, but we found that **10** was also formed as a single diastereomer, as shown by its ^1H and ^{13}C spectra. This has been assigned the exo structure shown, since the endo isomer would be expected to be sterically congested.



The ^1H NMR spectrum of **10** at room temperature shows a singlet at 7.40 ppm for the two vinylic protons,

(1) See, for example: (a) Chang, T. C. T.; Rosenblum, M. *J. Org. Chem.* **1981**, *46*, 4103. (b) Chang, T. C. T.; Rosenblum, M. *J. Org. Chem.* **1981**, *46*, 4676. (c) Chang, T. C. T.; Rosenblum, M. *Tetrahedron Lett.* **1983**, *24*, 695. (d) Rosenblum, M. *Pure Appl. Chem.* **1984**, *56*, 129.
(2) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.
(3) Marsi, M.; Rosenblum, M. *J. Am. Chem. Soc.* **1984**, *106*, 7264.
(4) Giering, W. P.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1972**, *94*, 7170.
(5) Turnbull, M. M.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1988**, *7*, 200.

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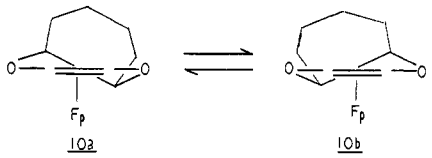
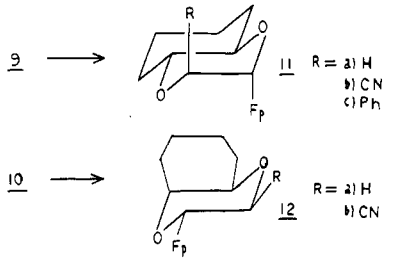
indicating a rapid conformational exchange between the two equivalent conformers **10a** and **10b**. At −45 °C, the signal begins to separate and is well resolved into two resonances at 7.60 and 7.20 ppm at −60 °C. Based on an observed coalescence temperature of −45 °C, the activation energy for the conformational inversion is calculated[6] to be 10.7 ± 0.4 kcal/mol. This value is in good agreement with the value calculated for ring inversion in the parent compound, Fp(η^2-dioxene)BF_4 of 7.3 ± 0.4 kcal/mol.[5]



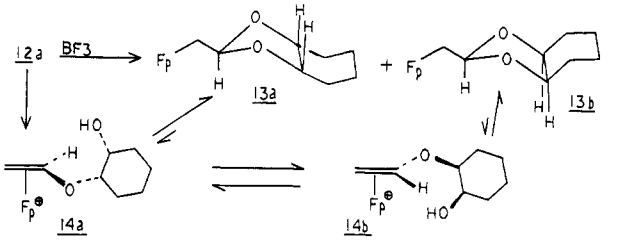
Hydride addition to **9** and **10**, following the procedure of Brookhart,[7] gave the corresponding neutral complexes **11a** (90%) and **12a** (66%), respectively. The proton NMR spectra of these substances confirm their assignments. In **11a**, the tertiary proton α to the Fp group is observed as a doublet (J = 3 Hz) at δ 6.05, while in **12a** this proton resonance appears at much higher field (δ 5.50) and, as is expected, appears as a double doublet (J = 11, 3 Hz). We have previously shown that the deshielding of this proton and the absence of significant equatorial–equatorial coupling for this proton are characteristic of axial substitution of the Fp group on the dioxane ring.[5] The ^1H NMR spectrum of **12a** shows no change on cooling the solution to −50 °C, suggesting that there is no appreciable population of the conformer with the Fp group in an axial position. This is in accord with the behavior of the parent Fp-substituted dioxane, which also shows no evidence in its NMR spectrum for the presence of the conformer with the Fp substituent in the axial position.[5]

Treatment of **9** and **10** with tetraethylammonium cyanide gave the corresponding adducts **11b** (86%) and **12b** (46%). Again, the relative chemical shifts and multiplicites of the α-proton signals for **11b** (δ = 6.1, singlet) and **12b** (δ = 5.36, doublet, J = 10.5 Hz) confirmed these assignments.

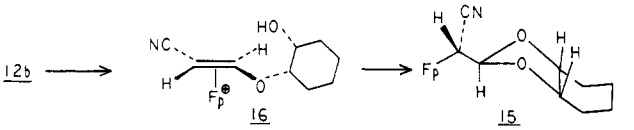
Finally, the phenyl-substituted complex **11c** was prepared (87%) by treatment of **9** with phenylmagnesium bromide. The absence of vicinal coupling for the ring proton α to the Fp group, and its low resonance (δ = 6.9) are in accord with this structural assignment.



Rearrangement studies of the compounds prepared were carried out in $CDCl_3$ or CH_2Cl_2 solution in the presence of a 0.1 molar equiv of BF_3·Et_2O and were monitored by observing IR, ^1H NMR, and ^{13}C NMR spectral changes. At −30 °C, no reaction of **12a** was observed after several hours, but at −10 °C, at the end of 3 h, the dioxane complex is incompletely transformed to a 2:1 mixture of isomeric dioxolane complexes **13a** and **13b**. The assignment of structure to the predominant product **13a** is based on the anticipated stereospecific ring opening and reclosure mechanism, which must proceed through the intermediate vinyl ether complex **14a**. The formation of the stereogen **13b** is the result of reversion of the kinetic product **13a** to the cation **14a** and slow conversion of this cation through rotation about the putative double bond to its diastereomer **14b**. Evidence for the low rotational barrier in Fp(η^2-vinyl ether) complexes has previously been given.[8] As anticipated, when acid-catalyzed ring opening of **12a** is carried out at room temperature, reaction is complete within 3 h, and **13a** and **13b** are formed in equal amounts.



The rearrangement of **12b** at room temperature in the presence of BF_3·Et_2O proceeded much more slowly than **12a** but was complete after 24 h. Unlike the latter reaction, only one stereogen **15** was formed in this reaction. The slower rate of rearrangement as well as the formation of a single isomer may reflect the effect of the electron-withdrawing cyano substituent in retarding the formation of the cationic intermediate **16**.



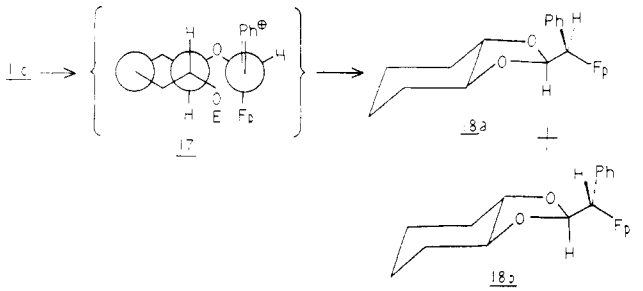
In sharp contrast to the behavior of **12a** and **12b**, the corresponding trans-fused dioxane complexes **11a** and **11b** resisted rearrangement and remained unchanged even after 2 weeks at room temperature or after 2 days in refluxing methylene chloride in the presence of BF_3·Et_2O.

The facile rearrangement of **12a,b** to the dioxolane complexes **13** and **15** and the resistance of **11a,b** to this transformation is in accord with a mechanism which requires an antiperiplaner stereochemistry for the leaving group and the Fp group. A very similar stereochemical requirement has earlier been observed in trityl cation promoted β-hydride abstraction reactions of (alkyl)-[9] and (cycloalkyl)Fp[10] complexes. Such a stereoelectronic requirement for Fp participation in these elimination reactions is closely analogous to that observed in acid-promoted elimination reactions of (β-hydroxyalkyl)silane compounds,[11] which have also been shown to require an antiperiplaner relationship of hydroxyl and assisting silyl groups.[12,13] These systems therefore show congruent behavior notwithstanding the presence of filled, nonbonding d orbitals on the iron atom, which are lacking in silicon.

(6) Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Heyden, London, 1981; p 167.
(7) Brookhart, M.; Tucker, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 979.
(8) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.
(9) Slack, D.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1974**, 701.
(10) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.
(11) Hurdlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464.
(12) Robbins, C. M.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1976**, 697.
(13) β-Hydroxy eliminations from chromium, cobalt, iron, and copper have also been observed under aqueous conditions. No discussion of the relevant stereochemical requirements has been made. See: (a) Cohen, H.; Meyerstein, D.; Shustermann, A. J.; Weiss, M. *J. Am. Chem. Soc.* **1984**, *106*, 1876. (b) Sorek, Y.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3431.

However, the symmetries of these a'_σ and a'_π orbitals[14] suggest that they, like the Fe–C bond orbital, are best able to stabilize the developing cationic center when the Fe–C bond is antiperiplaner to the departing group. Indeed, the high reactivity, and stereoselection observed for the Fp substituent as an "anchimeric" group may derive in some measure from the interactions of these nonbonding electrons, as from those in the Fe–C bonding orbital.[15]

Finally, in contrast to the behavior of **11a** and **11b**, treatment of the phenyl-substituted dioxane **11c** with $BF_3{\cdot}Et_2O$ at room temperature led to its transformation, after 3 h, to a mixture of the dioxolane complexes **18a** and **18b**.



As with **3**, the disparate behavior of **11c** is readily accounted for in terms of phenyl-assisted ring opening of **11c** through the phenonium ion **17**. The relatively facile rearrangement of this compound notwithstanding the lack of a favorably oriented Fp group and the observed racemization of **3** in its transformation to **6** are both consistent with the mechanism of ring opening.

In conclusion, in the absence of strong electron-donor groups in these dioxane complexes, the conformation of the Fp substituent controls the rate and stereochemistry of acid-promoted ring opening. However, if a sufficiently strong electron-donor substituent is positioned to stabilize the developing positive charge, ring opening without Fp participation may occur, with consequent racemization of optical centers. This alternative pathway must consequently be taken into account in the design of enantioselective reactions employing these systems.

Experimental Section

Reactions were carried out under argon or nitrogen atmosphere using standard Schlenk technique. Solvents were distilled under nitrogen from sodium/benzophenone (ether and THF) or CaH_2 (CH_2Cl_2 and hexane). Alumina refers to Basic Alumina Activity IV. Elemental analyses were carried out by Galbraith Labs (Knoxville, TN) or MultiChemLaboratories (Lowell, MA). IR spectra were recorded on a PE-683 or a PE-1330 spectrophotometer and are calibrated against a polystyrene standard. ^1H and ^{13}C NMR spectra were taken on a Varian XL-300 (NIH-1-S10RR01493-01-Al) or a Bruker AC-200 (courtesy of the Worcester NMR Consortium) spectrometer and referenced to TMS (^1H) or solvent (^{13}C).

Dicarbonyl(η^5-cyclopentadienyl)(η^2-*trans*-4a,5,6,7,8,8a-hexahydrobenzo-1,4-dioxin)iron(II) Tetrafluoroborate (9). Fp-dimethoxyethene tetrafluoroborate[3] (1.41 g, 4.0 mmol) and *trans*-1,2-cyclohexanediol (2.32 g, 20 mmol, 5 equiv) were slurried in 50 mL of CH_2Cl_2 at −10 °C. A constant flow of argon was applied during the reaction to entrain the methanol byproduct out of the system. The mixture was thus flushed to dryness and redissolved in CH_2Cl_2 three times over the course of 30 h, each time giving an orange solution. Finally, ether was added slowly to precipitate a solid, which was collected by suction filtration and washed with ether. The compound was dried in vacuo to give an orange solid (1.55 g, 96% crude). Recrystallization from CH_2Cl_2/ether gave pure **9** as a yellow powder (1.37 g, 85%): IR (CD_3NO_2) 2069, 2028 cm^{-1} (C≡O); ^1H NMR (CD_3NO_2/TMS) δ 7.68 (d, 1 H, J = 2 Hz, =C*H*), 7.22 (d, 1 H, J = 2 Hz, =C*H*), 5.53 (s, 5 H, Cp), 3.58, 3.32 (2 m, 2 H, OC*H*CHO), 2.10, 1.76 (2 m, 4 H, OCHCH_2's), 1.35 (m, 4 H, OCHCH$_2$CH_2's); ^{13}C NMR (CD_3NO_2/TMS) δ 211.4, 210.9 (C≡O), 109.5, 94.9 (HC=*C*H), 89.3 (Cp), 78.6, 77.7 (O*C*HCHO), 30.6, 30.4 (OCHCH$_2$'s), 24.6, 24.5 (OCHCH$_2$CH_2's). Anal. Calcd for $C_{15}H_{17}BF_4FeO_4$: C, 44.60; H, 4.24. Found: C, 40.06; H, 3.98. This was the best analysis result. Repeated attempts have failed to produce more accurate results.

***cis*-Dicarbonyl(η^5-cyclopentadienyl)(η^2-*cis*-4a,5,6,7,8,8a-hexahydrobenzo-1,4-dioxin)iron(II) Tetrafluoroborate (10).** Same procedure as in the preparation of **9** using *cis*-1,2-cyclohexanediol. Recrystallization gave a yellow powder, (0.86 g, 53%): IR (CD_3NO_2) 2068, 2027 cm^{-1} (C≡O); ^1H NMR (CD_3NO_2) δ 7.40 (br s, 2 H, =C*H*'s), 5.50 (s, 5 H, Cp), 3.93 (br s, 2 H, OC*H*CHO), 2.00–1.20 (m, 8 H, CH_2's); at −60 °C δ 7.60 (br s, 1 H, =C*H*), 7.20 (br s, 1 H, =C*H*), 5.50 (s, 5 H, Cp), 4.05, 3.82 (2 br s, 2 H, OC*H*CHO), 2.10–1.20 (m, 8 H, CH_2's); ^{13}C NMR (CD_3NO_2/TMS) δ 212.2, 211.5 (C≡O), 105.0, 95.0 (HC=*C*H), 89.5 (Cp), 73.6, 72.4 (O*C*HCHO), 30.1, 26.3 (OCHCH$_2$'s), 24.7, 20.2 (OCHCH$_2$CH_2's). Anal. Calcd for $C_{15}H_{17}BF_4FeO_4$: C, 44.60; H, 4.24. Found: C, 44.43; H, 4.28.

Dicarbonyl(η^5-cyclopentadienyl)(*cis*,*trans*-2,3,4a,5,6,7,8,8a-octahydrobenzodioxin-2-yl)iron(II) (11a). Sodium borohydride (0.076 g, 2.0 mmol) and sodium methoxide (0.118 g, 2.2 mmol, 10% excess) were slurried in 10 mL of THF and cooled to −20 °C. Compound **9** (0.808 g, 2.0 mmol) was added. A color change from yellow slurry to brown solution was observed within 10 min. The reaction was monitored by TLC (alumina, 50% ether/hexane) to detect formation of the product (R_f = 0.7, yellow) and quenched after 1 h by addition of 10 drops of H_2O. The reaction was stirred an additional 5 min and filtered through a short plug of alumina, and the solvent was removed from the filtrate to give 0.61 g of crude product (96%). Column chromatography (alumina, 50% CH_2Cl_2/hexane) removed traces of Fp_2 and gave the product as a yellow solid (0.57 g, 90%): IR (CH_2Cl_2) 2000, 1945 cm^{-1} (C≡O); ^1H NMR (C_6D_6/CS_2/TMS) δ 6.05 (d, 1 H, J = 3 Hz, Fp-C*H*), 4.50 (s, 5 H, Cp), 3.94 (d of d, 1 H, J = 3 Hz/12 Hz, Fp-CHCH_{ax}), 3.42 (d, 1 H, J = 12 Hz, Fp-CHCH_{eq}), 3.27, 2.96 (2 m, 2 H, OC*H*CHO), 1.61 (br m, 4 H, OCHCH_2's), 1.24 (br m, 4 H, OCHCH$_2$CH_2's); ^{13}C NMR (C_6D_6/CS_2/TMS) δ 218.4, 217.4 (C≡O), 86.8 (Cp), 76.9 (Fp-CH), 78.1 (Fp-CHCH$_2$), 80.9, 75.2 (O*C*HCHO), 31.5, 31.2 (OCHCH$_2$'s), 25.4, 25.2 (OCHCH$_2$CH_2's). Anal. Calcd for $C_{15}H_{18}FeO_4$: C, 56.63; H, 5.70. Found: C, 57.41; H, 5.76.

Dicarbonyl(*trans*,*cis*,*trans*-3-cyano-2,3,4a,5,6,7,8,8a-octahydrobenzodioxin-2-yl)(η^5-cyclopentadienyl)iron(II) (11b). Compound **9** (0.57 g, 1.41 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to 0 °C. Et_4NCN[16] (0.33 g, 2.12 mmol, 50% excess) was added in a single portion with stirring. A color change from yellow to brown was observed almost immediately. The reaction mixture was stirred for an additional half hour, and then Et_2O (10 mL) was added to precipitate salts. The mixture was then filtered through a short plug of alumina, and the solvent was removed in vacuo to give a red oil (0.41 g, 86%). Column chromatography on alumina (50% ether/petroleum ether) gave a yellow crystalline solid (0.36 g, 75%): IR (CH_2Cl_2) 2005, 1950 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$/TMS) δ 6.2 (s, 1 H, Fp-C*H*), 4.86 (s, 5 H, Cp), 4.30 (s, 1 H, N≡CC*H*), 3.60, 3.40 (2 m, 2 H, OC*H*CHO), 1.76 (br m, 4 H, OCHCH_2's), 1.40 (br m, 4 H, OCHCH$_2$CH_2's); ^{13}C NMR ($CDCl_3$) δ 216.8, 215.8 (C≡O), 118.3 (C≡N), 86.7 (Cp), 77.1, 75.0 (O*C*HCHO), 74.7 (Fp-CH), 73.3 (*C*HC≡N), 30.3, 29.7 (OCHCH$_2$'s), 24.5, 24.2 (OCHCH$_2$CH_2's). Anal. Calcd for $C_{16}H_{17}FeNO_4$: C, 56.00; H, 4.99; N, 4.08. Found: C, 55.61; H, 5.16; N, 3.90.

Dicarbonyl(η^5-cyclopentadienyl)(*trans*,*cis*,*trans*-3-phenyl-2,3,4a,5,6,7,8,8a-octahydrobenzodioxin-2-yl)iron(II) (11c). Compound **9** (0.50 g, 1.23 mmol) was slurried in 20 mL of THF and cooled to −60 °C. Phenylmagnesium bromide (0.45

(14) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(15) For a discussion of stabilization in analogous 12-electron $C_2H_5^+$ systems, see: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985; Chapter 10.

(16) Andreades, S.; Zahnow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 4181.

mL of 3 M in Et_2O, 1.35 mmol, 10% excess) was added dropwise via syringe over the course of 10 min. The reaction mixture was allowed to stir for an additional 4 h, and then Et_2O (20 mL) was added slowly to precipitate salts. The cold mixture was then quickly filtered through a plug of alumina, and the solvent was removed in vacuo to give a red solid (0.42 g, 87% crude). NMR spectroscopy showed the presence of Fp_2 and Fp-phenyl, but attempts to remove these via column chromatography led to significant decomposition and rearrangement to compound **18**. Only traces of pure **11c** were recovered and used for elemental analysis. Spectra were taken on samples containing the impurities: IR (CH_2Cl_2) 2000, 1940 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$/TMS) δ 7.6–7.2 (m, 5 H, Ph), 6.95 (br s, 1 H, Fp-C*H*), 4.75 (s, 5 H, Cp), 4.55 (s, 1 H, N≡CC*H*), 3.70, 3.50 (2 m, 2 H, OC*H*C*H*O), 1.75 (br m, 4 H, OCHCH_2's), 1.30 (br m, 4 H, OCHCH$_2$CH_2's); ^{13}C NMR ($CDCl_3$) δ 217.6, 217.1 (C≡O), 142.3 (iPh), 86.4 (Cp), 77.1, 75.0 (O*C*HCHO), 74.7 (Fp-*C*H), 73.3 (*C*HC≡N), 30.3, 29.7 (OCHCH$_2$'s), 24.5, 24.2 (OCHCH$_2$CH$_2$). Anal. Calcd for $C_{21}H_{22}FeO_4$: C, 63.98; H, 5.62. Found: C, 63.67; H, 5.42.

Dicarbonyl(η⁵-cyclopentadienyl)(*trans*,*trans*-2,3,4a,5,6,7,8,8a-octahydrobenzodioxin-2-yl)iron(II) (12a). Same procedure as **11a** using compound **10**. Crude yield was quantitative. Column chromatography gave a yellow solid (0.42 g, 66%). The lower yield after chromatography may be due to ring opening and decomposition as in the attempted purification of **11c**: IR (CH_2Cl_2) 2010, 1954 cm^{-1} (C≡O); ^1H NMR (C_6D_6/CS_2/TMS, 0 °C) δ 5.50 (d of d, 1 H, J = 3 Hz/11 Hz, Fp-C*H*), 4.23 (s, 5 H, Cp), 3.77 (app t, 1 H, J = 11 Hz/12 Hz, Fp-CHCH_{ax}), 3.67 (d of d, 1 H, J = 3 Hz/12 Hz, Fp-CHCH_{eq}), 3.41, 2.34 (2 m, 2 H, OC*H*C*H*O), 1.84–0.97 (br m, 8 H, CH_2's); ^{13}C NMR (C_6D_6/CS_2/TMS, 0 °C) δ 217.3, 216.9 (C≡O), 85.2 (Cp), 79.4 (Fp-CHCH$_2$), 76.9, 74.5 (O*C*HCHO), 68.5 (Fp-*C*H), 31.4, 24.9, 24.7, 20.6 (*C*H$_2$'s). Anal. Calcd for $C_{15}H_{18}FeO_4$: C, 56.63; H, 5.70. Found: C, 57.18; H, 5.34.

Dicarbonyl(*trans*,*trans*,*trans*-3-cyano-2,3,4a,5,6,7,8,8a-octahydrobenzodioxin-2-yl)(η⁵-cyclopentadienyl)iron(II) (12b). Same procedure as **11b**, using compound **10** as the starting material. Column chromatography on alumina (50% ether/petroleum ether) gave a yellow oil (0.22 g, 46%): IR (CH_2Cl_2) 2010, 1950 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$/TMS) δ 5.36 (d, 1 H, J = 10.5 Hz, Fp-C*H*), 4.90 (s, 5 H, Cp), 4.56 (d, 1 H, J = 10.5 Hz, N≡CC*H*), 3.90, 3.50 (2 m, 2 H, OC*H*C*H*O), 2.1–1.30 (br m, 8 H, CH_2's); ^{13}C NMR ($CDCl_3$) δ 215.7, 214.3 (C≡O), 118.1 (C≡N), 85.4 (Cp), 76.5 (*C*HC≡N), 75.7, 75.0 (O*C*HCHO), 66.1 (Fp-*C*H), 30.4, 24.0, 23.4, 19.6 (*C*H$_2$'s). Anal. Calcd for $C_{16}H_{17}FeNO_4$: C, 56.00; H, 4.99; N, 4.08. Found: C, 55.70; H, 5.21; N, 3.87.

Dicarbonyl(η⁵-cyclopentadienyl)(formylmethyl)iron(II) *cis*-Cyclohexane-1,2-diyl Acetal (13a and 13b). To a 5-mm NMR tube containing a solution of **12a** (100 mg, 0.31 mmol in 1 mL of $CDCl_3$) was added via syringe 0.29 mL of a solution of BF_3·Et_2O in $CDCl_3$ (0.109 M, 0.031 mmol, 0.1 equiv) at room temperature. The rearrangement was followed by ^1H NMR spectroscopy and was complete within 3 h. The reaction mixture was then filtered through a short plug of alumina, the plug was washed with ether, and the solvent was removed in vacuo from the combined organics to give a brown oil. Column chromatography of the oil on alumina with 50% ether/hexane gave two fractions: mixed products **13a** and **13b** (55 mg, 55%) and hydrolyzed product (Fp-acetaldehyde): IR ($CDCl_3$) 2010, 1957 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$/TMS) δ 5.31, 5.04 (2 t, 2 H, J = 6 Hz, Fp-CH$_2$C*H*), 4.82, 4.81 (2 s, 10 H, Cp's), 4.06, 4.00 (br s, 4 H, OC*H*C*H*O's), 1.74 (br s, 8 H, OCHCH_2's), 1.54, 1.28 (2 m, 8 H, OCHCH$_2$CH_2's), 1.45, 1.43 (2 d, 4 H, J = 6 Hz, Fp-CH_2); ^{13}C NMR ($CDCl_3$/TMS) δ 216.8 (C≡O), 110.6, 109.0 (Fp-CH$_2$*C*H), 85.04, 85.00 (Cp's), 74.5, 73.8 (O*C*HCHO), 28.9, 27.3 (OCH*C*H$_2$), 21.2, 21.0 (OCHCH$_2$*C*H$_2$), 5.3, 4.4 (Fp-*C*H$_2$).

Dicarbonyl(η⁵-cyclopentadienyl)(cyanoformylmethyl)iron(II) *cis*-Cyclohexane-1,2-diyl Acetal (15). This compound was prepared in the same manner as **13** using **12b** as the starting material. From 63 mg of **12b**, 28 mg (44%) of **15** was recovered: IR ($CDCl_3$) 2005, 1950 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$/TMS) δ 5.10 (d, 1 H, J = 7 Hz, Fp-CHC*H*), 4.75 (s, 5 H, Cp's), 4.10 (m, 2 H, OC*H*C*H*O), 2.40 (d, 1 H, J = 7 Hz, Fp-C*H*), 1.80 (br s, 4 H, OCHCH_2's), 1.30 (br m, 4 H, OCHCH$_2$CH_2's); ^{13}C NMR ($CDCl_3$/TMS) δ 216.8 (C≡O), 124.5 (C≡N), 98.3 (Fp-CH*C*H), 84.7 (Cp's), 75.2, 72.2 (O*C*HCHO), 29.7, 28.2 (OCH*C*H$_2$), 21.1, 20.5 (OCHCH$_2$*C*H$_2$), 1.5 (Fp-*C*H$_2$).

Dicarbonyl(η⁵-cyclopentadienyl)(formylphenylmethyl)iron(II) *trans*-Cyclohexane-1,2-diyl Acetal (18a and 18b). This compound was prepared in the same manner as **13** using **11c** as the starting material. From 121 mg of **11c**, 74 mg (61%) of **18** was recovered. The compounds are formed in a 3:1 ratio (by NMR). Where both are detected spectroscopically, values will be given as major/minor: IR ($CDCl_3$) 2000, 1945 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$/TMS) δ 7.3 (br m, 5 H, Ph), 5.40/5.35 (d, 1 H, J = 7 Hz, Fp-CHC*H*), 4.60 (s, 5 H, Cp), 3.90–3.60 (br m, 3 H, OC*H*C*H*O, Fp-C*H*), 2.10–1.40 (br m, 8 H, CH_2's); ^{13}C NMR ($CDCl_3$/TMS) δ 211.8 (C≡O), 145.9/147.1 (Fp-*C*H), 135.9/134.2 (ipso-Ph), 128.1, 127.9 (o-Ph, m-Ph), 125.6 (p-Ph), 105.9/108.1 (Fp-CH*C*H), 84.5/84.3 (Cp), 73.4, 73.5 (O*C*HCHO), 32.0, 30.6 (OCH*C*H$_2$), 24.0, 23.7 (OCHCH$_2$*C*H$_2$).

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Nickel-Mediated Elimination of Hydrogen Halide from Primary and Secondary Alkyl Bromides and Iodides. Synthetic Aspects

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Treatment of alkyl bromides or iodides with a low-valent nickel complex generated in situ and 1,8-diazabicyclo[5.4.0]undec-7-ene in THF under argon leads on oxidative workup to alkenes. Primary halides give predominantly or exclusively the terminal alkene whereas acyclic secondary halides give a mixture. The thermodynamically most stable alkene is isolated from the cyclic congeners, 3α- and 3β-bromocholestane, and from cholesteryl bromide.

The elimination of hydrogen halide from alkyl bromides or iodides can be achieved under a number of experimental conditions.[1] Most often bases of varying strengths are used with or without considerable heating. Subsitution

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