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The Radical Pair Mechanism in Hydrometalation and Stoichiometric Hydrogenation Reactions of η^5-$C_5H_5Fe(CO)_2H$ with Conjugated Dienes

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The hydride η^5-$C_5H_5Fe(CO)_2H$ reacts with a variety of 1,3-dienes to form both the products of irreversible 1,4-addition of the hydride to the diene and of stoichiometric hydrogen transfer to the diene, i.e.

$$\eta^5\text{-}C_5H_5Fe(CO)_2H + CH_2{=}CRCR'{=}CH_2 \rightarrow \eta^5\text{-}C_5H_5Fe(CO)_2CH_2CR{=}CR'Me$$

$$2\eta^5\text{-}C_5H_5Fe(CO)_2H + CH_2{=}CRCR'{=}CH_2 \rightarrow MeCHRCR'{=}CH_2 + CH_2{=}CRCHR'Me + MeCR{=}CR'Me + [\eta^5\text{-}C_5H_5Fe(CO)_2]_2$$

$$R, R' = H, \text{alkyl}$$

The hydrometalation reactions are first order in both η^5-$C_5H_5Fe(CO)_2H$ and diene and zero order in added carbon monoxide, while use of η^5-$C_5H_5Fe(CO)_2D$ shows that the reaction exhibits an inverse primary isotope effect. Monitoring of the early stages of the reactions also reveals the development of striking CIDNP polarizations, and it is suggested that these "insertion" reactions involve hydrogen atom abstraction from η^5-$C_5H_5Fe(CO)_2H$ by diene to give [allyl + η^5-$C_5H_5Fe(CO)_2$] radical pairs. In the spin-selective step, the component radicals can then either couple to give the geminate σ-allyl products of hydrometalation or diffuse from the solvent cage and react with a second molecule of η^5-$C_5H_5Fe(CO)_2H$ to give the nongeminate products, the monoolefins, and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. It is also shown that trace concentrations of thiophenol stabilize η^5-$C_5H_5Fe(CO)_2H$ with respect to decomposition to H_2 and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$.

Introduction

We have previously demonstrated that hydrometalation and stoichiometric hydrogenation reactions of $HMn(CO)_5$ with conjugated dienes (as in eq 1 and 2, respectively) both

$$HMn(CO)_5 + CH_2{=}CHCH{=}CH_2 \rightarrow \textit{cis-} \text{ and } \textit{trans-}MeCH{=}CHCH_2Mn(CO)_5 \quad (1)$$

$$2HMn(CO)_5 + CH_2{=}CHCH{=}CH_2 \rightarrow \textit{cis-} \text{ and } \textit{trans-}MeCH{=}CHMe + CH_2{=}CHCH_2Me + Mn_2(CO)_{10} \quad (2)$$

proceed via the radical pair mechanism outlined in general fashion in Figure 1 (R, R′ = H, alkyl; M = $Mn(CO)_5$).[1a] The first step in both eq 1 and eq 2 involves transfer of the hydride hydrogen atom to a terminal carbon atom of the diene to form a radical pair in a solvent cage. The thus-formed caged radicals can then couple to give geminate hydrometalation products (eq 1 or i–iv of Figure 1), or they can diffuse from the solvent cage and react with a second molecule of hydride to form the nongeminate products (eq 2 or v–vii of Figure 1).

Evidence for this type of mechanism was found in the product distributions from the reactions of several dienes, in the rate equations, which were first order in each of the reactants but zero order in carbon monoxide and which exhibited an inverse kinetic isotope effect when $DMn(CO)_5$ was used, and in the observations of striking CIDNP polarizations in the ^1H NMR spectra of reaction mixtures. There is an obvious parallel between the chemistry of Figure 1 and similar hydrometalation and diene hydrogenation reactions of η^5-$C_5H_5M(CO)_3H$ (M = Mo, W),[2a] $HMn(CO)_5$,[2b–e] and $HCo(CO)_4$[2e–n] with aromatic olefins, of $HMn(CO)_5$[2o] and $HCo(CO)_4$[2p] with polyaromatic hydrocarbons, and of $FeH(SiCl_3)(CO)_4$,[2q] $HMn(CO)_5$,[1,2r] and $HCo(CO)_4$[2r] with dienes. In all cases, radical pair intermediates have been proposed, although only nongeminate products are observed in most.

Since it has long been held that the formation of "insertion" products, as in eq 1, generally involves initial coordination of the olefin followed by migration of a metal-bonded hydrogen atom to C-2 of the incipient alkyl group,[3] the novelty of the radical pair mechanism clearly calls for further investigations into its possible generality. We have therefore been engaged in a search for other examples, one result of which has been the serendipitous discovery of a rather extensive chemistry of persistent chromium- and molybdenum-centered 17-electron radicals.[4] However, we have also found further examples of

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(1) (a) Wassink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* 1987, *109*, 1995. (b) Thomas, M. J.; Shackleton, T. A.; Wright, S. C.; Gillis, D. J.; Colpa, J. P.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* 1986, 312.

(2) (a) Sweaney, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* 1981, *216*, 57. (b) Sweaney, R. L.; Halpern, J. *J. Am. Chem. Soc.* 1977, *99*, 8335. (c) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* 1981, *222*, C5. (d) Matsui, Y.; Orchin, M. *J. Organomet. Chem.* 1983, *244*, 369. (e) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Mol. Catal.* 1982, *16*, 43. (f) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* 1979, *182*, 299. (g) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* 1980, *199*, 265. (h) Roth, J. A.; Wiseman, P. *J. Organomet. Chem.* 1981, *217*, 231. (i) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Organomet. Chem.* 1981, *221*, 193. (j) Nalesnik, T. E.; Orchin, M. *Organometallics* 1982, *1*, 222. (k) Ungváry, F.; Markó, L. *Organometallics* 1982, *1*, 1120. (l) Ungváry, F.; Markó, L. *J. Organomet. Chem.* 1983, *249*, 411. (m) Roth, J. A.; Wiseman, P.; Ruszala, L. *J. Organomet. Chem.* 1983, *240*, 271. (n) Bockman, T. M.; Garst, J. F.; King, R. B.; Markó, L.; Ungváry, F. *J. Organomet. Chem.* 1985, *279*, 165. (o) Sweaney, R. L.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* 1981, *213*, 487. (p) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* 1975, *97*, 7186. (q) Connolly, J. W. *Organometallics* 1984, *3*, 1333. (r) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* 1986, *108*, 1689.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

0276-7333/89/2308-2225$01.50/0

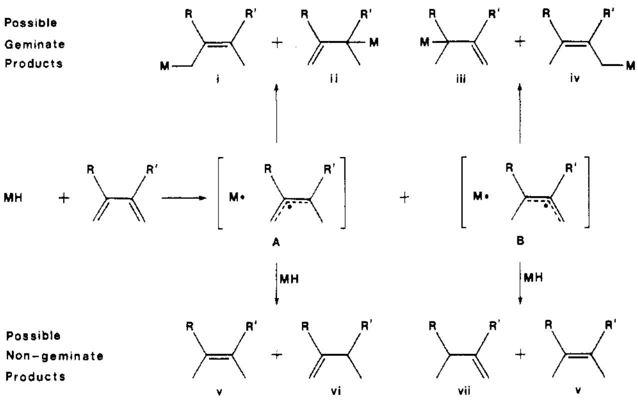

Figure 1. The radical pair mechanism proposed for the reactions of $HMn(CO)_5$ and η^5-$C_5H_5Fe(CO)_2H$ with 1,3-dienes, showing the intermediate radical pairs and the possible geminate and nongeminate products from each.

the radical pair mechanism in the "insertion" and hydrogen transfer reactions of η^5-$C_5H_5Fe(CO)_2H$ with conjugated dienes. A preliminary report of aspects of this work has appeared,[1b] and we now give a full account of our investigation.

Experimental Section

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere by using dried, deoxygenated solvents. NMR spectra were obtained on Bruker HX-60, CXP-200, and AM-400 FT NMR spectrometers, and chemical shifts are referenced to tetramethylsilane (TMS) or hexamethyldisiloxane (HMDS) for ^1H, $^2D\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra. NMR data for the organoiron complexes prepared in this investigation accompany details of the syntheses (see below).

IR spectra were obtained by using a Bruker IFS-85 FT-IR spectrometer and gas chromatographs by using a Hewlett-Packard HP 5880A gas chromatograph equipped with flame ionization and thermal conductivity detectors. Elemental analyses were performed by the Guelph Chemical Laboratories Ltd. in Guelph, Ontario.

Cyclopentadienyliron dicarbonyl hydride was prepared from $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ by using a method based on that of Whitesides and Shelley.[5] The compound $Na[\eta^5$-$C_5H_5Fe(CO)_2]$ was prepared by cleavage of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ with sodium amalgam in THF and, after removal of the THF under reduced pressure, was either stored under nitrogen at −25 °C in a freezer or at ambient temperature in a glovebox. η^5-$C_5H_5Fe(CO)_2H$ was generated from the anion as required by adding the desired amount of glacial acetic acid in pentane. The hydride solution was decanted from any remaining anion and NaOAc residue into a separate flask for subsequent reactions. Rapid elution of the solution through alumina removed any $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ generated, yielding a temporarily pure solution of hydride. IR: ν(CO) 2013, 1952 cm^{-1} in THF; 2023, 1967 cm^{-1} in pentane. ^1H NMR in benzene-d_6: δ 4.17 (s, η^5-C_5H_5), −11.77 (br s, FeH). ^{13}C NMR in benzene-d_6: δ 216.0 (CO), 81.8 (η^5-C_5H_5). The deuterium analogue η^5-$C_5H_5Fe(CO)_2D$ was generated by using DOAc prepared from the reaction of acetic anhydride with D_2O, although in this case elution of the solution through alumina was omitted in order to avoid exchange of the deuterium with residual water on the alumina.

General Procedure for Reactions of η^5-$C_5H_5Fe(CO)_2H$ with Conjugated Dienes. Mixtures of η^5-$C_5H_5Fe(CO)_2H$ and excesses of the conjugated dienes in pentane or THF were stirred under nitrogen at room temperature while being monitored by IR spectroscopy. When all of the η^5-$C_5H_5Fe(CO)_2H$ appeared to have been consumed (15–20 min, depending on the diene and the ratio of reactants), the solvent and any other low boiling organic compounds were removed in vacuo, yielding dark purple-brown residues. Chromatography on alumina was utilized to separate the organometallic products, the hydrometalated products forming mobile yellow bands that were removed by pentane as yellow eluates. Removal, in vacuo, of the solvent from the yellow eluates gave amber oils of the products, typically in low yields. The dimer $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, which was mobile as a red-purple band using a more polar solvent, accounted for the majority of the remaining iron-containing products.

To determine the fate of hydrogen atoms transferred from the iron, all the dienes were reacted with η^5-$C_5H_5Fe(CO)_2D$, following the procedures outlined above. The hydrometalated products were characterized by ^2H NMR and ^{13}C NMR spectroscopy.

A combination of GC and NMR spectroscopy was employed to identify the low-boiling organic products and to determine yields of all products from the reactions of η^5-$C_5H_5Fe(CO)_2H$ with isoprene, 2,3-dimethyl-1,3-butadiene, and 1,3-cyclohexadiene. Assignments of the resonances of the olefinic products of hydrogenation were made on the basis of comparisons with spectra of the pure materials.

The reaction of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-butadiene at 1 atm was complete within 15–20 min, and, after removal of the solvent, the crude product was chromatographed to yield 1.5 g (23%) of an amber oil, identified as a mixture of the cis and trans isomers of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHMe$ by comparison of the IR (ν(CO) 2001, 1945 cm^{-1} in THF; 2011, 1960 cm^{-1} in pentane) and ^1H NMR data with the literature,[6-9] and 2.0 g (40%) of the dimeric $[\eta^5$-$C_5H_5Fe(CO)_2]_2$.

***cis*-η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHMe$.** ^1H NMR in benzene-d_6: δ 1.73 (d, J = 7 Hz, Me), 2.24 (d, J = 8 Hz, CH_2), 4.03 (s, η^5-C_5H_5), 5.30 (dq, J = 11, 7 Hz, CH), 5.86 (m, CH). ^{13}C NMR in benzene-d_6: δ 4.4 (CH_2), 18.3 (Me), 85.7 (η^5-C_5H_5), 117.7 (=CH), 141.6 (=CH), 217.7 (CO).

***trans*-η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHMe$.** ^1H NMR in benzene-d_6: δ 1.67 (d, J = 6 Hz, Me), 2.20 (d, J = 8 Hz, CH_2), 4.00 (s, η^5-C_5H_5), 5.42 (dq, J = 15, 6 Hz, CH), 5.78 (dt, J = 15, 8 Hz, CH). ^{13}C NMR in benzene-d_6: δ −1.8 (CH_2), 13.1 (Me), 85.3 (η^5-C_5H_5), 116.6 (=CH), 140.8 (=CH), 217.5 (CO).

Reaction of η^5-$C_5H_5Fe(CO)_2H$ with isoprene was complete within 20–30 min, and purification by chromatography yielded 1.7 g (46%) of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ and 1.0 g (19%) of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$, identified by comparison with IR and NMR data in the literature.[8,9] IR ν(CO): 1999, 1943 cm^{-1} in THF; 2009, 1957 cm^{-1} in 30/60 petroleum ether. ^1H NMR data in benzene-d_6: δ 1.71 (s, 2 × Me), 2.27 (d, J = 9 Hz, CH_2), 4.10 (s, η^5-C_5H_5), 5.60 (t, m, $J \approx 9$, 1 Hz, CH). ^{13}C NMR in benzene-d_6: δ −0.1 (CH_2), 18.0 (Me), 26.3 (Me), 85.3 (η^5-C_5H_5), 124.4 (C=), 135.3 (C=), 217.6 (CO).

In a complementary experiment, a yellow-orange solution of η^5-$C_5H_5Fe(CO)_2H$ (11 mmol) in 150 mL of dry, degassed pentane was treated with 0.2 mL of a 0.49 M pentane solution of thiophenol (1 mol %). After being left standing for 2 h, the solution IR spectrum indicated that very little decomposition of the η^5-$C_5H_5Fe(CO)_2H$ had occurred. On addition of 2.2 mL (22 mmol) of isoprene, the color of the solution darkened. The reaction was monitored by IR spectroscopy for 4 h although it was determined to be complete in <1 h. The ν(CO) of the products indicated the formation of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$ and $[\eta^5$-$C_5H_5Fe(CO)_2]_2$. A precipitate of the latter formed during the reaction, as its solubility limit in pentane was exceeded.

Reaction of η^5-$C_5H_5Fe(CO)_2H$ with 2,3-dimethyl-1,3-butadiene was complete within about 1 h, after which chromatography

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(4) (a) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563. (b) Morton, J. R.; Preston, K. F.; Cooley, N. A.; Baird, M. C.; Krusic, P. J.; McLain, S. J. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 3535. (c) Cooley, N. A.; Baird, M. C.; Morton, J. R.; Preston, K. F.; LePage, Y. *J. Magn. Reson.* **1988**, *76*, 325. (d) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965. (e) Jaeger, T. J.; Baird, M. C. *Ibid.* **1988**, *7*, 2074. (f) Drake, P. R.; Baird, M. C. *J. Organomet. Chem.* **1989**, *363*, 131.

(5) Whitesides, T. H.; Shelley, J. *J. Organomet. Chem.* **1975**, *92*, 215.

(6) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189.

(7) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149.

(8) Downs, R. L.; Wojcicki, A. *Inorg. Chim. Acta* **1978**, *27*, 91.

(9) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

yielded 0.9 g (20%) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and 0.6 g (8%) of an amber oil. No literature data were found for the expected product η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$, but elemental analyses and spectral data support this structural formulation. Anal. Calcd for $C_{13}H_{16}FeO_2$: C, 60.03; H, 6.20. Found: C, 60.39, 60.03; H, 6.25, 6.74. IR: ν(CO) 1998, 1941 cm^{-1} in THF; 2007, 1955 cm^{-1} in pentane. ^1H NMR in benzene-d_6: δ 1.65 (s, Me), 1.74 (s, Me), 1.81 (s, Me), 2.32 (s, CH_2), 4.11 (s, η^5-C_5H_5). ^{13}C NMR in benzene-d_6: δ 6.2 (CH_2), 20.4 (Me), 21.2 (Me), 21.4 (Me), 85.4 (η^5-C_5H_5), 119.8 (C=), 137.8 (C=), 217.9 (CO).

Reaction of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-cyclohexadiene yielded after workup 2.6 g (61%) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and 1.4 g (21%) of an amber oil, identified as η^5-$C_5H_5Fe(CO)_2$(cyclohex-2-enyl) by comparison with the literature.[9] IR: ν(CO) 1993, 1950 cm^{-1} in THF; 2008, 1956 cm^{-1} in pentane. ^1H NMR in benzene-d_6: δ 2.18–1.38 (m, 3 × CH_2), 3.31 (br s, CH), 4.10 (s, η^5-C_5H_5), 5.44 (m, =CH), 5.87 (br d, =CH). ^{13}C NMR in benzene-d_6: δ 20.8 (FeCH), 25.1 (CH_2), 25.7 (CH_2), 38.1 (CH_2), 86.2 (η^5-C_5H_5), 119.9 (=CH), 142.4 (=CH), 218.0 (CO).

Reaction of η^5-$C_5H_5Fe(CO)_2H$ with myrcene ($CH_2{=}CHC(CH_2CH_2CHC{=}Me_2){=}CH_2$) was complete within 45 min. Chromatographic workup yielded a clear organic fraction containing predominantly unreacted myrcene and 0.98 g (17%) of an amber oil formulated as a mixture of two isomers of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMeCH_2CH_2CH{=}CMe_2$. Although purification to obtain good elemental analyses was unsuccessful (Anal. Calcd for $C_{17}H_{22}FeO_2$: C, 64.98; H, 7.06. Found: C, 66.76, 66.82; H, 7.84, 7.87), the identity of this product is certain based on spectroscopical analysis. IR: ν(CO) 1999, 1943 cm^{-1} in THF; 2009, 1957 cm^{-1} in pentane.

Major Isomer. ^1H NMR in benzene-d_6: δ 1.58 (s, Me), 1.69 (s, 2 × Me), 2.07 (t, J = 7 Hz, CH_2), 2.18 (t, J = 7 Hz, CH_2), 2.25 (d, J = 10 Hz, CH_2), 4.15 (s, η^5-C_5H_5), 5.23 (m, =CH), 5.60 (t, J = 10 Hz, =CH). ^{13}C NMR in benzene-d_6: δ 0.0 ($FeCH_2$), 16.3 (Me), 17.7 (Me), 25.8 (Me), 26.8 (CH_2), 40.9 (CH_2), 85.9 (η^5-C_5H_5), 124.7 (=CH), 128.5 (C=), 131.0 (C=), 135.6 (C=), 217.8 (CO).

Minor Isomer. ^1H NMR in benzene-d_6: δ 1.60 (s, Me), 1.70 (s, Me), 1.72 (s, Me), 2.30–2.15 (m, 3 × CH_2), 4.12 (s, η^5-C_5H_5), 5.30 (m, =CH), 5.55 (m, =CH). ^{13}C NMR in benzene-d_6: δ –0.2 ($FeCH_2$), 17.7 (Me), 24.1 (Me), 25.8 (Me), 26.6 (CH_2), 32.5 (CH_2), 85.9 (η^5-C_5H_5), 124.5 (=CH), 128.6 (C=), 131.2 (C=), 135.8 (C=), 217.8 (CO).

General Procedures for CIDNP Experiments. CIDNP experiments were carried out by using a Bruker HX-60 magnet interfaced to the Aspect 3000 computer of a Bruker AM-400 spectrometer. The procedure used involved the preparation of a number of samples of η^5-$C_5H_5Fe(CO)_2H$ in benzene-d_6, with hexamethyldisiloxane (HMDS) as an internal reference. These samples were kept frozen in a dry ice/2-propanol slush bath until they were required, when they were thawed and placed in the preheated probe of the HX-60. A spectrum of the η^5-$C_5H_5Fe(CO)_2H$ sample was then obtained, and the sample was removed from the probe and treated with 50 μL of diene. The tube was inverted twice to mix the contents and replaced in the preheated HX-60 probe. Each reaction was monitored every 10 s (two scans) for 3 min and then every minute for 4 more minutes. Reaction conditions (i.e. concentrations, temperatures) were normally chosen such that the CIDNP polarizations were maximized and that the reactions were completed during the program run time.

Kinetic Studies of the Reaction between η^5-$C_5H_5Fe(CO)_2H$ and 2,3-Dimethyl-1,3-butadiene. η^5-$C_5H_5Fe(CO)_2H$ (1.2 mmol), stabilized by the addition of thiophenol (0.004 mmol), was dissolved in 4.2 mL of benzene-d_6 containing 90 μL of benzene (internal standard for integration purposes, sufficient to swamp the thiophenol phenyl resonance). This solution of the hydride was then used to prepare six NMR samples, which were kept frozen in a dry ice/2-propanol slush bath until used. In a similar manner, samples of the deuteride under nitrogen and of the hydride under carbon monoxide were also prepared. Each kinetic run was carried out by adding a known excess of 2,3-dimethyl-1,3-butadiene thermostated at 294 (±1) K. After mixing, single-scan spectra (400 MHz) were obtained at 1-min intervals until the η^5-C_5H_5 resonance of the hydride had disappeared.

Attempted Reaction of η^5-$C_5H_5Fe(CO)_2H$ with Ethylene. A low-boiling petroleum ether solution of η^5-$C_5H_5Fe(CO)_2H$ (17 mmol) was treated with ethylene gas by slowly bubbling the ethylene through the hydride solution, the reaction being monitored by IR spectroscopy for 7 h. During this time, there were no indications that an insertion product had formed, only η^5-$C_5H_5Fe(CO)_2H$ and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ being identified in the IR spectra.

Results and Discussion

Syntheses of η^5-$C_5H_5Fe(CO)_2H$. η^5-$C_5H_5Fe(CO)_2H$ was prepared from the reaction of the sodium salt of the $[\eta^5\text{-}C_5H_5Fe(CO)_2]^-$ anion with glacial acetic acid according to the literature,[5] as in eq 3.

$$\mathrm{Na}[\eta^5\text{-}C_5H_5Fe(CO)_2] + \mathrm{HOAc} \rightarrow \eta^5\text{-}C_5H_5Fe(CO)_2H + \mathrm{NaOAc} \quad (3)$$

Solutions of η^5-$C_5H_5Fe(CO)_2H$ prepared in this way were found generally to decompose to $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ on sitting under nitrogen at ambient temperature, in accord with previous reports that η^5-$C_5H_5Fe(CO)_2H$ spontaneously decomposes thermally[10,11] to form $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and H_2. We have earlier suggested, however, that the decomposition arises not from an inherent thermal instability of the hydride at ambient temperatures but rather from reactions with trace impurities.[12] The impurities were thought to be unidentified, adventitious radicals which reacted via a nonchain process.

As will be discussed elsewhere,[13] decay in the concentration of the η^5-$C_5H_5Fe(CO)_2H$ generally appears to be exponential, but the rate and even the extent of the process are erratic and the mechanism of the decomposition is not yet known. Interestingly, the addition of as little as 1 mol % of thiophenol to solutions of η^5-$C_5H_5Fe(CO)_2H$ is found to almost completely shut down the decomposition of η^5-$C_5H_5Fe(CO)_2H$ to $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. After monitoring such solutions for 12 h, greater than 99% of the initial concentrations of η^5-$C_5H_5Fe(CO)_2H$ remains, as determined by IR spectroscopy.[13] For this reason, several of the experiments carried out in the course of this study were performed in the presence of 1 mol % thiophenol.

Although addition reactions of thiophenol with conjugated dienes have been reported,[14] such reactions take days and thus presumably cannot be a factor in the reactions of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-dienes, which are complete within 2 h. In order to investigate the possibility that thiophenol reacts with the hydride, a 1:1 ratio of thiophenol and η^5-$C_5H_5Fe(CO)_2H$ was refluxed overnight in hexanes. Periodic monitoring of the reaction by IR spectroscopy indicated that there was no apparent reaction between the two compounds, although there was slight decomposition of the η^5-$C_5H_5Fe(CO)_2H$ to $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. It would thus appear that thiophenol should not interfere directly with the reactions of η^5-$C_5H_5Fe(CO)_2H$ with the dienes, and interpretations of our observations have therefore been made on the basis of that assumption.

Reactions of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-Dienes. The reaction of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-butadiene yielded $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ as the major organoiron product. The other iron-containing products from this reaction were the cis and trans isomers of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHMe$, formed in a 2:3 ratio, respectively, in a total yield of 23%. This result confirms the postulate of Green and Nagy[11]

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[10] Green, M. L. H.; Street, C. N.; Wilkinson, G. *Z. Naturforsch., B* **1959**, *14B*, 738.

[11] Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58.

[12] Fergusson, S. B.; Sanderson, L. J.; Shackleton, T. A.; Baird, M. C. *Inorg. Chim. Acta* **1984**, *83*, L45.

[13] Shackleton, T. A.; Mackie, S. C.; Baird, M. C., unpublished results.

[14] Oswald, A. A.; Griesbaum, K.; Thaler, W. A.; Hudson, B. E. *J. Am. Chem. Soc.* **1962**, *84*, 3897.

that both isomers are formed. (No attempt was made to separate the two isomers although Cutler et al.[7] have reported separating the majority of the trans isomer from the cis isomer by chromatography.)

The infrared and ^{1}H NMR data of the products of hydrometalation compare well with the literature data[7,9,11] for these compounds and confirm the structures. In addition, the ^{13}C NMR spectrum contains separate resonances for each isomer, assignments being based on the relative intensity of the isomeric signals. The hydrometalated products from the reaction of 1,3-butadiene with η^5-$C_5H_5Fe(CO)_2D$ exhibited two methyl resonances, of approximately equal intensity, at δ 1.61 and 1.55 in the $^2H\{^1H\}$ NMR spectrum of the reaction mixture. That deuterium incorporation occurred specifically and only in the methyl positions was further supported by the appearance in the $^{13}C\{^1H\}$ NMR spectrum of 1:1:1 triplets which may be attributed to CH_2D groups but not to an Fe–CHD moiety. Thus the labeled products contain terminal CH_2D groups, implying 1,4-addition of η^5-$C_5H_5Fe(CO)_2D$ across the conjugated double bonds of 1,3-butadiene.

The formation of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$ from the reaction of η^5-$C_5H_5Fe(CO)_2H$ with isoprene required $\approx$30 min, and the IR and ^{1}H NMR data for the isolated product compare well with those of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$ prepared by Cutler et al.[9] from the reaction of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ with $BrCH_2CH{=}CMe_2$. The reaction took longer and the yield of isolated product was slightly lower than for the analogous reaction of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-butadiene, but no other hydrometalated product was observed. The isolated yield of 19% is considerably less than the spectroscopically determined yield of 45%, obtained from a thiophenol-stabilized ^{1}H NMR experiment (see below).

The reaction of a hexane solution of η^5-$C_5H_5Fe(CO)_2H$ with an excess of isoprene in the presence of 1 mol % of thiophenol was monitored by IR spectroscopy. Over a period of $\approx$45 min, ν(CO) of η^5-$C_5H_5Fe(CO)_2H$ disappeared, being replaced by ν(CO) of both the hydrometalated product η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$ and of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. Since the thiophenol acts to prevent the decomposition of η^5-$C_5H_5Fe(CO)_2H$ to $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, the longer period of time required for the disappearance of the η^5-$C_5H_5Fe(CO)_2H$ ($\gg$the 20–30-min period observed in the unstabilized reaction) can be explained by a reduction in the rate of decomposition of η^5-$C_5H_5Fe(CO)_2H$. Thus a larger percentage of the initial η^5-$C_5H_5Fe(CO)_2H$ reacts with the isoprene, and the time required for complete reaction is necessarily longer.

Because of overlap of the methyl resonances, the $^2H\{^1H\}$ NMR spectrum of the product from the reaction of η^5-$C_5H_5Fe(CO)_2D$ with isoprene exhibited only a single methyl resonance, at δ 1.66. However, a $^{13}C\{^1H\}$ NMR spectrum showed that deuterium incorporation into both methyl resonances had in fact occurred. Thus both methyl singlets of the unlabeled products were accompanied by 1:1:1 triplets shifted slightly to higher field, indicating that deuterium labeling had resulted in two distinct isomers. On the other hand, the $^2H\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra exhibited no evidence for deuterium incorporation into the methylene group of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$ or into the unreacted isoprene, and thus the hydrometalated product is formed via an irreversible process.

The products of hydrogenation were identified by both GC and ^{1}H NMR spectral analysis and by comparison of the obtained data with those of authentic samples of the compounds. It was found that isoprene was hydrogenated to form a mixture of olefins comprised of 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene in a ratio of 1–2:5:15. By comparison of the ^{1}H NMR data, the organic products accounted for 55% of the reaction.

A further reduction in the isolated yield of the single hydrometalated product, η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$, to 8% was observed for the reaction between η^5-$C_5H_5Fe(CO)_2H$ and 2,3-dimethyl-1,3-butadiene. A much higher yield (36%) observed for the hydrometalated product in a thiophenol-stabilized reaction monitored by ^{1}H NMR spectroscopy probably resulted from the greater amount of η^5-$C_5H_5Fe(CO)_2H$ available to react with the diene, since the decomposition reaction forming $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ would have been inhibited. Although the compound η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$ has not been reported previously, rather straightforward assignments of the ^{1}H and ^{13}C NMR data were made by comparison to the products from reactions with 1,3-butadiene and isoprene. In addition, elemental analyses for carbon and hydrogen support this formulation.

Labeling the η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$ with deuterium by reaction of η^5-$C_5H_5Fe(CO)_2D$ instead of η^5-$C_5H_5Fe(CO)_2H$ yielded results similar to those obtained with isoprene. The $^2H\{^1H\}$ NMR spectrum of the hydrometalated product exhibited two methyl resonances, at δ 1.71 and 1.60, in a 1:1 ratio, corresponding to deuterium incorporation into two of the three methyl groups. In addition, in the ^{13}C NMR spectrum, the only resonances which exhibited coupling to deuterium were to be attributed to two of the three methyl resonances; such coupling was not observed in the resonances of the unreacted diene, in the resonance attributed to the 2-methyl group of the 2,3-dimethylbut-2-enyl ligand, or in the resonance of the Fe–CH_2 group. Thus, as with isoprene, formation of the hydrometalated product from the reaction of η^5-$C_5H_5Fe(CO)_2D$ with 2,3-dimethyl-1,3-butadiene occurs via an irreversible reaction, resulting in both cis and trans isomers of the product.

The products of hydrogenation were identified as 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene. The thiophenol-stabilized ^{1}H NMR experiment yielded a product ratio of 2:1, respectively, accounting for 64% of the reaction products. The reversal of this ratio of hydrogenated products (1:2) found in the GC experiment may result from decomposition of the hydrometalated product.

Reaction of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-cyclohexadiene yielded a single hydrometalated product, η^5-$C_5H_5Fe(CO)_2$(cyclohex-2-enyl), after $\approx$30 min. The IR and ^{1}H NMR data compare well with the data reported in the literature for the product of the same formulation prepared from $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ and 3-chlorocyclohexene,[9] and the ^{13}C NMR data further support the formation of a single product of the suggested formulation. A higher yield in a ^{1}H NMR experiment (35%) compared to the isolated yield (21%) reflects to a certain extent the low thermal stability of this compound.

Assignment of the methylene resonances in the ^{1}H NMR spectrum was not possible because of overlap of the resonances and thermal instability[9] of the product prevented the employment of two-dimensional NMR experiments to assign the methylene resonances. Consequently, interpretation of a ^{2}H NMR spectrum of the deuterated compound could not be unambiguous, and no attempt to determine the position of deuterium addition was made on the basis of ^{1}H and ^{2}H NMR data.

The ^{13}C chemical shifts of the deuterated and nondeuterated organoiron products were assigned on the basis of spin–spin coupling to directly bonded hydrogen atoms, and

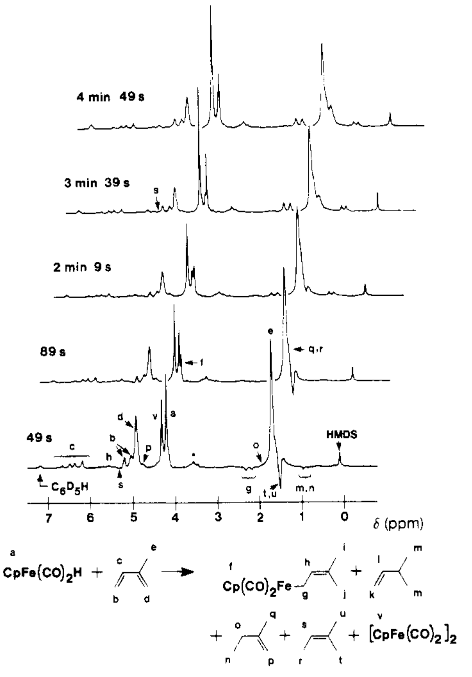

Figure 2. Stacked plot showing the CIDNP effects observed during the course of the reaction between η^5-$C_5H_5Fe(CO)_2H$ and isoprene.

in large part utilizing the deuterium isotope shifts on the positions of the carbon resonances.[15] On the basis of the assignments, it would appear that both 1,2- and 1,4-addition of η^5-$C_5H_5Fe(CO)_2D$ across 1,3-cyclohexadiene occurs. The unisolated product of hydrogenation was identified spectroscopically to be cyclohexene (65% yield).

η^5-$C_5H_5Fe(CO)_2H$ reacted with myrcene, $CH_2{=}CHC(CH_2CH_2CHC{=}Me_2){=}CH_2$, over a period of ≈50 min to yield a 3:1 mixture of hydrometalated products, presumably the cis and trans isomers of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(Me)CH_2CH_2CH{=}CMe_2$ although these compounds could not be completely separated from unreacted myrcene. Overlap of the methylene and methyl resonances in the ^1H NMR spectrum made it necessary to employ homonuclear 2D NMR spectroscopy to determine the proper assignments, which are listed above. The mixture of deuterium-labeled compounds obtained from the reaction of myrcene with η^5-$C_5H_5Fe(CO)_2D$ gave rise to a single methyl resonances at δ 1.68 in the $^2H\{^1H\}$ NMR spectrum, but the ^{13}C NMR spectrum exhibited two distinct CH_2D triplets, at δ 15.9 and 23.6, corresponding to the resonances of the 3-methyl groups of the major and minor isomers of the hydrometalated product, respectively.

CIDNP Results. The stacked spectra in Figure 2 illustrate the course of the reaction between η^5-$C_5H_5Fe(CO)_2H$ and isoprene in benzene-d_6 at 313 K, and, as this system is typical for the reactions of η^5-$C_5H_5Fe(CO)_2H$ with the dienes studied, it will be discussed in comparative detail. The initial spectrum at t = 49 s exhibits resonances attributed to isoprene (δ 6.39 (dd), 5.06, 4.92, and 1.70) and η^5-$C_5H_5Fe(CO)_2H$ (δ 4.16). The singlet at δ 4.27 is the η^5-C_5H_5 resonance of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$.

As can be seen, during the course of the reaction there appear product resonances in emission at δ 5.21 (assigned to the olefinic proton of 2-methyl-2-butene), 2.27 (d, methylene resonance of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$), 1.53 (methyl groups of the disubstituted end of 2-methyl-2-butene), and 0.94 (overlapping resonances of the two methyl groups of the disubstituted end of 3-methyl-1-butene and the terminal methyl group of 2-methyl-1-butene) and in absorption at δ 5.60 (t, olefinic resonance of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$) and 4.75 (geminal olefinic protons of 2-methyl-1-butene). At t = 89 s, the emissions at δ 2.27 and 0.94 have disappeared and new absorptions at δ 5.21 (assigned above), 4.12 (η^5-C_5H_5 of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$), and 1.64 (2-methyl group of 2-methyl-1-butene) have appeared, the lowest field resonance being very weak and the highest field resonance being in the form of a shoulder. Over the next few minutes, all resonances grow into absorption, yielding the final spectrum at t = 4 min 49 s.

The progress of the reaction of 2,3-dimethyl-1,3-butadiene with η^5-$C_5H_5Fe(CO)_2H$ in benzene-d_6 at 313 K is shown in a series of stacked spectra which are included with the supplementary material. Product resonances appearing in emission in this case were those of the two methyl groups bound to C-3 of 2,3-dimethyl-1-butene (δ 0.96), the methyl groups of 2,3-dimethyl-2-butene (δ 1.59), and the methylene group of η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$ (δ 2.32). A resonance appearing in apparent enhanced absorption was assigned to the geminal olefinic protons of 2,3-dimethyl-1-butene (δ 4.73). A similar experiment, run in the presence of 1 mol % thiophenol, resulted in an identical pattern of CIDNP polarizations. The only major difference from the reaction run in the absence of thiophenol was the very noticeable diminution in the relative intensity of the resonance of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$.

The results of a CIDNP experiment for the reaction of 1,3-cyclohexadiene and η^5-$C_5H_5Fe(CO)_2H$ in benzene-d_6 at 313 K is also shown in the supplementary material. In this case, weak emissions at δ 3.31 and 5.44 were assigned to the proton on the carbon bound to the iron center and the H-3 olefinic proton in the product η^5-$C_5H_5Fe(CO)_2$(cyclohex-2-enyl), respectively. Remaining emissions at δ 1.91 and 1.52 were assigned to the methylene groups of the hydrogenation product cyclohexene, the downfield resonance being assigned to the methylene group closer to the double bond.

Kinetic Investigation. The choice of 2,3-dimethyl-1,3-butadiene as the substrate for the kinetic investigation was made on the basis of the time of 45–70 min required for the disappearance of η^5-$C_5H_5Fe(CO)_2H$ in several synthetic reactions. This time of reaction is slow enough to allow the collection of a sufficient number of data points before the monitored η^5-C_5H_5 resonance of η^5-$C_5H_5Fe(CO)_2H$ disappeared into the base-line noise of the ^1H NMR spectrum.

Another consideration in the study of the kinetics of the hydrometalation reaction of the hydrometalation reaction of η^5-$C_5H_5Fe(CO)_2H$ with a conjugated diene was to ensure, as much as possible, that this was indeed the reaction being monitored; decomposition of the hydride to form $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ and hydrogen gas is well-noted in the literature.[10-12] However, as noted above, the addition of approximately 1 mol % of thiophenol to a hexane solution of η^5-$C_5H_5Fe(CO)_2H$ stabilized the hydride toward decomposition without affecting the nature of the reaction of the η^5-$C_5H_5Fe(CO)_2H$ with the dienes. Thus thiophenol-stabilized solutions of η^5-$C_5H_5Fe(CO)_2H$ in hexane were found to react with excesses of isoprene and 2,3-dimethyl-1,3-butadiene to yield the expected hydrometalated products. The reaction times had lengthened relative to that of unstabilized solutions, but this was presumably a

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[15] Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105.

[16] (a) Danno, S.; Moritani, I.; Fujiwara, Y. *Tetrahedron* **1969**, *25*, 4809. (b) Pouchert, C. J. *The Aldrich Library of NMR Spectra, Edition II*: Aldrich Chemical Company, Inc.: Milwaukee, WI, 1983.

result of the greater amounts of η^5-$C_5H_5Fe(CO)_2H$ reacting with the dienes as a result of the stabilization with respect to the decomposition pathway. Furthermore, stabilized benzene-d_6 ^1H NMR samples of η^5-$C_5H_5Fe(CO)_2H$ still exhibited the same CIDNP effects observed in the ^1H NMR monitoring of the reaction of unstabilized η^5-$C_5H_5Fe(CO)_2H$ with the diene 2,3-dimethyl-1,3-butadiene.

The kinetic runs were therefore performed with thiophenol-stabilized solutions of η^5-$C_5H_5Fe(CO)_2H$ under pseudo-first-order conditions at 294 K, the changes in intensities of the η^5-C_5H_5 resonances being monitored via single-scan ^1H NMR spectra collected at 1-min intervals on a Bruker AM-400 spectrometer. The disappearance of η^5-$C_5H_5Fe(CO)_2H$ under these conditions resulted in linear plots of ln $([\eta^5\text{-}C_5H_5Fe(CO)_2H]_t/[\eta^5\text{-}C_5H_5Fe(CO)_2H]_0)$ versus time for 4 half-lives, indicating a first-order dependence of the rate of reaction on the concentration of the hydride $[\eta^5\text{-}C_5H_5Fe(CO)_2H]$. From the slopes, $k_{obs} = (2.01 \pm 0.05) \times 10^{-3}\ s^{-1}$. Similar treatment of the rate data for formation of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$, while not as good as for that of η^5-$C_5H_5Fe(CO)_2H$ because of increased scatter, also indicated first-order formation of these two products. The pseudo-first-order rate constants for the formation of these products are $(2.27 \pm 0.55) \times 10^{-3}\ s^{-1}$ and $(2.27 \pm 0.52) \times 10^{-3}\ s^{-1}$, respectively, in good agreement with k_{obs} for disappearance of the hydride.

It was also found that plots of k_{obs} for the disappearance of η^5-$C_5H_5Fe(CO)_2H$ versus the concentration of diene were linear, verifying a first-order dependence of the rate on the concentration of the diene and yielding a second-order rate constant k_2 of $(1.22 \pm 0.07) \times 10^{-3}\ M^{-1}\ s^{-1}$ (average for five trials). Similar experiments under an atmosphere of carbon monoxide yielded a k_2 of $(1.14 \pm 0.09) \times 10^{-3}\ M^{-1}\ s^{-1}$, essentially identical with the value of k_2 for the reaction under nitrogen, and thus the rate of reaction appears to be independent of added carbon monoxide. A final experiment involved monitoring the disappearance of η^5-$C_5H_5Fe(CO)_2D$ on reaction with 2,3-dimethyl-1,3-butadiene under an atmosphere of nitrogen under pseudo-first-order conditions. A value of k_2 of $(1.42 \pm 0.06) \times 10^{-3}\ M^{-1}\ s^{-1}$ was obtained, significantly different from the k_2 determined for η^5-$C_5H_5Fe(CO)_2H$ and yielding an inverse kinetic isotope effect, k_H/k_D, of 0.86 ± 0.09.

Reaction Mechanism. The experimental observations presented above, including the product distributions, the rate laws, and, in particular, the CIDNP polarizations, can be shown to be best rationalized in terms of the radical pair process of Figure 1 ($M = \eta^5\text{-}C_5H_5Fe(CO)_2$). Thus the first step presumably involves irreversible transfer of the hydrogen atom from η^5-$C_5H_5Fe(CO)_2H$ to a terminal atom of the conjugated diene to form the [allyl + η^5-$C_5H_5Fe(CO)_2$] radical pairs. In Figure 1, the various possible products (i–vii) which may result from the reaction of η^5-$C_5H_5Fe(CO)_2H$ with a 1,3-diene in the s-cis conformation and via the two possible radical pair intermediates (A and B) are shown. The analogous s-trans conformation would result in the same distribution of products except that the compounds containing internal carbon–carbon double bonds (i, iv, v) would be formed as the corresponding trans isomers. Although it might be expected that thiophenol, added to various reaction mixtures to stabilize the iron hydride, would intercept several of the postulated intermediates, in fact the amount of thiophenol added was never more than 1 mol % of the amount of η^5-$C_5H_5Fe(CO)_2H$ present in solution. While this small amount of thiophenol was sufficient to deactivate the as yet unknown species which induce(s) the thermal decomposition of η^5-$C_5H_5Fe(CO)_2H$,[13] it should not be sufficient to skew the product distributions.

Subsequent reactions of the radical pairs are influenced by the nature of the organic radical. Given the considerable stability of allyl radicals,[17,18] there is, as mentioned above, an obvious parallel with the formation of stable benzylic radicals during reactions of η^5-$C_5H_5M(CO)_3H$,[2a] $HMn(CO)_5$,[2b–e] and $HCo(CO)_4$[2e–n] with aromatic olefins. In these cases, the conjugated aromatic olefins react to yield predominantly nongeminate products of olefin hydrogenation, whereas at least 35% of the products obtained from the reactions of η^5-$C_5H_5Fe(CO)_2H$ and $HMn(CO)_5$ with 1,3-dienes results from geminate coupling. A further contrast between reactions of aromatic olefins and conjugated dienes lies in the spin-selective step, which occurs via the reversible hydrogen abstraction step for the former but via the formation of products of both hydrogenation and hydrometalation for the latter.

Significantly, ethylene was found not to react with η^5-$C_5H_5Fe(CO)_2H$ in low-boiling petroleum ether at room temperature and atmospheric pressure. This observation is consistent with the low stability of the ethyl radical[17,18] and the apparent inapplicability of the conventional migratory insertion process.

The pattern of products formed from the reactions of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-butadiene, isoprene, myrcene, and 2,3-dimethyl-1,3-butadiene suggests that both the geminate coupling of the radical pairs and the hydrogen atom abstraction reactions are affected by steric hindrance. Thus hydrometalated products of the types ii, iii, and, in the cases of isoprene ($R = H$, $R' = Me$) and myrcene ($R = H$, $R' = CH_2CH_2CH{=}CMe_2$), iv of Figure 1 were neither isolated nor detected spectroscopically. The last of these compounds, at least for isoprene, would be expected to be stable enough to allow isolation in view of the observed stability of η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$. Similar behavior was also noted in the reactions of $HMn(CO)_5$,[1a] where it was noted that the hydrometalated products obtained were those expected to exhibit stronger metal–carbon bond dissociation energies rather than those anticipated on the basis of coupling at the sites of higher spin densities.[17–19]

Further to this point, in all cases, reaction of η^5-$C_5H_5Fe(CO)_2D$ with the acyclic aliphatic dienes resulted in deuterium incorporation in the hydrometalated products only into methyl groups, forming terminal CH_2D moieties. For the geminate products formed from isoprene and 2,3-dimethyl-1,3-butadiene, deuterium incorporation was observed in both of the 3-methyl groups of the allyl ligand, resulting in cis and trans isomers of the labelled, hydrometalated products. Both *cis*- and *trans*-2-butenyl isomers were also observed to be formed in the reaction of η^5-$C_5H_5Fe(CO)_2H$ with 1,3-butadiene, as previously reported,[4] and in the reaction of η^5-$C_5H_5Fe(CO)_2H$ with myrcene, in which the two inequivalent C-3 substituents resulted in cis and trans isomeric products. These observations indicate that the 1,4-addition reactions cannot be concerted processes, as was previously suggested[20] for the reaction of $HMn(CO)_5$ with $CD_2{=}C(CD_3)CH{=}CH_2$.

Reaction of η^5-$C_5H_5Fe(CO)_2D$ with 1,3-cyclohexadiene resulted in deuterium labeling in two separate sites on the

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(17) O'Neal, H. E.; Benson, S. W. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 17.

(18) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(19) Bennett, J. E.; Mile, B.; Thomas, A.; Ward, B. *Adv. Phys. Org. Chem.* **1970**, *8*, 1.

(20) Kormer, V. A.; Lobach, M. I.; Druz, N. N.; Klepikova, V. I.; Kiseleva, N. V. *Dokl. Akad. Nauk SSSR* **1979**, *246*, 1372.

cyclohex-2-enyl ligand, as determined by ^{13}C NMR spectroscopy of the labeled, hydrometalated product. The product mixture has been identified as a statistical mixture of the products of 1,2- and 1,4-addition of η^5-$C_5H_5Fe(CO)_2D$ to the cyclic diene, in which the deuterium atom can reside in either an axial or an equatorial site. As pointed out previously,[1a] the presumed intermediate allyl radical has a plane of symmetry, and thus the two ends of the allyl radical are indistinguishable as far as reaction with the $\{\eta^5$-$C_5H_5Fe(CO)_2\}$ radical is concerned. Consequently, when deuterium is incorporated into the allyl radical by reaction with η^5-$C_5H_5Fe(CO)_2D$, the plane of symmetry is disrupted and the products of 1,2- and 1,4-addition can be distinguished. It is this symmetrical intermediate that accounts for the observation of 1,2-addition.

Information concerning the reaction pathway(s) may also be inferred from the distributions of hydrogenated products, which may generally result from both 1,2- and 1,4-addition of two hydrogen atoms to the dienes. Thus vi and vii were both observed in CIDNP experiments with isoprene and 2,3-dimethyl-1,3-butadiene.

In addition to determining the fate of the transferred hydrogen atom(s), labeling studies using η^5-$C_5H_5Fe(CO)_2D$ confirmed the fact that no isolated product showed any evidence for the reversibility of the radical pair formation. For example, the ^{13}C NMR spectra of the metalated products of the reactions of the various dienes with η^5-$C_5H_5Fe(CO)_2D$ exhibited no resonances indicative of deuteration processes which would require scrambling arising from reversibility of the hydrogen transfer step.

Note that where the substituents R and R′ of Figure 1 are identical, as in 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene, the intermediate radical pairs A and B are indistinguishable. However, where R = H and R′ = alkyl, such as in the cases of isoprene and myrcene, then the allylic radical in radical pair A should be more stable[21] and might therefore be expected to account for the majority of the products. The observed product distribution for the reaction of thiophenol-stabilized η^5-$C_5H_5Fe(CO)_2H$ with isoprene (R = H, R′ = Me) is 45% η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$, 37% 2-methyl-2-butene, 13% 3-methyl-1-butene, and 5% 2-methyl-1-butene. This product distribution suggests that the presence of the methyl group hinders both hydrogen transfer to the internal carbon atom of the allylic radical in pair A (3-methyl-1-butene represents only 13% of the observed products) and coupling of the geminate radical pair B via the terminal carbon of the allylic radical (0% of the products). Furthermore, 95% of the products can be generated via radical pair A, whereas only 5% of the products have to be generated via radical pair B. (These numbers were obtained by attributing the entire yield of 2-methyl-2-butene to intermediate A, based on CIDNP observations; see below.) Consequently, the formation of radical pair B appears to occur to a much lesser extent than radical pair A.

The NMR emissions and enhanced absorptions observed during the CIDNP experiments require that at least a part of the products be formed via radical pair intermediates. Although the intensities of the polarizations can be influenced by a number of factors,[22-26] the CIDNP data for the reactions of η^5-$C_5H_5Fe(CO)_2H$ with the aliphatic conjugated dienes can be readily interpreted in terms of the mechanism of Figure 1 by recourse to the rules proposed by Kaptein.[24,25] It is necessary, but reasonable, to assume that the products of Figure 1 are derived from a singlet precursor and that the hydrometalated products result from geminate recombination of the components of the radical pair, whereas the products of hydrogenation result from secondary, nongeminate reactions following escape from the solvent cage. Utilization of g factor and hyperfine data from the literature for the allylic radicals[27-29] (see ref 1) and the assumption that the g factor for the $[\eta^5$-$C_5H_5Fe(CO)_2]$ radical is much larger than that of an organic radical[30] results in the phase predictions shown in Figure 3 for isoprene, 2,3-dimethyl-1,3-butadiene, and 1,3-cyclohexadiene. In fact, many metal-centered radicals[30] do exhibit relatively large g values, and the observation of all polarizations as net effects[31] is consistent with and supports the proposed large difference in g values for the allylic and $[\eta^5$-$C_5H_5Fe(CO)_2]$ radicals. In addition, the relative magnitudes of the polarizations in the spectrum of a particular product are expected to correlate with the magnitudes of the hyperfine couplings, in the allylic radical precursor, of the particular hydrogen atom(s) being observed,[22-26] as outlined in ref 1.

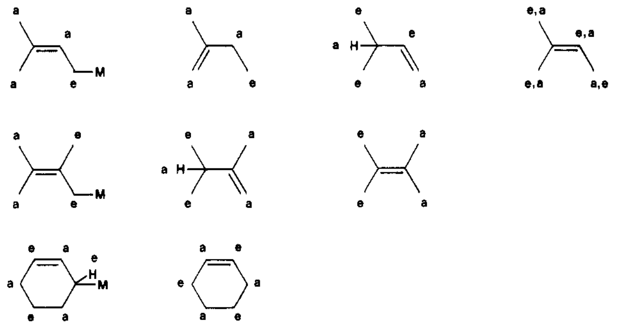

Figure 3. CIDNP phases anticipated for the observed reaction products from the reactions of η^5-$C_5H_5Fe(CO)_2H$ with isoprene, 2,3-dimethyl-1,3-butadiene, and 1,3-cyclohexadiene (e = emission, a = enhanced absorption).

Interestingly, as mentioned above, the experiments with η^5-$C_5H_5Fe(CO)_2D$ show that the hydrogen transfer step of Figure 1 is not reversible, and thus hydrogen transfer cannot be the spin-selective step. Spin selectivity must rather occur during the partitioning between geminate and nongeminate products, a conclusion reached also for reactions of $HMn(CO)_5$ with 1,3-dienes.[1a]

The complex CIDNP polarizations observed for the reactions of isoprene (see Figure 2) are in complete agreement with the predictions of the Kaptein rules.[24,25] Not all product resonances could be monitored because of overlap in some cases and distortion due to partial overlap of resonances in emission and enhanced absorption in others. However, for the isoprene system, it is clear that the methylene resonance of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CMe_2$, the methyl resonance of 3-methyl-1-butene, and the resonances of the olefinic proton and of the 1- and 2-methyl groups of 2-methyl-2-butene all appeared in

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(21) Jericevic, Z.; Sabljic, A.; Trinajstic, N. *Int. J. Biol. Macromol.* **1980**, *2*, 266.

(22) Lepley, A. R.; Closs, G. L. *Chemically Induced Magnetic Polarization*; Wiley: New York, 1973.

(23) Lowry, T. H.; Richardson, K. S. *Mechanisms and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 746.

(24) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732.

(25) Kaptein, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 6251.

(26) Hutton, R. S.; Roth, H. D.; Bertz, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6371.

(27) Fischer, H.; Hellwege, K. H. *Magnetic Properties of Free Radicals*; Springer-Verlag: New York, 1977; Landholt-Bornstein New Series, Group II, Vol. 9, Part b, pp 346–348, 410.

(28) Nakatsuji, H.; Kato, H.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 698.

(29) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 4201.

(30) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

emission, as predicted on the basis of their formation from radical pair A (R = H, R′ = Me). Interestingly, the phases of the resonances of 2-methyl-2-butene were completely incompatible with formation of this olefin from radical pair B (R = H, R′ = Me), although the emission observed for the 4-methyl group of 2-methyl-1-butene would appear to originate with radical pair B as would be predicted on that basis. The remaining signals were present but were interfered with except for the signal for the trans-terminal olefinic proton of 3-methyl-1-butene.

The phases of the polarizations for the products of the reaction of 2,3-dimethyl-1,3-butadiene were also as predicted by the Kaptein rules.[24,25] Thus, the methylene resonance of η^5-$C_5H_5Fe(CO)_2CH_2CMe{=}CMe_2$, the methyl resonance of 2,3-dimethyl-2-butene, and the 3,4-methyl resonance of 2,3-dimethyl-1-butene all appeared in emission, as predicted on the basis of either radical pair in Figure 1. Similarly the enhanced absorption of the geminal vinyl protons H-1 of 2,3-dimethyl-1-butene is consistent with the predictions made. The appearance of a single emission for the four methyl signals of 2,3-dimethyl-2-butene, two of which should be in absorption, is a result of smaller hyperfine couplings for the absorptions which allows the emission to dominate. The expected emission of the 2-methyl group of the hydrometalated product was obscured by the methyl signal of unreacted 2,3-dimethyl-1,3-butadiene. The remaining signals were present but were interfered with except for the signal of H-3 of 2,3-dimethyl-1-butene, which was not observed because of its heptet nature and its low intensity.

The case of 1,3-cyclohexadiene is interesting because the mirror planes of the cyclohexenyl radical intermediate and the cyclohexene product do not bisect the same pairs of atoms. Therefore, although the two vinyl hydrogen atoms of the cyclohexene are equivalent, they originate in sites in the allylic radical which are not only chemically nonequivalent but which exhibit nuclear hyperfine couplings which are of different magnitudes and signs.[1a] Application of the Kaptein rules[24,25] therefore results in the prediction that one of the olefin hydrogen atoms should appear in relatively weak enhanced absorption and the other in relatively strong emission. The expected polarization would be an emission but was not observed because of overlap with the olefinic protons of unreacted 1,3-cyclohexadiene. The same argument applies to the allylic hydrogen atoms of cyclohexene, the net result again being emission, while the hydrogen atoms in the 4- and 5-positions should be and are in emission. In the case of η^5-$C_5H_5Fe(CO)_2$(cyclohex-2-enyl), the weak emissions of the short-lived resonances for H-1 and the olefinic proton, H-3, are in accord with the predictions.

Kinetic studies showed that the hydrometalation reaction of 2,3-dimethyl-1,3-butadiene is first order in each of the reactants and is independent of free carbon monoxide. The latter observation indicates that coordination of the dienes to the iron is not a necessary step, while the first-order dependence of the rate of disappearance of η^5-$C_5H_5Fe(CO)_2H$ on the concentrations of both η^5-$C_5H_5Fe(CO)_2H$ and the diene suggests that formation of the geminate radical pairs is the rate-determining step. This conclusion is supported by the similarity in the observed rate constants for the disappearance of the hydride and for the appearance of both the hydrometalated product and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$.

In addition, the reaction exhibits an inverse isotope effect ($k_H/k_D = 0.86 \pm 0.09$), as observed for similar hydrometalation and diene hydrogenation reactions of η^5-$C_5H_5M(CO)_3H$ (M = Mo, W),[2a] $HMn(CO)_5$,[2b–e] and $HCo(CO)_4$[2e–n] with aromatic olefins, of $HMn(CO)_5$[2o] and $HCo(CO)_4$[2p] with polyaromatic hydrocarbons and of $FeH(SiCl_3)(CO)_4$,[2q] $HMn(CO)_5$,[1,2r] and $HCo(CO)_4$[2r] with dienes. This observation is consistent with a transition state consisting in part of an essentially linear Fe–H–C(diene) fragment and in which hydrogen transfer is almost completed.[32,33] Consequently, these reactions must be very similar mechanistically.

The much higher occurrence of geminate products from the reactions of aliphatic 1,3-dienes with η^5-$C_5H_5Fe(CO)_2H$ and $HMn(CO)_5$,[1] compared with the corresponding reactions of transition-metal monohydrides with aromatic olefins[2] presumably reflects the formation of stronger metal–carbon bonds in the σ-allylic compounds. The one notable exception, the product of hydrometalation of 1,3-cyclohexadiene, is probably relatively unstable thermally because of steric reasons arising from the metal–carbon bond involving a secondary rather than a primary carbon atom, as is the case in all the other isolated products of hydrometalation.

The possible involvement of either an electron-transfer step or a chain radical mechanism analogous to that observed for hydrostannation reactions[34] has been discussed in context with the reaction of $HMn(CO)_5$ with 1,3-dienes.[1a] It was concluded not only that an electron-transfer reaction would be exceedingly endothermic but also that the radical pair, if formed, would not have a sufficiently long lifetime to contribute to the CIDNP polarizations. In addition, even if the radical pair were formed, the predicted polarizations arising from this intermediate radical pair, containing a butadiene radical anion (all the hyperfine coupling constants are positive),[35] would not agree with the observed polarizations.

The chain radical mechanism was ruled out because this type of reaction normally exhibits a normal kinetic isotope effect ($\approx$1.2–1.4)[33] in contrast to the inverse kinetic isotope effect observed in this case and in similar reactions with $HMn(CO)_5$. It was thought that the primary reason for the difference in mechanism for stannanes and $HMn(CO)_5$ was the greater metal–hydrogen bond strength in stannanes, which was presumably too high for hydrogen atom abstraction by a conjugated diene to take place.

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Supplementary Material Available: Figures of hyperfine coupling constants *a* (in MT) for allylic radicals and stacked plots showing the CIDNP effects observed during the course of the reaction between η^5-$C_5H_5Fe(CO)_2H$ and 2,3-dimethyl-1,3-butadiene and the reaction between η^5-$C_5H_5Fe(CO)_2H$ and 1,3-cyclohexadiene (3 pages). Ordering information is given on any current masthead page.

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(31) Schaublin, S.; Hohener, A.; Ernst, R. R. *J. Magn. Reson.* **1974**, *13*, 196.

(32) Bigeleisen, J. *Pure Appl. Chem.* **1964**, *8*, 217.

(33) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295.

(34) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970; Chapter 9.

(35) Hamano, H.; Kondo, H. *Bull. Chem. Soc. Jpn.* **1979**, *33*, 1255.