Reaction of (η^5-C_5H_5)$(CO)_2$Fe(2-norbornyl) Complexes and Triphenylmethyl Tetrafluoroborate: Competitive β-Elimination and Redox-Catalyzed Migratory Carbonyl Insertion[1]

Robert S. Bly,* Gary S. Silverman, and Ruta K. Bly

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

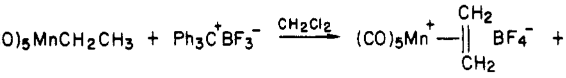
Received July 2, 1984

Both (η^5-C_5H_5)$(CO)_2$Fe(*endo*-2-norbornyl) and -(*exo*-2-norbornyl), **6** and **7**, respectively, react in dichloromethane with triphenylmethyl tetrafluoroborate (**8**) to give a mixture of (η^5-C_5H_5)$(CO)_2$Fe(*endo*-2-norbornylcarbonyl) or -(*exo*-2-norbornylcarbonyl), **4** or **5**, respectively, and (η^5-C_5H_5)$(CO)_2$Fe(η^2-*exo*-norbornene) tetrafluoroborate (**9**). No endo π-complex is observed. The yield and relative abundance of the acyl and π-complex are dependent upon the mole ratio of the starting materials, the temperature, whether the solution is blanketed with nitrogen or carbon monoxide, and whether triphenylmethyl radical (**8**·) is added at the start of the reaction. The mechanisms of these competitive β-eliminations and redox-catalyzed migratory CO insertions are discussed.

Introduction

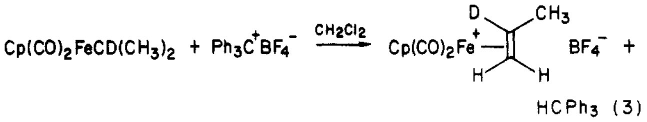
Organometallic σ-complexes having hydrogen on a β-carbon commonly react with triphenylmethyl cation. Main-group alkyls fragment to alkene, metal cation, and triphenylmethane (eq 1).[2] Comparable transition-metal derivatives produce rearranged, cationic olefin π-complexes and triphenylmethane (eq 2).[3] A number of such complexes, particularly those of dicarbonyl(η^5-cyclopentadienyl)iron(II), have been prepared in this manner.[3-6]

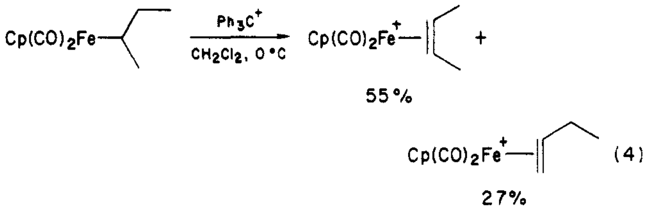
$$(CH_3)_3SnCH_2CH_3 + Ph_3C^+BF_4^- \xrightarrow[30\ °C]{CH_3CN} (CH_3)_3Sn^+BF_4^- + CH_2{=}CH_2 + HCPh_3 \quad (1)$$

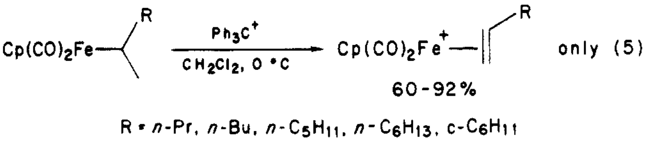


$$(CO)_5MnCH_2CH_3 + Ph_3\overset{+}{C}BF_3^- \xrightarrow{CH_2Cl_2} (CO)_5\overset{+}{Mn}—\underset{CH_2}{\overset{CH_2}{\|}}\ BF_4^- + HCPh_3 \quad (2)$$

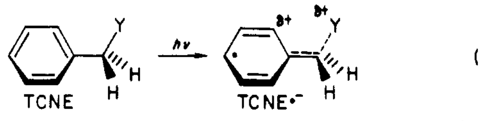
Normally, only β-hydrogen is lost during cation-induced σ–π rearrangement (eq 3).[3,7] The resulting η^2-olefin complexes are preferentially cis or terminal (eq 4),[6b,c] though 2-alkyl σ-complexes having more hindered internal β-hydrogens yield only terminal olefin π-complexes (eq 5).[6c]







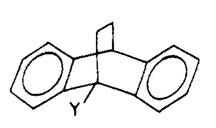
The β-hydrogen is thought to be abstracted as hydride by the cation.[2b,3-9] Theory supports this view. Reactions conjectured to proceed via a β-carbenium ion are known to be unusually facile in transition-metal σ-complexes.[9] Further, the log of the second-order rate constant for triphenylcarbenium-induced fragmentation of $(C_2H_5)_nMCH_2CH_3$ (M = Pb, Hg, Sn, Ge, Si) in acetonitrile at 30 °C (cf. eq 1) correlates linearly with the charge-transfer frequency of the corresponding Ph_nMCH_2Ph with tetracyanoethylene (TCNE) (eq 6).[2] The cation evidently abstracts a β-hydrogen as hydride in the rate-limiting step.



(6)

Y = PbPh$_3$, HgPh, SnPh$_3$, GePh$_3$, SiPh$_3$; ν = 17 060-22 220 cm^{-1}

Theory also suggests that β-hydride abstractions should be conformationally dependent. The shift in frequency of the charge transfer bands of benzyl-type dichloromaleic anhydride complexes when a benzylic hydrogen is replaced by a metal moiety is large if the carbon–metal bond can be perpendicular to the plane of the aromatic ring (eq 6: Y = H, $Sn(CH_3)_3$, HgC_6H_{11}; $\Delta\nu = \nu_H - \nu_M$ = 6800 and 9300 cm^{-1}, respectively) but virtually zero when it is constrained to be parallel.[2b]



Y = H, $Sn(CH_3)_3$, HgC_6H_{11}; $\Delta\nu$ = 0 and −400 cm^{-1}

---

[1] Portions of this work were reported at (a) the 34th Southeast Regional Meeting of the American Chemical Society, Nov 1982, Birmingham, AL, Abstr #324, and (b) the 37th Annual Meeting of the Florida Section of the American Chemical Society, May 1984, Lakeland, FLACS, 1984, XXXVII, No. 4, Abstr 20.

[2] (a) Jerkunica, J. M.; Traylor, T. G. *J. Am. Chem. Soc.* **1971**, *93*, 6278–6279. (b) Traylor, T. G.; Berwin, H. J.; Jerkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599–606 and references cited therein. (c) Hannon, S. J.; Traylor, T. G. *J. Org. Chem.* **1981**, *46*, 3645–3650. (d) Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651–3657.

[3] Green, M. L. H.; Nagy, P. L. I: (a) *Proc. Chem. Soc.* **1962**, 74; (b) *J. Organomet. Chem.* **1963**, *1*, 58–69.

[4] (a) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1963**, 889–894. (b) Green, M. L. H.; Stear, A. R. *J. Organomet. Chem.* **1964**, *1*, 230–234.

[5] Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122–128.

[6] (a) Slack, D. A.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1974**, 701. (b) Laycock, D. E.; Baird, M. C. *Tetrahedron Lett.* **1978**, 3307–3308. (c) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291–299.

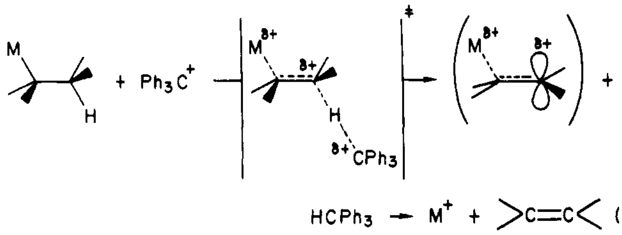
[7] Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V.; Sanders, A. *J. Organomet. Chem.* **1974**, *65*, C57–C60.

[8] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978: (a) p 247. (b) Chapters 3 and references cited therein.

[9] Green, M. L. H. In "Organometallic Compounds", 3rd ed.; Methuen: London, 1968; Vol. II, pp 211–217.

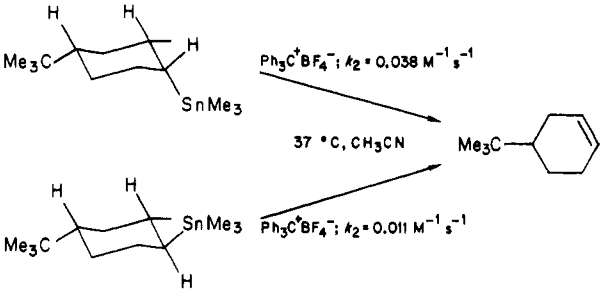
0276-7333/85/2304-0374$01.50/0

Also, calculations suggest that the β-hydrogen which is fartherest from the metal in an alkyllithium has the greatest electron density.[10] The implication is that an antiperiplanar transition state will be favored for β-hydride abstraction by cation (eq 7).[2b]



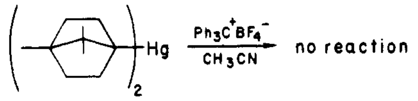
(7)

When appropriately tested, this prediction is sustained experimentally. Triphenylmethyl tetrafluoroborate reacts with (*cis*-4-*tert*-butylcyclohexyl)trimethyltin to form 4-*tert*-butylcyclohexene about 3.5 times as rapidly as it does with the trans isomer[2b] while bis[1-(4,7,7-trimethylnorbornyl)]mercury, which has no antiperiplanar hydrogen, is unreactive (eq 8–10).[2b] Similarly, dicarbonyl(η^5-cyclopentadienyl)[1-(*threo*-1,2-dideuterio-2-phenylethyl)]iron yields a 1:2.5 mixture of (*E*)-1-deuterio-2-phenyl- and (*Z*)-1,2-dideuterio-1-phenylethenes after decomplexation of the π-complexes with triphenylphosphine (eq 11).[6a] The primary kinetic isotope effect, $k_H/k_D = 2.5$, that is evident from the product distribution, reemphasizes the importance of β-C–H(D) bond breaking in the rate-limiting step.

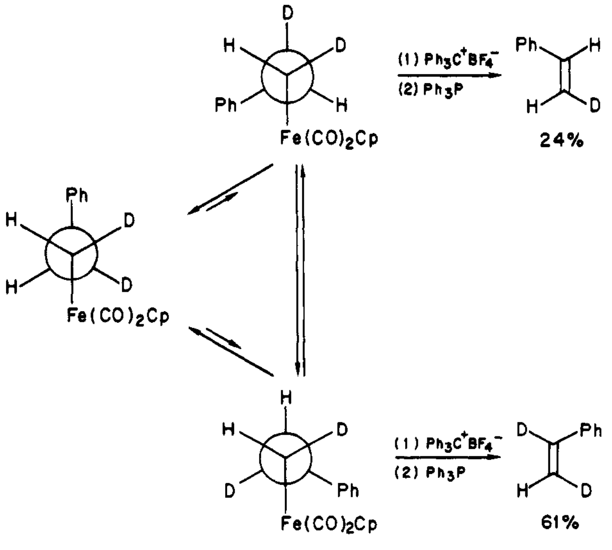


(8)

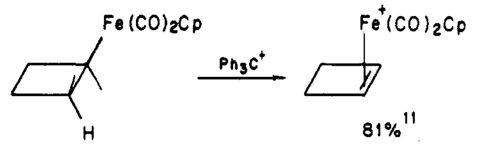
(9)



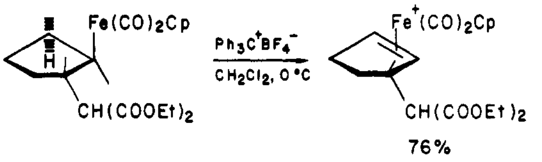
(10)



(11)



(12)

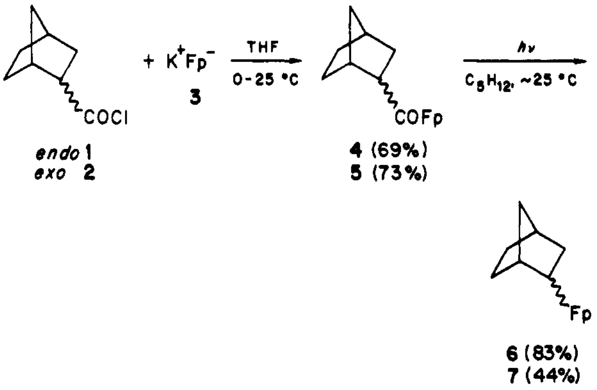


(13)

Precedent aside, isolated examples of apparent nonantiplanar β-hydrogen abstraction by triphenylmethyl cation are known (eq 12 and 13). Whether the reaction in such cases simply occurs via a somewhat distorted transition state, whether an intermediate β-carbocation is formed, whether a hydrogen other than β is abstracted initially, or whether the process differs in an even more fundamental way is not known. To learn more of such processes, we have examined the reaction of triphenylmethyl tetrafluoroborate (8) with dicarbonyl(η^5-cyclopentadienyl)iron—hereafter designated Fp—*endo*- and *exo*-2-norbornyls, 6 and 7, respectively.

Methods and Results

The starting materials were prepared from the known *endo*- and *exo*-2-norbornanecarbonyl chlorides,[13] 1 and 2, respectively. Treatment of each with potassium dicarbonyl(η^5-cyclopentadienyl)ferrate (3)[14] yields the corresponding oxidatively and thermally stable, yellow, crystalline acyl complex[15] 4 or 5. Photolysis of each acyl in Pyrex[16] affords the single Fp norbornyl 6 or 7, respectively, of retained configuration.[17]



(14)

The norbornyl complexes 5 and 6 are oxidatively, photolytically, and thermally labile amber oils. As monitored by low temperature ^{13}C NMR, 6 is stable for as long as a week at −20 °C under nitrogen and 7 is significantly decomposed after 2 days. This may explain the lower yield of 7 from photolysis (eq 14).

---

(10) Reetz, M. T.; Stephan, W. *Tetrahedron Lett.* **1977**, 2693–2696.

(11) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495–3507.

(12) (a) Rosan, A.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1976**, *95*, 3062–3064. (b) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426–8439.

(13) (a) Komppa, G.; Beckmann, S. *Justus Liebigs Ann. Chem.* **1934**, *512*, 172–185. (b) Alder, K.; Stein, G.; Rolland, E.; Schulze, G. *Justus Liebigs Ann. Chem.* **1934**, *514*, 197–211, 211–227. (c) Berson, J. A.; Suzuki, S. *J. Am. Chem. Soc.* **1959**, *81*, 4088–4094.

(14) Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284–285.

(15) King, R. B.; *J. Am. Chem. Soc.* **1963**, *85*, 1918–1922.

(16) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15–37.

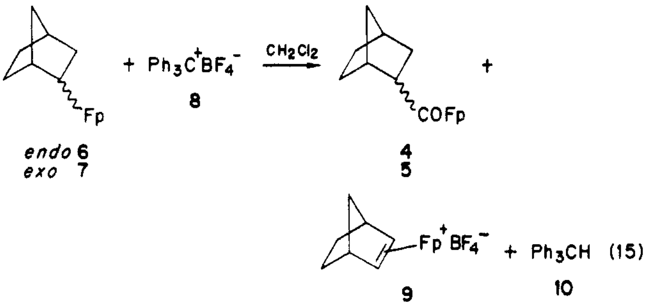
(17) Such decarbonylations of Fe(II) acyls are known to proceed with retention of configuration at carbon: (a) Alexander, J. J.; Wojciki, A. *Inorg. Chim. Acta* **1971**, *5*, 655–658. (b) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Dermers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814–2825.

Table I. Product Yields from the Reaction of $(\eta^5\text{-}C_5H_5)(CO)_2FeR$ (6 or 7) and $Ph_3C^+BF_4^-$ (8) in CH_2Cl_2 [a]

				% in product mixture[b]				
run	FpR	mol ratio 8/FpR	temp, °C time, h	FpCOR	9	10	FpR	8
1	6	1.1	25, 6	*c*	66	*d*	0	*c*
2[e]	6	1.2	25, 5	59	trace[f]	*c*	0	72
3	6	1.0	0, 15	45[g]	11[g]	42[g]	12	*c*
4[h]	6	1.0	0, 38[i]	*c*	16	*d*	0[f]	*d*
5	6	1.4	−20, 24	28[g]	trace[f]	*d*	23	*d*
6[h]	6	1.1	−20, 45	*c, f*	*c, f*	*c, f*	72	*d*
7[h]	6	0.0	25, 5			no reaction[f]		
8	7	1.0	25, 7	17[g]	11[g]	*d*	17	*d*
9a	7	1.1	−20, 24			no reaction[f]		
9b[e]	7	1.1	−20, 2[j]	40[k]	0	0	0	*d*

[a] Under 1 atm of N_2 or Ar unless otherwise indicated. [b] Isolated yield based on 6 or 7 uncorrected for recovered starting material unless otherwise indicated. [c] None detected. [d] Not analyzed. [e] Under excess CO at 1 atm. [f] By infrared. [g] Yields corrected for recovered starting material. [h] Also contains 1 mol equiv of 8·. [i] Solution yellow at 20 h, IR shows unreacted 6; dark green after 38 h, no 6. [j] Ar replaced with CO and mixture stirred for an additional 2 h. [k] Mixed with a trace of 7 and a trace of benzophenone; some unreacted 8 was also recovered.

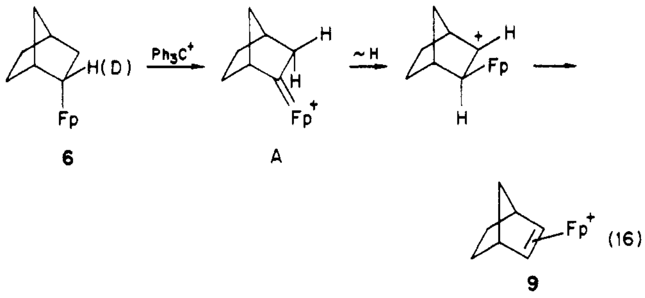
Both 6 and 7 react with triphenylmethyl tetrafluoroborate[18] (8) in dichloromethane. Depending somewhat upon the reaction conditions (Table I) each yields the acyl complex of retained configuration,[17] viz., 4 or 5, respectively, and/or dicarbonyl(η^5-cyclopentadienyl)(η^2-*exo*-norbornene)iron tetrafluoroborate (9) and triphenylmethane (10) (eq 15). At room temperature under nitrogen π-complex 9 is the only organometallic that can be isolated or detected from the reaction of endo Fp 6 and cation 8^+ (run 1) while at −20 °C only endo acyl 4 is observed (run 5). At 0 °C both are formed (run 3).

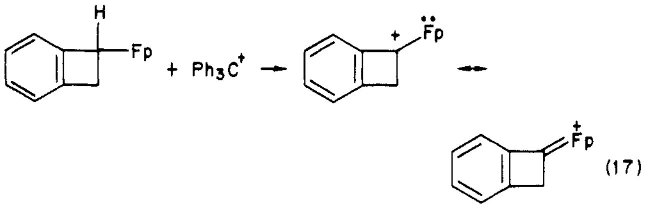


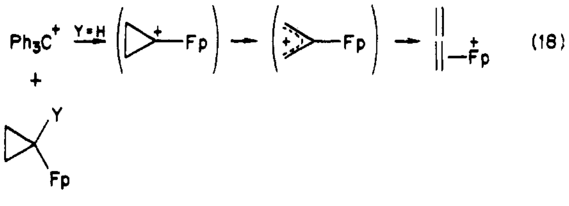
The thermally less stable (*exo*-norbornyl)Fp (7) is less reactive than 6 toward triphenylmethyl cation (8^+). Under comparable conditions at room temperature 7 reacts incompletely to produce a mixture of acyl 5 and π-complex 9 (run 7). At −20 °C, conditions sufficient to give 28% of acyl 4 from 6 (run 5), 7 does not react (run 9a).

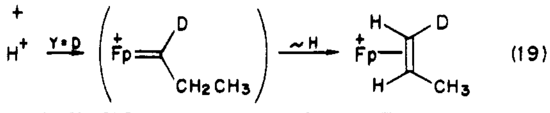
These reactions are unusual in several respects. The formation of exo π-complex 9 from endo σ-complex 6 more rapidly, more cleanly, and in better yield than from exo σ-complex 7 is unexpected. The formation of substantial amounts of acyl 4 or 5 in competition with or to the exclusion of π-complex in the absence of added carbon monoxide or of a coordinating ligand or solvent is surprising and, as far as we know, represents the first observation of competitive β-elimination and insertion under such conditions.[18] Considering these competing reactions in turn we focus first on the elimination.

How is exo π-complex 9 formed from endo σ-complex 6? Conceptionally, the most straightforward route would involve α-hydrogen abstraction to form the alkylidene A, followed by an endo 3,2 hydrogen shift and σ–π rearrangement (eq 16). There is precedent for each of these steps. α-Hydride abstraction by triphenylmethyl cation in preference to β can occur when, for either steric or electronic reasons, the latter is unusually unreactive. Both (benzocyclobutenyl)- and (cyclopropyl)Fp react in this manner (eq 17 and 18). β-Hydrogen shifts convert transition-metal alkylidenes to π-complexes. Protonation of (α-deuteriocyclopropyl)Fp, for example, produces the cationic α-deuteriopropylidene complex which shifts a β-hydrogen to yield [Fp(η^2-deuteriopropene)]$^+$ (eq 19).[21] Other examples are known.[22]









---

(18) Our earlier report[19] is an outgrowth of this study.

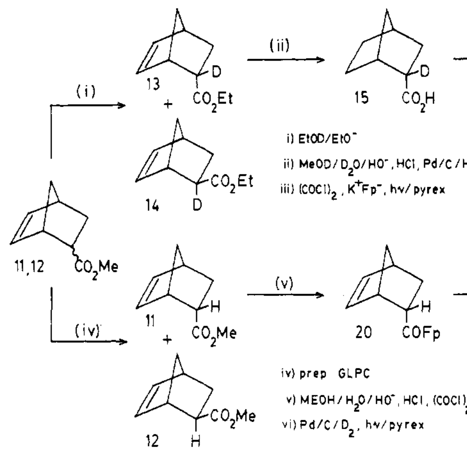
(19) Bly, R. S.; Silverman, G. S.; Hossain, M. M.; Bly, R. K. *Organometallics* **1984**, *3*, 642–644.

(20) (a) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430–5431. (b) Sanders, A.; Bauch, T.; Magatti, C. V.; Lorenc, G.; Giering, W. P. *J. Organomet. Chem.* **1976**, *107*, 359–375.

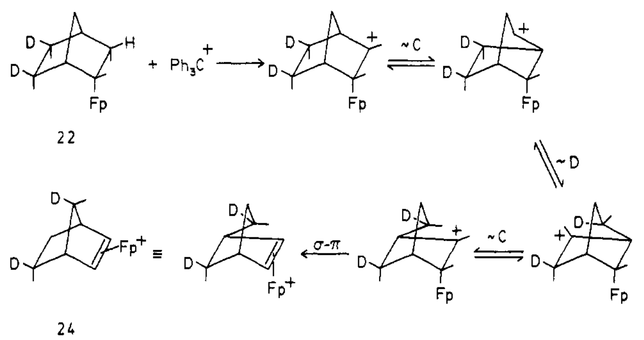
(21) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354–4355.

(22) (a) Labinger, J. A.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *97*, 1596–1597. (b) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533–2539. (c) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31–C36. (d) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761–3762. (e) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258–264 and references cited therein.

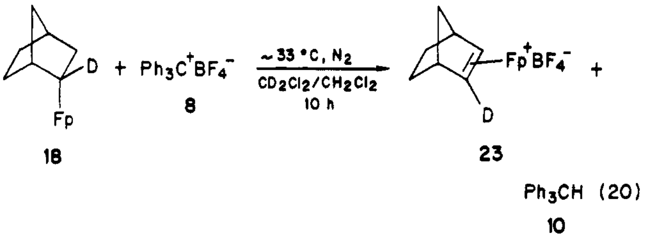
Scheme I. Synthesis of Deuterated Fp(2-norbornyl) Complexes



Scheme II. A Hypothetical Route from Fp(*endo*-2-norbornyl) to [Fp(η^2-*exo*-norbornene)]$^+$

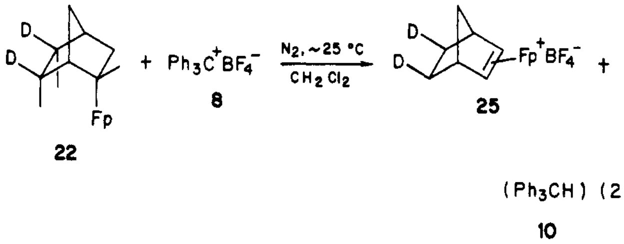


To determine whether the conversion of **6** to **9** *requires* an α-hydrogen abstraction, we prepared dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(2-deuterionorbornyl)]iron (**18**, 90% d_1, 10% d_0) as outlined in Scheme I and subjected it to our reaction conditions (eq 20). After 10 h at ~33 °C a $^{13}C\{^1H\}$ NMR of the reaction mixture exhibits only resonances of **23** (80% d_1 at C-2 and/or C-3 relative to **9**) and **10**. Clearly, replacement of α-hydrogen with deuterium does not retard the σ–π rearrangement to the point that CO insertion becomes competitive. A mass spectrum of isolated **10** reveals that fewer than 1% of the molecules are monodeuterated. On this basis it is apparent that the conversion of **5** to **9** (eq 15) does not *require* α-hydride abstraction.



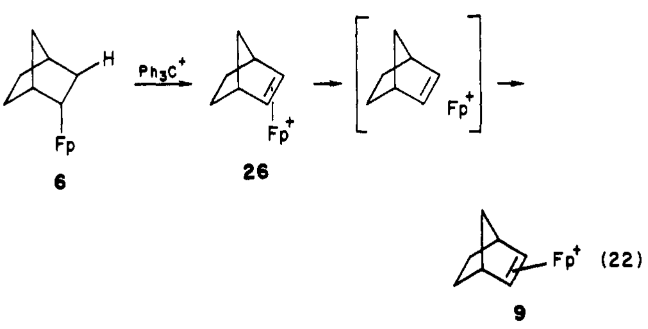
(20)

β-Hydride abstraction from **6** could produce **9** if it were followed by sequential carbon and/or hydrogen shifts as shown in Scheme II. Such consecutive rearrangements are well-known in norbornyl cations[23] though they are probably less likely in organometallic derivatives. To test this possibility, we synthesized dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(5,6-dideuterionorbornyl)]iron (**22**) (Scheme I) and examined its reaction with **8**. In nitrogen-blanketed dichloromethane at ambient temperature **22** forms dicarbonyl(η^5-cyclopentadienyl)(η^2-*exo*-5,6-dideuterionorbornene)iron (**25**) in 49% yield (eq 21). No deuterium-scrambled π-complexes could be detected by $^{13}C\{^1H\}$NMR. This result rules out the possibility of sequential carbon and hydrogen shifts in the conversion of **6** to **9**.

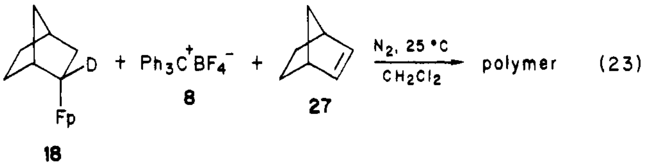


(21)

Attempts to trap or observe an intermediate in the conversion of **6** to **9** were unsuccessful. Thinking that perhaps the endo π-complex **26** might actually be formed but that being sterically crowded it dissociates and recombines to produce the less crowded, more stable exo π-complex **9**, we attempted to trap the organometallic cation Fp$^+$ by carrying out the reaction of **18** and **8** in the presence of a three-fold excess of norbornene (**27**) (eq 23).



(22)



(23)

No organometallic π-complex could be isolated, only polymer. When the reaction of **6** and **8** in nitrogen-blanketed dichloromethane was followed at 25 °C by $^{13}C\{^1H\}$ NMR, we could detect no endo π-complexed intermediate **26**. At −20 °C the extensive paramagnetic line broadening[24] that occurs as soon as **8** is added precludes observation of **26**. As the reaction progresses at this temperature, the resonances gradually sharpen and shift to those of the product acyl, **4**, cf. run 5, Table I. Little, if any, π-complex is formed under these conditions. If **26** is an intermediate in the conversion of **6** to **9**—and we suspect that it is—we do not detect it. Were dissociation–recombination to occur within a solvent cage, trapping could be difficult.

Our attempts to observe and/or trap an intermediate in the reaction of **6** and **8**$^+$ provide a clue to the origin of the acyl complex produced in these reactions (eq 15; Table I). The extensive polymerization observed in the presence of excess **27** and the paramagnetic line broadening associated with the increased amount of acyl formed at lower temperature speak clearly of electron transfer.

Oxidation of an organometallic σ-complex including those of iron(II) can result in cleavage of the metal-to-

---

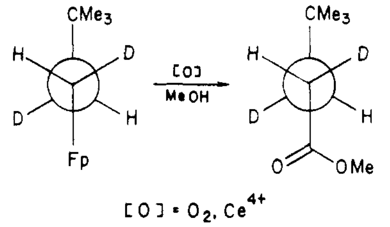
[23] Cf. Berson, J. A. In "Molecular Rearrangements"; DeMayo, P., Ed.; Interscience: New York, 1963; Vol. 1, pp 111–231 and references cited therein.

[24] Cf. Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: New York, 1977; pp 444–449.

carbon bond.[25] When terminal CO ligands are present insertion may occur prior to cleavage.[17b,26] With oxidants in the protic solvent, alcohol or water, the final organic product is an ester or carboxylic acid (eq 24). Both Anderson, Fong, and Johnson[26b] as well as Rosenblum and Nicholas[26c] suggest that insertion takes place in the 17-electron Fe(III) specie noting that oxidation would decrease back-bonding from iron to a terminal CO and make alkyl migration more likely. Whitesides et al. find that insertion in the 17-electron iron(III) complex occurs with retention of configuration in the migrating alkyl (eq 25).[17b]

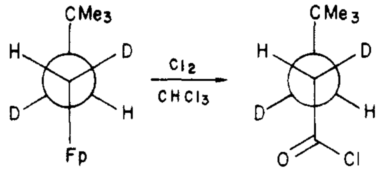
$$\text{Fp–R} \xrightarrow[\text{(CO)}]{[\text{O}]} [\text{Fp–R}]^{+\cdot} \rightarrow [\text{Cp(CO)FeCOR}]^{+\cdot} \xrightarrow{\text{R}'\text{OH}} \text{RCOOR}' \quad (24)$$

$$[\text{O}] = \text{Cu}^{2+}, \text{Fe}^{3+}, \text{Ce}^{4+}, \text{DDQ}; \text{R}' = \text{H, alkyl}$$



(25)

With chlorine as oxidant in the aprotic solvent $CHCl_3$, solvolysis of the acyl does not occur; rather, the Fe(III)–acyl bond is cleaved by the nucleophilic chloride generated in the initial electron transfer (eq 26).[17b] Given the occurrence of radicals in our reaction mixtures and these literature precedents for oxidative insertion, it is likely that the acyl products which we observe are formed in a similar manner.

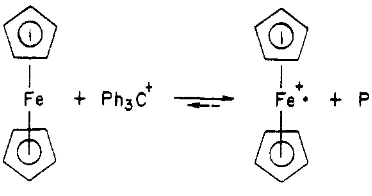


(26)

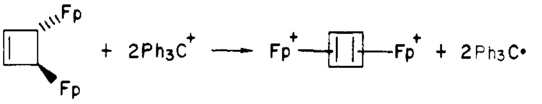
The presence of radicals in our solutions was confirmed, and the identity of the oxidant was established by EPR. Freshly prepared solutions of 8 and 6 or 7 at −20 °C exhibit a relatively intense resonance (g = 2.002) identical with that of triphenylmethyl (8·) and a less intense resonance at g = 2.067 attributable to an organometallic specie.[8b] Under comparable conditions at −20 °C the resonance of 8· is equally intense in each mixture; in solutions prepared at ambient temperature it is about 100 times less intense in the endo case. Clearly, triphenylmethyl cation (8^+) is acting as an oxidizing agent in these solutions. Control experiments confirm that it is the Fp σ-complex 6 or 7 which reduces 8^+ to 8· and is, in turn, converted to a radical cation (eq 27).

$$\text{FpR} + \text{Ph}_3\text{C}^+ \xrightarrow{\text{N}_2/\text{CO}} [\text{FpR}]^{+\cdot} \text{ and/or } [\text{FpCOR}]^{+\cdot} + \text{Ph}_3\text{C}\cdot \quad (27)$$

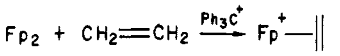
Triphenylmethyl cation (8^+) has traditionally been employed in organometallic chemistry to abstract hydride[2-8a] but only occasionally as a one-electron oxidant. It has been used by Hawthorne to generate ferrocenium ion from ferrocene (eq 28),[29a] by Sanders and Giering to prepare the bis Fp π-complex of cyclobutadiene (eq 29),[29b] and by Boyle and Nicholas to synthesize $[\text{Fp}(\eta^2\text{-olefin})]^+$ complexes from olefin and Fp dimer (eq 30).[29c] As far as we know 8^+ has not previously been reported to act as both a Lewis acid (hydride abstractor) and a one-electron oxidant toward the same organometallic under a single set of reaction conditions.



(28)



(29)



(30)

What is the source of the CO needed for conversion of 6 to 4 or 7 to 5? Rosenblum and Nicholas have observed that although it accelerates the rate, added CO is not required for the conversion of FpR to RCOOH (eq 24) when the former is oxidized in aqueous solution.[26c] The implication is that the necessary CO must come from the decomposition of free or complexed Fp. This being the case, the yield of Fp acyl should be greater, particularly at reduced temperature, if CO were to be provided as one of the initial reactants. To test this, we repeated the reaction of 8^+ and 6 using CO rather than N_2 to blanket the solution. The difference at 25 °C is striking: instead of 66% 9 and no 4 (run 1) we observe but a trace of 9 and 59% of 4 (run 2). Elsewhere[19] we have shown that under CO the insertion will also take place at lower temperatures as it is no longer necessary that the organometallic be decomposed to provide the needed carbon monoxide.

While this work was in progress, Magnuson, Giering, et al.[30] using a combination of chemical and electrochemical techniques demonstrated that in the presence of a coordinating solvent and/or ligand the equilibrium constant for CO insertion in $(\eta^5\text{-C}_5\text{H}_5)(\text{L})\text{COFeR}$ (L = $(i\text{-PrO})_3\text{P}$, Ph_3P, CO; R = CH_3) is greatly enhanced in the 17-electron radical cation (eq 32; L = $(i\text{-PrO})_3\text{P}$, Ph_3P; R = CH_3) relative to the 18-electron neutral complex (eq 31; L = $(i\text{-PrO})_3\text{P}$, Ph_3P; R = CH_3), i.e., that $K_3/K_1 = 10^{11}\text{–}10^{12}$.

$$(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{CO})\text{FeR} + \text{CO} \overset{K_1}{\rightleftharpoons} (\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{CO})\text{FeCOR} \quad (31)$$

$$[(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{CO})\text{FeR}]^{+\cdot} + \text{CO} \overset{K_3}{\rightleftharpoons} [(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{CO})\text{FeCOR}]^{+\cdot} \quad (32)$$

---

(25) (a) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539–5546. (b) Daub, G. W. *Prog. Inorg. Chem.* **1977**, *22*, 409–423 and references cited therein. (c) Rogers, W.; Page, J. A.; Baird, M. C. *J. Organomet. Chem.* **1978**, *156*, C37–C42. (d) Dong, D.; Slack, D. A.; Baird, M. C. *Inorg. Chem.* **1979**, *18*, 188–191.

(26) (a) Collman, J. P.; Winter, S. R.; Komoto, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 249–250. (b) Anderson, S. N.; Fong, C. W.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1973**, 163. (c) Nicholas, K. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 4449–4450.

(27) Ayers, C. L.; Janzen, E. S.; Johnston, F. J. *J. Am. Chem. Soc.* **1966**, *88*, 2610–2612.

(28) Okamoto, K.; Komatsu, K.; Shingu, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3249–3254.

(29) (a) Hawthorne, M. F. *J. Org. Chem.* **1956**, *21*, 363. (b) Sanders, A.; Magatti, C. V.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1610–1611. (c) Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *114*, 307–312. (d) Chaudhary, F. M.; Pauson, P. L. *J. Organomet. Chem.* **1974**, *69*, C21–C32. (e) Sanders, A.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 5247–5248. (f) Sanders, A.; Giering, W. P. *J. Organomet. Chem.* **1976**, *104*, 49–65. (g) Bauch, T. E.; Konowitz, H.; Giering, W. P. *J. Organomet. Chem.* **1976**, *114*, C15–C18. (h) Bauch, T. E.; Giering, W. P. *J. Organomet. Chem.* **1978**, *144*, 335–349.

(30) (a) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790–5791. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J., Giering, W. P. *Organometallics* **1983**, *2*, 460–462.

Table II. Electrochemical Potentials[a]

redox couple	$(E_a + E_c)/2$,[b] V
$4^{+\cdot} + 1e \rightleftarrows 4$	0.28[c,d]
$5^{+\cdot} + 1e \rightleftarrows 5$	0.41[e]
$6^{+\cdot} + 1e \rightleftarrows 6$	0.90[d]
$7^{+\cdot} + 1e \rightleftarrows 7$	0.90[e]
$8^{+} + 1e \rightleftarrows 8\cdot$	0.21

[a] From cyclic voltammetry studies at ambient temperature in nitrogen-blanketed CH_2Cl_2 containing 0.1 M tetraethylammonium perchlorate and ~0.03 M 4, 5, 6, or 7. [b] Vs. SCE. [c] Contains 10^4 equiv of added acetonitrile. [d] Scan rate is 100 mV/s. [e] Scan rate is 25 mV/s.

They also found that in CH_2Cl_2 under 1 atm of CO $(E_a + E_c)/2 \approx E°$ for the quasi-reversible one-electron reduction of $[(\eta^5\text{-}C_5H_5)(L)(CO)FeR]^{+\cdot}$ (eq 33) is less, $E°_2 \approx +0.38$ V, than the comparable value, $E°_4 \approx +0.47$ V, for the reduction of $[(\eta^5\text{-}C_5H_5)(L)(CO)FeCOR]^{+\cdot}$ (eq 34; L = Ph_3P, R = CH_3). Hence, the overall insertion for L = Ph_3P, R

$$[(\eta^5\text{-}C_5H_5)(L)(CO)FeR]^{+\cdot} + 1e \rightleftarrows (\eta^5\text{-}C_5H_5)(L)(CO)FeR\ (E°_2) \quad (33)$$

$$[(\eta^5\text{-}C_5H_5)(L)(CO)FeCOR]^{+\cdot} + 1e \rightleftarrows (\eta^5\text{-}C_2H_5)(L)(CO)FeCOR\ (E°_4) \quad (34)$$

= CH_3, i.e., eq 31 = + eq 32 − eq 33 + eq 34, is a radical chain process requiring only a catalytic amount of added oxidant for initiation.

The conditions for catalysis are easily defined: $K_1 > 1$ or $\log K_1 > 0$. From the above analysis (at 0 °C)[31] it follows that

$$\log K_1 = \log K_3 + (E°_4 - E°_2)/0.0542 > 0$$

or

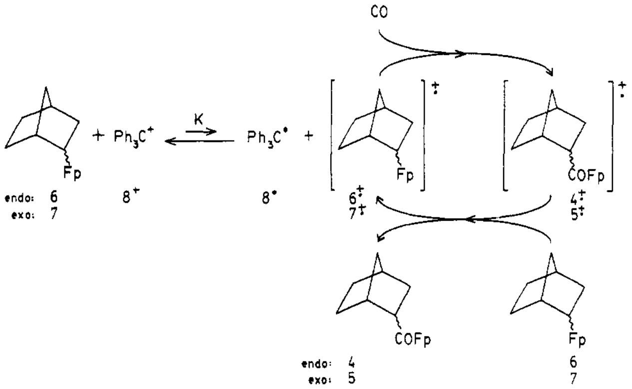
$$\log K_3 > -(E°_4 - E°_2)/0.0542$$

The Magnuson, Giering, et al. data[30b] for $(\eta^5\text{-}C_5H_5)(Ph_3P)(CO)FeCH_3$, require that K_3 exceeds 0.022 for catalysis to occur. They find $K_3 = 230 \pm 2$,[30a] and thus the condition for catalysis is satisfied.

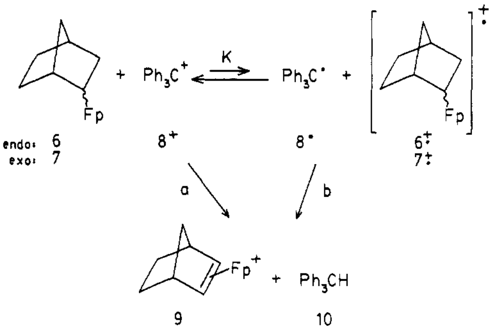
Since we have established chemically that CO insertions in $FpCH_2CH_2R$ (R = Me, *i*-Pr, *t*-Bu) also require less than a catalytic amount of oxidant[19] and since there is a hint of such catalysis in the reaction of 6 and 8^+ under CO at 25 °C (run 5), we have measured the electrochemical potentials for the quasi-reversible one-electron redox couples shown in Table II.

Application of the catalytic criterion to our data, Table II (eq 31–34; L = CO, R = 2-norbornyl) reveals that for CO insertion to require less than 1 equiv of added oxidant—as it apparently does in the case of 6 (run 2) —K_3 would have to exceed 10^{10}–10^{11} for the endo Fp 6 or 10^8–10^9 for the exo 7. However, Magnuson, Giering, et al. observe that when the redox reactions (eq 33 and 34; L = Ph_3P, R = CH_3) are carried out in acetonitrile under an atmosphere of N_2 instead of in CH_2Cl_2 under CO, $\Delta E° \approx E°_4 - E°_2 \approx [(E_a + E_c)_4/2 - (E_a + E_c)_2/2] = -0.625$ V[30a] instead of +0.090 V. In other words, the redox-initiated CO insertion is about 0.7 V more favorable in CH_2Cl_2 under CO! Were a similar effect to obtain in the Fp (*endo*-2-norbornyl) and Fp(*exo*-2-norbornyl) complexes, 6 and 7, respectively, the insertion(s) would likely be catalytic, for then K_3 (L = CO, R = 2-norbornyl) would need be only 0.045 and/or 10^{-4}–10^{-3}, respectively. Thus, we presume that the competitive CO insertions probably follow a radical chain process similar to that shown below.

Scheme III. The Probable Path of Triphenylcarbenium-Initiated Migratory Carbonyl Insertion



Scheme IV. Possible Paths of β-Hydrogen Loss during Redox-Catalyzed Migratory Insertion



We represent the initial electron transfer as reversible because of the effect of added triphenylmethyl radical (8·). When an equivalent of 8· is added to an equimolar mixture of 6 and 8^+ in argon-blanketed dichloromethane at 0 °C (Table I, run 4), no acyl, 4, is produced (compare with run 3) though 9 continues to form at about the same rate. At −20 °C, where π-complex formation is very slow, unreacted starting material, 6, can be recovered (run 5). Such strong inhibition establishes the chemical reversibility of the initial electron transfer and supports our electrochemical measurements (Table II) which indicate that the initial equilibrium (Scheme III) is thermodynamically quite unfavorable, viz., $\log K \approx (0.21\text{–}0.90)/0.059$ and $K \approx 10^{-11}$–10^{-12}.[33]

Apparently, it is the combined effect of CO upon both the rate of formation and the stability of the resultant 17-electron acyl radical cation[30b] that makes the initial unfavorable electron transfer to 8^+ a viable initiation step for the overall insertion. Likewise, it is the strong π-acidic character of CO[34] relative to that of other possible coordinating ligands that increases the reduction potential of the acyl radical to the point that it can serve as an oxidant for the starting Fp alkyl and thus render the overall reaction catalytic in initial oxidant.

---

[31] We thank Professor Dennis Evans, Department of Chemistry, University of Wisconsin, Madison, for this analysis.

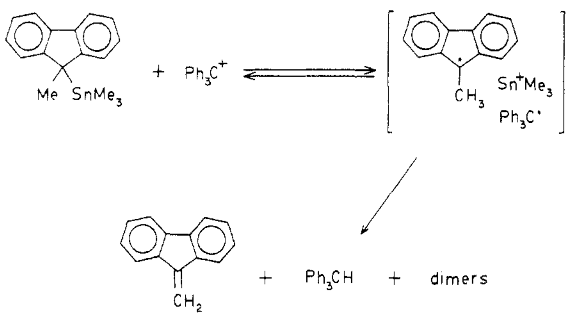
[32] (a) As an equilibrium mixture with the dimer prepared by treating triphenylchloromethane with excess zinc at room temperature[32b] and decanting the resultant clear supernatant solution. (b) Isaacs, N. S. "Experiments in Physical Organic Chemistry"; Macmillan: New York, 1969; pp 216–217.

[33] It may be estimated that in order for the addition of an equimolar amount of 8· to a 1:1 mixture of 6 or 7 and 8^+ to decrease the initial rate of formation of acyl 4 or 5 (as outlined in Scheme III) by a factor of 100, $K < \sim10^{-4}$.

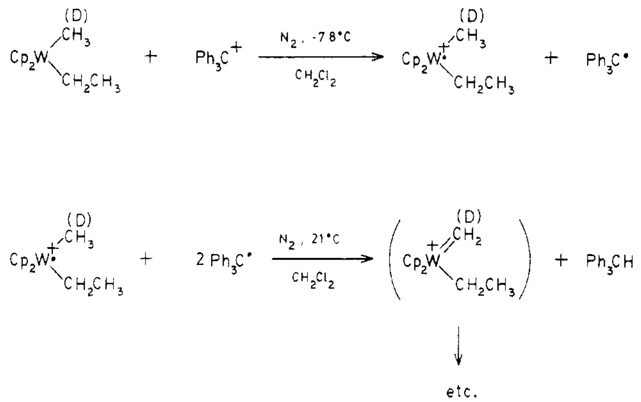
[34] (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 82 ff. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 81–89.

[35] Cf. Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 8.

Scheme V. β-Hydrogen Atom Loss during a Triphenylcarbenium-Initiated Reaction



Scheme VI. α-Hydrogen Atom loss during a Triphenylcarbenium-Initiated Reaction



Returning now to the elimination we consider whether the β-hydrogen is lost as a hydride or as a neutral atom. The formation of triphenylmethyl radicals in our solutions raises the possibility that instead of a cation abstracting hydride (path a), a radical may abstract a hydrogen atom (path b, Scheme IV).

There is no precedent for β-hydrogen *atom* loss during the reaction of an organometallic σ-complex with triphenyl methyl cation. Reutov, Beletskaya, et al.[36] report that (9-methyl-9-fluorenyl)trimethylstannane and triphenylmethyl tetrafluoroborate in dichloromethane at 20 °C yield 9-methylenefluorene, triphenylmethane, and bis-(9-methyl-9-fluorenyl), but, as the authors suggest (Scheme V), hydrogen abstraction probably occurs not from the organometallic cation radical but from the solvent-caged metal cation–organic radical pair instead.

There is precedent, however, for α-hydrogen *atom* loss in reactions with triphenylmethyl cation. Hayes, Cooper, et al.[37] observe that in dichloromethane at −78 °C this cation oxidizes a dialkylbis(cyclopentadienyl)tungsten to the radical cation which, when warmed to room temperature with 2 equiv of triphenylmethyl radical, loses α- rather than β-hydrogen to form a cationic tungsten alkylidene that inserts and rearranges to the cationic hydridotungsten π complex (Scheme VI). Gladysz et al.[38] report that the reaction of the neopentyl complex ($(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)[CH_2C(CH_3)_3]$) in dichlorodideuteriomethane with 1.1 equiv of triphenylmethyl hexafluorophosphate at −70 °C shows extensive line broadening in the ^1H NMR. Though no metal alkylidene could be detected, triphenylmethane was observed in some reaction mixtures. This is probably also a case of one-electron transfer followed by α- (not β-) hydrogen abstraction. The driving force for α-hydrogen atom loss is presumedly formation of the metal alkylidene. Both Cooper[37c] and Gladysz[38] have, in fact, suggested that hydrogen *atom* abstraction may be diagonostic of α- rather than β-hydrogen loss!

Paths "a" and "b" cannot be distinguished kinetically.[39] We have demonstrated elsewhere[19] in some acyclic Fp alkyls that, as predicted by the mechanism of Scheme IV, the addition of triphenylmethyl radical (8·) does not alter significantly the rate of elimination especially when K for the initial, reversible electron transfer is small.[40]

Whether they are intermediates in the formation of the π-complex or not (Scheme IV), the concentrations of both triphenylmethyl radical (8·) and the organometallic radical cation seem to mirror the extent acyl formation. At −20 °C under nitrogen in dichloromethane, where acyl 4 is the only isolable organometallic product (run 5), the radical concentrations in a solution of 6 and 8 are about 100 times greater than in a comparable solution at ambient temperature, which produces only π-complex 9 (run 1). Similarly, paramagnetic line-broadening in the $^{13}C\{^1H\}$ NMR spectrum of such a mixture is much greater at −20 °C than it is at ambient probe temperature (~33 °C). Further, at ambient temperature the radical concentrations in a solution of 7 and 8, which yields a mixture of acyl 5 and π-complex 9 (run 8), are much greater than they are in the comparable solution of 6 and 8. Apparently, one-electron transfer/migratory carbonyl insertion is favored relative to β-elimination/σ–π rearrangement in the Fp *endo*-norbornyl 6 and at lower temperatures.

We attribute the reactivity differences between the endo and exo isomers 6 and 7 to steric crowding. The anticlinal β-hydrogen in 7 is endo and, hence, less accessible to the Lewis acid or radical than is the exo β-hydrogen of 6; elimination is slower in 7. Analogously, the endo Fp of 6 is less accessible to the oxidant (8^+) than is the exo Fp of 7; electron transfer is retarded in 6. The steric bulk of triphenylmethyl cation (radical) accentuates these differences.

Both 6 and 7 are less reactive toward triphenylcarbenium-initiated β-elimination than the acyclic σ-complexes $FpCH_2CH_2CH_3$ and $FpCH_2CH_2CH(CH_3)_2$.[19] Although a direct comparison has not been made, the reactivity differences are obvious from the product ratios and the time required for complete reaction. Of the acyclic compounds that we have examined only $FpCH_2CH_2C(CH_3)_3$ with its highly hindered, conformationally unfavorable[17b] neopentyl-type β-hydrogens is less reactive toward elimination than 6 or 7. We assume that the inability of the conformationally immobile (norbornyl)Fp's to attain an antiperiplanar conformation in the transition state is largely responsible for their relative reluctance to eliminate β-hydrogen in the presence of triphenylmethyl cation.

Experimental Section

General Procedures. All operations were carried out under dry, oxygen-free nitrogen or argon atmospheres using standard

---

[36] Kashin, A. N.; Bumagin, N. A.; Beletskaya, I. P.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 98–102.

[37] (a) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648–4650. (b) Hayes, J. C. Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570–5572. (c) Hayes, J. C.; Jernakoff, P.; Miller, G. A.; Cooper, N. J., Proceedings, of the XI International Conference on Organometallic Chemistry, Pine Mountain, GA, Oct 1983, p 38.

[38] Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958–4972.

[39] Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; pp 78–79.

[40] It may be estimated that as K is varied from $-\infty$ to $+\infty$ (Schemes III and IV), $(k_i)_a = (k_i)_b$ changes from 1.0 to 2.0. (i.e., $1.0 < (k_i)_a = (k_i)_b < 2.0$) when an equimolar amount of 8· is added to a 1:1 mixture of 6 or 7 and 8^+. When $K < \sim 10^{-4}$ the initial rate of π-complex formation by either path a or path b is predicted to be unaffected experimentally by the addition of 8·.[33]

Schlenk-line and/or drybox techniques.[41] Glassware was flame-dried prior to use.

Instrumental and Analytical Methods. Proton NMR spectra were recorded on a Varian EM 360 or EM 390 spectrometer or on an IBM NR 80 and ^{13}C NMR spectra on a Varian CFT 20 or on the NR 80. All NMR spectra are reported in parts per million (δ) relative to tetramethylsilane. Infrared spectra were recorded on either a Beckman IR 4210 or a Perkin-Elmer 727B spectrometer and are reported in inverse centimeters. Mass spectra were determined on a Finigan 4021 GC–MS spectrometer using a direct probe at ionization potentials of 15 and 70 eV. Melting points were determined in sealed capillary tubes under nitrogen on a Mel-Temp apparatus; the temperatures reported are uncorrected. Cyclic voltammetry (CV) measurements were made on a Bio-Analytical Inc. Model CV-1A system equipped with a Hewlett-Packard Moseley 7035B X-Y recorder using a carbon working electrode, a platinum counterelectrode, and a potassium chloride saturated calomel reference electrode. Electron spin resonance (ESR) spectra were determined on a Varian E-9 ESR spectrometer. Microanalyses were performed by Atlanta Microlab, Inc., Atlanta, GA.

Solvents and Reagents. Reagent grade benzene, diethyl ether, and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane was distilled under nitrogen from P_2O_5. Technical grade pentane was purified by sequential overnight stirring with concentrated sulfuric acid, distillation, stirring with a second batch of sulfuric acid, washing with water, and distillation from P_2O_5. The purified pentane was stored over sodium ribbon and distilled from sodium under nitrogen immediately prior to use. Solvents used for spectral and electrochemical determinations were degassed by the freeze–pump–thaw technique and stored under an inert atmosphere.

Column chromatography was carried out on Merck EM Reagent neutral "Aluminum Oxide 90" activity state I with the activity adjusted by adding appropriate amounts of water according to the manufacturers label directions.

Dicarbonyl(η^5-cyclopentadienyl)(*endo*-2-norbornylcarbonyl)iron. (4). To a stirred solution of 0.43 g (2.7 mmol) of *endo*-2-norbornanecarbonyl chloride (1)[13,42] in 10 mL of THF, cooled in an ice-bath, was added in small portions from a side-arm-equipped solid addition tube over a period of ~10 min 0.70 g (3.2 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate (3, K^+Fp^-).[14] The mixture was allowed to warm to room temperature, and stirring was continued for an additional 10 h. The solvent was removed under reduced pressure (~0.5 mm), and the residual solid was washed with ~150 mL of pentane. The pentane suspension was filtered through Celite, and the volume of the filtrate was reduced to ~5 mL under reduced pressure. The concentrate was chromatographed on activity III alumina at 10 °C using 2% ether-in-pentane as eluant. Removal of the solvent under reduced pressure yielded 0.56 g (69%) of an air-stable yellow solid: mp 111.5–113.5 °C; IR (CH_2Cl_2) 2018, 1958 (C≡O, Fp), 1652 cm^{-1} (C=O, acyl); ^{1}H NMR (CCl_4) δ 4.83 (s, Cp), 3.30 (m, >CHCOFp), 2.97 (br s, >CH, bridgehead) 2.18 (br s, >CH, bridgehead), 1.31 (m, 8 H); ^{13}C{^{1}H} NMR (20% CD_2Cl_2/CH_2Cl_2) δ 254.9 (>C=O), 215.1, 214.7 (-C≡O), 86.6 (Cp), 76.2 (C-2), 46.6 (C-1), 39.6 (C-7), 37.9 (C-4), 31.2 (C-3), 29.3 (C-5), 24.4 (C-6); MS, *m/e* 300 $[M]^{+\cdot}$, 272 $[M - CO]^{+\cdot}$, 244 $[M - 2CO]^{+\cdot}$, 123 $[M - Fp]^{+\cdot}$. Anal. Calcd for $C_{15}H_{16}FeO_3$: C, 60.03; H, 5.37. Found: C, 60.10; H, 5.75.

Dicarbonyl(η^5-cyclopentadienyl)(*exo*-2-norbornylcarbonyl)iron (5) was prepared in the same manner as 4 using 2.8 g (13 mmol) of 3,[14] 1.7 g (11 mmol) of *exo*-2-norbornanecarbonyl chloride (2),[13,42] and 40 mL of THF. A yield of 2.4 g (73%) of yellow crystalline solid was obtained after workup and purification (vide supra): mp 91–92 °C; IR (CH_2Cl_2) 2015, 1958 (C≡O, Fp), 1652 cm^{-1} (C=O, acyl); ^{1}H NMR (CCl_4) δ 4.77 (s, Cp), 2.76 (m, >CHCOFp), 2.41 (br s, >CH, bridgehead), 2.18 (br s, >CH, bridgehead) 1.21 (m, 8 H); ^{13}C{^{1}H} NMR (20% CD_2Cl_2/CH_2Cl_2) δ 256.7 (>C=O), 215.5, 215.0 (-C≡O), 86.9 (Cp), 76.5 (C-2) 40.2 (C-1), 36.9 (C-7), 36.2 (C-4), 34.7 (C-3), 29.7 (C-5), 29.3 (C-6); MS, *m/e* 300 $[M]^{+\cdot}$, 272 $[M - CO]^{+\cdot}$, 244 $[M - 2CO]^{+\cdot}$, 123 $[M - Fp]^{+\cdot}$. Anal. Calcd for $C_{15}H_{16}FeO_3$: C, 60.03; H, 5.37; Found: C, 60.30; H, 5.41.

Dicarbonyl(η^5-cyclopentadienyl)(*endo*-2-norbornyl)iron (6). A magnetically stirred solution containing 0.28 g (0.93 mmol) of 4 in 180 mL of pentane was irradiated for 8 min at ambient temperature in a water-cooled photochemical reactor equipped with a Pyrex insert and a Hanovia 450-W medium-pressure mercury lamp. At this time the reaction mixture had darkened and no longer showed any absorption at 1652 cm^{-1} (C=O, acyl) in the IR spectrum. The solution was concentrated to ~3 mL and chromatographed on activity IV alumina at 10 °C using pentane as eluant. Removal of the solvent by vacuum evaporation gave 0.21 g (83%) of a thermally and oxidatively labile amber oil: IR ($CHCl_3$) 1998, 1940 cm^{-1} (C≡O); ^{1}H NMR ($CDCl_3$) δ 4.67 (s, Cp), 2.83 (m, >CHFp), 2.03 (br s, 2 H, >CH, bridgehead), 1.45 (m, 8 H); ^{13}C{^{1}H} NMR (20% CD_2Cl_2/CH_2Cl_2) δ 218.9, 218.5 (C≡O), 86.0 (Cp), 47.9 (C-1), 43.9 (C-7), 40.6 (C-4), 37.0 (C-3), 30.1 (C-5), 29.0 (C-6), 27.0 (C-2); MS, *m/e* 272 $[M]^{+\cdot}$, 244 $[M - CO]^{+\cdot}$, 216 $[M - 2CO]^{+\cdot}$, 95 $[M - Fp]^{+\cdot}$.

Dicarbonyl(η^5-cyclopentadienyl)(*exo*-2-norbornyl)iron (7). This compound was prepared and isolated in the same manner as 6 by irradiating 0.45 g (1.5 mmol) of 5 in ~180 mL of pentane for ~4 min. The product (0.18 g, 44%) is an oxidatively and thermally labile amber oil: IR 1997, 1939 cm^{-1} (C≡O); ^{1}H NMR ($CDCl_3$) δ 4.78 (s, Cp), 2.55 (m, >CHFp), 2.21 (br s, >CH, bridgehead), 2.07 (br s, >CH, bridgehead), 1.61 (m, 5 H), 1.21 (m, 3 H); ^{13}C{^{1}H} NMR (20% CD_2Cl_2/CH_2Cl_2) δ 218.9, 218.6 (-C≡O), 86.9 (Cp), 49.1 (C-1), 47.9 (C-3) 39.6 (C-4), 37.2 (C-7), 35.0 (C-5), 29.0 (C-6), 27.4 (C-2); MS, *m/e* 272 $[M]^{+\cdot}$, 244 $[M - CO]^{+\cdot}$, 216 $[M - 2CO]^{+\cdot}$, 95 $[M - Fp]^{+\cdot}$.

Dicarbonyl(η^5-cyclopentadienyl)(η^2-*exo*-norbornene)iron Tetrafluoroborate (9). A solution of 1.50 g (16 mmol) of freshly distilled norbornene in 2 mL of dichloromethane was added dropwise with stirring to 20 mL of an ~0.75 M solution of dicarbonyl(η^5-cyclopentadienyl)iron tetrafluoroborate[43] in dichloromethane and allowed to react at room temperature for 40 min. The mixture was cooled to 0 °C combined slowly (~10 min) with 25 mL of diethyl ether and placed in a dry ice–isopropyl alcohol bath for 2 h. Filtration followed by several washings with diethyl ether and drying at room temperature under reduced pressure yielded 2.6 g (56%) of pale yellow crystals, the IR and ^{1}H NMR of which are identical in all respects with those of the π-complex 9 prepared previously in a different manner[11,44] ^{13}C{^{1}H} NMR (20% CD_2Cl_2/CH_2Cl_2) δ 210.3 (-C≡O), 89.6 (Cp), 77.7 (C-2, C-3), 41.3 (C-1, C-4), 36.7 (C-7), 25.4 (C-5, C-6).

The Reaction of Dicarbonyl(η^5-cyclopentadienyl)(*endo*-2-norbornyl)iron (6) and Triphenylmethyl Tetrafluoroborate (8). Run 1. A nitrogen-blanketed solution containing 0.38 g (1.2 mmol) of 8[45] in 6 mL of dichloromethane was cannulated into a stirred, nitrogen-blanketed solution of 0.29 g (1.1 mmol) of 6 in 6 mL of dichloromethane at room temperature. Progress of reaction was monitored by periodically withdrawing small samples and scanning the 2200–1800 cm^{-1} region in the IR. After ~6 h the spectrum showed strong terminal C≡O absorptions of the π-complex 9 (2065, 2027 cm^{-1}) and virtually none of the starting material 6 (1998, 1940 cm^{-1}) or acyl complex 4 (2018, 1958 cm^{-1}). The mixture was stirred for an additional 4 h, cooled to −78 °C, slowly combined with 25 mL of diethyl ether, and, after ~1 h, filtered to give 0.25 g (66%) of pale yellow product identical in all respects with authentic dicarbonyl(η^5-cyclopentadienyl)(η^2-*exo*-norbornene)iron tetrafluoroborate (9).

Run 2. Carbon monoxide blanketed solutions containing 0.192 g (0.706 mmol) of 6 in ~2 mL of dichloromethane and 0.272 g (0.824 mmol) of 8 in 5 mL of dichloromethane were combined at room temperature and stirred under 1 atm of CO for 5 h. The reaction mixture was cooled to −78 °C, combined with ~15 mL of diethyl ether and filtered to give 0.197 g (72%) of unreacted

---

(41) Shriver, D. F. "Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

(42) Prepared by the method of Wilt, J. W.; Parsons, C. F.; Schneider, C. A.; Schultenover, D. G.; Wagner, S. J.; Wagner, W. J. *J. Org. Chem.* **1968**, *33*, 694–708.

(43) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73–84.

(44) Nicholas, K. M. *J. Am. Chem. Soc.* **1976**, *97*, 3254–3255.

(45) Dauben, H. J.; Honnen, L. R.; Harman, E. M. *J. Org. Chem.* **1960**, *25*, 1442–1444.

8 (identified by IR) containing only a trace of π-complex **9**. The filtrate was concentrated to $\sim$2 mL and chromatographed on activity III alumina using 10% ether-in-pentane as eluant. A yield of 0.126 g (59%) of pure acyl complex **4** was obtained after evaporation of the solvent.

Run 3. Argon-blanketed solutions of dichloromethane containing 0.94 g (0.36 mmol) of **6** in 5.0 mL and 0.115 g (0.348 mmol of **8** in 5.0 mL were cooled to 0 °C and mixed. The solution turned dark green within 15 min. The mixture was held at 0 °C for 15 h, then cooled to -78 °C, diluted with diethyl ether, allowed to stand for $\sim$1 h, and filtered. The pale yellow precipitate was redissolved in dichloromethane, the solution was agitated vigorously with cold water to convert any unreacted **8** into triphenylmethanol, the layers were separated, and the organic layer was diluted with diethyl ether. Filtration of the resulting pale yellow precipitate gave 0.012 g of pure **9**. The original filtrate was concentrated under vacuum, placed on an activity III alumina column, and eluted with 2% ether-in-pentane. Two fractions were collected: an initial 0.045-g fraction consisting of a 1:3 mixture of **6** and **10** and a second, 0.042-g fraction of essentially pure **4**. Thus, the isolated product yields are 0.042 g (0.14 mmol) of **4**, 0.012 g (0.034 mmol) of **9**, and 0.032 g (0.13 mmol) of **10**. When corrected for the 0.013 g (0.048 mmol) of recovered **6**, this amounts to 45% **4**, 11% **9**, and 42% **10**.

Run 4. A solution of 0.094 g (0.36 mmol) of **6** in 5 mL of dichloromethane was degassed by the freeze-thaw method, blanketed with argon, cooled to 0 °C, and combined by syringe with 2.0 mL of a similarly treated, $\sim$0.2 M solution of triphenylmethyl radical (**8·**) ($\sim$0.4 mmol, in equilibrium with the dimer[32]) in dichloromethane. There was no appreciable reaction. The stirred mixture at 0 °C was combined by cannula with a cold solution of 0.115 g (0.348 mmol) of **8** in 5.0 mL of dichloromethane. Progress of the reaction at 0 °C was monitored by periodically scanning the 2400–1600 cm^{-1} IR regions of aliquots withdrawn for this purpose. After 20 h the yellow solution contained π-complex **9** and starting material **6**, but no acyl **4**. The reaction was discontinued after 36 h when **6** could no longer be detected in the now green solution. Workup as before (run 1) gave a mixture of **9** and triphenylmethyl peroxide from which 0.021 g (16%) of **9** could be recovered after recrystallization.

Run 5. The reaction was carried out under nitrogen at -20 °C as otherwise described under "run 1" using 0.38 g (1.2 mmol) of **8** and 0.23 g (0.85 mmol) of **6** each in 6 mL of dichloromethane. After having been stirred at -20 °C for 24 h, the reaction mixture showed strong C=O stretches of unreacted **6** and of acyl **4**, but only very weak absorptions attributable to **9**. The solvent was evaporated under reduced pressure, and the residual paste was washed thoroughly with 10% ether-in-pentane and filtered through a thin layer of alumina. The filtrate was concentrated to $\sim$3 mL and chromatographed on activity III alumina at 10 °C using 2% diethyl ether-in-pentane. Two yellow bands separated and were isolated: 0.053 g (23%) of **6** and 0.056 g—28% when corrected for recovered **6**—of **4**.

Run 6. A solution containing 0.086 g (0.32 mmol) of **6** in 5 mL of dichloromethane was degassed by the freeze-thaw method, placed under an atmosphere of argon, cooled to -78 °C, and combined by syringe with 2.4 mL of an 0.14 M solution (0.34 mL) of triphenylmethyl radical[32] (**8·**) in dichloromethane. The mixture was stirred and combined by cannula with a cold (-78 °C), degassed solution of 0.12 g (0.36 mmol) of **8** in 10 mL of dichloromethane. Stirring was continued at -20 °C for 45 h. IR analysis of a small aliquot showed only the presence of unreacted **6**. The starting material **6** (0.062 g, 72%) was recovered by removal of the solvent under reduced pressure and chromatography on activity IV alumina.

Run 7. A solution of 0.1 g of **6** in 3 mL of dichloromethane was stirred under a carbon monoxide atmosphere at room temperature for 5 h. The IR spectrum of the reaction mixture showed no C=O peaks attributable to **4**, only those of unreacted **6**.

The Reaction of Dicarbonyl(η^5-cyclopentadienyl)(*exo*-2-norbornyl)iron (7) and Triphenylmethyl Tetrafluoroborate (8). Run 8. A solution containing 0.258 (0.782 mmol) of **8** in 5 mL of dichloromethane was added by cannula to a stirred solution of 0.207 g (0.761 mmol) of **7** in 5 mL of dichloromethane. The mixture was stirred at room temperature for 7 h, cooled in an ice bath, combined dropwise with 16 mL of ether, allowed to stand at 0 °C for $\sim$1 h, and filtered through a glass frit. The crystalline solid was washed with three 7-mL portions of ether. The combined filtrate and washings were concentrated under reduced pressure to $\sim$3 mL and chromatographed on activity III alumina at 10 °C using 2% ether-in-pentane as eluant. Two yellow fractions separated: the first, 55 mg, consisted mainly of unreacted **7** and the second, 54 mg, of **5**. Both fractions contained some triphenylmethane (**10**). Each fraction was rechromatographed on alumina giving 0.035 g (17%) of **7** and 0.033 g (17%) of **5**. The solid material from the diethyl ether precipitation was washed through the frit with dichloromethane. Evaporation of the washings under reduced pressure gave 0.046 g of residue which by $^{13}C\{^1H\}$ NMR consisted of **9** and **10**. Recrystallization from diethyl ether/dichloromethane gave 0.025 g (9%)—11% when corrected for recovered **5**—of pure **9**.

Run 9. To an argon-blanketed, stirred solution of 0.120 g (0.444 mmol) of **7** in 1 mL of dichloromethane cooled in a dry ice–isopropyl alcohol bath was added by cannula 0.162 g (0.491 mmol) of **8** in 3 mL of dichloromethane. The mixture was stirred at -20 °C and monitored by IR as described for the endo complex, "run 1". Only unreacted starting material was detected after 24 h. The argon atmosphere was then replaced with CO, and the solution was stirred for an additional 2 h. Now the only detectable CO stretches were those of the acyl complex **5** (2002, 1948 cm^{-1}). The solution was cooled to -78 °C and combined with 8 mL of ether. The precipitated, unreacted **8** was separated by filtration and washed with 3 mL of ether. Column chromatography of the combined filtrate and washings as described in "run 8" yielded 0.053 g (40%) of **5**, the only identifiable complexed product, mixed with a trace of benzophenone.

***endo*-2-Carbethoxy-*exo*-2-deuterio-5-norbornene (13).** A solution containing 2.0 g (13 mmol) of the mixed isomeric esters **11** and **12** (prepared by treatment of the commercially available [Frinton Laboratories] mixed acids with diazomethane) and $\sim$12 mmol of sodium ethoxide in 13 mL of anhydrous C_2H_5OD was heated under reflux for 4 h. The mixture was cooled, combined with 150 mL of pentane, and washed with four 4-mL portions of D_2O. The pentane solution was dried (Na_2SO_4) and the solvent evaporated under reduced pressure to give 1.9 g (88%) of a 55:45 mixture of *endo*- and *exo*-2-carbethoxy-5-norbornene, **13** and **14**, respectively. The mixture was separated by GLPC at 125 °C on a 20 ft × $^3/_8$ in. column packed with 20% diethylene glycol succinate (DEGS) on 45/60 mesh Chromosorb P. Mass spectral analysis of each isomer showed >90% d_1 and <10% d_0.

***exo*-2-Deuterio-*endo*-2-norbornanecarboxylic Acid (15).** A solution of 0.830 g (4.96 mmol) of **13** in 5 mL of CH_3OD was combined with an equal volume of 5% NaOH in D_2O. The mixture was heated under reflux for 2 h, cooled, and washed with 50 mL of diethyl ether. The acidified solution was extracted with four 50-mL portions of ether, the combined extract was washed with saturated sodium chloride and dried over Na_2SO_4, the solvent was removed under aspirator pressure, and the residual oil was combined with 10 mL of methanol and 0.25 g of 10% palladium-on-charcoal. The mixture was hydrogenated for 2 h at atmospheric pressure. The catalyst was removed by filtration and the solvent evaporated under aspirator pressure to give 0.488 g (70%) of the crystalline acid **15**. The $^{13}C\{^1H\}$ NMR spectrum of this material is identical with that reported for the nondeuterated acid[46] except for the singlet at δ 46.3 (C-2) which now appears as a triplet of reduced intensity shifted slightly to higher field.[47]

***exo*-2-Deuterio-*endo*-2-norbornanecarbonyl Chloride (16).** To a solution of 0.48 g (3.4 mmol) of **15** in 10 mL of anhydrous benzene at room temperature was added dropwise with stirring 0.50 mL (5.8 mmol) of oxalyl chloride. The mixture was slowly warmed to reflux temperature. After 30-min reflux, the solvent was removed by distillation at atmospheric pressure. Distillation of the residue under reduced pressure gave 0.433 g (81%) of a colorless liquid, bp 55–60 °C (3 mm), which was used without further purification or characterization.

Dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(*exo*-2-deuterionorbornyl)carbonyl]iron (17) was prepared in the

---

[46] Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107–7120.

[47] Stothers, J. B. in "Topics in Carbon-13 NMR Spectroscopy"; Levy, G. C., Ed.; Wiley: New York, 1974; Chapter 6.

same manner as **4** in 70% yield using 0.43 g (2.7 mmol) of **16**. The $^{13}C\{^1H\}$ NMR spectrum of **17** is identical with that of **4** except for the deuterium splitting and upfield isotopic shift[47] of the C-2 singlet at δ 76.4.

Dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(*exo*-2-deuterionorbornyl)]iron (18) was prepared in the same manner as **6** in 77% yield using 0.28 g (0.93 mmol) of **17** in 180 mL of pentane. The $^{13}C\{^1H\}$ NMR spectrum of the product is consistent with structure **18**: all signals except that at δ 27.8, which is split and shifted slightly upfield by deuterium,[47] coincide with the corresponding resonances in the spectrum of **6**.

The reaction of dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(*exo*-2-deuterionorbornyl)]iron (18) and triphenylmethyl tetrafluoroborate (8) was monitored by $^{13}C\{^1H\}$ NMR on the NR-80. Samples of 0.10 g (0.40 mmol) of **18** and 0.15 g (0.50 mmol) of **8** were combined with 1.25 mL of 20% CD_2Cl_2/CH_2Cl_2 in a 5-mm tube and allowed to react at probe temperature (~33 °C). After 10 h no unreacted starting material, **18**, could be detected. The only identifiable absorptions were those of **10** and of dicarbonyl(η^5-cyclopentadienyl)(*exo*-η^2-2-deuterionorbornene)iron (**23**). The relative intensity of the singlet at δ 77.7 (C-2, C-3) is about 60% that of the corresponding resonance of the nondeuterated π-complex **9**. The triphenylmethane, recovered from the reaction mixture by chromatography on activity III alumina, contains less than 1% deuterium by mass spectroscopy.

Dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(5-norbornenyl)carbonyl]iron (20) was prepared in the same manner as **4**: adding 1.24 g (5.74 mmol) of **3** to a solution of 0.69 g (4.4 mmol) of 5-norbornene-*endo*-2-carbonyl chloride[48] (**19**) in 10 mL of THF and stirring at room temperature for 18 h. Workup followed by chromatography on activity III alumina with 4% diethyl ether-in-pentane as eluant yielded 1.11 g (84%) of yellow, crystalline **20**: mp 74–76 °C; IR (CH_2Cl_2) 2017, 1960 (C≡O), 1660 cm^{-1} (>C═O); ^1H NMR (CCl_4) δ 5.85 (m, 2 H, ═CH), 4.77 (s, Cp) 3.40 (m, >CHCOFp), 3.25 (b s, >CH, bridgehead), 2.79 (b s >CH, bridgehead) 1.3 (m, 4 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 255.5 (>C═O), 214.9 (–C≡O), 136.4 (C-5), 132.6 (C-6), 86.6 (Cp), 73.5 (C-2), 48.7 (C-1), 46.0 (C-7), 42.6 (C-4), 29.5 (C-3); MS, *m/e* 298 $[M]^{+\cdot}$, 270 $[M - CO]^{+\cdot}$, 242 $[M - 2CO]^{+\cdot}$, 121 $[M - Fp]^{+\cdot}$. Anal. Calcd for $C_{15}H_{14}FeO_3$: C, 60.43; H, 4.73. Found: C, 60.58; H, 4.78.

Dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(*exo*,*exo*-5,6-dideuterionorbornyl)carbonyl]iron (21). A solution of 0.95 g (3.2 mmol) of **20** in 8 mL of absolute ethanol was combined with 0.25 g of 10% palladium-on-charcoal and stirred under a dideuterium atmosphere for 2 h. The mixture was filtered and the solvent removed on a rotary evaporator. Chromatography of the residual solid on activity III alumina at 10 °C with 2% diethyl ether-in-pentane as eluant gave 0.70 g (73%) of a yellow solid, the $^{13}C\{^1H\}$ NMR spectrum of which is consistent with structure **21**: all resonances coincide with those of **4** except for the signals at δ 29.3 and 24.4 which are of reduced intensity and show splitting and slight upfield shifts characteristic of deuteration at C-5 and C-6.[47]

Dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(*exo*,*exo*-5,6-dideuterionorbornyl)]iron (22) was prepared in 89% yield by irradiation of 0.31 g (1.0 mmol) of **21** as described in the case of the nondeuterated analogue **6**. The $^{13}C\{^1H\}$ NMR spectrum is identical with that of **6** except for the splitting and the slight upfield shift of the singlets at δ 30.1 and 29.0 caused by deuterium at C-5 and C-6.[47]

The reaction of dicarbonyl(η^5-cyclopentadienyl)[*endo*-2-(*exo*,*exo*-5,6-dideuterionorbornyl)]iron (22) and triphenylmethyl tetrafluoroborate (8) for 36 h at room temperature as described for **6** (run 1) gave 49% of π-complex. The product **25** was shown to be deuterated exclusively at C-5 and C-6 by the $^{13}C\{^1H\}$ NMR spectrum: only the resonance at δ 25.4 (due to C-5 and C-6) is coupled and shifted slightly upfield by the deuteriums;[47] all other resonances appear as singlets whose chemical shifts are identical with those of the corresponding signals in the nondeuterated π-complex **9**.

The Stability of Norbornene (27) in the Presence of Triphenylmethyl Radical (8·). A 0.07-g sample of **27** in 2 mL of nitrogen-blanketed dichloromethane was added to 4 mL of a 0.19 M solution of **8·**[32] in dichloromethane under nitrogen at 0 °C. After 42 h at this temperature the solvent was removed by vacuum evaporation. The waxy, yellow-brown solid was washed with four 10-mL portions of diethyl ether and dried under vacuum. As indicated by the absence of vinyl hydrogen resonances in the ^1H NMR (CD_3COCD_3) no **27** remained.

The Stability of Dicarbonyl(η^5-cyclopentadienyl)(η^2-*exo*-norbornene)iron Tetrafluoroborate (9) in the Presence of Triphenylmethyl Radical (8·). A 0.13-g sample of **9** dissolved in 2 mL of nitrogen-blanketed dichloromethane was added to 5 mL of a 0.072 M solution of **8·**[32] in nitrogen-blanketed dichloromethane at 0 °C. After 28 h the solution was concentrated to ~1 mL and mixed at –78 °C with an equal amount of cold diethyl ether. A yellow precipitate, identical in all respects with **9**, formed and was isolated in 84% yield. There was no evidence of polymerization.

Cyclic voltammetry measurements were made using a jacketed cell similar to the design of Van Duyne and Reilly[49] thermostated at ~0 °C under an atmosphere of nitrogen. To minimize Ohmic drop, the distance between the carbon working electrode and the tip of the salt bridge was held to less than 2 mm. The dichloromethane solutions were 3 × 10^{-3} M in sample and 0.1 M in tetraethylammonium perchlorate (TEAP). All scans were initially swept positive from an initial potential of 0.65–1.5 V. The return sweep went to –0.7 V. All potentials are relative to a saturated calomel reference electrode, cf. Table II.

Electron paramagnetic resonance studies were carried out in flat, quartz cells at –20 °C and at ambient temperature. Nitrogen-blanketed solutions 0.08 M in **8** and in **6** or **7** in dichloromethane were allowed to react for 2 h, and then the spectrum of each was recorded. The spectra were calibrated by comparison with a solution of triphenylmethyl radical[32] (**8·**), *g* = 2.0024.[27] After reaction at ambient temperature both spectra showed a sharp, intense resonance at *g* = 2.002 corresponding to **8·** and a broader less intense one at *g* = 2.0665, but the signals of the reaction mixture from **7** were about 100 times as intense as those of the mixture from **6**. The same resonances were observed after reaction at –20 °C but were now of comparable intensity in each mixture.

Acknowledgment. We are indebted to Professor Horacio Farach and Charles P. Poole of the Physics and Astronomy Department for help with the EPR measurements and to Professor Robert H. Philp for his interest in and help with the cyclic voltammetry. We thank Professors Philp and Daniel L. Reger for many helpful discussions and Professor Dennis Evans of the Chemistry Department, University of Wisconsin, Madison, for providing the catalytic analysis cited earlier. Partial support for this work was provided by the National Science Foundation under its EPSCOR program.

Registry No. **1**, 934-27-0; **2**, 1195-11-5; **3**, 60039-75-0; **4**, 93757-21-2; $\mathbf{4}^{+\cdot}$, 93757-22-3; **5**, 93859-91-7; $\mathbf{5}^{+\cdot}$, 93859-92-8; **6**, 93757-23-4; $\mathbf{6}^{+\cdot}$, 93757-24-5; **7**, 93859-93-9; $\mathbf{7}^{+\cdot}$, 93859-94-0; **8**, 341-02-6; $\mathbf{8}^{+}$, 13948-08-8; **8·**, 2216-49-1; **9**, 60363-48-6; **10**, 519-73-3; **11**, 2903-75-5; **12**, 769-85-7; **13**, 93757-17-6; **14**, 93757-18-7; **15**, 93757-19-8; **16**, 93757-20-1; **17**, 93757-25-6; **18**, 93757-26-7; **19**, 37750-50-8; **20**, 93757-27-8; **21**, 93757-28-9; **22**, 93757-29-0; **23**, 93757-31-4; **25**, 93781-82-9; **27**, 498-66-8; $Fp^+BF_4^-$, 93757-32-5; *endo*-2-carboxy-5-norbornene, 1195-12-6; *exo*-2-carboxy-5-norbornene, 934-30-5.

---

[48] Parham, W. E.; Hunter, W. T.; Hanson, R. *J. Am. Chem. Soc.* **1951**, *73*, 5068–5070.

[49] Van Duyne, R. P.; Reilly, C. N. *Anal. Chem.* **1972**, *44*, 142–152.