The Nature of the Ring-Opening Process in a Substituted Cyclopropylmethyliron Complex

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Irradiation of $CpFe(CO)_2$(2,2-dimethylcyclopropylmethyl) (**4**) in the absence and presence of triphenylphosphine leads to the ring-opened products $CpFe(CO)CH_2CMe_2CH{=}CH_2$ (**6**) and $CpFe(CO)(PPh_3)CH_2CMe_2CH{=}CH_2$ (**7**). These are interconverted on further irradiation and on heating are more slowly converted to the π-allylic complex $CpFe(CO)(\eta^3CH_2$-$CHCHCHMe_2)$ (**8**). Ring-opening rearrangement in the sense to produce mainly **6** or **7** (with a primary σ-bonded alkyl group) rather than products derived from a tertiary σ-bonded alkyl group is most consistent with a concerted four-center organometallic rearrangement process. A radical route, previously proposed for the unsubstituted cyclopropylmethyl complex, is unlikely. Complex **4** also undergoes normal migratory insertion to an acyl complex, without opening of the cyclopropylmethyl group.

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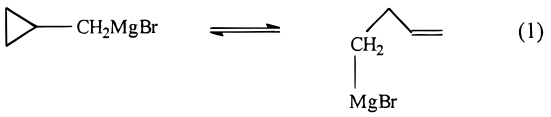
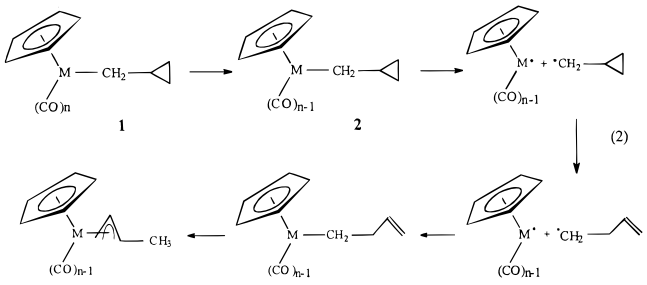
Introduction

Rearrangements interconverting cycloalkylmethyl and unsaturated organometallic compounds have long been known[2,3] (e.g., the conversion of cyclopropylmethyl to 3-butenyl Grignard reagents, eq 1).[4] In 1987, Pannell



(1)

and co-workers[5] published a study of transition-metal cyclopropylmethyl derivatives **1a**−**c**. When treated with triphenylphosphine in THF, all three underwent facile migratory insertion without rearrangement of the cyclopropylmethyl group to yield the corresponding metal acyls, $CpM(CO)_{n-1}(PPh_3)COCH_2C_3H_5$. However, in refluxing hexane, **1a** and **1b** were converted into phosphine-free η^3-crotyl complexes **3a** and **3b**. Reaction was faster in the presence of PPh_3, but the same products were formed in its absence, accompanied by much decomposition. Irradiation of **1a** or **1b** or their migratory insertion products led to more rapid formation of the crotyl π-complexes. The crotyl compounds were considered to be the result of a cyclopropylmethyl/3-butenyl rearrangement, followed by shift of a hydrogen (eq 2). The presumed intermediates were not



a. M = Fe, n = 2; **b.** M = Mo, n = 3; **c.** M = W, n = 3

detected, but irradiation of **1c** in hexane with Ph_3P did produce a rearanged migraory insertion product, $CpW(CO)_2(COCH_2CH_2CH{=}CH_2)$.

The authors assumed that rearrangement of the cyclopropylmethyl group had occurred by a *radical* mechanism. Loss of a CO ligand from the metal would leave a 16-electron intermediate **2**, and subsequent homolytic cleavage of the metal−C bond would form a 15-electron species and a cyclopropylmethyl radical. The known, very rapid rearrangement of the latter[6] to a 3-butenyl radical, followed by radical recombination, would complete conversion to the 3-butenylmetal compound.

(1) (a) Taken in part from the Ph.D. Thesis of B. Li, University of Wisconsin-Milwaukee, 1995. (b) Presented in preliminary form at the 204th American Chemical Society National Meeting, Chicago, IL, August 1993, Abstract O-280 and at the IUPAC 12th Conference on Physical Organic Chemistry, Padova, Italy, 1994.

(2) (a) Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123. (b) Hill, E. A. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1977; Vol. 16, p 131. (c) Stirling, C. M. J. *Chem. Rev.* **1978**, *78*, 517.

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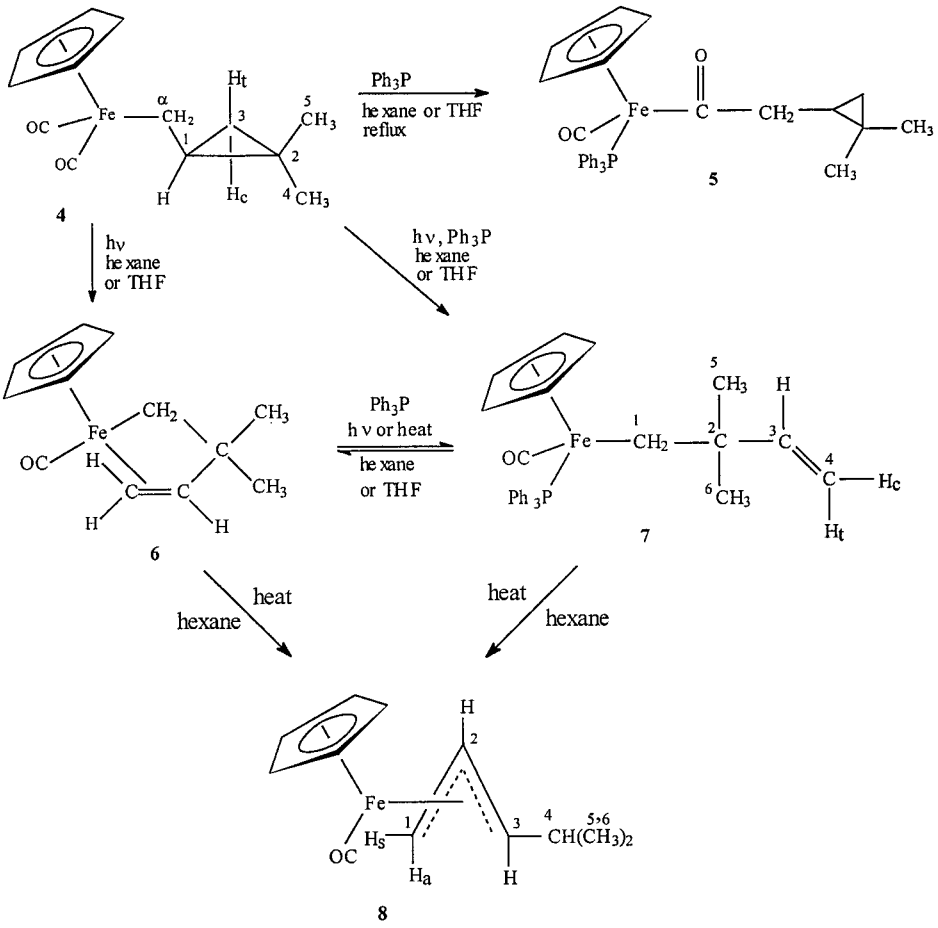
Scheme 1



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The proposal of only the radical mechanism for rearrangement of the cyclopropylmethyl group was unexpected for two reasons. First, a number of other rearrangements of cycloalkylmethylmetal compounds are likely to occur via concerted mechanisms involving neither radical nor carbanionic intermediates.[2,3] It would seem reasonable to at least consider a similar mechanism in the current case. Second, the mechanism proposed involves cleavage of the metal−carbon σ bond in the short-lived, reactive, coordinatively unsaturated intermediate **2**, forming a 15-electron species which is also expected to be unstable. To be significant, this cleavage would have to be very fast. The case has been made for homolytic cleavage of this sort in similar 16-electron intermediates.[5,7] However, it also appears that alternative pathways for reaction of the 16-electron intermediate are preferred if they are available,[8] and the mechanism involving a 15-electron intermediate has been questioned.[8e] For this reason, we have investigated an analogous cyclopropylmethyliron compound, substituted on the cyclopropane ring in a manner which distinguishes between a radical mechanism and a nonradical "organometallic" mechanism. Our conclusion, as detailed below, is that the reaction does not involve rearrangement of a cyclopropylmethyl radical, but is instead a concerted rearrangement of the 16-electron intermediate.

Results

The 2,2-dimethylcyclopropylmethyliron complex **4** [$CpFe(CO)_2DMCPM$] was prepared by reaction of $Na^+CpFe(CO)_2^-$ with 2,2-dimethylcyclopropylmethyl bromide or chloride. Its NMR and IR spectra are consistent with published data for other Fp−alkyl complexes;[5,9−11] in common with other 2,2-dimethylcyclopropylmethyl compounds prepared, the diastereotopic methylene protons are magnetically nonequivalent. The reactions of **4**, described below, are summarized in Scheme 1.

(7) (a) Severson, R. G.; Wojcicki, A. J. *J. Organomet. Chem.* **1978**, *157*, 173. (b) Mahmoud, K. A.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2199. (c) Gismondi, T. E.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *284*, 59. (d) Pourreau, D. B.; Geoffroy, G. L. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West R., Eds.; Academic: New York, 1985; Vol. 24, p 249.

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Refluxing **4** with excess Ph_3P in THF or hexane led to the corresponding migratory insertion product, **5**, with no apparent side reactions. Spectroscopic data were again consistent with published data for similar compounds.[5,10] The presence of two diastereomers of **5** in approximately equal amounts was evident from the ^{13}C and ^{1}H NMR spectra, and the diastereotopic α-methylene protons of both were distinguishable. In the absence of Ph_3P, no sign of reaction was noted in the IR spectrum after 54 hours of refluxing in hexane. In refluxing heptane, decomposition occurred without formation of identifiable organometallic products.

Irradiation of **4** in THF or hexane, in the absence of Ph_3P, led to the loss of CO and formation of the ring-opened complex **6**, in which the newly generated double bond is coordinated to the iron. This compound has previously been prepared in another fashion by Green and Smith.[11] The relatively high-field shift of the "olefinic" carbons and protons is characteristic of the iron-coordinated double bond.[11,12] The same photochemical reactions in the presence of excess Ph_3P yielded **7**, in which the phosphine replaces the double bond in its coordination to the metal. The olefinic carbon and proton resonances of **7** are within normal ranges,[13] and other NMR parameters are consistent with those of analogous complexes.[16] In the NMR spectra of both **6** and **7**, the methylene hydrogens H_1 and $H_{1'}$ and the methyl groups are nonequivalent because of the stereogenic iron center. In the presence of a 2-fold excess of Ph_3P, irradiation led to an apparent photostationary mixture of **6** and **7** with approximate composition 40:60.

When either **6** or **7** was heated at reflux in hexane, or when **4**, **6**, or **7** was subjected to an extended period of irradiation, the allylic π-complex **8** was formed. Its proton and carbon NMR parameters are consistent with the stereochemical features shown—exo orientation of the allyl fragment and syn configuration of the isopropyl group—which are favored in other allylic complexes.[17] The structure is chiral, so the methyl groups are nonequivalent.

Discussion

The migratory insertion reaction of **4** to form **5** appears unexceptional and warrants no discussion beyond noting that the absence of cyclopropylmethyl ring opening confirms the lack of involvement of radicals in that process.

As in the reported[5] study of compounds **1a**−**c**, we presume that the photochemical reactions leading to ring-opened products are initiated by the dissociation of a CO ligand from the metal, forming the 16-electron intermediate **9**. Homolytic cleavage of the Fe−C bond at this stage, as proposed[5] for compounds **1a** and **1b** and detailed in Scheme 2, would generate a 2,2-dimethylcyclopropylmethyl radical, **11**, paired with the 15-electron iron species **10**. Radical **11** has been studied previously by Newcomb, Glenn, and Williams[18] and by Beckwith and Bowry,[6b] using scavenging methods, and in our laboratory[19] via perester photolysis. It undergoes ring cleavage with an overall rate constant (at 25 °C) about 6−9 times greater than that of the unsubstituted cyclopropylmethyl radical, and the tertiary radical **12** is kinetically favored by a ratio of about 7:1 over the primary radical **13** in this rearrangement. Therefore, the major intermediate formed by radical recombination after ring cleavage should be the tertiary iron alkyl **14**. Subsequent hydrogen migration (as in the reactions of **1a** and **b**) would produce the η^3-allylic complex **8** as the principal kinetically controlled product. Although **8** is formed on heating or further photolysis of **6** or **7**, it is not a significant initial reaction product. Alternative disproportionation of the radical pair [**10**• •**12**] would produce CpFe(CO)H and dienes. The former is likely to decompose, and the latter might polymerize under reaction conditions. The formation of products **6** and **7** in moderately good yields, the absence of **8** as an important initial product, and the lack of major decomposition during the photolysis combine to make it unlikely that the radical-pair mechanism contributes significantly in the photochemical reaction of **4** to **6** and **7**.

An alternative to the radical-pair mechanism is a concerted molecular mechanism of rearrangement (Scheme 3). On the basis of several kinds of mechanistic evidence, this type of mechanism has been favored over alternative radical-pair or ion-pair routes for the ring-opening rearrangements of cyclopropylmethyl and cyclobutylmethyl organomagnesium compounds.[2a] For steric and, probably, electronic reasons, these rearrangements favor cleavage of the less-substituted ring bond, leading to the preferential formation of 1° > 2° > 3° organometallic product.[2,3b,20] This is the opposite of the radical's behavior but in line with observations for **4**.

Seen in the reverse direction, the mechanism of Scheme 3 is analogous to the addition step in transition-metal-catalyzed coordination polymerization reactions, in which a coordinated alkene molecule is believed to insert into an alkyl−metal bond.[21] This mechanism implies that a vacant coordination site on the metal is important, perhaps essential, for the ring cleavage of the cyclopropylmethyl organometallic compound to occur. In this context, it might be noted that analogous rearrangements of cyclopropylmethyl- and cyclobutylmethylboranes are strongly retarded by the addition of pyridine, which coordinates to the vacant orbital on the

(12) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1365.

(13) The olefinic carbon shifts of 106.01 and 153.37 ppm are at relatively high and low fields, respectively, in comparison with the hydrocarbon 3,3-dimethyl-1-butene at 109.0 and 149.8 ppm.[14] These shifts are consistent with a "linear electric field" effect, with the metal as a moderately electropositive group.[15]

(14) Sadtler Standard Carbon-13 NMR Spectra, Sadtler Research Laboratories, Philadelphia, #282.

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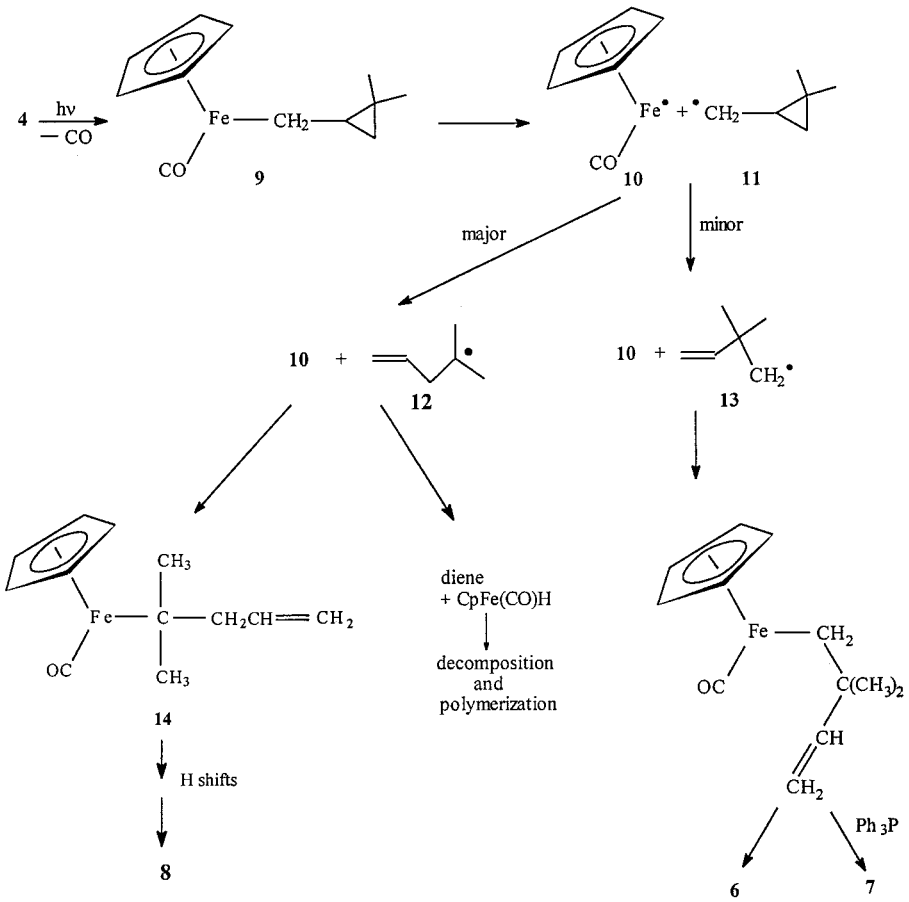
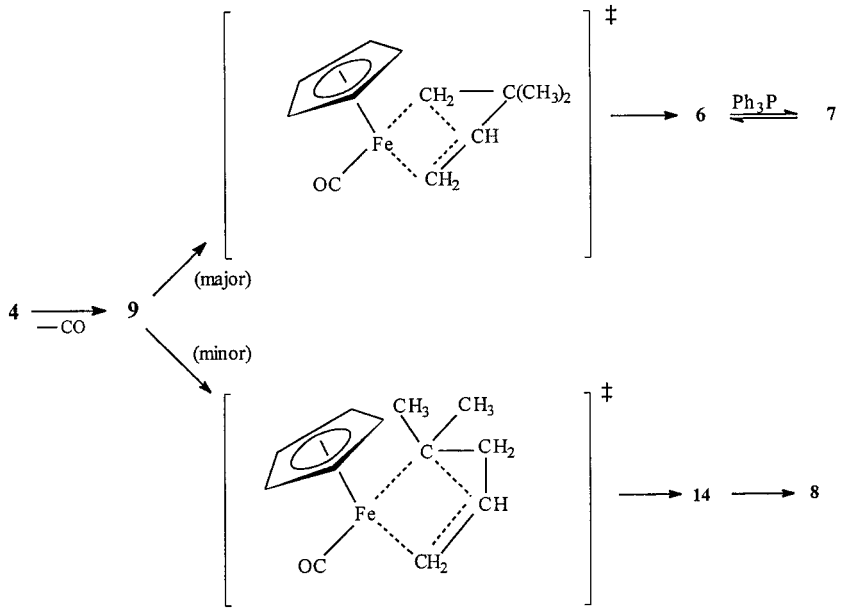
Scheme 2



Scheme 3



boron.[22] In the present reaction, rearrangement of the cyclopropylmethyl group appears to require initial loss of a carbonyl ligand in order to free a coordination site on the iron, after which rearrangement occurs very rapidly.

In the absence of Ph_3P, the product isolated (**6**) retains coordination of the double bond with the iron. With the phosphine present, the major product is **7**, in which the double bond is replaced in the coordination sphere of the metal. Since photochemical equilibration between **6** and **7** occurs faster than the photolysis of **4**, it is reasonable that **7** resulted from subsequent displacement by the added phosphine.

(22) (a) Koster, R.; Arora, S.; Binger, P. *Angew. Chem., Int. Ed.* **1969**, *8*, 205. (b) Hill, E. A.; Nylen, P. A.; Fellinger, J. H. *J. Organomet. Chem.* **1982**, *239*, 279.

Heating or further irradiation of either **6** or **7** leads to a slower formation of the η^3-allylic complex **8**, the apparent thermodynamic sink in the system. This final conversion might be formulated to involve reversible recyclization of **6** to the 16-electron intermediate **9**, followed by the alternative ring cleavage of the dimethylcyclopropane ring to produce the tertiary organoiron complex **14**. The latter ring opening might occur by the same type of molecular mechanism as proposed above for interconversion of **4** and **6** but in the kinetically less-favored sense. Alternatively, it might, in fact, occur by a radical pathway. In any event, the *gem*-dimethyl substitution of the alkenyl ligand blocks direct conversion of **6** or **7** to an η^3-allylic complex, in addition to directing the regiochemistry of the ring opening.

Conclusion

The present study appears to definitively rule out a radical mechanism in the rearrangement of **4** to **6** and **7** and to cast doubt upon its occurrence in the rearrangements of **1a** and **1b**.[5]

However, the behavior of **4** does not completely parallel that of **1a** and **1b**, and so it might be argued that our results do not preclude the previously suggested homolytic pathway for rearrangement of the latter. Most notably, we found only the migratory insertion product **5** on *heating* **4** with PPh_3 in either hexane or THF. We observed the ring-opened rearranged products from **4** only on irradiation. In contrast, the cyclopropylmethyl groups of **1a** and **1b** did rearrange on heating in *hexane* solution to form the π-crotyl complexes **3a** and **3b** (both in the presence of PPh_3 or more slowly in its absence). Also, **1a** appears to have reacted more rapidly than **4**, particularly in the migratory insertion, though not all of the experiments were reported in detail.

The methyl substituents in **4** clearly influence the quantitative balance among competing pathways of decomposition, migratory insertion, and rearrangement, relative to compound **1a**. We do not have a simple rationalization for differences in reactivity between **1a** and **4**. It remains possible that the methyl groups have in fact produced a qualitative change in the mechanism of the rearrangement of **4**, either preventing the homolytic dissociation of the Fe−C bond in the 16-electron intermediate **9** or accelerating its molecular rearrangement. However, we prefer the alternative that a single mechanism, the molecular mechanism consistent with the results in the present study of **4**, is responsible for the cyclopropylmethyl ring openings in all cases.

Experimental Section

Reactions involving organometallic compounds were carried out under dry nitrogen that had additionally passed through a tube of Drierite. Photochemical reactions were run under nitrogen in a quartz tube in a Rayonet photochemical reactor (Srinivasan-Griffin, with 16 low-pressure mercury lamps). During photolysis, the temperature held at 31 ± 1 °C. Column chromatography was generally performed under nitrogen on a 2 × 50-cm column of Brockman grade I acidic alumina; variations from this are noted. THF and ether were distilled under nitrogen from sodium/benzophenone. Pentane, hexane, and heptane were distilled from sodium metal. Melting and boiling points are uncorrected. IR spectra were taken in hexane solution in a 0.1-mm sodium chloride cell on a Nicolet 5DXC FT-IR spectrometer. NMR spectra were recorded in $CDCl_3$ solution on a Bruker WM 250 spectrometer (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz). Chemical shifts are vs internal TMS, either directly or via solvent at 7.24 or 77.0 ppm, respectively. The numbering of the protons and carbons is as shown in structures **4**, **7**, and **8**. Resonances were assigned with the assistance of DEPT, single-frequency off resonance, and homonuclear H−H decoupling experiments and comparison of chemical shifts and coupling constants with those of analogous compounds. Mass spectra were run on a Hewlett-Packard 5985 mass spectrometer using electron impact ionization (solid inlet, 70 eV). Abbreviations Cp and DMCPM represent η^5-cyclopentadienyl and 2,2-dimethylcyclopropylmethyl, respectively.

2,2-Dimethylcyclopropylmethyl Chloride. 2,2-Dimethylcyclopropanecarboxylic acid was prepared via the corresponding nitrile;[23] bp 195 °C (lit.[23] bp 198 °C). The acid was then reduced to 2,2-dimethylcyclopropylmethanol with lithium aluminum hydride in ether; bp 135 °C (lit.[24] bp 93−94 °C (118 Torr)).

Tri-*n*-butylphosphine (90 mL, 0.36 mol) was added dropwise to a vigorously stirred solution of the alcohol (21 g, 0.21 mol) in 350 mL of CCl_4, chilled to 0 °C. The solution became viscous, and after 72 h at 0 °C, the ^{1}H NMR indicated that reaction was complete. Pentane (100 mL) was added, the upper (pentane) layer was separated, and the lower layer was extracted three more times with pentane. Solvent was stripped (10 Torr), and the product was transferred under high vacuum to a cold trap and redistilled; 17.9 g, 72%; bp 120 °C (760 Torr). ^{1}H NMR: δ 0.19 (H_{3t}, t, $J_{3c,3t} \approx J_{1,3t} = 4.8$ Hz), 0.59 (H_{3c}, d/d, $J_{3c,3t} = 4.8$, $J_{1,3c} = 8.3$ Hz), 0.96 (H_1, m), 1.07 and 1.11 (3H each, H_4 and H_5, s), 3.41 (H_α, d/d, $J_{\alpha,\alpha'} = 11.2$, $J_{\alpha,1} = 9.3$ Hz), 3.71 ($H_{\alpha'}$, d/d, $J_{\alpha,\alpha'} = 11.2$, $J_{\alpha',1} = 6.8$ Hz). ^{13}C NMR: δ 18.13 (C_2), 19.40 (C_5), 20.82 (C_3), 26.55 (C_1), 26.95 (C_4), 47.43 (C_α).

2,2-Dimethylcyclopropylmethyl Bromide. Tri-*n*-butylphosphine (17 mL, 0.068 mol) was added dropwise to a vigorously stirred solution of 2,2-dimethylcyclopropylmethanol (5 g, 0.05 mol) and carbon tetrabromide (20 g, 0.06 mol) in 75 mL of pentane, cooled on a −78 °C bath. The reaction flask was wrapped with a black cloth, warmed to room temperature, and stirred for 60 h. A viscous lower layer separated, and the absence of alcohol peaks in the ^{1}H NMR spectrum indicated that reaction was complete. The lower layer was extracted 3 times with pentane, and solvent was stripped (10 Torr) from the combined pentane layers. The bromide (6 g, 73%) was transferred under high vacuum to a −78 °C trap, stored in the dark at −78 °C, and used within 8 h. The ^{1}H NMR spectrum indicated less than 3% of rearrangement to open-chain bromide. ^{1}H NMR: δ 0.20 (H_{3t}, t, $J_{3c,3t} \approx J_{1,3t} = 4.9$ Hz), 0.64 (H_{3c}, d/d, $J_{3c,3t} = 4.9$, $J_{1,3c} = 8.5$ Hz), 1.07 and 1.11 (3H each, H_4 and H_5, s), 1.1 (H_1, m), 3.28 (H_α, d/d, $J_{\alpha,\alpha'} = 10.2$, $J_{\alpha,1} = 9.3$ Hz), 3.59 ($H_{\alpha'}$, d/d, $J_{\alpha,\alpha'} = 10.2$, $J_{\alpha',1} = 7.1$ Hz). ^{13}C NMR: δ 18.97 (C_5), 19.46 (C_2), 22.31 (C_3), 26.80 (C_4), 26.89 (C_1), 36.19 (C_α).

$CpFe(CO)_2(DMCPM)$ (4). A solution of $Na^+[CpFe(CO)_2]^-$ was prepared[8a,25] by addition of $[CpFe(CO)_2]_2$ (1.167 g, 3.30 mmol) in 20 mL of THF to sodium amalgam (from 0.76 g, 33 mmol of Na, and 5.8 mL of Hg) and 10 mL of THF. The supernatant was transferred to centrifuge tubes via cannula, centrifuged until clear, transferred to a reaction flask, and cooled to 0 °C. 2,2-Dimethylcyclopropylmethyl bromide (1.0 g, 6.2 mmol) was added by syringe, and the reaction mixture was stirred at 0 °C for 3 h. The solvent was distilled to a cold trap under vacuum, and the residue was dissolved in pentane and transferred by cannula to a column of alumina (Brockman

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grade I acidic, deactivated with 10% of water). A yellow band eluted with pentane was concentrated to an orange oil (0.77 g, 48%). Similar preparation from the chloride yielded **4** of similar purity in 61% yield. IR: 1955 and 2010 cm^{-1}. MS 260 (M^+, 2), 232 (3), 204 (16), 200 (21), 178 (31), 177 (10), 162 (13), 160 (9), 149 (32), 134 (18), 121 (100). ^1H NMR: δ −0.10 (H_{3t}, t, $J_{3c,3t} \approx J_{3t,1} = 3.9$ Hz), ca. 0.55 (2H, H_{3c} and H_1, m), 0.97 and 1.03 (3H each, H_4 and H_5, s), 1.39 (H_α, t, $J_{\alpha,\alpha'} \approx J_{\alpha,1} = 8.6$ Hz), 1.70 ($H_{\alpha'}$, d/d, $J_{\alpha,\alpha'} = 8.6$, $J_{\alpha',1} = 5.1$ Hz), 4.73 (5H, Cp, s). ^{13}C NMR: δ 4.16 (C_α), 19.56 (C_5), 20.53 (C_2), 24.95 (C_3), 27.66 (C_4), 33.48 (C_1), 85.25 (Cp), 217.67 (CO). Anal. Calcd for $C_{13}H_{16}FeO_2$: C, 60.03; H, 6.20. Found: C, 60.45; H, 6.40.

CpFe(CO)(PPh_3)(CO-DMCPM) (5); Reaction of 4 with PPh_3. A solution of **4** (1.1 g, 4.2 mmol) and PPh_3 (2.22 g, 8.46 mmol) in 75 mL of hexane was refluxed under nitrogen. After 48 h, the color had changed from yellow to pink and changes in the IR carbonyl absorption indicated that the reaction was nearly complete. The reaction mixture was passed through a column of silica gel. Unreacted **4** and PPh_3 were eluted with hexane, followed by an orange fraction with ether−hexane (1:4). Removal of the solvent under vacuum yielded **5** as a yellow powder (1.57 g, 71%); mp 112−117 °C. IR: 1920 and 1619 cm^{-1}. MS 439 (M − C_6H_{11}, 37), 411 (2), 383 (99), 262 (54), 204 (9), 200, (11), 183 (100), 152 (15), 149 (17), 121 (57), 108 (38). The NMR spectra indicated an inseparable mixture of diastereomers in a ratio of about 1:1; spectra for the two are summarized together, because resonances are not clearly assignable to the two isomers. ^1H NMR: δ −0.47 and −0.18 (H_{3t}, t, $J_{3t,3c} \approx J_{1,3t} = 4.5$ Hz), 0.17 and 0.33 (H_{3c}, d/d, $J_{3t,3c} = 4.2$, $J_{1,3c} = 8.5$ Hz), 0.58 (H_1, m), 0.79, 0.90, 0.91, and 0.94 (each 3H, H_4 and H_5, s), 2.36 and 2.50 (H_α, d/d, $J_{\alpha,\alpha'} = 16.8$ and 16.1, $J_{\alpha,1} = 8.0$ and 6.1 Hz), 3.01 and 2.81 ($H_{\alpha'}$, d/d, $J_{\alpha,\alpha'} = 16.9$ and 16.0, $J_{\alpha',1} = 6.0$ and 7.7 Hz), 4.38 and 4.40 (Cp, d, $J_{PH} = 1.15$ and 1.12 Hz), 7.35 and 7.45−7.53 (Ph). ^{13}C NMR: δ 14.33 (C_2), 19.17 and 19.38 (C_3), 19.81 and 19.90 (C_5), 20.87 (C_1), 26.79 and 26.94 (C_4), 65.98 and 66.98 (C_α), 84.85 (Cp), 127.64 (Ph C_m, d, $J_{PC} = 9$ Hz), 129.27 (Ph C_p), 133.01 (Ph C_o, d, $J_{PC} = 11$ Hz), 136.25 (Ph C_{ipso}, d, $J_{PC} = 42$ Hz), 220.29 (CO, d, $J_{PC} = 31.5$ Hz). Anal. Calcd for $C_{31}H_{31}FeO_2P$: C, 71.27; H, 5.98. Found: C, 71.62; H, 5.93.

A similar reaction of **4** (1.1 g, 4.2 mmol) with PPh_3 (3.0 g, 11.4 mmol) in THF (60 mL) yielded 1.35 g (61%) of **5** (77 h reflux).

A solution of **4** (0.538 g, 2.07 mmol) in 60 mL of hexane was heated at reflux for 54 h without PPh_3. No reaction was indicated in the IR or ^1H NMR spectra.

CpFe(CO)(σ-2,2-dimethylbut-3-π-enyl) (6); Irradiation of 4. A solution of **4** (1.62 g, 6.23 mmol) in 75 mL of hexane was irradiated for 28 h; the reaction was judged by IR to be complete. On chromatography, a yellow band eluted with ether/pentane (1/1) yielded, after vacuum removal of solvent, 1.26 g (87%) of **6** as an orange oil.[11] IR: 1947 cm^{-1}. MS: 232 (M^+, 9), 204 (44), 200 (56), 186 (11), 176 (10), 167 (10), 162 (25), 160 (18), 149 (28), 148 (26), 134 (36), 121 (100). ^1H NMR: δ −1.13 (H_1, d, $J_{1,1'} = 5.7$ Hz), 0.20 (3H, H_5 or H_6, s), 1.04 ($H_{1'}$, d, $J_{1,1'} = 5.4$ Hz), 1.12 (3H, H_5 or H_6, s), 1.83 (H_{4t}, d, $J_{3,4t} = 12.5$ Hz), 2.37 (H_{4c}, d, $J_{3,4c} = 8.0$ Hz), 3.03 (H_3, d/d, $J_{3,4t} = 12.4$, $J_{3,4c} = 8.05$ Hz), 4.51 (5H, Cp, s). ^{13}C NMR: δ −22.37 (CH_2), 23.97 and 33.14 (CH_3), 34.30 (C), 35.61 (CH_2), 45.03 (CH), 83.31 (Cp), 227 (CO).

Similar irradiation of **4** (0.81 g, 3.11 mmol) in THF (37 mL) for 35 h yielded 0.47 g (65%) of **6**.

CpFe(CO)(PPh_3)(σ-2,2-dimethylbut-3-enyl) (7); Irradiation of 4 with PPh_3. A solution of **4** (2.5 g, 9.6 mmol) and PPh_3 (3.85 g, 14.68 mmol) in 100 mL of hexane was irradiated for 62 h. The solution was chromatographed. Unreacted starting materials were eluted with hexane, and an orange product band followed with hexane/ether (1/1). After removal of solvent under vacuum, 3.32 g (70%) of **7** was obtained as an orange oil. IR: 1912 cm^{-1}. MS (15 eV): 466 (M − CO, 0.2), 464 (0.3), 383 (2), 277 (11), 262 (100), 232 (5), 204 (31), 200 (29), 183 (59), 176 (7), 162 (14), 160 (9), 148 (21) 134 (19), 121 (21), 108 (64). ^1H NMR: δ 0.83 (H_1, partially obscured, but consistent with d/d, $J_{1,1'} = 9.8$, $J_{1,P} = 15.0$ Hz), 0.85 and 0.86 (3H each, H_5 and H_6, s), 1.96 ($H_{1'}$, d, $J_{1,1'} = 9.8$, $J_{1',P} \approx 0$ Hz), 4.27 (5H, Cp, d, $J_{P,H} = 1.0$ Hz), 4.65 (H_{4c}, d/d, $J_{4c,4t} = 1.85$, $J_{3,4c} = 10.5$ Hz), 4.73 (H_{4t}, d/d, $J_{4c,4t} = 1.82$, $J_{3,4t} = 17.65$ Hz), 5.80 (H_3, d/d, $J_{3,4c} = 10.7$, $J_{3,4t} = 17.5$ Hz), 7.28−7.45 (Ph, m). ^{13}C NMR: δ 17.26 (C_1, d, $J_{P,C} = 18$ Hz), 29.74 and 31.05 (C_5 and C_6), 41.73 (C_2), 84.62 (Cp), 106.01 (C_4), 127.87 (Ph C_m, d, $J_{P,C} = 8.8$ Hz), 129.31 (Ph C_p), 133.25 (Ph C_o, d, $J_{P,C} = 9.4$ Hz), 136.80 (Ph C_{ipso}, d, $J_{P,C} = 40$ Hz), 153.37 (C_3), 224.5 (CO, d, $J_{P,C} = 32$ Hz).

Similar irradiation of **4** (0.132 g, 0.51 mmol) and PPh_3 (0.35 g, 1.3 mmol) in 10 mL of THF for 16 h yielded 0.166 g (66%) of **7**.

Equilibration of 6 and 7. A solution of **6** (0.4 g, 1.72 mmol) and PPh_3 (0.81 g, 3.08 mmol) in 10 mL of hexane was irradiated for 22 h. Monitoring by IR showed that the reaction had reached a stationary state with **6** and **7** in a ratio of 40/60. The mixture was separated by chromatography; unreacted PPh_3 and **6** were eluted with pentane, followed by **7** (0.29 g, 34%) with 1:1 pentane−ether. Repetition in THF led to similar results; **7** was isolated in 29% yield.

A solution of **6** (0.6 g, 2.59 mmol) and PPh_3 (1.00 g, 3.8 mmol) in 20 mL of hexane was refluxed for 3.5 h. The IR carbonyl spectrum indicated the presence of **6** and **7** in a ratio of 55/45. Compound **7** was isolated by column chromatography in 30% yield.

CpFe(CO)[η^3-(1-isopropylallyl)] (8); Thermal Rearrangement of 6 or 7. A solution of **6** (0.6 g, 2.59 mmol) in 100 mL of hexane was refluxed for 4 h and chromatographed. A yellow band eluted with hexane yielded **8** as an orange oil after removal of solvent (0.45 g, 75%). IR: 1950 cm^{-1}. MS: 232 (M^+, 11), 204 (38), 200 (51), 186 (44), 176 (9), 148 (12), 134 (30), 121 (100). ^1H NMR: δ 0.32 (H_{1a}, d/d, $J_{1a,2} = 10.6$, $J_{1a,1s} = 1.4$ Hz), ca. 1.15 (H_3, m, obscured), 1.13 and 1.17 (H_5 and H_6, 3H each, d, $J_{4,5} = J_{4,6} = 6.55$ Hz), 1.82 (H_4, d/sept, $J_{3,4} = 9.5$, $J_{4,5} = J_{4,6} = 6.5$ Hz), 2.55 (H_{1s}, d/d, $J_{1s,2} = 6.9$, $J_{1a,1s} = 1.4$ Hz), 4.32 (H_2, d/t, $J_{1s,2} = 7.1$, $J_{1a,2} = J_{2,3} = 10.5$ Hz), 4.46 (Cp, 5H, s). ^{13}C NMR: δ 24.13 and 26.15 (C_5 and C_6), 28.30 (C_1), 34.70 (C_4), 70.12 (C_3), 71.48 (C_2), 78.85 (Cp), 221.8 (CO).

Similar reaction of **7** (0.5 g, 1.01 mmol) in hexane (50 mL) also produced **8** (0.17 g, 71%).

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