Mechanisms of the Hydrometalation ("Insertion") and Stoichiometric Hydrogenation Reactions of Conjugated Dienes Effected by Manganese Pentacarbonyl Hydride: Processes Involving the Radical Pair Mechanism

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Abstract: Manganese pentacarbonyl hydride (I) reacts with 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene to form predominantly the hydrometalated products of 1,4-addition of H–Mn(CO)$_5$ to the dienes, i.e.

$$\mathrm{I + CH_2{=}CRCR'{=}CH_2 \rightarrow MeCR{=}CR'CH_2Mn(CO)_5}$$

$$\mathrm{R, R' = H, Me}$$

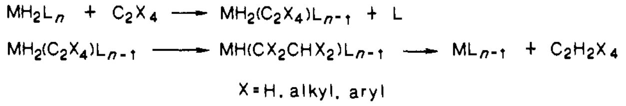
Monoolefins, the products of stoichiometric 1,2- and 1,4-addition of two hydrogen atoms to the dienes, are also formed as minor products, i.e.

$$\mathrm{2I + CH_2{=}CRCR'{=}CH_2 \rightarrow MeCHRCR'{=}CH_2 + CH_2{=}CRCHR'Me + MeCR{=}CR'Me + Mn_2(CO)_{10}}$$

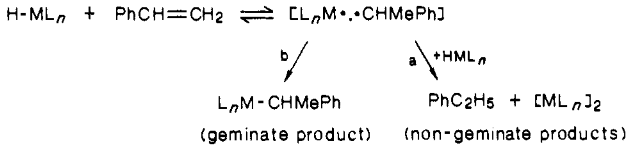
Hydrogenation is the predominant process with 1,3-cyclohexadiene. The hydrometalation reactions are first order in both I and diene, and the reaction rates are unaffected by added carbon monoxide (1 atm), while careful NMR monitoring of the early stages of the reactions under appropriate conditions reveals striking CIDNP polarizations for the ^{1}H resonances of both the products of hydrometalation and of hydrogenation. The experimental evidence thus suggests that the reactions do not proceed via prior coordination of the olefin to the metal followed by conventional migratory insertion and reductive elimination processes but rather via hydrogen atom abstraction from I by the diene to give the corresponding [allyl + Mn(CO)$_5$] radical pair. The latter can couple to give the hydrometalated compounds or diffuse apart to react with a second molecule of I to give Mn$_2$(CO)$_{10}$ and the monoolefins. For both types of products, the signs and, where measureable, the relative intensities of the CIDNP polarizations are completely consistent with the radical pair mechanism.

The roles of transition-metal dihydrides as intermediates in the catalytic hydrogenation of simple monoolefins have been much studied,[1] with the result that the mechanisms of many catalytic hydrogenation reactions seem well understood. In general, the olefin must occupy a site within the inner coordination sphere of the metal atom or ion prior to the hydrogen transfer steps. The latter normally occur consecutively and involve initial 1,2-migration of one of the hydrogen atoms from the metal to the olefin to form a σ-alkyl group. The second carbon–hydrogen bond is then formed via reductive elimination of the remaining hydride ligand and the newly formed alkyl ligand (Scheme I).

Scheme I



Scheme II



More recently, several transition-metal monohydrides, notably of molybdenum,[2] tungsten,[2] manganese,[3] and cobalt,[4] have been observed to effect stoichiometric hydrogen transfer to conjugated olefins, i.e.

$$\mathrm{2CpMo(CO)_3H + PhCMe{=}CH_2 \rightarrow PhCHMe_2 + [CpMo(CO)_3]_2} \quad (1)$$

$$\mathrm{2HMn(CO)_5 + PhCMe{=}CH_2 \rightarrow PhCHMe_2 + Mn_2(CO)_{10}} \quad (2)$$

$$\mathrm{2HCo(CO)_4 + PhCH{=}CH_2 \rightarrow PhCH_2Me + Co_2(CO)_8} \quad (3)$$

These reactions share several notable features which distinguish them mechanistically from the above-mentioned catalytic process involving dihydrides.[1] For instance, in several cases the rate of reaction is first order in each reactant but is independent of the CO concentration,[2,3a,4a-c,g] suggesting that a vacant site on the metal is not necessary and that the reactions proceed without involving coordination of the olefin. Also observed in several instances are the effects of chemically induced dynamic nuclear polarization (CIDNP) in the NMR spectra of the reaction mixtures, which result in emissions and enhanced absorptions in

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(1) For comprehensive discussions, see: (a) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (b) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. (c) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; pp 291–298. (d) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Co.: Monterey, CA, 1985; pp 256–259.

(2) Sweany, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57.

(3) (a) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (b) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5. (c) Matsui, Y.; Orchin, M. *J. Organomet. Chem.* **1983**, *244*, 369.

(4) (a) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299. (b) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1980**, *199*, 265. (c) Roth, J. A.; Wiseman, P. *J. Organomet. Chem.* **1981**, *217*, 231. (d) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Organomet. Chem.* **1981**, *221*, 193. (e) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Mol. Catal.* **1982**, *16*, 43. (f) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222. (g) Ungvâry, F.; Markô, L. *Organometallics* **1982**, *1*, 1120. (h) Ungvâry, F.; Markô, L. *J. Organomet. Chem.* **1983**, *249*, 411. (i) Roth, J. A.; Wiseman, P.; Ruszala, L. *J. Organomet. Chem.* **1983**, *240*, 271. (j) Bockman, T. M.; Garst, J. F.; King, R. B.; Markô, L.; Ungvâry, F. *J. Organomet. Chem.* **1985**, *279*, 165.

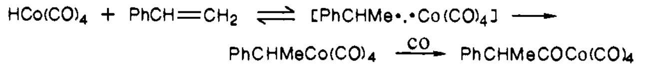
0002-7863/87/1509-1995$01.50/0

Table I. Spectroscopic Data for the Compounds $RMn(CO)_5$

R	$\nu_{(CO)}$ (cm^{-1})	δ (H)	δ (C)
$CH_2{=}CHCH_2^-$	2109 (m), 2047 (m), 2014 (vs), 1992 (s)[11d]	1.77 (2 H, d, J = 9 Hz, H_1), 4.77 (2 H, dd, H_3), 6.15 (1 H, m, H_2)[11a]	9.0 (C_1), 106.2 (C_3), 147.7 (C_2)[11c]
cis-$MeCH{=}CHCH_2^-$	2110, 2070, 1992 (br)[11a]	1.58 (3 H, dd, J = 6.9, 1.5 Hz, Me), 1.74 (2 H, dd, J = 9.2, 1.0 Hz, H_1), 5.20 (1 H, m, H_3), 5.82 (1 H, m, H_2)[11b]	
trans-$MeCH{=}CHCH_2^-$	2110, 2070, 1992 (br)[11a]	1.61 (3 H, dd, J = 6.5, 1.5 Hz, Me), 1.73 (2 H, dd, J = 8.7, 1.0 Hz, H_1), 5.32 (1 H, m, H_3), 5.76 (1 H, m, H_2)[11b]	
$Me_2C{=}CHCH_2^-$	2103 (m), 2012 (s), 2007 (s), 1989 (s)[a]	1.60 (3 H, s, Me), 1.67 (3 H, s, Me), 1.75 (2 H, d, J = 9.2 Hz, H_1), 5.63 (1 H, t, J = 9.2 Hz, H_2)[b]	5.6 (C_1), 17.4 (Me), 25.5 (Me), 125.6 (C_3), 132.7 (C_2)[b]
$Me_2C{=}CMeCH_2^-$	2101 (m), 2012 (s), 2004 (s), 1988 (s)[a]	1.62 (3 H, s, Me), 1.66 (3 H, s, Me), 1.68 (3 H, s, Me), 1.87 (2 H, s, H_1)[b]	12.9 (C_1), 20.3, 20.8, 20.9 (3 × Me), 121.3, 135.2 (C=C)[b]
cyclohex-3-enyl		2.9 (m, H_1), 5.3 (m, $H_{2,3}$)[b]	
Me	2110 (m), 2011 (vs), 1990 (s), 1976 (m)[c]		

[a] In hexanes. [b] In benzene-d_6. [c] Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844.

Scheme III



$$HCo(CO)_4 + PhCH{=}CH_2 \rightleftharpoons [PhCHMe\cdot.\cdot Co(CO)_4] \longrightarrow PhCHMeCo(CO)_4 \xrightarrow{CO} PhCHMeCOCo(CO)_4$$

resonances of the products.[3a,4f,j] CIDNP effects are to be taken as clear and unambiguous evidence that the reactions proceed at least in part via a radical pair process,[5] and the mechanism shown in Scheme II is generally regarded as being applicable to this class of olefin hydrogenation reactions. Thus the first step, which is postulated to involve direct, often reversible transfer of the hydrogen atom from the metal to the olefin, is consistent with generally observed negative entropies of activation[2,3a,b,4a,b] and results in the formation of a radical pair in a solvent cage. The components of the radical pair then appear to dissociate (route a) and are believed to react further with a second molecule of metal hydride to form nongeminate products as shown. Supporting this proposed mechanism is the general observation of an inverse kinetic isotope effect ($k_H/k_D \sim 0.4$) when the corresponding transition-metal deuterides are used,[2,3a,4a,b,e,f] a result consistent with a transition state in which the hydrogen atom being transferred is almost completely attached to the carbon atom.[6]

Several points may be made concerning the radical pair mechanism. In the first place, in only one instance have quantitative data been presented to demonstrate that the radical pair process constitutes the major pathway of a particular reaction.[3a] In most cases, it is at least possible that the more conventional steps of Scheme I could provide a parallel or even dominant route to products. A factor which clearly distinguishes those reactions which, on the basis of CIDNP data, must involve to at least some extent the radical pair process is that the unsaturated substrates can form a relatively stable radical[7] by the addition of a hydrogen atom. (In no case has an olefin such as ethylene been observed to lead to hydrogenation products exhibiting CIDNP). Consistent with this observation, a series of polycyclic aromatic hydrocarbons is also hydrogenated via the radical pair mechanism by manganese and cobalt carbonyl hydrides.[8]

In general, it seems likely that the components of the radical pair of Scheme II could also couple to give a geminate product containing a new metal–carbon σ-bond (route b of Scheme II). Such a hydrometalation product was in fact anticipated in earlier work but not observed,[3a] possibly because of low thermodynamic stability of the benzylic–metal compound which would have resulted. However, such species have been successfully trapped via carbonylation processes which lead to acyl complexes and/or the products of olefin hydroformylation,[3b,c,4g,h] as in Scheme III. The products of geminate coupling and their derivatives are, of course, also typical of nonradical, migratory insertion processes,[1] but it seems likely that the two mechanisms may be distinguishable on the basis of product distributions. The initial product of the radical process involving, say, styrene derivatives should be and is in several cases the corresponding 1-phenethyl–metal compounds,[4g,h,j,7] although the primary alkyl products are likely to be more stable and to be formed preferentially in a conventional migratory insertion reaction.[4g,9]

By analogy with the above described reactions of aryl olefins, it seems likely that similar reactions of conjugated dienes might also occur. Allylic radicals are known to be thermodynamically very stable,[7] and both hydrogenation of dienes to the monoolefins and "insertion" (or hydrometalation) reactions of dienes with $CpM(CO)_3H$[10] (M = Cr, Mo, W), $HMn(CO)_5$,[11a,b] and $HCo(CO)_4$[12] have been reported. Hydrogenation to the monoolefin stage only should, in fact, be a useful criterion for the identification of a radical pair rather than the conventional olefin hydrogenation process of Scheme I, because the latter would result in hydrogenation of the monoolefin as well. We are accordingly engaged in an investigation of the possibility of radical pair participation in such reactions and have earlier communicated preliminary CIDNP and related evidence for radical pair intermediates in diene hydrogenation and hydrometalation reactions with both $CpFe(CO)_2H$ and $HMn(CO)_5$.[13] We now report full details of our investigation into the relevant chemistry of $HMn(CO)_5$, with reports of related studies of chromium, molybdenum, tungsten, and iron hydrides to follow. While this work was in progress, it was reported elsewhere that hydrogenation reactions of conjugated dienes by both $HFe(CO)_4(SiCl_3)$[14] and $HCo(CO)_4$[15] also proceed via radical pair processes, although the latter observation may be somewhat at variance with an earlier report.[12]

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(5) (a) Lepley, A. R.; Closs, G. L. *Chemically Induced Magnetic Polarization*; Wiley: New York, 1973. (b) Lowry, T. H.; Richardson, K. S. *Mechanisms and Theory in Organic Chemistry*; Harper and Row: New York, 1981; p 746. (c) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732. (d) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251. (e) Hutton, R. S.; Roth, H. D.; Bertz, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6371.

(6) Bigeleisen, J. *Pure Appl. Chem.* **1964**, *8*, 217. (b) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295.

(7) (a) O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 17. (b) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(8) (a) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186. (b) Sweany, R. L.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487.

(9) See, for instance: Bennett, M. A.; Charles, R.; Mitchell, T. R. B. *J. Am. Chem. Soc.* **1978**, *100*, 2737.

(10) (a) Miyake, A.; Kondo, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 631. (b) Miyake, A.; Kondo, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *7*, 880.

(11) (a) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601. (b) Kormer, V. A.; Lobach, M. I.; Druz', N. N.; Klepikova, V. I.; Kiseleva, N. V. *Dokl. Akad. Nauk SSSR* **1979**, *246*, 1372 (see, also: Druz', N. N.; Klepikova, V. I.; Lobach, M. I.; Kormer, V. A. *J. Organomet. Chem.* **1978**, *162*, 343). (c) Oudeman, A.; Sorensen, T. S. *J. Organomet. Chem.* **1978**, *156*, 259. (d) Clarke, H. L.; Fitzpatrick, N. J. *J. Organomet. Chem.* **1972**, *40*, 379.

(12) Ungváry, F.; Markó, L. *Organometallics* **1984**, *3*, 1466 and references therein.

(13) 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.

(14) Connolly, J. W. *Organometallics* **1984**, *3*, 1333.

(15) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* **1986**, *108*, 1689.

Experimental Section

All reactions were carried out under nitrogen by using dried, deoxygenated solvents. Dimanganese decacarbonyl was purchased from Strem Chemicals, 1,3-butadiene from Matheson, isoprene, 2,3-dimethyl-1,3-butadiene, 2,3-dimethyl-2-butene, 2,3-dimethyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1,3-cyclohexadiene, cyclohexene, and α-methylstyrene from Aldrich Chemical Co. All olefins were characterized by their ^{1}H NMR spectra at 60 and 400 MHz. ^{1}H NMR spectra were run on Bruker HX60 and AM 400 FT NMR spectrometers, ^{13}C and ^{2}H NMR spectra on the latter instrument, and IR spectra on a Bruker IFS 85 FTIR spectrometer; spectroscopic data are listed in Table I. Gas chromatography experiments were performed on a Hewlett Packard HP 5880A gas chromatograph equipped with a 24-m methylsilicone (SP-2100) Carbowax 20M deactivated capillary column.

Manganese pentacarbonyl hydride (I) was prepared by using a modification of the method of King.[16] A solution of $Mn_2(CO)_{10}$ (3 g) in 20 mL of ethyl ether was combined with sodium amalgam in a flask fitted with both a dropping funnel containing 25 mL of degassed 85% phosphoric acid and a glass adapter leading to a second flask which contained ~20 g of P_2O_5 and was cooled to −196 °C with liquid nitrogen. After cleavage of the $Mn_2(CO)_{10}$ was complete (1 h at room temperature), the system was exposed (via the second flask) to a sufficiently reduced pressure that the ethyl ether began to boil, whereupon the phosphoric acid was added dropwise to the stirred suspension of $NaMn(CO)_5$. As the addition proceeded, the pressure in the system was reduced considerably so that the $HMn(CO)_5$ was carried over into the second flask with the boiling ether and condensed onto the P_2O_5. When all the acid had been added, the system was filled with nitrogen, and the mixture in the second flask was brought to room temperature and stirred for 10 min. The mixture was then heated up to ~60 °C, and the $HMn(CO)_5$ and the ethyl ether were distilled under reduced pressure into a third flask cooled to −196 °C. The mixture was then held at −40 °C in an acetone bath, and residual ethyl ether was removed by pumping to leave pure (by NMR spectroscopy) $HMn(CO)_5$ (mp ~ −25 °C). The corresponding deuteride, $DMn(CO)_5$ (I-d_1), was prepared in the same manner by using D_3PO_4 synthesized by treating freshly sublimed P_2O_5 with D_2O.

The compound **$Me_2C{=}CHCH_2Mn(CO)_5$ (II)** was synthesized as reported,[11] via reaction of I with isoprene (2-methyl-1,3-butadiene); II was purified by recrystallization from pentane at −40 °C. The compound **$Me_2C{=}CMeCH_2Mn(CO)_5$ (III)** has not been reported previously but was synthesized by treating 0.60 g of I (3.1 mmol) with excess (10 mL) 2,3-dimethyl-1,3-butadiene at room temperature for 2.5 h. The yellow mixture was then cooled to −10 °C, and the volatile hydrocarbons were removed at low pressure to leave a yellow solid which melted on warming to room temperature. Although the material could be recrystallized from hexanes at low temperature, it was not found possible to remove all traces of $Mn_2(CO)_{10}$, and III was characterized spectroscopically by comparisons with spectroscopic data for II, $CH_2{=}CHCH_2Mn(CO)_5$[11a,c] and *cis*- and *trans*-$MeCH{=}CHCH_2Mn(CO)_5$[11b] (Table I).

The identities of the products from reactions of I with 1,3-butadiene, 1,3-cyclohexadiene, isoprene, and 2,3-dimethyl-1,3-butadiene in benzene under a variety of conditions were investigated by using IR, NMR, and GC techniques. CIDNP experiments (involving 75 μL I i.e., ~1.1 M and 50 μL liquid diene in sufficient C_6D_6 to make 0.5 mL solutions, i.e., ~0.9 M in diene) were normally carried out in benzene-d_6 by using a Bruker HX60 magnet interfaced to the Aspect 3000 computer of an AM 400 spectrometer. Hexamethyldisiloxane (HMDS) was used as internal reference, and reaction conditions (i.e., concentrations, temperature) were normally chosen such that the reactions required 7–10 min to go to completion. Samples (room temperature) were placed in the preheated probe (55 °C), and each reaction was monitored as it warmed every 10 s (2 scans, $\pi/4$ pulse angle, no delay time) until half finished, then every minute until essentially complete.

Kinetics studies of the reactions of I and I-d_1 with isoprene and 2,3-dimethyl-1,3-butadiene were carried out in benzene-d_6 solutions. Samples were prepared for kinetics runs by adding weighed amounts of I to 1 mL of benzene-d_6 in an NMR tube in a glovebox. The desired amount of diene was then syringed into the NMR sample, which was quickly immersed in liquid nitrogen, evacuated, and flame sealed. Reactions were monitored by ^{1}H NMR spectroscopy at 400 MHz. In cases where the diene was in excess ([diene] ~1–1.7 M, [I] ~0.09–0.19 M, ratios ~ 9–14), the decay of the hydride resonance of I at δ −7.89 was followed. A value of ~5.3 s was determined for T_1 at the hydride resonance of I in benzene-d_6 at 25 °C, and accurate integrations were obtained by employing pulse angles of 35° and pulse delays of 5 s in all experiments. In a case where I was in excess ([I] ~0.7 M, [diene] ~0.05 M, ratio ~14), the change in concentration of 2,3-dimethyl-1,3-butadiene was monitored by using the vinyl resonances at δ 5.03 and 4.92, the formation of the products by integrating their methyl resonances. Although no T_1 measurements were made for this system, a pulse delay of 30 s and a pulse angle of 30° were found to give consistent integrations. Each data point of a run consisted of 8 scans.

Results and Discussion

The Products from Reactions of I with Conjugated Dienes. A number of experiments was carried out in order to obtain, as definitively as possible, mass balances for the reactions of interest. As many of the reactants and products were either very volatile or were air sensitive, most products were characterized utilizing spectroscopic techniques complemented by GC analyses. Relevant spectroscopic data for all organometallic compounds are listed in Table I.

Only brief investigations of the reactions of I with 1,3-butadiene and 1,3-cyclohexadiene were carried out. As reported in the literature, I reacts rapidly with 1,3-butadiene in benzene-d_6 at room temperature to form a mixture of *cis*- and *trans*-2-butenylmanganese pentacarbonyl[11b] (IV) in a 6:1 ratio. Careful inspection of the NMR spectrum of a reaction carried out at 40 °C showed the presence also of 1- and 2-butenes. In contrast, the reaction with 1,3-cyclohexadiene proceeded rather slowly at room temperature to give cyclohexene, $Mn_2(CO)_{10}$, and an unidentified, red, manganese-containing product, while reaction at ~60 °C yielded predominantly cyclohexene and $Mn_2(CO)_{10}$. Inspection of the NMR spectrum of the latter reaction showed the *temporary* presence of multiplet resonances at δ ~5.3 and ~2.9, tentatively assigned to the vinyl and methyne resonances, respectively, of 3-cyclohexenylmanganese pentacarbonyl (V) on the basis of comparisons with spectra of the hydrometalated products obtained from the reactions of 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene (Table I). Compound V is the hydrometalated product expected from 1,4-addition of I to 1,3-cyclohexadiene.

Reactions of I with various ratios of isoprene to I (15:1 to 1:2) in benzene-d_6 were generally complete within 2.5–13 h at room temperature. Compound II was the major product (80–90% yield), although $Mn_2(CO)_{10}$, 2-methyl-1-butene (4–8%), 2-methyl-2-butene (6–10%), and 3-methyl-1-butene (1–2%) were also formed in much lower albeit significant quantities. Reactions of I and isoprene in the temperature range 50–65 °C were generally finished within 30 min, forming II as the major product (~60% yield) and rather more significant amounts of $Mn_2(CO)_{10}$ and the monoolefins than at the lower temperature. In addition, small amounts of η^3-1,1-(dimethylallyl)manganese tetracarbonyl (~ 14%) and *syn*- and *anti*-η^3-1,2-(dimethylallyl)manganese tetracarbonyl (~9%)[11b] were also formed as secondary products. In separate experiments, mixtures of I and II were found to be stable with respect to secondary reactions for at least 20 h at room temperature and for at least 15 min in benzene at ~55 °C. Compound II also decomposes significantly over 3 h at 55 °C to form the η^3-allylmanganese tetracarbonyl compounds, isoprene, and the monoolefins, but both this process and any reactions with I occur very slowly on the time scale of the CIDNP-generating reactions.

Reactions of I with 2,3-dimethyl-1,3-butadiene were found to proceed somewhat more slowly in benzene than those of isoprene under comparable conditions. Compound III was the predominant product (~95% yield) at room temperature when the diene was present in excess, although lesser amounts of 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, and $Mn_2(CO)_{10}$ were also formed. The same products were formed when I was present in excess, but I and III were found to react slowly even at room temperature to form the monoolefins and $Mn_2(CO)_{10}$. Compound III is stable in C_6D_6 for at least 3 h at room temperature but was found to decompose slowly at 55 °C to regenerate I and 2,3-dimethyl-1,3-butadiene as primary products. Total thermolysis of III at 55 °C yielded principally 2,3-dimethyl-1,3-butadiene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, and $Mn_2(CO)_{10}$, but this process is very slow compared with the reactions of interest here and thus cannot contribute to the observed CIDNP effects. In

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(16) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 158.

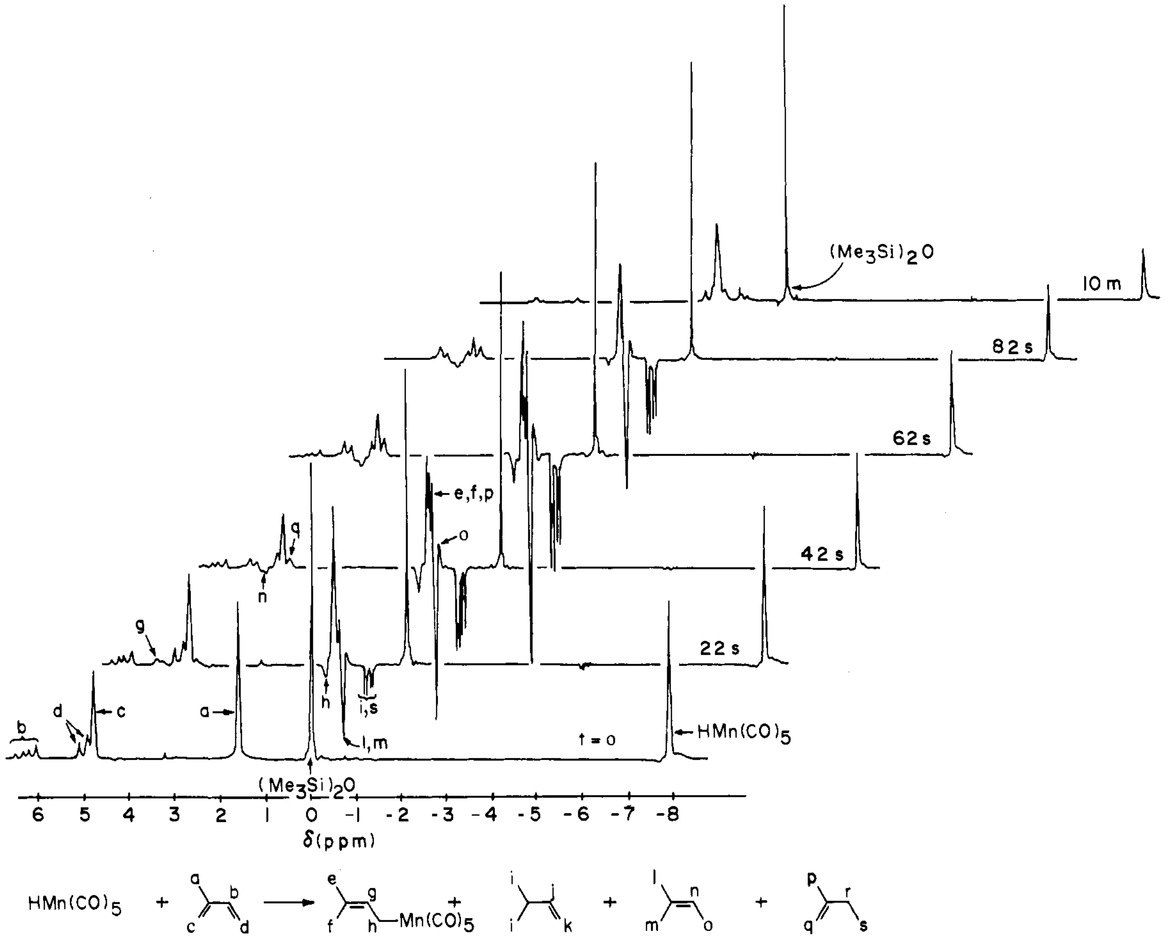


Figure 1. Stacked plot showing the course of the reaction between I and isoprene.

contrast to the thermal behavior of II, there was little evidence for the formation of η^3-allyl compounds.

Experiments involving addition of $DMn(CO)_5$ (I-d_1) to isoprene in benzene-d_6 at room temperature and at 55 °C were monitored by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. At both temperatures, deuteriation occurred predominantly at the methyl group exhibiting upfield resonances in both the ^1H and ^{13}C spectra of the II-d_1 formed, although deuteriation also occurred to a small extent at the other methyl group. This result is not completely congruent with a report that addition of I to isoprene-d_5 ($CD_2{=}C(CD_3)CH{=}CH_2$) results in hydrometalated product with a ^1H NMR spectrum exhibiting evidence for the hydrogen atom *only* in the upfield resonance, assigned, presumably on the basis of comparisons with the analogous of cis and trans crotyl compounds, to the cis methyl group.[11b] Addition of I-d_1 to 2,3-dimethyl-1,3-butadiene at room temperature also resulted in the deuterium occurring almost exclusively at one methyl group (δ_H 1.66, δ_C 20.9). Although these resonances have not been assigned, we assume again that the label resides in the methyl group cis to the methylene group. For the reactions of both dienes, the ^1H and ^{13}C spectra of the reaction mixtures and of the isolated products were carefully examined for evidence of deuterium incorporation into either the dienes or into other sites of the products. No such evidence was found, although 3% deuterium at any site would have been detectable. Furthermore, careful integration of the spectra during several such deuteriation studies failed to give any evidence for growth of the hydride resonance of the residual I.

CIDNP Experiments. All CIDNP experiments were carried out at the lowest field possible, 1.41 T, in order to maximize the polarizations,[5] and reaction conditions were chosen so that the evolution and decay of the polarizations could be readily followed. Use of the superior capabilities of the Aspect 3000 computer permitted the acquisition of high quality spectra at any time intervals desired. In general, the time scales of the reactions of all dienes except 1,3-cyclohexadiene were such that secondary reactions of the hydrometalated products, both thermal decomposition and reactions with I, were not observed. A CIDNP experiment involving 1,3-butadiene at 40 °C surprisingly exhibited polarization only for the methyl resonance of the 1-butene (emission), none for the isomeric hydrometalated products. This system was accordingly not studied in detail.

The stacked spectra shown in Figure 1 provide a very good illustration of the type of data obtained for the reaction of I with isoprene in benzene-d_6. At time $t = 0$, the initial spectrum exhibits a hydride resonance at δ −7.83 and the isoprene resonances at δ 1.72 (s, methyl), ~4.9, 5.12 (m, CH_2), and ~6.41 (m, CH). At $t = 22$ s, new resonances appear in emission at δ ~0.95 (m), 1.52 (s), and 1.90 (s), and there are also new, weak resonances in absorption at δ ~1.44, 1.61, 4.77, and ~5.6. Over the next 20–40 s, all of the polarizations become more intense, and a new multiplet at δ ~5.3 (in emission) appears. The methyl region at δ ~1.6 also becomes a complex cluster of lines in absorption although unambiguous assignments are impossible. The intensities of all the emissions are clearly decreasing by 80 s, and a spectrum after 10 min exhibits only the normal resonances of the products and unreacted I. Comparison of the intensities of the final spectrum with those at t = 22–62 s shows that several of the product resonances exhibit enhanced absorptions. This is especially clear in the methyl region, although the line separations are too small for definitive assignments to be made. The vinyl resonances centered at δ 4.77 and ~5.6 clearly appeared in enhanced absorption, but no CIDNP polarization was observed for the hydride resonance of I.

Assignments of many of the product resonances were made on the basis of comparisons with samples of the pure II, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene. We can thus assign the overlapping resonances in emission at δ ~0.95 to the methyl resonance of 3-methyl-1-butene and the 4-methyl resonance of 2-methyl-1-butene, the singlet in emission at δ 1.52 to the 1- or the 2-methyl resonance of 2-methyl-2-butene, the singlet in

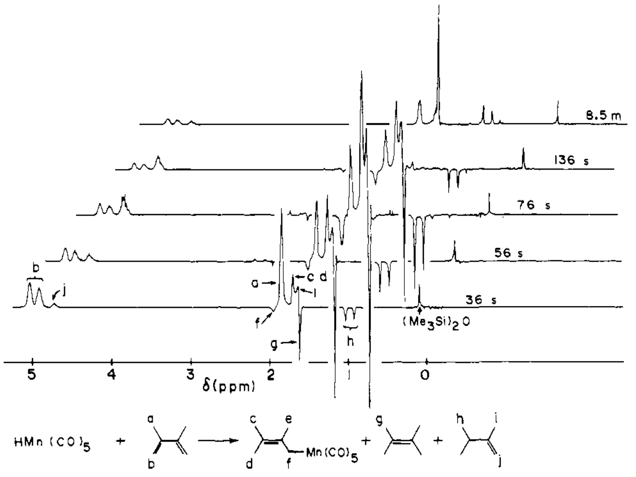


Figure 2. Stacked plot showing the course of the reaction between I and 2,3-dimethyl-1,3-butadiene.

emission at δ 1.90 to the lower field half of the methylene doublet resonance of II, and the resonance in emission at δ ~5.3 to H_3 of 2-methyl-2-butene. The singlets in apparent enhanced absorption at δ ~1.6 are probably to be assigned to the methyl resonances of II, the 2-methyl resonance of 2-methyl-1-butene, and the 2- or 1-methyl resonance of 2-methyl-2-butene, the resonance in absorption at δ 4.77 to the vinyl CH_2 multiplet resonance of 2-methyl-1-butene, and the resonance (clearly not in emission) at δ 5.6 to the vinyl hydrogen of II. The resonance in absorption at δ ~1.44 would appear to be the high field half of the 4-methyl doublet of 2-methyl-2-butene. The significance of these results will be discussed below.

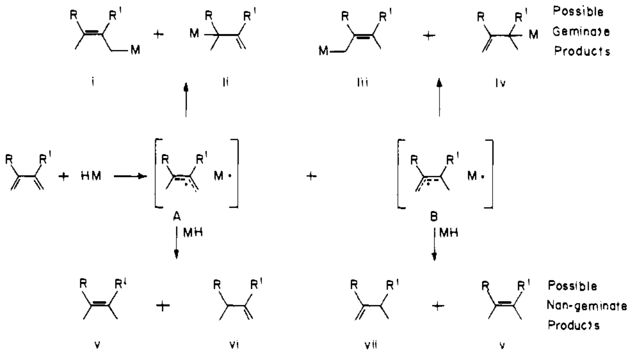
The stacked spectra of Figure 2 show the spectral progression during a reaction of 2,3-dimethyl-1,3-butadiene (same conditions as for isoprene reaction). Again assignments were made on the basis of comparisons with spectra of pure materials, and thus the doublet ($J = 6.9$ Hz) in emission at δ 0.96 can be assigned to the isopropyl methyl groups of 2,3-dimethyl-1-butene, the singlet in emission at δ 1.61 to 2,3-dimethyl-2-butene, and the broad singlet in emission at δ 1.87 to the methylene group of III. Enhanced absorption occurs in the olefinic resonance of the 2,3-dimethyl-1-butene at δ 4.76 and in the methyl region at δ ~1.7; although the close proximity of the latter resonances precludes firm assignments, they probably include methyl resonances of II and the 2-methyl resonance of 2,3-dimethyl-1-butene. As with isoprene, no polarization of the hydride resonance of I was observed.

In a study of the reaction of I with 1,3-cyclohexadiene, the aliphatic resonances of the product cyclohexene were observed in emission, the vinyl resonance in ehanced absorption. Interestingly, the two ephemeral resonances at δ ~5.3 and ~2.9, tentatively assigned to a short-lived hydrometalated compound, both appeared in emission.

For purposes of comparison, a CIDNP study of the hydrogenation of α-methylstyrene by I was carried out under conditions reported elsewhere.[3a] It was found that the degrees of emissions and enhanced absorptions exhibited by the α-methylstyrene, isoprene, and 2,3-dimethyl-1,3-butadiene systems, all at the same concentration, were qualitatively comparable in magnitude.

Kinetic Studies. Attempts to obtain reliable kinetics data utilizing IR spectroscopy were hampered by overlap of the carbonyl peaks of I, II, or III and $Mn_2(CO)_{10}$. NMR studies were somewhat hampered by the air sensitivity of the manganese compounds (most particularly $HMn(CO)_5$) and by the volatility of isoprene, 2,3-dimethyl-1,3-butadiene, and their monoolefinic products of hydrogenation; the extent of evaporation into the head-space of the NMR tubes was always impossible to assess. Useful results were ultimately obtained, however, by running samples syringed into NMR tubes in a glovebox, followed by freezing, evacuating, and flame sealing the tubes.

Scheme IV



For the reaction of I with excess isoprene at 25 °C, the disappearance of I under pseudo-first-order conditions resulted in linear plots of ln [I] for 3–4 half-lives in two separate experiments, and thus the reaction to form II (by far the predominant product under these conditions) is first order in I. From the slopes, k_1 ~3.2 × 10^{-4} s^{-1} and, assuming a first-order dependence on [diene] (as is shown below to be true for 2,3-dimethyl-1,3-butadiene), k_2 ~2.4 × 10^{-4} M^{-1} s^{-1}. Separate experiments of a similar nature with 2,3-dimethyl-1,3-butadiene, in which either I or the diene was in excess, showed that the disappearance of both reactants exhibited pseudo-first-order rate laws, resulting in a second-order rate constant $k_2 = 1.5\ (\pm 0.1) \times 10^{-4}\ M^{-1}\ s^{-1}$. Here also the hydrometalated product was by far the dominant species formed, although monoolefinic products were detected. Careful integrations demonstrated a good mass balance between the amount of diene which disappeared and the total amounts of products formed. Interestingly, identical pseudo-first-order rate constants were obtained for the reaction of 2,3-dimethyl-1,3-butadiene with I under 1 atm of carbon monoxide.

The kinetic isotope effect in the reaction of I with isoprene was determined at room temperature and at 55 °C via competition experiments. Solutions containing a 45:55 ratio of I and I-d_1, respectively, in benzene-d_6 were prepared and mixed with deficiencies (~1:10) of isoprene. The solutions were monitored until all of the diene had reacted, forming II as the major product. The relative amounts of II-d_0 and II-d_1 were determined by careful determinations of the deuterium contents of the methyl resonances in the NOE-suppressed $^{13}C\{^1H\}$ NMR spectra, and kinetic isotope effects k_H/k_D of ~0.45 and ~0.57 at the two temperatures, respectively, were found.

Similar treatment of the corresponding data from an experiment with α-methylstyrene, for which an inverse kinetic isotope effect of 0.4 has been measured directly,[3a] was also attempted (ratio I:I-d_1 45:55) but was complicated by extensive hydrogen–deuterium exchange between I-d_1 and the olefin.[3a] Interestingly, however, careful analysis of the $^{13}C\{^1H\}$ NMR spectrum of a reaction mixture containing both product and unreacted α-methylstyrene showed that while the latter had incorporated statistically comparable amounts of deuterium into both the methylene[17] and methyl groups, the isopropylbenzene product had incorporated deuterium essentially *only into the methyl groups*. Thus the methyl resonance of the isopropylbenzene contained an intense singlet at δ 24.1, a 1:1:1 triplet at δ 23.8 (J_{CD} = 20 Hz, isotope shift ~0.3 ppm), and a weaker multiplet centered at δ 23.7 (J_{CD} ~ 20 Hz, isotope shift ~0.4 ppm). On the basis of the observed intensities, multiplet patterns, and isotope shifts,[18] the resonances are to be assigned to isopropylbenzene-d_0, -d_1, and -d_2,[19] respectively. In contrast, an experiment involving reaction of a sevenfold excess of α-methylstyrene with I-d_1 (90% deuterated) resulted in the formation of isopropylbenzene containing deuterium in both the methyl and the methyne groups (1.7:1, respectively).

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(17) The isotopically shifted methylene carbon resonance consisted of triplet of doublets, presumably reflecting a slight (~0.04 ppm) chemical shift difference of the *E* and *Z* isomers.

(18) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105.

(19) The dideuteriated material is presumably $PhCH(CH_2D)_2$ rather than $PhCH(CH_3)(CHD_2)$, but the spectrum was not of sufficient quality to distinguish between the possible triplet and quintet structures.

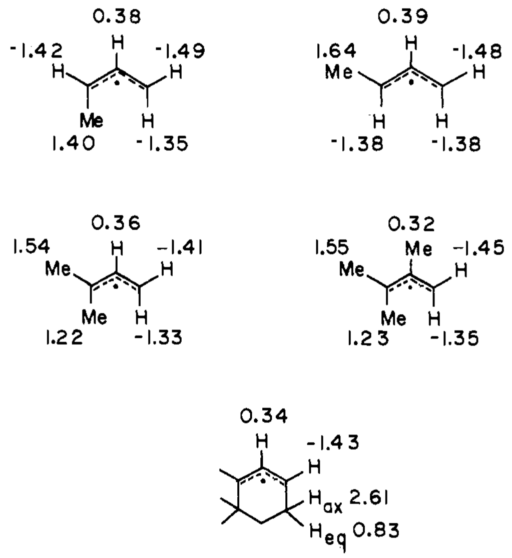

Figure 3. Hyperfine couplings (mT) for allylic radicals.

Mechanism. As will be shown, all of the experimental observations discussed above, including the product distributions, the rate laws, and, in particular, the CIDNP polarizations, are best rationalized in the context of the radical pair processes of Scheme IV. Thus the first step probably involves transfer of the hydrogen atom from I to the conjugated diene to form the allylic component of the geminate radical pair. In Scheme IV, we indicate the various possible products (i–vii) which may derive from the two possible radical pairs (A and B) anticipated from reaction of I with a 1,3-diene in the s-cis conformation. Note that the analogous s-trans conformation would result in principle in the same distribution of products except that the compounds containing internal carbon–carbon double bonds (i, iii, v) would be formed as the corresponding trans isomers. Given the considerable stability of allyl radicals,[7] there is an obvious parallel with the formation of stable benzylic radicals in the initial steps of Schemes II and III. The major difference between the reactions of I with conjugated aromatic olefins and conjugated dienes (except 1,3-cyclohexadiene) is that the former give predominantly nongeminate products involving olefin hydrogenation, while the latter give predominantly the products of geminate coupling. Indeed, the ratio of geminate to total nongeminate products for the isoprene system is ≥9:1 at room temperature, ~4:1 at 55 °C. Ethylene (atmospheric pressure) was found not to react with I in benzene at room temperature, consistent with the low stability of the ethyl radical[7] and the apparent inapplicability of the conventional migratory insertion process.

Let us discuss first the CIDNP data. As mentioned above, the observed NMR emissions and enhanced absorptions require that at least a part of the products be formed via radical pair intermediates. Although many factors may influence the phases and the intensities of the polarizations,[5] the CIDNP data are readily interpreted in terms of the mechanisms of Scheme IV by recourse to the protocol proposed by Kaptein.[5c,d] It is necessary but reasonable to assume that the reaction products of Scheme IV are derived from singlet precursors and that the hydrometalated products result from geminate recombination of the components of the radical pairs, the monoolefins from secondary, nongeminate reactions of the allyl radicals as shown. Utilization of g value and hyperfine couplings (representative hf data are shown in Figure 3) from the literature for the allylic[20] and manganese[21] radicals then leads to the phase predictions shown in Figure 4. Furthermore, 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.[5] Interestingly, and in further contrast to the reactions of I with aromatic olefins, the experiments with I-d_1 show that the hydrogen transfer step of Scheme IV is not reversible and hence cannot be the spin-selective step. Spin selectivity must rather occur during the partitioning between geminate and nongeminate products.

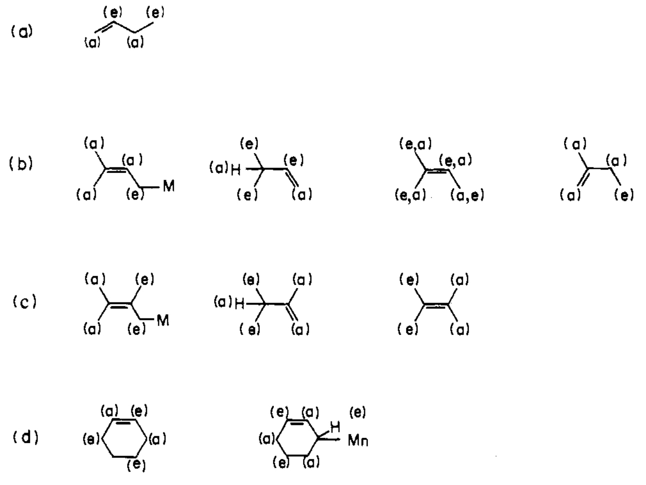

Figure 4. CIDNP phases anticipated for the observed reaction products (e = emission, a = enhanced absorption).

The observation of emission in the methyl resonance of 1-butene during the reaction of I with 1,3-butadiene is consistent with the radical pair mechanism, although the apparent lack of CIDNP in the resonances of the hydrometalated products is rather puzzling. The 1,3-butadiene reaction is the most rapid; however, it is possible that coupling of the geminate product occurs more rapidly than the singlet–triplet mixing required (typically 10^{-9} s[5a]) for the polarization effects to be established. Consistent with this hypothesis, we note that the polarizations of the products of hydrogenation of isoprene and 2,3-dimethyl-1,3-butadiene are comparable with those of the hydrometalated products (Figures 1 and 2) even though the latter are the major products.

The complex CIDNP polarizations observed for the reactions of isoprene and 2,3-dimethyl-1,3-butadiene (Figures 1 and 2, respectively) are in complete agreement with the predictions of the Kaptein formulation shown in Figure 4. Not all product resonances from the reactions of the two dienes could be monitored because of overlap in some cases and distortion in others when resonances in emission and enhanced absorption overlapped partially. However, for the isoprene system, it is clear that the methylene resonance of II, the methyl resonance of 3-methyl-1-butene, and the resonances of H_3 and of the 1- or 2-methyl groups of 2-methyl-2-butene all appeared in emission, as predicted on the basis of their formation from radical pair A (R = Me, R′ = H). Similarly the resonances of the 4-methyl group of 2-methyl-2-butene, of the methyl groups of II, and/or the 2-methyl group of 2-methyl-1-butene appeared in enhanced absorption, while the vinyl resonances of II appeared to be in absorption rather than emission, all as anticipated on the basis of formation from radical pair A. Interestingly, the phases of the resonances of 2-methyl-2-butene were completely incompatible with formation of this olefin from radical pair B (R = Me, R′ = H), although the 2-methyl-1-butene present in solution would appear to originate with radical pair B and the terminal methyl resonance of this olefin did appear in emission as would be predicted on that basis.

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 formulation. Thus the methylene resonance of III, the 3,4-methyl resonance of 2,3-dimethyl-1-butene, and the methyl resonance of 2,3-dimethyl-2-butene all appeared in emission, while the olefinic resonance and, probably, the 2-methyl resonance of

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[20] (a) Fischer, H.; Hellwege, K. H. *Magnetic Properties of Free Radicals*; Springer-Verlag: New York, 1977; Landolt-Bornstein New Series, Group II, Vol. 9, Part b. (b) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 4201. (c) Nakatsuji, H.; Kato, H.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 698.

[21] (a) Howard, J. A.; Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1981**, *83*, 226. (b) Symons, M. C. R.; Sweany, R. L. *Organometallics* **1982**, *1*, 834.

the 2,3-dimethyl-1-butene appeared in enhanced absorption. The enhancement of the latter should be weak in any case because of the relatively small magnitude of the hyperfine coupling of the methyl hydrogen atoms in the radical. As noted above, there are also enhanced absorptions in the methyl region of the NMR spectrum, and these are presumably to be assigned to the 3-methyl and the 2-methyl resonances of III and 2,3-dimethyl-1-butene, respectively. Interestingly, we note that two of the methyl resonances of 2,3-dimethyl-2-butene should be in emission and two in enhanced absorption. As one of the latter should be relatively weak because of the magnitude of the hyperfine splitting in the radical, the resulting resonance is in emission.

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 hyperfine couplings which are of different magnitudes and signs. Application of the Kaptein formula 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 observed net polarization is, as expected, emission. The same argument applies to the allylic hydrogen atoms of the 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 the putative cyclohex-3-enylmanganese compound, H-1 should be in emission, H-2 in (relatively) weak enhanced absorption, and H-3 in (relatively) strong emission. The observed phases of the ephemeral resonances at $\delta \sim 2.9$ and ~ 5.3 are in accord with these predictions and strengthen the assignments.

Consistent with the large differences in g values for the allylic and $Mn(CO)_5$ radicals,[20,21] all polarizations were observed as net effects.[22] The nuclear spin polarizations are thus also expected to be small and hence not readily quantifiable.[4j,5d] However, we have found that the magnitudes of the polarizations for both geminate and nongeminate products were qualitatively comparable with those of the reaction between I and α-methylstyrene, for which careful kinetics studies have established the dominant role of the mechanism of Scheme II.[3a] Given the similarities in magnitudes of g values for benzylic and allylic radicals,[20a] it may be tentatively inferred that the reactions under consideration here, both hydrometalation and hydrogenation, also proceed predominantly via radical pair intermediates.

A notable difference between the benzylic and allylic systems is alluded to by the initial hydrogen transfer step, which is reversible in the former but not in the latter. One line of the evidence for reversibility in the former lies in observations that, when I-d_1 is used, deuterium appears in unreacted olefin starting material accompanied by formation of I-d_0. However, as we have found for reactions of α-methylstyrene with mixtures of I and I-d_1, the deuterium exhibits a strong preference for the methyl groups of the isopropylbenzene product, much less appearing in the methyne group. These results have very interesting mechanistic implications, as they suggest that a [(dimethylphenyl)methyl]-d_1 radical does not readily acquire a second deuterium atom from a second molecule of I-d_1. Instead, prior to significant formation of isopropylbenzene, many manganese atoms may take part in hydrogen–deuterium exchange via the reversible first step of Scheme II. As well, there may be a significant kinetic isotope effect for the abstraction of the hydrogen isotopes from I by the benzylic radical (Scheme II, path a), as has been demonstrated for tin hydrides.[23] Hydrogen–deuterium exchange may also occur between [(dimethylphenyl)methyl]-d_1 radicals and α-methylstyrene, as has been observed for similar hydrogenation reactions of conjugated aromatic olefins by $HCo(CO)_4$.[4c]

The formation of the hydrometalated σ-allylic products, via formal 1,4-addition of the manganese–hydrogen bond of I to the dienes, is reminiscent of many radical addition reactions to conjugated dienes.[24] We have drawn the generalized conjugated diene of Scheme IV in the s-cis conformation because our deuterium labeling results appear to suggest a preference for attack on the s-cis conformations of isoprene and 2,3-dimethyl-1,3-butadiene. While it is well known that conversion between the s-cis conformer of a conjugated diene and the more stable s-trans conformer is facile,[25] syn–anti isomerization of allylic radicals should be relatively slow at the temperature utilized here,[26] and thus the product distributions should reflect the relative reactivities of the conformers. We note that similar 1,3-butadiene addition reactions with I[11b] and $CpFe(CO)_2H$[27] are much less stereoselective, however, and both the s-cis and the s-trans conformers of 1,3-dienes would appear to be receptive to interaction with metal hydrides. Thus the previously postulated[11b] concerted process would appear not to pertain.

Interestingly, several of the products possible from reactions of I with 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene were apparently not formed, and it seems that both the coupling and the hydrogen atom abstraction reactions of the radicals are very susceptible to steric hindrance. Thus hydrometalated compounds of the types ii, iv, and, in the case of isoprene ($R = Me$, $R' = H$), iii, of Scheme IV were neither isolated nor detected spectroscopically, although the last mentioned should, in view of the stability of III, be isolable if formed. Even an NMR experiment involving the reaction of I with 1,3-butadiene ($R, R' = H$) at ~ -5 °C in toluene-d_8 failed to reveal the presence of a methyl resonance which might indicate the initial formation of an unstable isomer such as ii. Similarly, in the case of isoprene ($R = Me$, $R' = H$), the product distribution suggests that the methyl group hinders both hydrogen transfer to the internal carbon atom of radical A and coupling of the $Mn(CO)_5$ radical to the terminal carbon of radical B. Thus in all three cases, attack does not occur at the sites of higher spin densities.[28] Indeed, as noted previously,[13] the hydrometalated products obtained are rather those expected on the basis of electronic factors to exhibit the stronger metal–carbon bond dissociation energies.[7]

Kinetics 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 hydrometalation reaction of isoprene is also first order in I. Thus coordination of the dienes to the manganese is not a necessary step, and it appears that formation of the geminate radical pairs is rate-determining. In addition, the reaction of isoprene, at least, exhibits an inverse kinetic isotope effect ($k_H/k_D \sim 0.5$), consistent with a transition state consisting in part of an essentially linear $Mn{\cdot\cdot}H{\cdot\cdot}C$ (diene) fragment and in which hydrogen transfer is almost completed.[6] These observations are all very similar to those reported for reactions involving hydrogenation of conjugated aromatic olefins by I[3], and, as suggested above, the two types of reactions must be very similar mechanistically. The much higher occurrence of geminate products from the diene reactions may result from the fact that lower temperatures were used and/or may reflect the formation of stronger metal–carbon bonds in the σ-allylic compounds.[7] The one notable exception, the product of hydrometa-

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

(23) Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19.

(24) (a) Afanas'ev, I. B.; Samokhvalov, G. I. *Russ. Chem. Rev.* **1969**, *38*, 318. (b) Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol II, Chapter 13. (c) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley Interscience: New York, 1970; pp 93–95. (d) Sawyer, A. K. *Organotin Compounds*; Marcel Dekker, Inc.: New York, 1971; Vol. 1, Chapter 2.

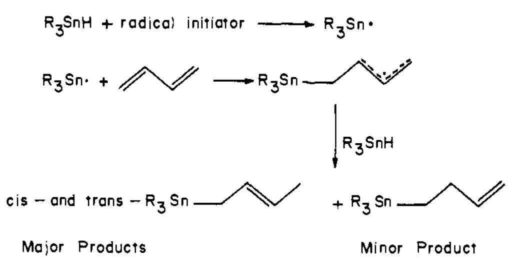
(25) Squillacote, M. E.; Semple T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842.

(26) (a) Kochi, J. K.; Krusic, P. J. In *Essays on Free-Radical Chemistry*; *Chem. Soc. Spec. Publ.* 1970, No. 24, p 147. (b) Krusic, P. J.; Meakin, P.; Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 6211.

(27) Addition of the iron hydride to 1,3-butadiene gives a 2:1 mixture of the trans and cis isomers, respectively, of $MeCH{=}CHCH_2Fe(CO)_2Cp$. Shackleton, T. A.; Baird, M. C., unpublished results. Similarly reaction of isoprene with the iron deuteride, which is also believed to proceed via a mechanism as in Scheme IV, results in extensive scrambling of deuterium between the two 3-methyl groups.[13]

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

Scheme V



lation of 1,3-cyclohexadiene, may be thermally unstable for steric reasons.

Transition-metal hydrides are known to exhibit nucleophilic properties,[29] and the initial interaction between the hydrogen atom of I and a 1,3-diene presumably involves overlap between the Mn–H σ-bonding orbital and the LUMO of the diene. The latter is of π^* character and is partially localized on a terminal carbon atom in both the s-trans and the s-cis conformations.[30] Although hydride transfer is known to be preceded by electron transfer in some cases of hydride addition,[31] electron transfer presumably does not occur in the system under consideration here. Given the ionization potential of I ($\sim$9 eV)[32] and the electron affinity of 1,3-butadiene ($\sim$0.6 eV),[33] formation of the radical pair [$HMn(CO)_5^+$, $C_4H_6^-$] would be exceedingly endothermic. It is also possible to show that, even if formed, the radical pair originating from electron transfer does not live sufficiently long to contribute to the CIDNP polarizations. The pattern of the hydrogen hyperfine couplings of the butadiene radical anion (all of the same sign)[34] is different from that of the butenyl radical (Figure 3), and thus different CIDNP phases would be predicted by the Kaptein formula. Interestingly, the initial hydrogen transfer step of Scheme IV is endothermic by about 15 kcal/mol,[35] and it is the subsequent steps which make the net chemistry exothermic.

Finally, we note that although the hydrometalation of 1,3-dienes by I gives a distribution of hydrometalated products very similar to that obtained with tin hydrides, the latter reaction (hydrostannation) involves a chain radical process rather than direct interactions of diene with metal hydride (Scheme V).[24c,d] Thus hydrostannation reactions are catalyzed by UV light and radical initiators and are retarded by radical scavengers. Furthermore the trialkyltin radical intermediates can add to simple as well as to conjugated olefins, and thus hydrostannation of simple olefins (and alkynes) is facile. Interestingly, addition of a trialkyltin radical to an olefin such as styrene yields the thermodynamically more stable secondary radical, which in turn abstracts a hydrogen atom from a second molecule of stannane to form the 2-phenethylmetal product.[24c,d] Abstraction by styrene of a hydrogen atom from a transition-metal hydride also yields a secondary rather than a primary radical, of course, but now coupling of a metal radical with the radical intermediate yields the 1-phenethylmetal product.[3] Hydrostannation of alkynes is also believed to involve the type of chain radical process shown in Scheme V, and it is interesting to note that this type of reaction exhibits a normal kinetic isotope effect ($\sim$1.2–1.4),[6b] typical for abstraction of hydrogen from tin by carbon centred radicals.[23] The primary reason for the differences in mechanisms for metalation reactions of the two types of metal hydrides probably lies in the relative metal–hydrogen bond strengths, which are $\sim$74 kcal/mol for stannanes[39] and $\sim$63 kcal/mol for I.[36] Thus the tin–hydrogen bond is presumably too strong to be broken by a conjugated diene.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this research and J. P. Colpa for useful discussions.

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(29) (a) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Organometallics* **1982** *1*, 1624. (b) Sweany, R. L.; Owens, J. W. *J. Organomet. Chem.* **1983**, *255*, 327. (c) Kao, S. C.; Spillet, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83. (d) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33.

(30) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; pp 175, 178.

(31) (a) Klinger, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626. (b) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208.

(32) Fenske, R. F. *Prog. Inorg. Chem.* **1976**, *21*, 179 and references therein.

(33) Burrow, P. D.; Jordan, K. D. *Chem. Phys. Lett.* **1975**, *36*, 594.

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

(35) The Mn–H bond strength of I is 63 kcal/mol,[36] while the enthalpies of formation of 1,3-butadiene and the butenyl radical are 26 kcal/mol[37] and 30 cal/mol,[38] respectively.

(36) Billmers, R.; Griffith, L. L.; Stein, S. E. *J. Phys. Chem.* **1986**, *90*, 517.

(37) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

(38) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(39) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17.