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Reactions of $(CO)_2(\eta^5\text{-}C_5H_5)Fe$ Alkyls and $Ph_3C^+BF_4^-$: A Search for Hydrogen-Atom Abstraction following One-Electron-Transfer

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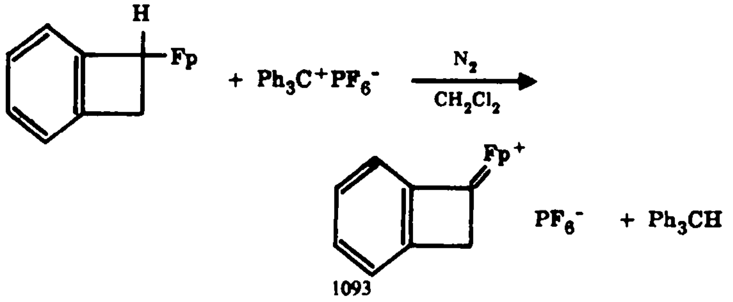
Abstract—The reaction products of $Ph_3C^+BF_4^-$ (**2**) and $(CO)_2$-$(\eta^5\text{-}C_5H_5)$Fe-(2-cyclopropylethyl) (**1**), -neopentyl (**10**), and -(1-norbornylcarbinyl) (**13**) under N_2 and under CO have been determined in an effort to detect evidence of hydrogen-atom abstraction from the 17e, Fe(III) cation-radical intermediate produced by one-electron transfer to the starting cation. None was observed. Labeling studies reveal that migratory CO insertion to produce $(CO)_2(\eta^5\text{-}C_5H_5)$FeCO(2-cyclopropylethyl) (**8**) is accompanied by β- not α-hydride abstraction to form $[(CO)_2(\eta^5\text{-}C_5H_5)Fe(\eta^2\text{-cyclopropylethene})]^+BF_4^-$ (**3**) when **1** reacts with **2** under CO. The insertion is catalytic in **2**. Hydrogen is not lost from **10** or **13** under these conditions; the acyl complexes $(CO)_2(\eta^5\text{-}C_5H_5)FeCOCH_2$-$C(CH_3)_3$ (**11**), 71%, or $(CO)_2(\eta^5\text{-}C_5H_5)$FeCO(1-norbornylcarbinyl) (**14**), 80%, respectively, are the only organometallic products.

INTRODUCTION

Dicarbonylcyclopentadienyliron- (Fp) and other midfirst-row transition-metal alkyls which have an appropriately oriented β-hydrogen typically react with triphenylmethyl cation to form cationic η^2-olefin complexes and triphenylmethane, e.g. eq 1.[1]

$$FpCH_2CH_2CH_3 + Ph_3C^+ClO_4^- \xrightarrow[THF]{} [Fp(\eta^2\text{-}CH_2{=}CHCH_3)]^+ClO_4^- + Ph_3CH \quad (1)$$

The reaction is thought to involve the concerted loss of hydride antiperiplanar to the metal moiety.[2] Only one Fp alkyl is known to transfer α- rather than β-hydrogen under these conditions, eq 2.[3]



(2)

This bias for β-hydrogen loss on the part of first-row transition-metal alkyls contrasts with the preferential α-hydrogen transfer that occurs between several third-row alkyls and triphenylmethyl cation,[4,5] e.g. eqs 3 , 4 and 5.

$$\mathrm{Cp(NO)(Ph_3P)ReCH_2R} + \mathrm{Ph_3C^+PF_6^-} \xrightarrow[\mathrm{CD_2Cl_2}]{\mathrm{N_2},\,-78^\circ\mathrm{C}}$$

$$[\mathrm{Cp(NO)(Ph_3P)Re{=}CHR}]^+\mathrm{PF_6^-} + \mathrm{Ph_3CH} \qquad (3,4)$$

$$\mathrm{R{=}H}\ (87\%)^{4b};\ \mathrm{R{=}C_2H_5}\ (78\%)^{4a}$$

$$\mathrm{Cp_2(C_2H_5)WCH_3} + \mathrm{Ph_3C^+BF_4^-} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{N_2},\,25^\circ\mathrm{C}}$$

$$[\mathrm{Cp_2WH(\eta^2\text{-}CH_2{=}CHCH_3)}]^+\mathrm{BF_4^-} + \mathrm{Ph_3CH} \qquad (5)$$

$$89\%$$

Some α-hydrogen abstractions clearly involve initial one-electron transfer to triphenylmethyl cation. Cooper, *et al.* have demonstrated that the tungsten dialkyl, eq 5, reacts in this manner – rapid oxidation followed by slower hydrogen atom transfer to triphenylmethyl radical,[5] Scheme 1. Likewise, Gladysz, *et al.* report that

$$\mathrm{Cp_2(C_2H_5)WCD_3} + \mathrm{Ph_3C^+} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{N_2},\,-78^\circ\mathrm{C}} [\mathrm{Cp_2(C_2H_5)WCD_3}]^{+\cdot} + \mathrm{Ph_3C\cdot}$$

$$[\mathrm{Cp_2(C_2H_5)WCD_3}]^{+\cdot} + \mathrm{Ph_3C\cdot} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{N_2},\,21^\circ\mathrm{C}} \mathrm{Ph_3CD} + \left([\mathrm{Cp_2(C_2H_5)W{=}CD_2}]^+\right)$$

$$\left([\mathrm{Cp_2(C_2H_5)W{=}CD_2}]^+\right) \xrightarrow{\mathrm{P(CH_3)_2Ph}} [\mathrm{Cp_2(C_2H_5)WCD_2P(CH_3)_2Ph}]^+$$

Scheme 1

the ^{1}H NMR of $\mathrm{Cp(NO)(Ph_3P)ReCH_2C(CH_3)_3}$ in $\mathrm{CD_2Cl_2}$ at -79°C shows extensive line broadening in the presence of this cation. Though no rhenium (I) alkylidene could be detected, triphenylmethane was observed in some reaction mixtures,[4a] *cf.* Scheme 2.

$$\mathrm{Cp(NO)(Ph_3P)ReCH_2C(CH_3)_3} + \mathrm{Ph_3C^+} \longrightarrow$$

$$\left([\mathrm{Cp(NO)(Ph_3P)ReCH_2C(CH_3)_3}]^{+\cdot}\right) + \mathrm{Ph_3C\cdot} \longrightarrow$$

$$\left([\mathrm{Cp(NO)(Ph_3P)Re{=}CHC(CH_3)_3}]^+\right) + \mathrm{Ph_3CH}$$

$$?$$

Scheme 2

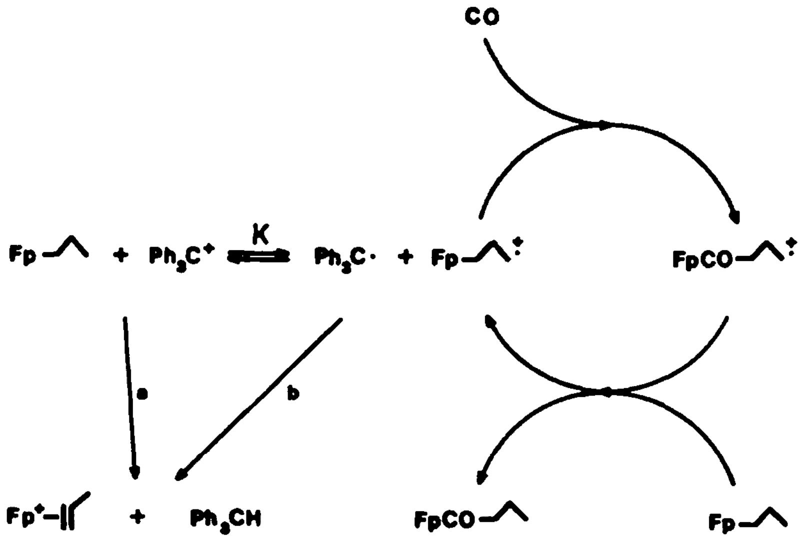
Both Gladysz, *et al.* and Cooper and Hayes have speculated that α-hydrogen loss may be uniquely associated with initial one-electron transfer.[4,5] They reason that, as the first-row transition-metal alkyls are more difficult to oxidize,[6] they should show less tendency to lose α-hydrogen than their third-row counterparts.[4,7]

This speculation caught our attention for we had noted that at reduced temperatures in the presence of CO, carbonyl insertion competes with β-hydrogen abstraction in the reactions of several Fp alkyls and triphenylmethyl cation,[7] eq 6.

$$FpCH_2CH_2CH_3 + Ph_3C^+BF_4^- + CO \xrightarrow[CH_2Cl_2]{-78^\circ C}$$

$$\underset{71\%}{[Fp(\eta^2\text{-}CH_2{=}CHCH_3)]^+BF_4^-} + \underset{13\%}{FpCOCH_2CH_2CH_3} + Ph_3CH \quad (6)$$

The insertion is a radical-chain process catalyzed by reversible[8,9] one-electron transfer to the cation, Scheme 3. Its observation in competition with the formation of



Scheme 3

η^2-olefin complex clearly indicates that a first-row Fp alkyl can be oxidized by triphenylmethyl cation under conditions compatible with β-hydrogen loss. Thus, the possibility of β-hydrogen-atom abstraction arises in these cases as well (path b, Scheme 3).

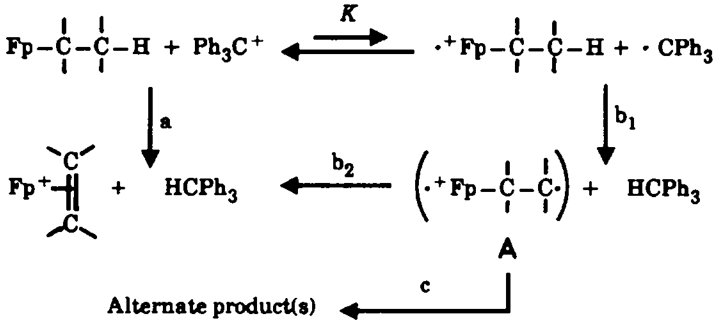
This possibility is not a probability since the equilibrium constant, K, for electron transfer to the cation is quite small: chemical studies suggest less than 10^{-4} while electrochemical measurements[8,9] indicate $10^{-10}-10^{-12}$. The observed, competitive insertion is possible only because it is highly favored in the 17e radical-cation relative to the neutral 18e Fp alkyl and because concerted loss of β-hydride is slowed by stereoelectronic factors and/or the reduced temperature at which the reaction is carried out.[8b]

Conversely, the transfer of a β-hydrogen atom from a 17e cation-radical might also be favored for it would lead to a more stable, 18e, cationic η^2-olefin complex. In fact, because cationic Fp alkylidenes routinely rearrange to cationic η^2-olefin complexes,[10] eq 7, β-hydrogen-atom abstraction should be favored thermodynamically over α-hydrogen-atom loss from a 17e cation-radical. Here we describe attempts to detect hydrogen-atom transfer in the reaction of triphenylmethyl cation with some Fp alkyls.

$$\cdot(Fp{=}CHCH_2CH_3)^+ \xrightarrow{\sim H} [Fp(\eta^2\text{-}CH_2{=}CHCH_3)]^+ \quad (7)$$

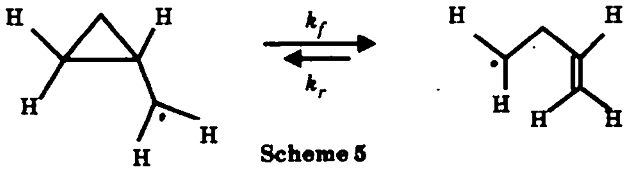
RESULTS AND DISCUSSION

A fairly convincing demonstration of electron-transfer/β-hydrogen-atom loss would be demonstrable diversion of the putative cation-diradical intermediate, **A**, Scheme 4, to an alternate product (path c).



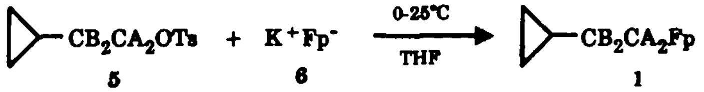
Scheme 4

An approach frequently utilized to display the development of an unpaired electron at a particular carbon during the course of a radical reaction is the rearrangement of cyclopropylcarbinyl to homoallyl, Scheme 5.[11] Ingold, *et al.* report



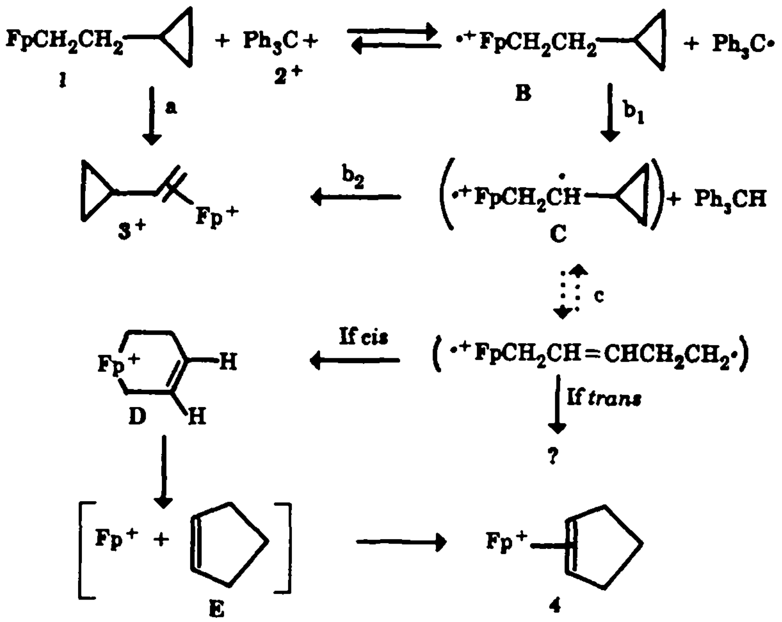
Scheme 5

that at 25°C $k_f \approx 6.5\text{x}10^7\ s^{-1}$, $k_r \approx 5\text{x}10^3\ s^{-1}$ ($4.1\text{x}10^5$ and $2.1\ s^{-1}$, respectively, at -78°C),[12] thus radical reactions which develop significant spin density at a cyclopropylcarbinyl carbon usually form ring-opened products. Should the reaction of $FpCH_2CH_2\overline{CHCH_2CH_2}$ (**1a**) and **2** occur by electron-transfer/hydrogen-atom-abstraction (path "b", Scheme 4) rather than by concerted loss of hydride (path "a", Scheme 4) a product other than $[Fp(\eta^2\text{-}CH_2{=}CH\overline{CHCH_2CH_2})]^+BF_4^-$ (**3a**),[10c] perhaps $[Fp(\eta^2\text{-}\overline{CH_2CH{=}CHCH_2CH_2})]^+BF_4^-$ (**4a**),[13] could result, *cf.* Scheme 6.[14] To test this possibility we have prepared the 2-cyclopropylethyl complexes, **1**, as outlined in eq 8 and examined their reaction with **2** under conditions compatible with electron transfer.[8]



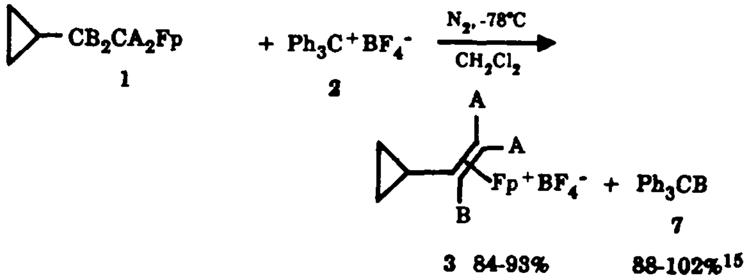
(8)

a: A = B = H b: A = D, B = H c: A = H, B = D



Scheme 6

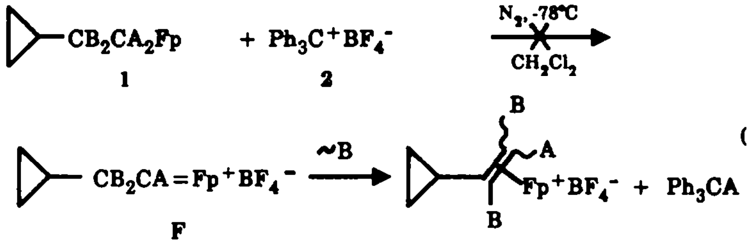
When stirred under N_2 with 1.1 eq of **2** in CH_2Cl_2 at reduced temperature 1.0 eq of **1a** forms crystalline **3a** in 93% yield, eq 9.



(9)

a: A = B = H b: A = D, B = H c: A = H, B = D

Under identical conditions the dideuterium-labeled complex **1b** forms **3b** and triphenylmethane, **7b**, while **1c** yields **3c** and triphenyldeuteriomethane, **7c**.[15] These results confirm that β- not α-hydrogen is lost and exclude the possibility of a cationic alkylidene intermediate, $(\text{Fp}=\text{CACB}_2\overline{\text{CHCH}_2\text{CH}_2})^+\text{BF}_4^-$ (F) being formed then undergoing a β-to-α hydrogen shift[10] to produce the observed η^2-olefin complex, eq 10.

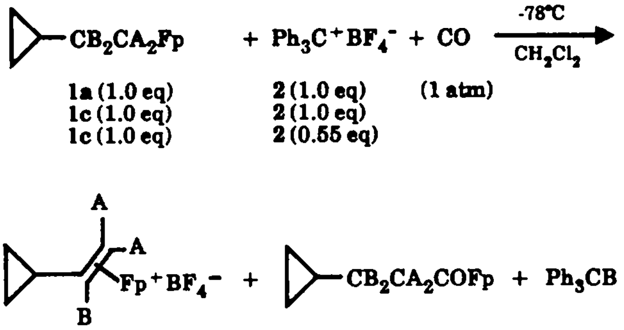


(10)

a: A = B = H b: A = D, B = H c: A = H, B = D

In spite of the fact that no product of insertion or rearrangement is isolated when 1 and 2 react at reduced temperature under nitrogen, eq 9, there is evidence of one-electron transfer under these conditions. When cold, initially yellow solutions of 1 and 2 in CH_2Cl_2 are mixed at -78°C a clear, green-brown solution results whose color persists at that temperature but changes to yellow as the mixture is allowed to warm to -20°C. Similar color changes have been observed to accompany CO insertion in 17e Fe(III) alkyls.[8,9a]

To confirm that one-electron transfer to triphenylmethyl cation (2^+) occurs we repeated the reactions of 1 and 2 under CO instead of N_2. When 1.0 eq of 1a or 1c and 1.0 eq of 2 are used both 3 and the insertion product, 8, are formed, eq 11. We attribute the higher proportion of insertion evident with 1c to a primary kinetic isotope effect, $k_H/k_D > 1$, that retards the rate of elimination in this β-dideuterated



(11)

3a 85%	8a 7%	7a 87%
3c 50%[16]	8c 9%[16]	7c
3c 42%	8c 52%	7c

a: A = B = H c: A = H, B = D

isomer.[16] Its presence emphasizes the fact that β- not α-hydrogen (deuterium) is lost in the rate-limiting step of the elimination.

The insertion is catalytic in cation 2^+ as revealed by the fact that when the reaction of 1c is repeated under CO with but half an equivalent of cation, eq 11, the combined isolated yield of 3c and 8c (0.94 eq) exceeds the amount of 2 (0.55 eq) initially present in the reaction mixture.[8a] Since neither insertion nor elimination occur in the absence of **2** the reactions of **1** with **2** exhibit the characteristics of competitive β-elimination and redox-catalyzed CO insertion delineated earlier, *cf.* Scheme 4.[8c]

Thus, under conditions consistent with competitive one-electron oxidation, we can find no evidence that the β-hydrogen (deuterium) which is abstracted from 1 when 1 is converted to 3 is lost as a hydrogen (deuterium) atom from a cation-radical intermediate (path c, Scheme 6) rather than as a hydride (deuteride) from the starting Fp alkyl (path a). It is possible of course that this particular cyclopropylcarbinyl/homoallyl rearrangement (path c, Scheme 6) is either too slow or too thermodynamically unfavorable relative to path b_2 to intercept a cation diradical such as C[18] but we know of no evidence supporting either of these possibilities.

In view of our inability to demonstrate β-hydrogen-atom loss from an Fe(III) cation-radical (path "b", Scheme 4), it seemed appropriate to attempt α-hydrogen-atom abstraction from a comparable intermediate. To avoid competing β-hydride transfer to triphenylmethyl cation (2^+), eq 1, we have utilized an Fp alkyl having no β-hydrogens. Two examples had been studied previously. Green, *et al.*.[1a] report $FpCH_3$ to be essentially unreactive toward triphenylmethyl perchlorate: after 10 h a little $(Fp{\cdot}H_2O)^+$ was noted but no $[Fp(\eta^2\text{-ethene})]^+ClO_4^-$ or triphenylmethane, expected products of α-hydrogen abstraction,[20] were observed, eq 12. Giering, *et al.*[3a] report only 1,1,1,2-tetraphenylethane as the reaction product of $FpCH_2Ph$ and triphenylmethyl hexafluorophosphate, eq 13. Although it is not clear that either of these reactions was attempted under conditions appropriate for one-electron transfer, rather than reexamine them we decided to concentrate instead on $FpCH_2C(CH_3)_3$ (**10**) as it promised a better comparison with the recent work of Gladysz, *et al.*[4a], Scheme 2.

$$FpCH_3 + Ph_3C^+ClO_4^- \xrightarrow[\text{THF}]{10\text{ h}} (Fp{\cdot}H_2O)^+ClO_4^- + \;? \qquad (12)$$

$$FpCH_2Ph + Ph_3C^+PF_6^- \longrightarrow Ph_3CCH_2Ph \qquad (13)$$

The required starting material was prepared from pivaloyl chloride as outlined in eq 14, 15.[21] When yellow solutions of **2** and **10** in CH_2Cl_2 are mixed under one atmosphere of CO at -78°C and the resulting green solution[9a] is stirred for 4 h at that temperature, then at -20°C for 2.5 h, the product mixture contains only $FpCOCH_2C(CH_3)_3$ (**11**), the insertion product, eq 16. No unreacted starting material **10**,

$$\underset{}{(CH_3)_3CCOCl} + \underset{\mathbf{6}}{K^+Fp^-} \xrightarrow[CH_2Cl_2]{N_2,\,25^\circ C} \underset{\mathbf{9}\;\;55\%}{(CH_3)_3CCOFp} \qquad (14)$$

$$\underset{\mathbf{9}}{(CH_3)_3CCOFp} + BH_3{\cdot}THF \xrightarrow[\text{THF}]{N_2,\,0^\circ C} \underset{\mathbf{10}\;\;39\%}{(CH_3)_3CCH_2Fp} \qquad (15)$$

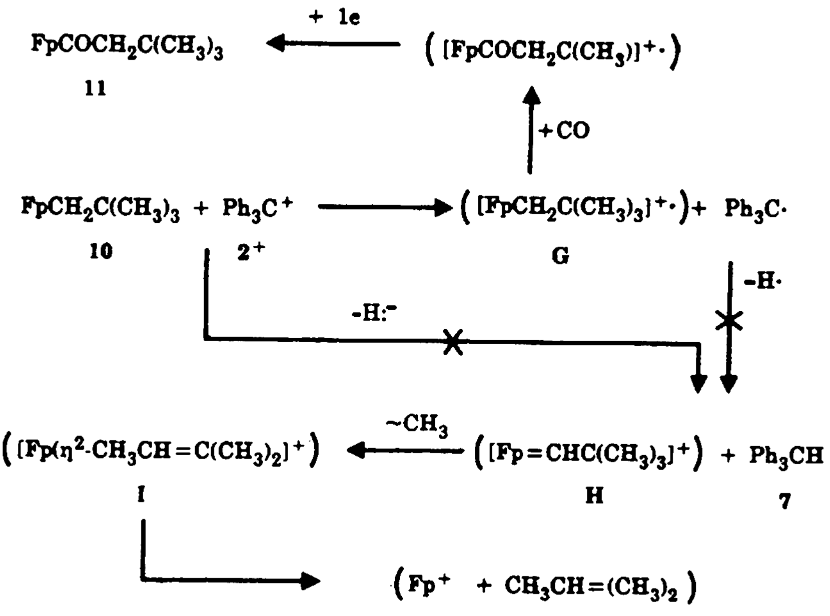
$$\underset{\mathbf{10}}{FpCH_2C(CH_3)_3} + \underset{\mathbf{2}}{Ph_3C^+BF_4^-} + CO \xrightarrow[CH_2Cl_2]{1)\ -78°C,\ 4\ h \quad 2)\ -20°C,\ 2.5\ h} \underset{\mathbf{11}\ \ 71\%}{FpCOCH_2C(CH_3)_3} \qquad (16)$$

$[Fp{=}CHC(CH_3)_3]^+BF_4^-$, or triphenylmethane is apparent. When carried out analogously under N_2 instead of CO the reaction exhibits a more persistent green color but the reaction mixture contains only unreacted starting material. After an additional 20 h at room temperature, 10 is no longer evident; workup reveals a small amount of 11, some triphenylmethanol and benzophenone, and a polyaromatic which we believe may be 3,3-dimethyl-1,1,1-triphenylbutane,[3a] eq 17. The transient green

$$\underset{\mathbf{10}}{FpCH_2C(CH_3)_3} + \underset{\mathbf{2}}{Ph_3C^+BF_4^-} \xrightarrow[N_2,\ CH_2Cl_2]{1)\ -78°C,\ 4\ h \quad 2)\ -20°C,\ 2.5\ h} \xrightarrow[N_2,\ CH_2Cl_2]{\sim 25°C,\ 20\ h}$$

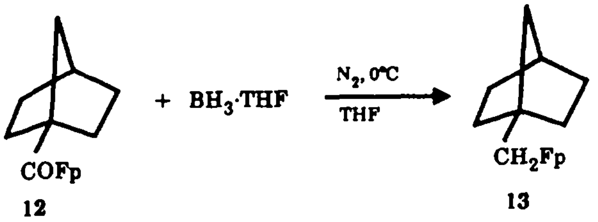
$$\underset{\mathbf{11}\ \ 17\%}{FpCOCH_2C(CH_3)_3} + Ph_3COH + Ph_2C{=}O + Ph_3CCH_2C(CH_3)_3 \qquad (17)$$

color,[9a] the formation of the acyl complex,[8a] 11, and the observation of benzophenone after workup[22] suggest one-electron transfer to produce cation-radical G and triphenylmethyl radical, Scheme 7. The absence of [Fp-alkylidene]$^+$ (H), of [Fp(η^2-alkene)]$^+$ (I), and probably of free alkene as well, indicate that α-hydrogen is not lost, either as an atom from the cation-radical G or as hydride from the starting material, 10.



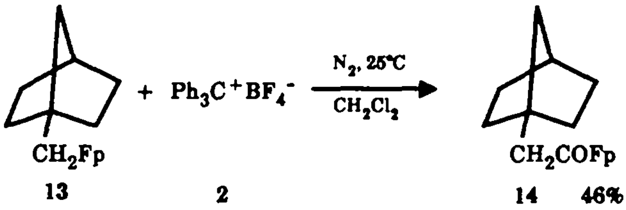
Scheme 7

Thinking that perhaps the steric bulk of the triphenylmethyl cation (2^+) and the hindered nature of the neopentyl hydrogens in 10 may inhibit hydrogen transfer[23] we attempted a similar reaction with the slightly less hindered $FpCH_2$-(1-norbornyl) (13) prepared by reduction[21] of the known acyl,[24] 12, eq 18. After 43 h



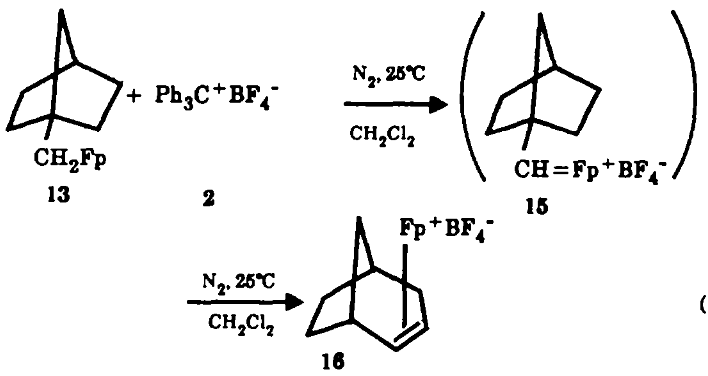
(18)

under nitrogen in dichloromethane at ambient temperature an approximately equimolar mixture of 13 and 2 forms $FpCOCH_2$(1-norbornyl) (14) in 46% yield, eq 19.



(19)

When carried out under CO instead of N_2 the yield of 14 is 80%. No other organometallics were detected. That α-hydrogen is not lost in this case either is evident from the absence of 16, the rearrangement product of the cationic Fp alkylidene, 15, that would have resulted, eq 20.[24]



(20)

There are many similarities in the behavior of Fp neopentyls and $Cp(NO)(Ph_3P)ReCH_2(CH_3)_3$ toward triphenylmethyl cation.[4a] In no case is α-hydride abstracted even though it is in many nonneopentyl Re(I) alkyls.[4a,25] Instead, one-electron transfer occurs in all cases though in none is it followed by α-hydrogen-atom loss from the metal cation-radical to the resulting triphenylmethyl radical as happens in some $[Cp_2WR_2]^{+\cdot}$ cases (Scheme 1).[5a] Insertion of CO follows in the Fe(III) cation-radicals but the Re(II) cation-radical, lacking a terminal CO, reacts or decomposes another way.

Our studies and those of Gladysz, *et al.* constitute interesting examples of sterically induced mechanistic switching between alternate electronic modes of reaction. Neopentyl-type α-hydrogens are apparently too hindered to be abstracted either as hydride by the bulky triphenylmethyl cation or as an atom by the corresponding radical. One-electron transfer, not being subject to such steric constraint,[28] occurs instead.

CONCLUSION

We can find no evidence of an electron-transfer/hydrogen-atom-abstraction path in the reaction of Fp alkyls with triphenylmethyl cation. Hydrogen-atom abstraction by triphenylmethyl radical from a 17e, Fe(III) cation-radical apparently is not the kinetically favored process that we had hoped it might be. Unlike CO insertion following one-electron oxidation, it is not competitive with concerted β-hydride abstraction.

EXPERIMENTAL[29]

2,2-Dideuterio-2-cyclopropylethanol.

Methyl cyclopropylacetate (1.5 g, 13.0 mmol), prepared according to the procedure of Turnbull and Wallis[30] was combined with an ~0.3 M solution of sodium methoxide in O-deuteriomethanol. The mixture was heated under reflux for an hour, cooled, combined with 100 ml of pentane and extracted with 15 ml of D_2O. The methanol-deuterium oxide layer was extracted with two additional portions of pentane. The extract was dried (Na_2SO_4) and the solvent was distilled at atmospheric pressure. The residue was treated with a second 15-ml portion of 0.3 M sodium methoxide in deuteriomethanol. Work-up, followed by distillation at atmospheric pressure (bp 131-134°C) gave 0.871 g (7.51 mmol, 57%) of methyl 2-cyclopropyl-2,2-dideuterioacetate: ^1H NMR (C_6D_6) δ 3.32 (s, OCH_3), ~1.0-0 (m, 5H, $\text{-}\overline{\text{CHCH}_2\text{C}}\text{H}_2$).

Reduction of the dideuterio ester with lithium aluminum hydride (0.928 g, 24.0 mmol) gave 2-cyclopropyl-2,2-dideuterioethanol in 76% yield: ^1H NMR (CCl_4) δ 3.69 (s, 2H), ~2 (br s, concentration dependent, OH), ~1.0-0 (m, 5H).

2-Cyclopropyl-1,1-dideuterioethanol was prepared in 72% yield by the reduction of methyl cyclopropylacetate (1.48 g, 13.0 mmol) with lithium aluminum deuteride (1.0 g, 24 mmol): ^1H NMR ($CDCl_3$) δ 1.44 (d, 2H), ~2 (s, concentration dependent, OH) ~1.0-0 (m, 5H).

2-Cyclopropylethyl, 2-cyclopropyl-1,1-dideuterioethyl and 2-cyclopropyl-2,2-dideuterioethyl p-Toluenesulfonates (**5a**,[31b] **5b**[31b] and **5c**, respectively) were prepared according to the procedure of Sauers and Ubersax[31a] for the synthesis of the corresponding protio p-bromobenzenesulfonate. The tosylates are liquids at room temperature. The spectra for **5a** are as follows: ^1H NMR (CCl_4) δ 7.72, 7.38 (AB-quartet, J = 8 Hz, 4H), 4.01 (t, J = 7 Hz, 2H), 2.44 (s, 3H), 1.52 (q, J = 7 Hz, 2H), ~1-0 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 144.3, 132.9, 129.5 (2C), 127.4 (2C), 70.4, 33.4, 21.1, 6.8, 3.7 (2C). The ^1H NMR spectra of the deuterated tosylates differ from that of **5a** in the following ways: **5b** has a doublet (instead of a quartet) at δ 1.52 and the triplet at 4.01 is absent, **5c** has a singlet at δ 4.01 and no absorption at 1.52.

Dicarbonyl(η^5-cyclopentadienyl)(2-cyclopropylethyl-, 2-cyclopropyl-1,1-dideuterioethyl-, and 2-cyclopropyl-2,2-dideuterioethyl)iron (**1a**, **1b**, and **1c**, respectively).

A degassed solution of 1.05 g (4.6 mmol) of 2-cyclopropylethyl p-toluenesulfonate (**5a**) in 50 ml of tetrahydrofuran was cooled to 0°C and 1.5 g (7.0 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate[32] (**6**) was added slowly with stirring under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and stirred for 5 h. The solvent was removed under reduced pressure. The residue was digested with pentane and filtered through a Celite mat. The Celite was washed with several portions of pentane and the combined filtrate and washings concentrated to ~10 ml under reduced pressure. The concentrate was chromatographed on neutral alumina (Activity III) at 0°C using pentane as eluent. After removal of the solvent under reduced pressure, 0.895 g (79%) of a yellow oil was obtained: IR ($CDCl_3$) 2000, 1940 cm^{-1} ($C\equiv O$); ^1H NMR ($CDCl_3$) δ 4.65 (s, Cp), ~1.5 (m, 4H $-CH_2CH_2Fe$), 0.9-0 (m, 5H, $-\overline{CHCH_2C}H_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0°C) δ 217.6 ($C\equiv O$), 85.2 (Cp), 43.1 (C-2), 15.1 ($-\overline{CHCH_2C}H_2$), 4.9 (2C, $-\overline{CHCH_2C}H_2$), 4.5 (C-1); MS, *m/e* 246 $[M]^{+\cdot}$, 218 $[M\text{-}CO]^{+\cdot}$, 190 $[M\text{-}2CO]^{+\cdot}$, 121 $[M\text{-}(2CO+C_5H_9)]^{+\cdot}$.

The deuterated complexes **1b** and **1c** were prepared in comparable yields from the corresponding tosylates (**5b** and **5c**). Their mass spectra, determined at an ionzation potential of 15 ev, showed 99.3% d_2, (248$[M]^+$); 0.7% d_1 (247 $[M]^+$) for **1b** and 96.2% d_2, 3.8% d_1 for **1c**.

The Reaction of Dicarbonyl(η^5-cyclopentadienyl)(2-cyclopropylethyl)iron (**1**) *and Triphenylmethyl Tetrafluoroborate* (**2**).

A nitrogen-blanketed solution containing 0.30 g (0.91 mmol) of **2**[33] in 10 ml of dichloromethane was cooled to -78°C and cannulated into a stirred, nitrogen-blanketed solution of 0.22 g (0.89 mmol) of **1a** in 10 ml of dichloromethane, also at -78°C. The mixture was stirred at -78°C for 4 h and at -20°C for an additional 14 h. The IR spectrum, determined on a small aliquot of the reaction mixture, showed absorptions at 2075 and 2040 cm^{-1} ($C\equiv O$ of **3a**) but none at 1955 or 1640 cm^{-1} ($C\equiv O$ and $C=O$ of **8a**). The solution was concentrated to ~5 ml under reduced pressure, combined with 10 ml of diethyl ether and the yellow precipitate was isolated by filtration. Complex **3a** (0.28 g) was obtained in 93% yield after two recrystallizations from dichloromethane/ether, mp 128-130°C (dec): IR (CH_2Cl_2) 2075, 2040 cm^{-1} ($C\equiv O$); ^1H NMR [$(CD_3)_2CO$] δ 5.74 (s, Cp), ~5.3 (sextet, $>CHCH=CH_2$), 3.70 (d, J = 9 Hz, *cis*-$CH=CHH$), 3.54 (d, J = 16 Hz, *trans*-$CH=CHH$), ~1.3-0.6 (m, 5H, $-\overline{CHCH_2C}H_2$); $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$] δ 212.0, 208.8 (CO), 101.4 (C-2), 89.6 (Cp), 49.6 (C-1), 18.2, 13.4, 12.1 ($-\overline{CHCH_2C}H_2$); Anal. Calcd for $C_{12}H_{13}BF_4FeO_2$: C, 43.43; H, 3.95. Found: C, 43.49; H, 4.00.

A similar experiment with **1b** (0.63 mmol) produced 84% of η^2-olefin complex (**3b**) and 88% of triphenylmethane (**7b**) while with **1c** (0.75 mmol) 90% of **3c** and 102% of **7c** were isolated.[15] The $^{13}C\{^1H\}$ NMR spectrum of **3b** exhibits a singlet of full intensity at δ 101.4 ($=CH-$) but shows no detectable resonance at δ 49.6 where that of undeuterated C-1 ($=CH_2$) would normally appear; the spectrum of **3c** displays a very weak triplet for C-2 ($=CD-$) at δ 101.2 but a singlet of full intensity for C-1 ($=CH_2$). The triphenylmethanes, **7b** and **7c**, were analyzed for deuterium content by mass spectroscopy and found to contain no deuterium in the case of **7b** but 87.8% d_1 ($[M]^+ = 245$) and 12.2%d_0 ($[M]^{+\cdot} = 244$) in the case of **7c**.[15]

The Reaction of **1** *and* **2** *Under a Carbon Monoxide Atmosphere* was carried out as described in the preceeding experiment using equimolar amounts (0.79 mmol each) **1a** and **2**. After the reaction mixture had been stirred under carbon monoxide at -

78°C for 4 h and at -20°C for 14 h, the IR spectrum of the mixture showed strong absorptions of 2075 and 2040 cm^{-1} and weaker ones at 1955 and 1640 cm^{-1}. The η^2-olefin, **3a**, was isolated in 85% yield as described above. After filtration, the mother liquor was concentrated to ~5 ml and chromatographed on neutral alumina (Activity III). Elution with pentane gave 0.167 g (87%) of triphenylmethane (**7a**). Elution with a 2% ether/pentane mixture gave 0.016 g (7%) of dicarbonyl(η^5-cyclopentadienyl)(3-cyclopropylpropionyl)iron (**8a**) as a yellow oil: IR (CH_2Cl_2) 2015, 1955 ($C\equiv O$), 1641 cm^{-1} ($C=O$); ^1H NMR ($CDCl_3$) δ 4.80 (s, Cp), 2.96 (t, J = 7 Hz FeCOCH$_2$-), 1.40 (q, J = 7 Hz, -CH$_2$-), ~0.6-0 (m, 5H, $-\overline{\text{CHCH}_2\text{C}}\text{H}_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0°C) δ 258.3 ($C=O$), 214.3 ($C\equiv O$), 86.2 (Cp), 66.6 (C-2), 30.2 (C-3), 10.3 ($-\overline{\text{CHCH}_2\text{C}}\text{H}_2$), 4.4 (2C, $-\overline{\text{CHCH}_2\text{C}}\text{H}_2$); MS, *m/e* 274 $[M]^{+\cdot}$, 246 $[M\text{-}CO)]^{+\cdot}$, 205 $[M\text{-}C_5H_9]^{+\cdot}$, 190 $[M\text{-}3CO]^{+\cdot}$, 121 $[M\text{-}(3CO+C_5H_9)]^{+\cdot}$.

The above procedure was repeated by combining solutions of **1c** (0.85 mmol) and **2** (0.87 mmol), each dissolved in 12 ml of dichloromethane. After completion of the reaction, **3c** (50%) was isolated by concentration of the solution, addition of ether, and filtration as described above. The solvent was removed from the filtrate and the residue was washed with pentane. Chromatography of the pentane-soluble portion gave triphenylmethane (**7c**) and acyl **8c** (9% after a second chromatography), mixed with some unidentified ametallic aromatic compound(s), presumably formed during work-up from unreacted **2**.[16] The portion of the residue which did not dissolve in pentane apparently contains a complexed salt, probably formed from **8c** and **2**.[16] Its $^{13}C\{^1H\}$ spectrum (d_6-acetone) shows at δ 318.8, 209.8 (CO), several plans in the 148-126 region (phenyl), 106.1, 89.7 (Cp), 62.5 and 9.4.

The reaction was repeated using 0.78 mmol of **1c** and 0.44 mmol of **2** (a 1:0.55 molar ratio) and the products were isolated in the same manner. The yields of **7c** and **8c** were 42% and 52%, respectively; very little of the unknown complexed product was formed.

Dicarbonyl(η^5-cyclopentadienyl)iron(2,2-dimethylpropionyl) (**9**).

To a stirred, nitrogen-blanketed solution of 1.3 g (11.8 mmol) of pivaloyl chloride in 50 ml tetrahydrofuran was added gradually at room temperature 3.2 g (14.8 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate[32] (**6**). After the mixture had been stirred for 20 h at room temperature, the solvent was removed under reduced pressure. The residue was extracted with several portions of 10% ether/pentane and the washings were filtered through a Celite mat. The filtrate was concentrated to ~10 ml under reduced pressure and the concentrate was chromatographed on neutral alumina (Activity III) at 10°C using 2% ether/pentane as eluent. The solvent was removed under reduced pressure to give 1.7 g (55%) of yellow crystalline product, **9**,: mp 70-71°C; IR (CH_2Cl_2) 2005, 1950 ($C\equiv O$), 1620 cm^{-1} ($C=O$); ^1H NMR ($CDCl_3$) δ 4.76 (s, Cp), 1.0 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 262.7 ($C=O$), 215.4 ($C\equiv O$), 86.3 (Cp), 57.9, 26.9 (3C); MS, *m/e* 234 $[M\text{-}CO]^{+\cdot}$, 205 $[M\text{-}t\text{-}Bu]^{+\cdot}$. Anal. Calcd for $C_{12}H_{16}FeO_3$: C, 55.00; H, 5.38; O, 18.31. Found: C, 54.91; H, 5.21; O, 18.32.

Dicarbonyl(η^5-cyclopentadienyl)iron(neopentyl) (**10**).

To a stirred, nitrogen-blanketed solution of 0.18 g (0.69 mmol) of **9** in 5 ml of tetrahydrofuran at 0°C was added slowly by syringe 5.0 ml of 0.97 M borane in tetrahydrofuran.[34] The solution was stirred for 10 h at room temperature, cooled to -78°C and excess borane was decomposed by adding 2 ml of methanol. The solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina (Activity IV) using pentane as eluent. After removal of the solvent under reduced pressure 0.066 g (39%) of 10 ws obtained as an amber oil:[35] IR (CH_2Cl_2) 2000, 1940 cm^{-1} ($C\equiv O$); ^1H NMR ($CDCl_3$) δ 4.73 (s, Cp), 1.76 (s, 2H), 0.96 (s, 9H); $^{13}C\{^1H\}$ NMR ($CHCl_3$, -5°C) δ 218.8 ($C\equiv O$), 85.6 (Cp), 35.2 (>C<), 33.1 (3C, CH_3), 19.5 (-CH_2Fe). Anal. Calcd for $C_{12}H_{16}FeO_2$: C, 58.10; H, 6.50; O, 12.89. Found: C, 58.25; H, 6.54; O, 13.01.

The Reaction of Dicarbonyl(η^5-cyclopentadienyl)iron(neopentyl) (10) *and Triphenylmethyl Tetrafluoroborate* (2) *in the Presence and in the Absence of Carbon Monoxide.*

A solution of 0.055 g (0.17 mmol) of 2[33] was cooled to -78°C and cannulated into a stirred solution of 0.040 g (0.16 mmol) of 10 also at -78°C *under a carbon monoxide atmosphere*. The progress of the reaction was monitored by periodically withdrawing small samples and scanning the 2200-1600 cm^{-1} region in the IR. Absorptions at 2010, 1950 and 1640 cm^{-1}, characteristic of complex 11, were evident after ~3 h at -78°C. After 4 h at -78°C and an additional 2.5 h at -20°C the reaction was virtually complete as evidenced by the absence of absorptions at 2000 and 1940 cm^{-1} ($C\equiv O$ of the starting material). The solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina (Activity III) at 10°C with 10% ether/pentane as eluent. A yield of 0.031 g (71%) of 10 was obtained: IR (CH_2Cl_2) 2010, 1950 ($C\equiv O$), 1640 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 4.70 (s, Cp), 2.80 (s, >CH_2), 0.83 (s, 9H, -CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 257.2 (C=O), 214.6 ($C\equiv O$), 86.3 (Cp), 79.2 (-CH_2COFe), 32.7 (>C<), 29.3 (3C, CH_3); MS, *m/e* 276 $[M]^{+\cdot}$, 248 $[M\text{-}CO]^{+\cdot}$, 220 $[M\text{-}2CO]^{+\cdot}$, 205 $[M\text{-}C_5H_{11}]^{+\cdot}$. Anal. Calcd for $C_{13}H_{16}FeO_3$: C, 56.50; H, 5.84; O, 17.38. Found: C, 56.42; H, 5.90, O, 17.19.

A second sample of 10 was treated with 2 under identical conditions but *under a nitrogen atmosphere*. After 4 h at -78°C and 2.5 h at -20°C only unreacted starting material was detected by IR. After an additional 20 h at room temperature unreacted starting material could no longer be detected; the product, 11, was isolated in ~17% yield by chromatography together with benzophenone, some triphenylmethanol, and a compound which we believe to be 3,3-dimethyl-1,1,1-triphenylbutane. The presence of the dimethyltriphenylbutane is suggested by resonances at δ 1.01 (s, ~9H), 2.52 (s, ~2H) and 7.1 (s, ~15H) in the ^1H NMR ($CDCl_3$) spectrum of the mixture.

Dicarbonyl(η^5-cyclopentadienyl)iron(1-norbornylcarbinyl) (13) was prepared and isolated by a procedure similar to that employed for 10. A sample of 0.10 g (0.33 mmol) of dicarbonyl(η^5-cyclopentadienyl)iron(1-norbornanecarbonyl) (12)[24] in 7 ml of tetrahydrofuran was combined with 1.75 ml of a 0.97 M solution of borane in tetrahydrofuran[34] at 0°C. The reaction mixture was stirred at 0°C for 30 min and at room temperature for an additional 2.5 h. A yield of 0.055 g (58%) of the oxidatively and thermally sensitive oil 13 was obtained: IR (CH_2Cl_2) 1998, 1941 cm^{-1} ($C\equiv O$); ^1H NMR (CD_2Cl_2) δ 4.78 (s, Cp), 2.05 (br s, >CH, bridgehead), 1.90 (s, -CH_2Fe), 1.40 (m, 10H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 218.0 ($C\equiv O$), 85.9 (Cp), 53.8 (C-1), 46.9 (C-4), 38.0 (C-7), 37.9 (C-3, C-5), 31.7 (C-2, C-6), 9.42 (C-8); MS, *m/e* 286 $[M]^{+\cdot}$, 258 $[M\text{-}CO]^{+\cdot}$, 230 $[M\text{-}2CO]^{+\cdot}$, 109 $[M\text{-}Fp]^{+\cdot}$.

The Reaction of Dicarbonyl(η^5-cyclopentadienyl)iron(1-norbornylcarbinyl) (13) *and Triphenylmethyl Tetrafluoroborate* (2) *in the Presence and in the Absence of Carbon Monoxide.*

A solution of 0.061 g (0.19 mmol) of 2[33] in 5 ml of dichloromethane was added by syringe to a stirred solution of 0.048 g (0.18 mmol) of 13 in 5 ml of dichloromethane *under a carbon monoxide atmosphere*. The mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure and the product was chromatographed on neutral alumina (Activity III) at 10°C with 5% ether/pentane as eluent to give 0.042 g (80%) of **14** as a yellow oil. Purification by sublimation (60°C/0.1 mm) gave a crystalline product:[10c] mp 50.5-51.5°C; IR 2001, 1947 ($C\equiv O$), 1652 cm^{-1} ($C=O$); ^1H NMR ($CDCl_3$) δ 4.89 (s, Cp), 3.41 (s, $-CH_2Fe$), 2.03 (br s, $>CH$, bridgehead), ~1.3 (m, 10H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 255.7 ($C=O$), 214.6 ($C\equiv O$), 86.4 (Cp), 72.4 (C-8) , 47.2 (C-1), 43.5 (C-7), 36.3 (C-4), 34.3 (C-3, C-5), 30.6 (C-2, C-6); MS, *m/e* 314 $[M]^{+\cdot}$, 286 $[M\text{-}CO]^{+\cdot}$, 258 $[M\text{-}2CO]^{+\cdot}$, 230 $[M\text{-}3CO]^{+\cdot}$, 137 $[M\text{-}Fp]^{+\cdot}$. Anal. Calcd for $C_{16}H_{18}O_3Fe$: C, 61.17; H, 5.78. Found: C, 60.67; H, 5.92.

A second solution of 0.055 g (0.19 mmol) of **13** in 5 ml of dichloromethane was combined with an equimolar solution of **2** and *stirred under a nitrogen atmosphere* at room temperature. Infrared analysis of a small aliquot after 5 h showed mostly unreacted starting material. Workup after 43 h followed by chromatography yielded two fractions. The first fraction (0.030 g) was a mixture of unreacted starting material, **13**, and benzophenone; the second fraction (0.028 g, ~46%) was the acyl complex, **14**, contaminated with some benzophenone.

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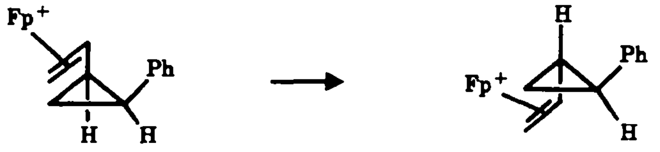
[14] Casey, *et al.*[10c] have recently proposed a mechanism for the isomerization of J to K which involves an intermediate similar to D (Scheme 6). If this mechanism is



J K

subsequently substantiated then perhaps even the one-electron-transfer/hydrogen-atom-abstraction mechanism of Scheme 6 would produce 3. We regard this as unlikely for to our knowledge *cis-to-trans* isomerizations such as J-to-K have not been observed when the $[Fp(\eta^2\text{-vinylcyclopropane})]^+$ lacks a phenyl substituent on the ring.

[15] Control experiments reveal that the "excess" (based on 3c) triphenylmethane isolated from this reaction as well as at least a portion of the slightly reduced deuterium content which it exhibits arises from the reaction of the excess 2^+ with diethyl ether added during work up.

[16] By retarding the stoichimetric elimination relative to the catalytic CO insertion the affect of the deuterium isotope effect in 1c is to cause unreacted cation, 2^+ to remain after the initial σ-complex 1c has been depleated. The cation reacts with some of the acyl, 8c, to produce a cationic Lewis acid-base complex, $[Fp(R)COCPh_3]^+$[17] which complicates the isolation of the primary reaction products and reduces the isolated yield of the neutral acyl 8c.

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[18] If the metal-centered cation-radical B (Scheme 6) assists β-hydrogen transfer, step "b", then the diradical C could well be a singlet and might better be regarded as a transition state[19] whose lifetime, τ, equals the inverse stretching frequency of a β-C−H bond of B, $\sim 10^{-14}$s. With no assistance C should be a triplet with a lifetime at least as long as the rate of intersystem crossing, $\sim 10^{-7}$s.[19]

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[23] We have noted previously[8a] that the reaction of $FpCH_2CH_2C(CH_3)_3$ and $Ph_3C^+BF_4^-$ forms no $[Fp(\eta^2\text{-}CH_2{=}CHC(CH_3)_3]^+BF_4^-$ or Ph_3CH. Evidently the neopentyl-like β-hydrogens are too sterically hindered to be abstracted by the bulky cation.

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[25] This failure to form cationic metal neopentylidenes by α-hydride abstraction is not a consequence of their instability or reactivity for each of these neopentylidenes can be prepared another way[8b,26] and $[Cp(NO)(Ph_3P)Re=CHC(CH_3)_3]^+$ itself is stable as a crystalline salt.[27]

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[27] We thank John Gladysz for informing us of this result prior to its publication.

[28] *Cf.* Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; John Wiley & Sons: New York, 4th Edition, 1980, pp. 1205-1217 and references cited therein.

[29] All operations were carried out using standard Schlenk-line and/or drybox techniques. Solvents were dried, distilled under nitrogen and degassed using the freeze-pump-thaw method immediately prior to use. Proton NMR spectra were recorded on a Varian EM390 spectrometer at 90 MHz and ^{13}C NMR spectra on an IBM NR80 spectrometer operating at 20.13 MHz. Chemical shifts (δ) are reported in ppm downfield from TMS. The ^{13}C assignments were made with the help of the refocused INEPT technique [Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* 1979, *101*, 760].

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