The mechanism of formation of 6 from the reaction of 2 with $Ni(COD)_2$ is not known. However, it is noteworthy that in the related reaction involving of $Cp_2V(SPh)_2$ and [Cp₃Ni₂][BF₄], redox chemistry is accompanied by ligand transfer, yielding $[Cp_2V][BF_4]$ and $[CpNi(\mu-SPh)]_2$. Isolation of 3 suggests that the initial step in the reaction may be coordination of 2 to Ni. Although the V byproduct is not isolated or characterized in this reaction, the isolation of a Ni(II) product from the reaction suggests the V(IV)dithiolate 2 is reduced to a V(III) species. These data suggest that the formation of the Ni(II) product 6 may proceed via two inner-sphere, one-electron transfers from Ni to V, which are accommodated by the formation of a V_2Ni intermediate analogous to 3.

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Summary

Complexes 1 and 2 have been prepared and characterized. In reactions with $Ni(COD)_2$, use of 1 affords the heterobimetallic complex 3. The structural data for 3 are consistent with the presence of a dative bond between the d¹⁰ Ni(0) center and the d⁰ Ti(IV) metal centers. In contrast, reaction of 2 with $Ni(COD)_2$, results in electron and ligand transfer affording the hexameric Ni(II) species 6. It is suggested that the formation of 6 proceeds through an V_2Ni analogue of 3. In a subsequent paper, we will describe a series of stable V(IV) heterobimetallics of the form $[Cp_2V(\mu-SR)_2CuPR_3]^{+.36}$

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Supplementary Material Available: Tables of thermal and hydrogen atom parameters (3 pages); listings of values of $10F_{o}$ and $10F_c$ (18 pages). Ordering information is given on any current masthead page.

Formal Transfers of Hydride from Carbon–Hydrogen Bonds. Synthesis, Structure, and Reactions of $[Cp(CO)_2FeCH_2]_3CH$

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The reaction of Cp(CO)₂FeNa with (CH₃SO₂OCH₂)₃CH (4) provided [Cp(CO)₂FeCH₂]₃CH (3) in 50% yield. Thermal decomposition of compound 3 occurred rapidly in solution at 25 °C and produced approximately equimolar amounts of $[Cp(CO)_2Fe]_2$ (5) and dicarbonyl(cyclopentadienyl)(cyclopropylmethyl)iron (6). These products presumably result from decarbonylation of compound 3, formation of carbonyl-bridged intermediate 8, and reductive elimination. The reaction of compound 3 with 2 equiv of $Ph_3C^+PF_6^-$ yielded the $Cp(CO)_2Fe^+$ complex 11 of $Cp(CO)_2FeCH_2CH_2CH=CH_2$ and negligible amounts of triphenylmethane. Ph₃C⁺ may accept an electron from compound 3, triggering loss of $Cp(CO)_2Fe^+$ and a shift of $Cp(CO)_2FeCH_2$ that converts the isobutyl skeleton of the starting material into the *n*-butyl skeleton of product 11. Irradiation of compound 3 at 350 nm produced $[Cp(CO)_2Fe]_2$ (5) and an exo/endo mixture of carbonyl(cyclopentadienyl) $(\eta^3$ -2-methyl-2-propenyl)iron (34). These products appear to result from decarbonylation, formation of carbonyl-bridged intermediate 8, further decarbonylation, formation of iron hydride 33 by β -elimination, reductive elimination, and further irradiation of dicarbonyl(cyclopentadienyl)(2-methyl-2-propenyl)iron (21).

Carbon-hydrogen bonds act as formal donors of hydride in many well-known redox reactions, including enzymatic reductions involving the coenzyme NADH, Cannizzaro reactions, and Meerwein-Ponndorf-Verley reductions. The subdued reactivity of these bonds is a distinct advantage since it allows a reducible substrate to be recognized and oriented by a receptor before the transfer of hydride takes place. Ordinary carbon-hydrogen bonds are not reactive enough to be useful, but those activated by adjacent lone pairs or carbon-metal bonds are very good formal donors of hydride. For example, tris[(triphenylstannyl)methyl]methane (1) contains a carbon-hydrogen



bond activated by adjacent carbon-tin bonds, and it is therefore able to reduce $Ph_3C^+PF_6^-$ to triphenylmethane

in high yield.^{1a} Similar carbon-hydrogen bonds constrained to be antiperiplanar to several carbon-metal bonds are even more reactive formal donors of hydride. For example, the central carbon-hydrogen bond of stannaadamantane 2 is weaker than typical tin-hydrogen bonds,² allowing compound 2 to reduce activated halides to the corresponding hydrocarbons.1c Since related compounds containing more electropositive metals like iron promised to be even more reactive formal donors of hydride, we decided to synthesize $[Cp(CO)_2FeCH_2]_3CH$ (3)³ and study its reactions.

After extensive experimentation, we found that compound 3 could be prepared efficiently by treating a solution

(3) Cp = η^{5} -2,4-cyclopentadien-1-yl.

⁽⁴²⁾ Darensbourg, M. Y.; Silva, R.; Reibenspies, J.; Prout, C. K. Or-ganometallics 1989, 8, 1315.

⁽⁴³⁾ Dance, I. G.; Scudder, M. L.; Secomb, R. Inorg. Chem. 1985, 24, 1201.

^{(1) (}a) Ducharme, Y.; Latour, S.; Wuest, J. D. Organometallics 1984, 3, 208-211. (b) Beauchamp, A. L.; Latour, S.; Olivier, M. J.; Wuest, J. D. J. Organomet. Chem. 1983, 254, 283-291. (c) Ducharme, Y.; Latour, S.; Wuest, J. D. J. Am. Chem. Soc. 1984, 106, 1499-1500. Beauchamp,

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⁽²⁾ Burkey, T. J.; Majewski, M.; Griller, D. J. Am. Chem. Soc. 1986, 108, 2218–2221. Dewar, M. J. S.; Grady, G. L. Organometallics 1985, 4, 1327-1329.

of $Cp(CO)_2$ FeNa in tetrahydrofuran at -40 °C with trimesylate $4.^{4,5}$ Solvent was then evaporated at -40 °C, and



the residue was extracted with benzene. Rapid, low-temperature chromatography of the extracts on silica yielded compound 3, which could be obtained pure in 50% yield by recrystallization from benzene/hexane. The simplicity of its ¹³C NMR spectrum confirmed that the product had an effective axis of C_3 symmetry, and the ¹H NMR spectrum contained only the expected singlet for fifteen cyclopentadienyl hydrogens at δ 4.33, doublet for six methylene hydrogens at δ 2.12, and septet at δ 1.66 for the unique methine hydrogen of the activated carbon-hydrogen bond.

Although purified solid samples of compound 3 could be kept for several days at 25 °C, decomposition occurred readily in solution. In benzene, for example, the half-life at 25 °C was approximately 8 h. This decomposition produced nearly equimolar amounts of $[Cp(CO)_2Fe]_2$ (5) and dicarbonyl(cyclopentadienyl)(cyclopropylmethyl)iron (6),⁶ which could be separated by chromatography on silica and isolated in 89% and 90% yields, respectively (eq 1).



No other significant products could be detected when the decomposition of compound 3 in benzene- d_6 was followed by ¹H NMR spectroscopy. The decomposition is therefore similar to that of a closely related compound, $[Cp-(CO)_2FeCH_2]_2CH_2$ (7),^{7,8} which is known to produce $[Cp-(CO)_2FeC$



 $(CO)_2Fe]_2$ (5) and cyclopropane in high yields at 125–196 °C, along with small amounts of propene.⁹ Like the

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(9) Cooke, M.; Forrow, N. J.; Knox, S. A. R. J. Chem. Soc., Dalton Trans. 1983, 2435-2440. Kao, S. C.; Thiel, C. H.; Pettit, R. Organo-1400 (2010) metallics 1983, 2, 914-917.

thermolysis of diiron compound 7, decomposition of triiron compound 3 is presumably initiated by loss of carbon monoxide and carbonyl bridging. These steps would produce hypothetical intermediate 8, from which the observed products can then be formed by reductive elimination. Formation of intermediate 8 may be accelerated by relief of strain created in compound 3 by interactions of the three large $Cp(CO)_2$ Fe groups. This would explain why compound 3 is much less stable than its simpler, less-congested relative 7. Carbonyl-bridged intermediate 8 could not be detected, however, so that even if its formation is accelerated by the relief of strain, its decomposition is faster still.

In dichloromethane at 25 °C, diiron compound 7 has been shown to reduce an equivalent amount of $Ph_3C^+PF_6^$ by a normal transfer of hydride, producing triphenylmethane and complex 9.10 Unexpectedly, triiron com-



pound 3 did not react similarly to form triphenylmethane and complex 10. Instead, complete consumption of compound 3 required 2 equiv of $Ph_3C^+PF_6^-$, and the reaction cleanly produced complex 11,11,12 which precipitated in



pure form in 64% yield when ether was added to the reaction mixture. Furthermore, little triphenylmethane (<5%) could be detected. A similar reaction occurred when $Ph_3C^+BF_4^-$ was used as the oxidant. We were surprised to find that the isobutyl skeleton of compound 3 had been converted into the *n*-butyl skeleton of complex 11, so we subjected the product to a particularly careful characterization. It proved to be identical with samples independently prepared by treating Cp- $(CO)_2FeCH_2CH_2CH_2CH_2Fe(CO)_2Cp$ with 1 equiv of $Ph_3C^+PF_6^{-12}$ or by treating (3-butenyl)dicarbonyl(cyclopentadienyl)iron (12) with sources of $Cp(CO)_2Fe^{+.11}$

Since the butyl skeletons of starting material 3 and product 11 contain the same number of hydrogens and since negligible amounts of triphenylmethane were formed, formal transfer of hydride cannot be the major reaction of compound 3 with $Ph_3C^+PF_6^-$. A possible alternative is summarized in Scheme I. Ph_3C^+ accepts an electron from compound 3, producing Ph_3C^+ and radical cation 13.¹³ This triggers the loss of carbon monoxide and formation

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⁽¹⁰⁾ King, R. B.; Bisnette, M. B. J. Organomet. Chem. 1967, 7, 311-319.

 ⁽¹¹⁾ Bodnar, T. W.; Cutler, A. R. Organometallics 1985, 4, 1558–1565.
 (12) Johnson, J. W.; Moss, J. R. Polyhedron 1985, 4, 563–565.

⁽¹³⁾ Chemical and electrochemical studies have established that oneelectron oxidations of alkyldicarbonyl(cyclopentadienyl)iron compounds by Ph₃C⁺ are feasible but distinctly endothermic.¹⁴

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of carbonyl-bridged radical cation 14. Reductive elimination then yields dicarbonyl(cyclopentadienyl)(cyclopropylmethyl)iron (6) and the radical cation of [Cp- $(CO)_2Fe]_2$, which is further oxidized to two $Cp(CO)_2Fe$ cations by the second equivalent of $Ph_3C^{+,15}$ In the final steps of this hypothetical scheme, combination of triphenylmethyl radicals gives the known dimer 15,¹⁶ and electrophilic ring opening of cyclopropane 6 by $Cp(CO)_2Fe^+$ produces the observed complex 11.¹⁷



The key proposals of Scheme I are that Ph_3C^+ is converted to Ph₃C[•] by a one-electron oxidation of compound 3 or its fragments and that electrophilic cleavage of cyclopropane 6 accounts for the unexpected conversion of branched-chain starting material 3 to straight-chain product 11. Evidence consistent with a one-electron oxidation was provided by detection of the characteristic vinyl hydrogen signals of dimer 15 when the reaction was followed by ¹H NMR spectroscopy.^{16b} However, cyclopropane 6 could not be detected during these NMR experiments. To test the second key postulate of Scheme I more rigorously, we treated independently prepared samples of hypothetical intermediate 6^{6b} with equivalent amounts of sources of $Cp(CO)_2Fe^+$, including $Cp(CO)_2Fe(THF)^+BF_4^{-18}$ and $Cp(CO)_2FeFBF_3$, generated by the known reaction of $Cp(CO)_2$ FeI with AgBF₄.¹⁹ These

⁽¹⁵⁾ The use of $Ph_3C^+BF_4^-$ to oxidize $[Cp(CO)_2Fe]_2$ is described by: Boyle, P. F.; Nicholas, K. M. J. Organomet. Chem. 1976, 114, 307-312. See also: Legzdins, P.; Martin, D. T.; Nurse, C. R.; Wassink, B. Or-ganometallics 1983, 2, 1238-1244. (16) (a) Colle, T. H.; Glaspie, P. S.; Lewis, E. S. J. Org. Chem. 1978, 43, 2722-2725. McBride, J. M. Tetrahedron 1974, 30, 2009-2022. Sholle, V. D.; Rozantsev, E. G. Russ. Chem. Rev. (Engl. Transl.) 1973, 42, 1011-1019. (b) Volz, H.; Lotsch, W.; Schnell, H.-W. Tetrahedron 1970, 26, 5343-5352. 26, 5343-5352.

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^{153 - 162} (b) Rosenblum, M.; Scheck, D. Organometallics 1982, 1, 397-399.

control reactions failed to produce detectible amounts of complex 11, so we doubt that Scheme I is correct.²⁰

Reasonable alternatives are summarized in Scheme II. Loss of Cp(CO)₂Fe[•] from radical cation 13,²¹ accompanied by a simultaneous shift of $Cp(CO)_2FeCH_2^{22,24}$ and movement of the remaining $Cp(CO)_2Fe$ group, could lead directly to complex 11. Alternatively, loss of $Cp(CO)_2Fe^{\bullet}$ and a simultaneous shift of $Cp(CO)_2FeCH_2$ would produce the stabilized open carbocation 16,25 from which product 11 could be formed in a simple second step. Further oxidation of $Cp(CO)_2$ Fe[•] to the corresponding cation would require a second equivalent of Ph_3C^+ and would eventually yield dimer 15, as observed.

Initial loss of the radical $Cp(CO)_2Fe^*$ rather than the cation $Cp(CO)_2Fe^+$ may be favored by the stability of the resulting cation 11 or 16. A concerted process of cleavage and migration is energetically advantageous because it avoids formation of an unstable primary isobutyl cation. In addition, conformational preferences make a concerted process favorable for the following reasons. Repulsion of the large $Cp(CO)_2$ Fe groups presumably forces compound **3** and its radical cation 13 to adopt the C_3 conformation 17, which is closely analogous to the structure known to be favored by tristannane 1.1b Experimental evidence for the congested conformation 17 was provided by the infrared spectrum of compound 3 in Nujol. Simple alkyldicarbonyl(cyclopentadienyl)iron compounds show two characteristic bands near 2000 and 1950 cm⁻¹,²⁶ but those of compound 3 are further split into doublets of approximately equal intensity. This splitting suggests that rotation around the $Cp(CO)_2Fe-CH_2$ bonds is relatively slow, which is likely in congested conformer 17.26a Despite this



congestion, rotational barriers in structure 17 are not high enough to be measured by NMR. Racemization caused by rotation around the $Cp(CO)_2FeCH_2$ -CH bonds (eq 2) appears to be fast even at -80 °C in toluene- d_8 , since the diastereotopic methylene hydrogens appear as a single broadened doublet. In structures 17 and 17', each Cp-

(19) Mattson, B. M.; Graham, W. A. G. Inorg. Chem. 1981, 20, 3186-3189.

(20) The novel reaction that occurs when dicarbonyl(cyclopentadienyl)(cyclopropylmethyl)iron (6) is treated with sources of Cp-(CO)₂Fe⁺ will be described in a separate publication. Kobayashi, M.; Wuest, J. D., unpublished results.

(21) Oxidation of iron alkyls to the corresponding radical cations is known to weaken the iron-carbon bond. Daub, G. W. Prog. Inorg. Chem. 1977, 22, 409-423.

(22) Two other reactions have been reported in which cleavage of an

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 (23) (a) Sanders, A.; Bauch, T.; Magatti, C. V.; Lorenc, C.; Giering, W. P. J. Organomet. Chem. 1976, 107, 359-375. Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. J. Am. Chem. Soc. 1973, 95, 5430-5431. (b) Rogers, W. N.; Page, J. A.; Baird, M. C. Inorg. Chem. 1981, 20, 3521-3528. Slack, D. A.; Baird, M. C. J. Am. Chem. Soc. 1976, 96, 5546. Flood T. C. DiSchrif, F. J. Chem. Soc. 067. 98, 5539-5546. Flood, T. C.; DiSanti, F. J. J. Chem. Soc., Chem. Commun. 1975, 18-19.

(24) Direct coordination of Ph₃C⁺ to the iron or oxygen atoms of compound 3, which might be able to initiate a similar cleavage of an iron-carbon bond and migration of Cp(CO)₂FeCH₂, is sterically improbable

(25) Carbocations adjacent to carbon-metal bonds are strongly stabilized even when the empty orbital and the carbon-metal bond are not parallel. Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Teramura, D. H. J. Am. Chem. Soc. 1987, 109, 7838-7845.

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 $(CO)_2$ Fe-CH₂ bond is antiperiplanar to one adjacent Cp-(CO)₂FeCH₂-CH bond, permitting the concerted cleavage and migration proposed in Scheme II. Moreover, this process would undoubtedly be facilitated by the partial relief of strain created by interactions of the three Cp- $(CO)_2$ Fe groups. At the same time, the hypothetical preference for conformation 17 may disfavor formation of cyclopropane 6. Direct generation of compound 6 from radical cation 13 by 1,3-elimination of $Cp(CO)_2Fe^+$ and $Cp(CO)_2Fe^*$ would require inversion of configuration at one carbon and retention at the other, whereas double inversions are known to be preferred in related 1,3-eliminations.27,28

To test the implications of Scheme II, we treated the labeled derivative $[Cp(CO)_2FeCH_2]_3CD$ with $Ph_3C^+PF_6^-$. The location of deuterium in the observed product, complex 18, is consistent with the concerted cleavage and migration of Scheme II and is inconsistent with sequences requiring cleavage of carbon-hydrogen bonds.



A similar process in which $Cp(CO)_2Fe^{\bullet}$ and Cp^{\bullet} $(CO)_2Fe = CH_2^+$ are lost simultaneously from radical cation 13 would also be stereoelectronically favorable (eq 3).



Readdition of $Cp(CO)_2Fe=CH_2^+$ to $Cp(CO)_2FeCH_2CH=$ CH₂ would then be expected to generate the observed complex 11.11 This mechanism is consistent with the labeling experiment but seems incompatible with other observations. For example, the independent reaction of $Cp(CO)_2Fe=CH_2^+$ with $Cp(CO)_2FeCH_2CH=CH_2$ is known to provide significantly lower yields of complex 11 than we observe.¹¹ Furthermore, Cp(CO)₂FeCH₂CH=CH₂ is trapped irreversibly by Ph_3C^+ to produce complex 19.²⁹ Efficient recombination of $Cp(CO)_2Fe=CH_2^+$ and Cp- $(CO)_2FeCH_2CH=CH_2$ is therefore unlikely under our conditions, since large amounts of Ph_3C^+ are present.

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Formal Transfers of Hydride from C-H Bonds

We believe that the activated central carbon-hydrogen bond of compound 3 fails to transfer hydride to Ph_3C^+ for three major reasons. The likely preference of compound 3 for conformation 17 disfavors hydride transfer because the activated carbon-hydrogen bond lies hidden in a cavity created by the large $Cp(CO)_2$ Fe groups. In addition, all three iron-CH₂ bonds are gauche to the activated carbon-hydrogen bond, and more reactive conformations in which these bonds are antiperiplanar may be inaccessible.^{25,30} Finally, the expected product of hydride transfer, complex 10, may not be highly stabilized. The simpler analogue 9 derived from diiron compound 7 is stabilized electronically by extensive delocalization of the positive charge. This delocalization, represented by the incompletely symmetrical structure 20, makes the transfer of $Cp(CO)_2Fe^+$ from 2-methylpropene to dicarbonyl(cyclopentadienyl)(2-methyl-2-propenyl)iron (21) an exothermic reaction, since a more stabilized cationic complex 22 is produced (eq 4).³² For complex 10, a similar but even



more extensive delocalization can be represented by structure 23. Despite this hypothetical stabilization, however, formal loss of hydride from compound 3 does not occur.

We therefore tried to produce complex 10 independently by transferring $Cp(CO)_2Fe^+$ to compound 24 (eq 5), which could be prepared in two ways. Addition of 3-chloro-2-(chloromethyl)propene (25) to 2 equiv of $Cp(CO)_2FeNa$ at -40 °C produced compound 24 in satisfactory yield, but the product was invariably contaminated by small amounts of $[Cp(CO)_2Fe]_2$ and methallyl compound 21. The high chemical reactivity and thermal sensitivity of compound 24 precluded purification by chromatography or distillation, so we were forced to develop an alternative synthesis. Bis(methanesulfonate) 27 could be prepared from diol 26^{1a} by standard procedures,³³ and addition of compound 27



to 2 equiv of $Cp(CO)_2$ FeNa at -40 °C produced acceptably pure samples of compound 24.

Like its close relatives 2-methylene-1,3-propanediylbis[triphenylstannane] (28) and 2-methylene-1,3propanediylbis[trimethylstannane] (29),^{34b} compound 24 proved to be exquisitely sensitive to acids. Addition of hexafluorophosphoric acid to a solution of compound 24 in ether provided an 87% yield of the hexafluorophosphate salt of the expected complex 22. Like allylstannanes 28 and 29, compound 24 also reacted with trichloromethyl radicals derived from carbon tetrachloride to give 1,1,1,5,5,5-hexachloro-3-methylenepentane (30),^{34b,c} which could be isolated in 64% yield.

Although compound 24 reacted avidly with certain radicals and small electrophiles like the proton, it refused to accept $Cp(CO)_2Fe^+$ from complexes with THF or 2methylpropene. The $Cp(CO)_2Fe^+$ complex of 2-methylpropene transferred a proton instead, giving compound 21 and complex 22. This is partly because compound 24 is likely to adopt the C_2 conformation 31, which minimizes



interaction of the large Cp(CO)₂Fe groups and maximizes hyperconjugation involving the π bond and the iron-CH₂ σ bond.^{34a,b} Since both faces of the π bond are sterically shielded, addition of Cp(CO)₂Fe⁺ may be kinetically difficult. The reaction may also be thermodynamically unfavorable, since interactions of the Cp(CO)₂Fe groups make the highly delocalized structure 23 sterically improbable. If all three Cp(CO)₂Fe groups simultaneously stabilize the

⁽³⁰⁾ Transfer of hydride from a carbon-hydrogen bond antiperiplanar to an iron-carbon bond is known to be favored in simple alkyldicarbonyl(cyclopentadienyl)iron compounds.³¹

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positive charge, at least two will necessarily be forced into energetically unfavorable proximity.

We conclude that steric factors, stereoelectronic effects, and product instability all oppose the direct transfer of β -hydride from the central carbon-hydrogen bond of compound 3 to sterically demanding acceptors like Ph_3C^+ . These same factors presumably disfavor a similar transfer of a β -hydrogen atom from radical cation 13 to a triphenylmethyl radical.³⁵ Reasonable alternative reactions, including a synperiplanar transfer of β -hydride, transfer of α -hydride from a methylene carbon-hydrogen bond,^{23a,36} loss of an α -hydrogen from radical cation 13,^{355,37} alkylation of Ph₃C⁺,^{23a} or carbonyl insertion,^{14a} all appear to be slower than electron transfer followed by cleavage of an iron-CH₂ bond and migration (Scheme II). This is true even when compound 3 is treated with Ph_3C^+ under conditions (low temperatures under an atmosphere of carbon monoxide)

that normally favor carbonyl insertion.^{14a} Compound 3 is therefore unique among iron alkyls, since its primary reaction with Ph_3C^+ under these conditions is neither hydride transfer nor carbonyl insertion.

Hypothetical loss of carbon monoxide and formation of carbonyl-bridged intermediate 8 during the thermal decomposition of compound 3 suggested that photolysis might promote more extensive decarbonylation and ultimately yield the novel carbonyl-bridged ferraadamantane 32 (eq 6).³⁸ Since its central carbon-hydrogen bond is



sterically accessible and antiperiplanar to three weak

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iron-carbon bonds, compound 32 should be a formal donor of hydride even more reactive than stannaadamantane 2. Unfortunately, we could not detect ferraadamantane 32 among the products formed when compound 3 was photolyzed under a variety of conditions. Although compound 32 may be present as a short-lived intermediate, the results of the photolysis of compound 3 in Pyrex vessels at 350 nm in benzene or acetone at 25 °C are more simply rationalized by the reactions of Scheme III. Irradiation presumably stimulates decarbonylation and produces carbonyl-bridged intermediate 8. Further irradiation causes a second decarbonylation and yields iron hydride 33 by β -elimination. Reductive elimination then produces dicarbonyl(cyclopentadienyl)(2-methyl-2-propenyl)iron (21) and $[Cp(CO)_2Fe]_2$ (5). These steps are completely analogous to those triggered by irradiation of the related compound $Cp(CO)_2FeCH_2CH_2CH_2Fe(CO)_2Cp$ (7), which is known to yield propene and $[Cp(CO)_2Fe]_2$.

Compound 21 could not be detected, since further irradiation rapidly converted it into the final products, the exo and endo isomers of π -allyl complex 34.³⁹ We confirmed by ¹H NMR spectroscopy that an identical exo/ endo mixture was formed when compound 21 itself was photolyzed independently under the same conditions. Additional experimental evidence for Scheme III was provided by isolation of $[Cp(CO)_2Fe]_2$ in low yields by chromatography of the crude photolysate on silica. During this separation, the approximately 1:1 exo/endo mixture of π -allyl complex 34 was converted cleanly into the thermodynamically more stable exo isomer, which was isolated in 85% yield. Since irradiation of dicarbonyl-(cyclopentadienyl)(cyclopropylmethyl)iron (6), the product of thermal decomposition of compound 3, did not produce π -allyl complex 34, compound 6 plays no role in the photochemical decomposition of compound 3.

Although the thermolyses and photolyses of [Cp- $(CO)_2FeCH_2]_2CH_2$ (7) and its more complex analogue $[Cp(CO)_2FeCH_2]_3CH$ (3) are very similar, compound 7 efficiently reduces Ph_3C^+ to triphenylmethane whereas compound 3 does not. This difference is instructive. In the solid state, compound 7 is known to adopt conformation 35.40 In solution, an energetically inexpensive rotation



of 120° around a carbon-carbon bond would provide alternative conformation 35', which contains a carbon-hydrogen bond activated by an antiperiplanar iron-carbon bond.^{25,30} Subsequent transfers of β -hydride from reactive conformer 35' to Ph_3C^+ in a single step or of β -hydrogen from the corresponding radical cation to Ph₃C[•] are sterically and stereoelectronically favorable. Since similarly reactive conformations of analogue 3 and its radical cation 13 are undoubtedly less accessible, transfers of β -hydride or β -hydrogen do not occur.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. Bruker WH-90 and WH-400 spectrometers were used to obtain ¹H and ¹³C nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million

downfield from internal tetramethylsilane (δ). Mass spectra were recorded on a V.G. Micromass 12-12 or V.G. Trio-1 quadrupole spectrometer using chemical ionization (CI) mass spectrometry. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. Photolyses were carried out in a standard Rayonet RPR-100 reactor. Chromatographic separations were typically effected by flash column chromatog-raphy^{41a} under N₂.^{41b} Dichloromethane was dried by distillation from CaH₂, and benzene, ether, and tetrahydrofuran (THF) were dried by distillation from the sodium ketyl of benzophenone. $Ph_3C^+PF_6^-$ and $Ph_3C^+BF_4^-$ were prepared by the standard procedure⁴² and stored at -20 °C. All other common reagents were commercial products of the highest purity available.

Triiron Compound 3. A mixture of sodium amalgam (5.62 g, 3%, 7.3 mg-atom of sodium) and [Cp(CO)₂Fe]₂ (0.336 g, 0.949 mmol) in THF (5 mL) was stirred at 25 °C under N₂ for 1 h. The supernatant was removed, cooled to -40 °C, and treated dropwise with a solution of 2-[((methylsulfonyl)oxy)methyl]-1,3-propanediol bis(methanesulfonate) (4; 0.330 g, $0.987 \text{ mmol})^5$ in THF (6 mL). The mixture was stirred at -40 °C for 2 h, treated with a second portion of $Cp(CO)_2$ FeNa prepared from the same amounts of sodium amalgam and $[Cp(CO)_2Fe]_2$ as the first, and kept at -40 °C for an additional 2 h. Solvent was then removed by evaporation in vacuo at -40 °C, and the residue was extracted with benzene at 5 °C. Flash chromatography⁴¹ of the extracts at 10 °C using a jacketed column (silica, dichloromethane) separated a leading yellow band that contained pure triiron compound 3 (0.288 g, 0.491 mmol. 49.7%). Recrystallization from benzene/hexane provided yellow needles of analytically pure compound 3: mp 109-110 °C dec; IR (Nujol) 1997, 1987, 1932, 1919 cm⁻¹; ¹H NMR (400 MHz, C_6D_6) δ 1.66 (septet, 1 H), 2.12 (d, 6 H), 4.33 (s, 15 H); ¹³C NMR (100.62 MHz, C_6D_6 , gated proton decoupling) δ 18.08 (CH₂), 56.15 (CH), 85.89 (Cp), 219.27 (CO); mass spectrum (CI, isobutane), m/e 354, 326, 298, 186, 177, 149. Anal. Calcd for C25H22Fe3O8: C, 51.24; H, 3.78. Found: C, 50.72; H, 3.78.

Thermolysis of Triiron Compound 3. A solution of triiron compound 3 (23.9 mg, 40.7 μ mol) in benzene (1 mL) was kept at 25 °C in the dark for 7 days. Flash chromatography⁴¹ of the product (silica, hexane (80%)/dichloromethane (20%)) resolved a leading yellow band and a trailing red-brown band. The trailing band yielded $[Cp(CO)_2Fe]_2$ (12.8 mg, 36.2 µmol, 88.9%), and the leading band contained dicarbonyl(cyclopentadienyl)(cyclopropylmethyl)iron (6; 8.5 mg, 37 μ mol, 90%), which was identical by IR and NMR with an authentic sample.⁶

Reaction of Triiron Compound 3 with Ph₃C⁺PF₆. A solution of $Ph_3C^+PF_6^-$ (30.2 mg, 77.8 μ mol)⁴² in dichloromethane (0.4 mL) was stirred at 0 °C under N_2 and treated dropwise with a solution of triiron compound 3 (22.5 mg, 38.4 μ mol) in dichloromethane (0.6 mL). The mixture was kept at 25 °C for 1.5 h and then treated with ether (2 mL). The resulting precipitate was separated by centrifugation, washed with ether, and dried in vacuo. This yielded a pure sample of complex 11 as an orange solid (13.6 mg, 24.5 µmol, 63.8%).^{11,12} IR (Nujol) 2065, 2035, 2000, 1940 cm⁻¹; ¹H NMR (400 MHz, acetone- d_6) δ 1.30 (m, 1 H), 1.66 (m, 1 H), 1.68 (m, 1 H), 2.54 (m, 1 H), 3.52 (d, J = 14.6 Hz, 1 H),3.94 (d, J = 8.1 Hz, 1 H), 4.99 (s, 5 H), 5.36 (m, 1 H), 5.86 (s, 5 H)H). Complex 11 was identical by IR and NMR with a sample independently independently prepared by treating C (CO)₂FeCH₂CH₂CH₂CH₂Fe(CO)₂Cp with 1 equiv of Ph₃C⁺PF₆ Cp-- 12

Reaction of Triiron Compound 3 with Ph₃C⁺PF₆⁻ under CO. A mixture of $Ph_3C^+PF_6^-$ (20.5 mg, 52.8 μ mol)⁴² and triiron compound 3 (15.4 mg, 26.3 µmol) was cooled at -78 °C under CO (1 atm) and treated with dichloromethane- d_2 (1.0 mL) saturated with CO. A steady stream of additional CO was passed through the mixture, the cooling bath was removed, the temperature was allowed to rise to 25 °C, and the mixture was kept at 25 °C for 2 h. A similar reaction was carried out under N₂ as a control. The ¹H NMR spectra of the resulting solutions were essentially identical.

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Preparation of $[Cp(CO)_2FeCH_2]_3CD$. Reaction with $Ph_3C^+PF_6^-$. Treatment of 2-[((methylsulfonyl)oxy)methyl]-2nitro-1,3-propanediol bis(methanesulfonate)⁵ with tributyltin deuteride under the standard conditions⁶ yielded (CH₃SO₂OCH₂)₃CD: ¹H NMR (90 MHz, CDCl₃) δ 3.08 (s, 9 H), 4.35 (s, 6 H). Further reaction with Cp(CO)₂FeNa according to the procedure described above provided [Cp(CO)₂FeCH₂]₃CD: ¹H NMR (90 MHz, C₆D₆) δ 2.12 (s, 6 H), 4.33 (s, 15 H). Its reaction with 2 equiv of Ph₃C⁺PF₆⁻ under the standard conditions yielded labeled complex 18: ¹H NMR (90 MHz, acetone-d₆) δ 3.52 (s, 1 H), 3.94 (s, 1 H).

Preparation of Compound 24 from 3-Chloro-2-(chloromethyl)propene (25). A solution of Cp(CO)₂FeNa in THF (1.0 mL) was prepared from sodium amalgam (1.4 g, 3%, 1.8 mg-atom of sodium) and [Cp(CO)₂Fe]₂ (81 mg, 0.23 mmol) by the procedure described above. The solution was stirred, cooled to -40 °C, and treated dropwise with neat 3-chloro-2-(chloromethyl)propene (25; 29 mg, 0.23 mmol). The resulting mixture was kept at -40 °C for 4 h, and then solvent was removed by evaporation under reduced pressure at 0 °C. Extraction of the residue with ether, followed by removal of solvent from the extracts by evaporation under reduced pressure at 25 °C, yielded compound 24 as a yellow-brown oil of acceptable purity: IR (Nujol) 2010, 1960 cm⁻¹; ¹H NMR (90 MHz, $C_{e}D_{e}$) δ 2.47 (s, 4 H), 4.13 (s, 10 H), 4.74 (s, 2 H); mass spectrum (CI, isobutane), m/e 354, 186, 177. Attempts to purify this material by distillation in vacuo or by chromatography led to extensive decomposition, so it was used directly in subsequent reactions.

Preparation of 2-Methylene-1,3-propanediol Bis(methanesulfonate) (27). A mixture of 2-methylene-1,3-propanediol (26; 0.868 g, 9.85 mmol), triethylamine (2.00 g, 19.8 mmol), and KOH (0.127 g, 2.26 mmol) in dichloromethane (30 mL) was stirred at 0 °C and treated dropwise with methanesulfonyl chloride (2.29 g, 20.0 mmol). The mixture was then stirred at 0 °C for 2.5 h, warmed to 25 °C, and filtered. The supernatant was washed with water, and solvent was removed from the organic phase by evaporation under reduced pressure. Recrystallization of the residue from dichloromethane/hexane provided colorless crystals of bis(methanesulfonate) 27 (1.74 g, 7.12 mmol, 72.3%): mp 64–66 °C; IR (KBr) 1350, 1200 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.07 (s, 6 H), 4.79 (m, 4 H), 5.55 (m, 2 H); mass spectrum (CI, methane), m/e 245, 149.

Alternative Synthesis of Compound 24 from Bis(methanesulfonate) 27. Reaction of Compound 24 with Cp- $(CO)_2Fe(THF)^+BF_4^-$. A solution of Cp(CO)₂FeNa in THF (5 mL) was prepared from sodium amalgam (683 mg, 3%, 0.891 mg-atom of sodium) and $[Cp(CO)_2Fe]_2$ (51.5 mg, 0.146 mmol) by the procedure described above. The supernatant was added dropwise at -40 °C to a stirred solution of bis(methanesulfonate) 27 (28.5 mg, 0.117 mmol). The mixture was kept at -40 °C for 6 h, then solvent was removed by evaporation in vacuo, and the residue was extracted with benzene- d_6 (0.6 mL). A ¹H NMR spectrum of the extracts showed that compound 24 was the major component. The extracts were then treated at 25 °C with a solution of $Cp(CO)_2Fe(THF)^+BF_4^-$ (23.8 mg, 0.0709 mmol)^{18b} in dichloromethane- d_2 (0.6 mL), and the resulting mixture was kept at 25 °C for 12 h. Centrifugation then separated traces of solid, and the supernatant was concentrated by partial evaporation under reduced pressure. Addition of ether (5 mL) to the concentrate provided a solid orange precipitate of the tetrafluoroborate salt of complex 22 (58.1 mg, 0.117 mmol, 100%).

Protonation of Compound 24. Compound 24 was prepared from 3-chloro-2-(chloromethyl)propene (25; 29 mg, 0.23 mmol) by the previously described procedure and dissolved in ether (1.3 mL). The solution was stirred at 5 °C and treated dropwise with aqueous HPF₆ (60–65%, 33 μ L). The resulting precipitate was separated by centrifugation, washed with ether and chloroform, and dried in vacuo. This yielded a pure sample of the hexa-fluorophosphate salt of complex 22 as an orange solid (110 mg, 0.20 mmol, 87%).³²

Reaction of Compound 24 with CCl₄. Compound 24 was prepared from 3-chloro-2-(chloromethyl)propene (25; 27 mg, 0.22 mmol) by the above procedure and dissolved in benzene (0.5 mL). The solution was treated with CCl₄ (0.2 mL) and azobis(isobutyronitrile) (3.3 mg, 20 μ mol) and heated at 70 °C for 8 h. Solids were then separated by centrifugation, and volatiles were removed from the supernatant by evaporation under reduced pressure. Preparative thin-layer chromatography (silica, CCl₄) of the residue yielded pure 1,1,1,5,5,5-hexachloro-3-methylenepentane (30; 41 mg, 0.14 mmol, 64%), which was identical by IR and NMR with an authentic sample.^{34b}

Reaction of Compound 24 with the Hexafluorophosphate Salt of the $Cp(CO)_2Fe^+$ Complex of 2-Methylpropene. Compound 24 was prepared from 3-chloro-2-(chloromethyl)propene (25; 31 mg, 0.25 mmol) by the previously described procedure and dissolved in 1,2-dichloroethane (0.3 mL). This solution was added to a solution of the hexafluorophosphate salt of the $Cp(CO)_2Fe^+$ complex of 2-methylpropene (37 mg, 0.098 mmol)⁴³ in 1,2-dichloroethane (1.1 mL) at 70 °C. The mixture was kept at 70 °C for 10 min, then cooled to 0 °C, and treated with ether (3 mL). The resulting precipitate was separated by centrifugation, washed with ether, and dried in vacuo. This yielded a pure sample of the hexafluorophosphate salt of complex 22 as an orange solid (42 mg, 0.076 mmol, 78%).³²

Photolysis of Compound 3. A solution of compound 3 (24 mg, 41 μ mol) in benzene (0.6 mL) in a thin-walled Pyrex tube was irradiated at 350 nm for 4 h in a standard Rayonet reactor. Flash chromatography⁴¹ of the photolysate at 10 °C using a jacketed column (silica, hexane (80%)/dichloromethane (20%)) separated a leading yellow band and a trailing red-brown band. The trailing band provided small amounts of [Cp(CO)₂Fe]₂ (2.7 mg, 7.6 μ mol, 19%), and the leading band contained the exo isomer of π -allyl complex 34 (7.2 mg, 35 μ mol, 85%).³⁹

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Registry No. 3, 123168-81-0; 4, 113967-52-5; 6, 34788-98-2; 11, 97011-64-8; 18, 123168-83-2; **22**[BF₄], 81161-08-2; **22**[PF₆], 62259-75-0; **24**, 123168-84-3; **25**, 1871-57-4; **26**, 3513-81-3; **27**, 123150-59-4; **30**, 86854-56-0; **34**, 123238-54-0; [Cp(CO)₂Fe]₂, 12154-95-9; Cp(CO)₂FeNa, 12152-20-4; Cp(CO)₂Fe(CH₂)₄Fe-(CO)₂Cp, 36655-41-1; Cp(CO)₂Fe(THF)⁺BF₄⁻, 63313-71-3; [Cp-(CO)₂FeCH₂]₃CD, 123168-85-4; (CH₃SO₂OCH₂)₃CD, 123150-60-7; [Cp(CO)₂Fe(2-methylpropene)]⁺PF₆⁻, 67771-63-5; 2-[((methylsulfonyl)oxy)methyl]-2-nitro-1,3-propanediol bis(methanesulfonate), 113967-51-4; tributyltin deuteride, 6180-99-0; azobis(isobutyronitrile), 78-67-1.

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