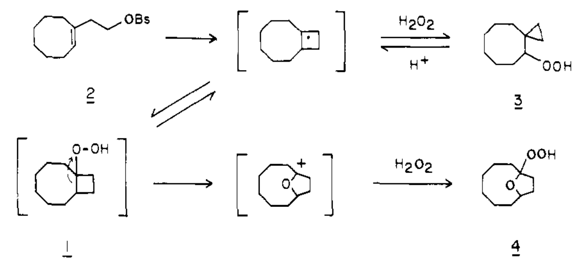
Scheme III



0 °C produced a pair of hydroxyesters that could be separated chromatographically, after *p*-nitrobenzoylation, into the cis (mp 143–145 °C)[9] and trans (mp 158–159 °C) diesters.

Optimal conversions (see Table I) of brosylates[10] are conveniently achieved by a one-pot, two-stage solvolysis procedure. Initially, the brosylate is dissolved in THF containing 1.1 equiv of powdered, suspended buffer ($K_2HPO_4 \cdot 3H_2O$). The mixture is cooled in an ice bath to avoid the small, but significant, exotherm that accompanies the mixing of high-strength H_2O_2 with organic solvents, and then the calculated amount of 90% H_2O_2 required to achieve a substrate concentration of 0.25–1.0 M in 50% THF is carefully added. The reaction vessel is then placed in a bath at the desired reaction temperature. Subsequently, when all of the brosylate has reacted, the second stage is completed by acidification with 2.1 equiv of $TsOH \cdot H_2O$ to convert **3** to **4**. The hydroperoxy hemiketal product is isolated by normal aqueous workup.

The oxa-bridged hydroperoxide products are only modestly stable. While they could be isolated and chromatographed on silica gel, concentrated solutions and purified samples rapidly lost H_2O_2 and became contaminated with dimeric peroxides. To facilitate handling, the crude hydroperoxides were immediately reduced (H_2/PtO_2 in THF).

The formation of **4** from **2** and **3**, as well as the homologous expansions, can be rationalized on the basis of a reversibly formed bicyclobutonium ion intermediate,[7,8] which, when trapped by H_2O_2 affording the fused cyclobutyl isomer, i.e., **1**, rapidly undergoes an irreversible Criegee type migration (Scheme III). As yet, we have been unable to observe any fused cyclobutyl derivatives directly. In the unbuffered system, the cyclopropylcarbinyl isomer, e.g., **3**, is observable by TLC[12] but remains in relatively low concentration throughout the course of the reaction. Although other modes of migration are possible from **1** and **3**, the principal if not exclusive pathway involves only the ring fusion atoms.

In addition to the brosylates we also find that the cyclopropylcarbinols are excellent substrates for ring expansion. Treatment of spiro[2.7]decane-4-ol[6] with TsOH in 1:1 H_2O–THF results in almost immediate conversion to **3** followed by reaction to form **4**. Since the cyclopropylcarbinols are readily available from cyclopropyl ketones, this provides an alternative route to ring expansion precursors; we are investigating the rearrangements of the cyclopropylcarbinols as well as other homoallylic systems to further explore this novel ring expansion reaction.

Acknowledgment. We thank the Boeing Co. for the gift of the Nicolet Technology Inc. 200-MHz NMR spectrometer. T.S.L. thanks the Graduate School of Washington State University for an assistantship.

Supplementary Material Available: Additional experimental data for brosylate **9**, **11**, **13**, and **15**, phenylurethane from **10** and **12**, *p*-nitrobenzoate from **4**, bicyclourethane from **14**, and urethane from **16** (2 pages). Ordering information is given on any current masthead page.

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[10] The brosylates were obtained in four steps from ketones by the following: $(MeO)_2POCHLiCO_2Me$ in THF/HMPA; LDA followed by 5% HCl; $LiAlH_4$; brosyl chloride in pyridine.

[11] 4-Hydroxycyclooctanone: Moell, H.; Urbanek, F. *Festschr. Carl Wurster 60. Geburstag* 1960, 91–97.

[12] Hydroperoxides and peroxides are conveniently and sensitively detected by TLC using Wurster dyes. [Solutions of 1% w/v *N*,*N*,*N'*,*N'*-tetramethylphenylenediamine in 50% aqueous MeOH containing 1% HOAc (Smith, L.; Hill, F. *J. Chromatogr.* **1972**, 66, 101–10).] Peroxy compounds appear as blue spots; the color from hydroperoxides develops rapidly, while some peroxides require gentle heating for development of color within a few minutes.

Cis Addition of Hydride to η^2-Alkyne Complexes by Initial Reaction at an η^5-C_5H_5 Ring. Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)FeCO(PPh_3)(\eta^1\text{-}(E)\text{-}C(CO_2Et){=}C(H)Me)$

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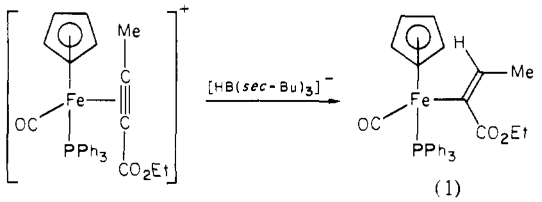
We have reported that a variety of nucleophiles will react with $[(\eta^5\text{-}C_5H_5)FeCO(L)(\eta^2\text{-alkyne})]^+$ (L = PPh_3, $P(OPh)_3$) complexes to yield η^1-alkenyl derivatives. In our initial report,[1] trans addition of the nucleophile was assumed[2] and partially verified by ^1H nuclear Overhouser effect (NOE) enhancement experiments. Subsequently, the preparation of both the *Z* and *E* isomers of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3](\eta^1\text{-}C(Me){=}C(Ph)Me)$ coupled with the solid-state structure of the *Z* isomer definitively proved trans addition of carbon nucleophiles delivered from organocuprate reagents.[3] Although trans addition of other nucleophiles, such as $[SPh]^-$, also seems certain,[4] NOE experiments tentatively indicated that the addition of hydride was overall cis. We initially believed this result to arise from trans addition followed by a cis–trans isomerization,[1] a process shown to be reasonable for other metal–alkenyl systems.[5] We show here that the course of the hydride addition reaction is first addition to the η^5-C_5H_5 ring followed by internal cis transfer of hydrogen to the alkyne from the η^4-C_5H_6 ring that forms in the first step.

In order to definitively assign the stereochemistry of an η^1-alkenyl complex formed from hydride addition, the X-ray crystal structure of the product of reaction 1 was determined.[6] The crystal and molecular structure of **1**, illustrated in Figure 1, clearly shows that the hydrogen atom at the β-alkenyl position is disposed cis with respect to iron. The regiochemistry of the reaction, addition away from the electron-withdrawing ester substituent, is as expected from our earlier structure of $(\eta^5\text{-}C_5H_5)FeCO(PPh_3)(\eta^1\text{-}C(CO_2Et){=}CMe_2)$ (**2**).[7] Bond lengths and angles are



(1)

(1)

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[1] Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923.

[2] Trans addition of nucleophiles to $[CpFe(CO)_2(\eta^2\text{-alkene})]^+$ complexes has been previously demonstrated: (a) Nicholas, K. M.; Rosan, A. M. *J. Organomet. Chem.* **1975**, *84*, 351. (b) Sanders, A.; Magatti, C. V.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1610.

[3] Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101.

[4] Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *J. Am. Chem. Soc.*, submitted for publication.

[5] Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

[6] Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with cell parameters; $a = 9.075$ (4) Å, $b = 9.414$ (4) Å, $c = 30.574$ (7) Å, $\beta = 92.31$ (4)°, with $Z = 4$. A total of 2323 reflections were measured to 2θ max of 38°. Of these 1658 reflections were considered observed ($I > 3\sigma(I)$). The final R and R_w values were 0.062 and 0.068.

[7] Reger, D. L.; McElligott, P. J.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1982**, *1*, 443.

0002-7863/83/1505-5710$01.50/0

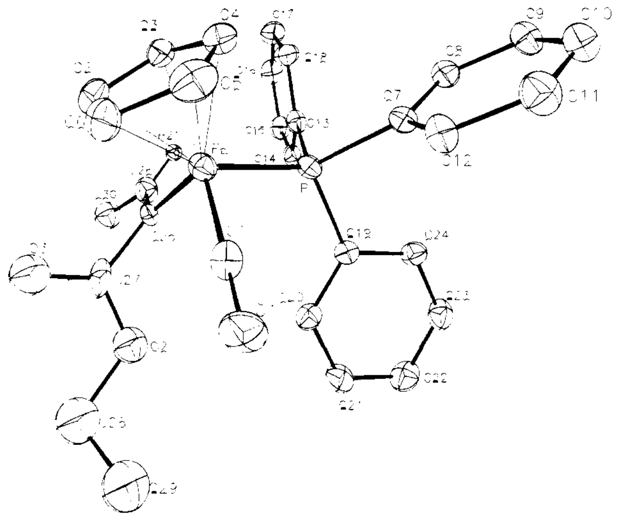
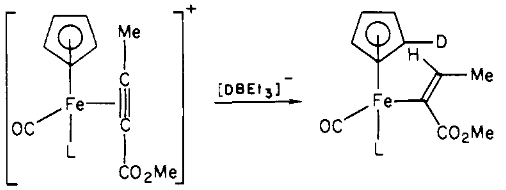


Figure 1. ORTEP plot of the molecular structure of $(\eta^5\text{-}C_5H_5)FeCO(PPh_3)(\eta^1\text{-}(E)\text{-}C(CO_2Et)=C(H)Me)$.

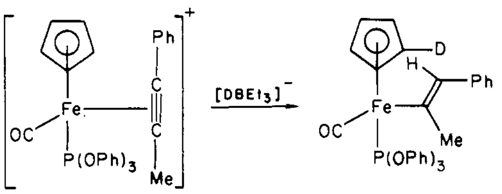
normal and quite similar to those for **2**. Most notably, the Fe–C(alkenyl) distance of 2.02 (1) Å is that expected for a single bond and is similar to the 2.030 (2) Å distance found in **2**.

Insight into how hydride adds cis is demonstrated by reactions 2 and 3. A combination of ^1H, ^{13}C and ^2H NMR spectroscopy



(2)

L = PPh$_3$, P(OPh)$_3$

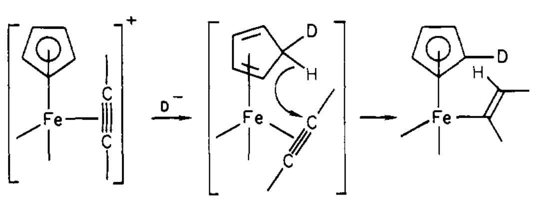


(3)

has been used to show that the added deuteride is in the Cp ring for each case. First, careful integration of the ^1H spectra shows a 3:4 ratio for the Me group(s) resonance vs. the Cp ring resonance. Also, the vinyl methyl group resonance in the product of reaction 2 is a normal doublet ($J = 7$ Hz) showing that H, not D, is geminal to it. Second, ^2H NMR spectra show a single resonance at the location expected for the Cp resonance from the ^1H NMR spectra. Again, integration vs. the natural abundance solvent resonance shows approximately one deuterium per ring. Finally, ^{13}C NMR spectra show that there is one deuterium in *each* Cp ring for all three cases. Although, we have been unable to observe the C–D carbon atom resonance in the proton decoupled spectra,[8] the remaining C–H ring carbon atoms appear as two equal-intensity resonances separated by ca. 0.1 ppm. This is what would be expected for a β-deuterium isotope shift in a C_5H_4D ring.[9]

Scheme I shows a reasonable course for these reactions. The first step, exo nucleophilic addition to an $\eta^5\text{-}C_5H_5$ ring, is a well-documented reaction.[10] The second step, transfer of an endo $\eta^4\text{-}C_5H_6$ hydrogen atom to an auxiliary ligand appears to be unique. Metal orbitals could potentially be involved in the transfer (or even a formyl type intermediate), but generation of a discrete $(\eta^5\text{-}C_5H_5)Fe(L)(\eta^2\text{-alkyne})H$ intermediate (a ligand, either CO or L, needs to dissociate in order to have an 18-electron species) seems unlikely. We note that cis addition of hydride to the 16-electron complex $[(\eta^5\text{-}C_5H_5)Mo[P(OMe)_3](\eta^2\text{-}HC{\equiv}C\text{-}t\text{-}Bu)]^+$ has been reported.[11] In contrast to our results presented above, a deuterium label (from $[BD_4]^-$) was shown to be incorporated exclusively at the β-alkenyl carbon atom.

Scheme I



Acknowledgment is made to the National Science Foundation for its support of this research through Grant CHE-8019513 (D.L.R.) and Grant CHE-8205871 (J.L.A.).

Registry No. 1, 86563-30-6; **2**, 80485-08-1; CpFeCO(P(OPh)$_3$)(η^1-(*E*)-C(CO$_2$CH$_3$)=C(H)CH$_3$), 86563-31-7; (CpFeCO(P(OPh)$_3$(η^1-(*E*)-C(Me)=C(H)Ph), 86563-32-8; $[(\eta^5\text{-}C_5H_5)FeCO(PPh_3)B]^+$ (B = ethyl 2-butynoate), 80501-95-7; $[(\eta^5\text{-}C_5H_5)FeCO(PPh_3)B]^3$ (B = methyl 2-butynoate), 86563-34-0; $[(\eta^5\text{-}C_5H_5)FeCO(P(OPh)_3)B]^+$ (B = methyl 2-butynoate), 86563-35-1; $[(\eta^5\text{-}C_5H_5)FeCO(P(OPh)_3)B]^+$ (B = 1-phenyl-1-propyne), 83096-11-1; $[HB(sec\text{-}Bu)_3]^-$, 86563-33-9; $[DBEt_3]^-$, 86563-36-2.

Supplementary Material Available: Characterization of new η^1-complexes, additional structural information, tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[8] A C–D carbon atom resonance would be split into a triplet (^2H has s = 1), line broadened due to the ^2H quadrupole and significantly lose intensity because of the loss of NOE.[9] They are generally not observed.

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Contribution of Intrinsic Volume Change of the Reactants to the Pressure Effect on Outer-Sphere and Intramolecular Electron-Transfer Reactions Involving Cobalt(III) to Cobalt(II) Reduction

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Activation volume has been used extensively for elucidating the mechanism of ligand substitution and isomerization reactions of metal complexes in solution.[1-5] On the other hand, much less study has been carried out on the electron-transfer reactions.[1,6-8]

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