Synthesis and Reactivity of Cyclic and Acyclic (1-(acyloxy)pentadienyl)Fe(CO)$_2$LX and (1-alkoxypentadienyl)Fe(CO)$_2$LX Salts (L = CO, PPh$_3$)

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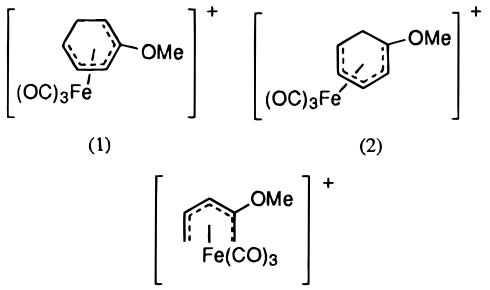
A variety of cyclic and acyclic [(pentadienyl)Fe(CO)$_2$L]X complexes (L = CO, PPh$_3$) containing terminal acyloxy or alkoxy substituents have been prepared. *In situ* NMR studies indicate that for the acyclic series where L = CO, stability is limited by solvolysis reactions. The position of nucleophilic attack (ipso for alkoxy, internal for acyloxy) in the acyclic series indicates an electron-donating and electron-withdrawing nature for alkoxy and acyloxy substituents, respectively. In the cyclic series, the different regiodirecting powers of alkoxy and acyloxy groups provide access to regioisomeric substituted cyclohexadienyl salts. Crystal structures of the Ψ-exo and Ψ-endo stereoisomers of [5-(benzoyloxy)-2,4-hexadien-1-ol]Fe(CO)$_2$PPh$_3$ (**34** and **35**) and of [(1,3,4,5-*η*)-1-(benzoyloxy)-2-methyl-3-pentene-1,5-diyl]Fe(CO)$_2$PPh$_3$ (**57**) have been determined.

Introduction

The efficient application of chiral electrophilic complexes such as [(pentadienyl)Fe(CO)$_3$]X salts in C−C bond-forming reactions in asymmetric synthesis depends on control of both regio- and stereoselectivity.[1,2] Though the latter is usually guaranteed because of the lateral coordination of the metal moiety, regioselectivity has generally been controlled through the nature of the substituent either on the pentadienyl ligand or on the metal. Alkoxy substituents in particular have been shown to exhibit high regiocontrol, promoting nucleophilic addition at C5 and C1 exclusively in complexes **1**[1a] and **2**, respectively.[3] This directing influence of the 2-methoxy substituent is maintained in the acyclic cation **3**.[4] Good regiocontrol, however, inevitably precludes access to the alternative regioisomer series, thus limiting synthetic applications if compounds from the inaccessible regioisomer series are required. We wish to report here our complete results[5] on the preparation and reactivity toward nucleophiles of cyclic and acyclic 1-acyloxy- and 1-alkoxy-substituted [(pentadienyl)Fe(CO)$_2$L]X complexes (L = CO, PPh$_3$). The results demonstrate a reversal of regioselectivity that offers novel possibilities for complementary control strategies in applications in asymmetric synthesis (since the acyloxy and alkoxy series can be obtained from the same precursors) and, for the acyloxy complexes, shows an important variation in regioselectivity between the cyclic and acyclic series.



(1) (2) (3)

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) For reviews, see: (a) Pearson, A. J. *Iron Compounds in Organic Synthesis*; Academic Press: London, 1994. (b) Grée, R.; Lellouche, J. P. *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; Jai Press: Greenwich, CT, 1995; Vol. 4, p 129. (c) Grée, R. *Synthesis* **1989**, 341.

(2) For recent examples of applications in synthesis see: (a) Hachem, A.; Toupet, L.; Grée, R. *Tetrahedron Lett.* **1995**, *36*, 1849. (b) Benvegnu, T.; Schio, L.; Le Floch, Y.; Grée, R. *Synlett* **1994**, 505. (c) Donaldson, W. A.; Bell, P. T.; Wang, Z; Bennett, D. W. *Tetrahedron Lett.* **1994**, *35*, 5829. (d) Donaldson, W. A.; Jin, M. J. *Tetrahedron* **1993**, *49*, 8787. (e) Knölker, H. J.; Baum, E.; Hoffmann, T. *Tetrahedron Lett.* **1995**, *36*, 5339. (f) Knölker, H. J.; Baum, G.; Kosub, M. *Synlett* **1994**, 1012. (g) Knölker, H. J.; El-Ahl, A. A.; Weingaertner, G. *Synlett* **1994**, 194. (h) McKillop, A.; Stephenson, G. R.; Tinkl, M. *Synlett* **1995**, 669. (i) Genet, J. P.; Hudson, R. D. A.; Meng, W. D.; Roberts, E.; Stephenson, G. R.; Thorimbert, S. *Synlett* **1994**, 631. (j) Franck-Neumann, M.; Kastler, A. *Synlett* **1995**, 61. (k) Roush, W. R.; Wada, C. K. *J. Am. Chem. Soc.* **1994**, *116*, 2151.

(3) (a) Stephenson, G. R.; Howard, P. W.; Owen, D. A.; Whitehead, A. J. *J. Chem. Soc., Chem. Commun.* **1991**, 641. (b) Owen, D. A.; Stephenson, G. R.; Finch, H.; Swanson, S. *Tetrahedron Lett.* **1990**, *31*, 3401. (c) Palatoi, I. M.; Stephenson, G. R.; Ross, W. J.; Tupper, D. E. *J. Organomet. Chem.* **1989**, *364*, C11.

(4) Donaldson, W. A.; Jin, M. J. *Bull. Soc. Chim. Belg.* **1993**, *102*, 297.

(5) For a preliminary communication, see ref 3a.

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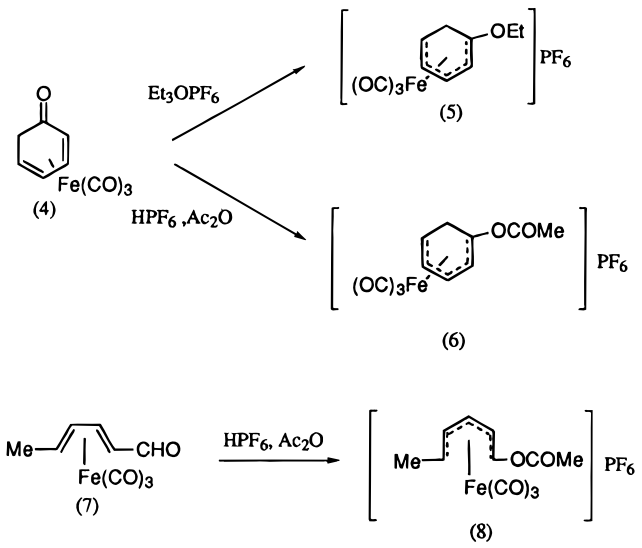
Scheme 1



Results and Discussion

(A) Synthesis. The cyclic cations **5** and **6** were readily prepared as stable salts by alkylation or acylation of the easily available cyclohexadienone complex **4** (Scheme 1). Attempts to extend this to the acyclic series were successful only in the acylation of (sorbaldehyde)-$Fe(CO)_3$ (**7**) to give **8** as a hygroscopic, unstable salt which reverted easily to starting material on exposure to moisture.

In order to improve stability and provide access to the 1-alkoxy series, an alternative synthetic strategy was investigated in the acyclic series. $NaBH_4$ reduction of the 5-(acyloxy)- or 5-alkoxypentadienyl complexes **9**−**14** (all available *inter alia* from sodium glutaconaldehyde)[6] gave the primary alcohol complexes **15**−**20** in good yield (Scheme 2). The availability of **9**−**11** in homochiral form may be noted.[6] While protonation of the PPh_3-substituted complexes provided the pentadienyl salts **21**−**23** as yellow precipitates in good yield, no such precipitates were observed in the cases of the tricarbonyl analogues. Intermediacy of the required pentadienyl cations **24**−**26** is indicated both by *in situ* NMR studies (*vide infra*) and by the products generated on neutralization. Evidence for intermediates **24** and **25** was also obtained by FT-IR measurements on samples withdrawn directly from the reaction mixture. Typical ν-(CO) bands for $[(\text{pentadienyl})Fe(CO)_3]^+$ complexes were observed at 2119, 2072 and 2113, 2083 cm^{-1}, respectively. Infrared bands due to the neutral starting materials were not present. In the case of the methoxy complex, neutralization after reaction with HPF_6 yields the methyl ether **27** together with an *inseparable* mixture of (*E*)- and (*Z*)-(pentadienal)$Fe(CO)_3$ (**28** and **29**), while neutralization of **25** and **26** yields only starting material. Given the water sensitivity of complexes such as **8** and the aqueous nature of the protonating medium, the results may perhaps best be interpreted as involving an equilibrium between protonated and nonprotonated complex which in the case of the methoxy complex collapses through alkylation of starting complex **15** by cation **24** to give the observed products. The greater sensitivity toward solvolysis of acyclic as opposed to cyclic and of tricarbonyl as opposed to dicarbonyl phosphine complexes has been noted by other workers.[7,8] The PPh_3-substituted cation **23** does undergo hydrolysis under more vigorous conditions, though via deacylation to give a *separable* 7:1 mixture of the (*E*)- and (*Z*)-pentadienal complexes **30** and **31**.

Availability of the formyl derivatives **9**−**14** provides potential access to 1-substituted dienyl salts via the intermediacy of secondary alcohols produced by reaction with Grignard or alkyllithium reagents. Thus, reaction of **11** and **14** with MeMgI proceeds smoothly to yield the separable diastereoisomeric Ψ-*exo* and Ψ-*endo* products **32**/**33** and **34**/**35** in ratios of 1:1.3 and 2.1:1, respectively (Scheme 3). The isolated yield of 1:3.3 for **32**/**33** is a result of more rapid decomposition of **32** on chromatography. The change in the Ψ-*exo*/Ψ-*endo* product ratio between tricarbonyl and dicarbonyl phosphine complexes has been observed previously in the (sorbaldehyde)$Fe(CO)_2L$ series and may be associated with the change in the s-cis/s-trans conformational preference of the formyl moiety.[9] Again, while protonation of **34** proceeds cleanly to yield **36**, no precipitates are observed on protonation of either **32** or **33**. Hydrolysis of **36** proceeds in a similar fashion as for **23** to yield the separable (*E*,*E*)- and (*E*,*Z*)-(sorbaldehyde)Fe-$(CO)_2PPh_3$ complexes **37** and **38**, but in a ratio of 1:1.

(B) Crystal and Molecular Structures of 34 and 35. Reaction of (dienal)$Fe(CO)_3$ complexes with Grignard or alkyllithium reagents proceeds with poor stereoselectivity in many cases to give Ψ-exo and Ψ-endo mixtures which are usually easily separable. Crystallographic determinations have confirmed the Ψ-exo or Ψ-endo stereochemistry in several cases,[2a,10a−c] but we are not aware of the structural characterization of both diastereoisomers of the same complex.

The molecular structures of **34** and **35** (Figure 1) confirm the assumed relative stereochemistries at iron and C1. The staggered conformation at C1 relative to the diene is in agreement with modeling predictions,[11] with hydrogen occupying the most sterically demanding position between the diene plane and the basal carbonyl. The complexes exhibit the typical square-based-pyramidal structure of (diene)$Fe(CO)_2L$ complexes. While **35** crystallizes as a single basal phosphine isomer, the solid-state structure of **34** contains an equimolar mixture of axial and basal phosphine isomers. In both **35** and the basal isomer of **34**, the phosphine occupies the least sterically demanding basal position *cis* to the benzoyloxy substituent, which is nearly coplanar with the diene fragment.

Intermolecular hydrogen-bonded interactions involving OH and benzoyloxy C═O groups are shown in Figure 2. The structure of **35** exhibits centrosymmetric dimers with O---O contacts of 2.84 Å. The structure of **34** contains two molecules (axial and basal phosphine) per asymmetric unit. The OH groups of the basal

(6) Howell, J. A. S.; Bell, A. G.; O'Leary, P. J.; McArdle, P.; Cunningham, D.; Stephenson, G. R. *Organometallics* **1994**, *13*, 1806.

(7) Donaldson, W. A.; Ramaswamy, M. *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 49.

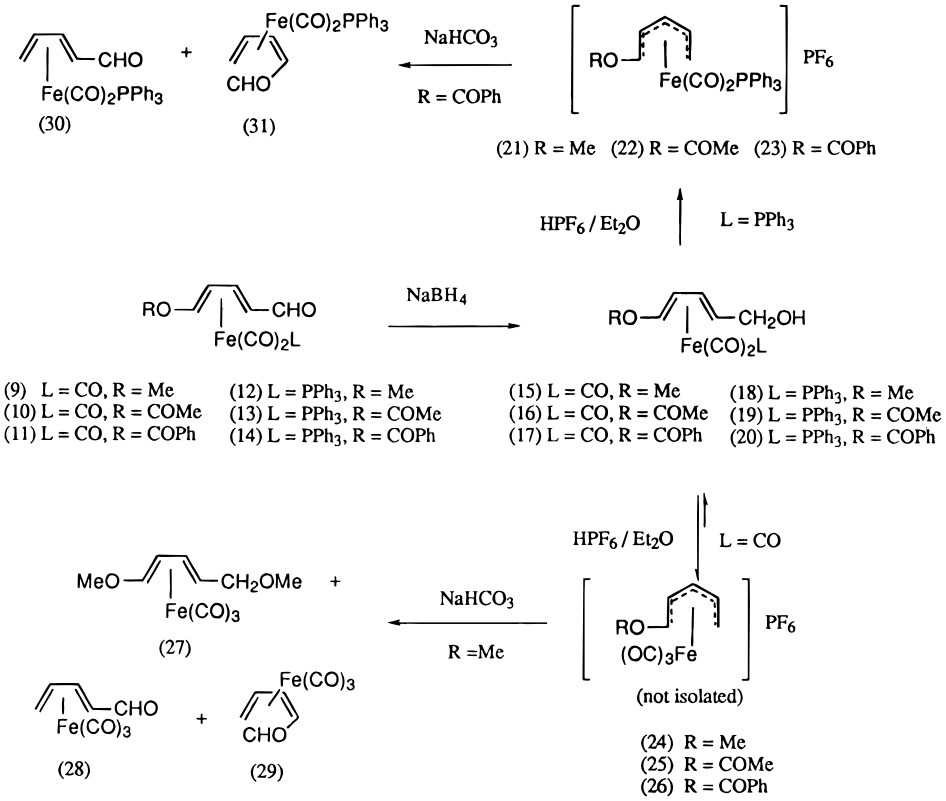
(8) Donaldson, W. A.; Shang, L. *Tetrahedron Lett.* **1995**, *36*, 1575.

(9) Howell, J. A. S.; Squibb, A. D.; Bell, A. G.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D.; Grée, R. *Organometallics* **1994**, *13*, 4336.

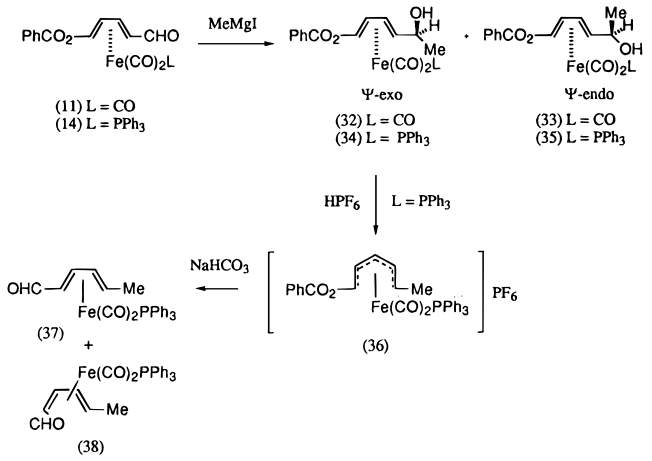
(10) (a) Riley, P. E.; Davis, R. E. *Acta Crystallogr.* **1976**, *32B*, 381. (b) Grée, D. M.; Martelli, J. T.; Grée, R. L.; Toupet, L. J. *J. Org. Chem.* **1995**, *60*, 2316. (c) Lellouche, J. P.; Breton, P.; Beaucourt, J. P.; Toupet, L. J.; Grée, R. *Tetrahedron Lett.* **1988**, *29*, 2449. (d) Roush, W. R.; Wada, C. K. *Tetrahedron Lett.* **1994**, *35*, 7347.

(11) Clinton, N. A.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3058.

Scheme 2



Scheme 3



phosphine isomer form bifurcated hydrogen bonds with the C═O and OH groups of molecules which have the phosphine apical. The structure thus consists of centrosymmetric tetramers with O- - -O contacts of 2.71 and 2.74 Å; the angle generated by the bifurcated hydrogen bond is 102°. A feature of the hydrogen bonding is that the **34** diene fragments of both unique molecules define planes that make an angle of 54.2°. The tetramers are packed to produce alternating hydrophobic and hydrophilic layers containing the phosphine aryl rings and the hydrogen-bonding regions, respectively. The probable reason for the presence of both axial and basal isomers is that the hydrogen-bonding arrangement requires the relative rotation of the metal coordination sphere, and to maintain the layer structure, the phosphines alternate between apical and basal positions. In solution the isomer distribution is opposite; complex **34** exists mainly as the basal isomer (axial to basal ratio 1:3.9), whereas for **35**, the distribution is close to equimolar (axial to basal ratio 1:1.4).

(C) *In Situ* Protonation Studies of Tricarbonyl Complexes. The lack of precipitation of isolable salts in the cases of complexes **15**−**17**, **32**, and **33** has prompted *in situ* NMR studies using HSO_3F/CD_2Cl_2 of the species produced on protonation. The results confirm the formation of the required pentadienyl cation, provide evidence for facile C−C rotational processes which augment earlier work in this area, and also indicate facile solvolysis reactions of the [(acyloxypentadienyl)$Fe(CO)_3$]$^+$ cations.

Protonation of the Ψ-exo and Ψ-endo diastereoisomers **32** and **33** at −20 °C (Scheme 4) yields spectra which are fully consistent with the *cis-syn, syn* and *cis-syn, anti* cations **39** and **40**, respectively (Figure 3). Particularly characteristic are the H5 resonances at 3.06 and 4.70 ppm with J_{4-5} values of 13.7 and 9.3 Hz, respectively. We have observed no resonances attributable to the presumed initial *trans* cation under these conditions.[12] Cation **39** undergoes a smooth first-order solvolysis at −20 °C ($k_2 = 5.3 \times 10^{-4}$ s^{-1}) to give **41**, identified unambiguously by comparison with the spectrum of protonated (sorbaldehyde)$Fe(CO)_3$ (**7**). Changes in the spectrum of **40** with time show formation of both **39** and **41**. The kinetics are in excellent agreement with those expected for *consecutive* reactions;[13] i.e., isomerization of **40** to **39** is followed by solvolysis to **41** and no direct conversion of **40** to **41** occurs ($k_1 = 3.8 \times 10^{-4}$ s^{-1}, $k_2 = 5.3 \times 10^{-4}$ s^{-1}). The phosphine-substituted complexes are not stable to HSO_3F, but *in situ* proto-

(12) For *in situ* characterizations of *trans* cations, see: (a) Lillya, C. P.; Sahatjian, R. A. *J. Organomet. Chem.* **1971**, *32*, 371. (b) Sorensen, T. S.; Jablonski, C. R. *J. Organomet. Chem.* **1970**, *25*, C62. (c) Lillya, C. P.; Sahatjian, R. A. *J. Organomet. Chem.* **1970**, *25*, C67. (d) Brookhart, M.; Harris, D. L. *J. Organomet. Chem.* **1972**, *42*, 441.

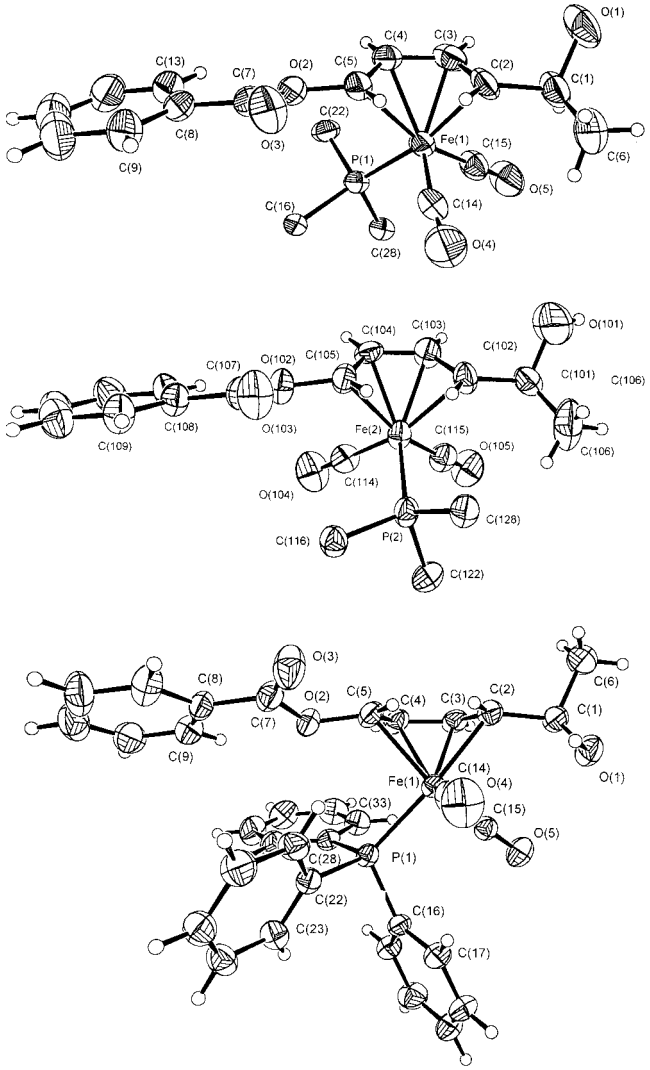


Figure 1. Molecular structures of **34** (basal) (top), **34** (axial), and **35** (bottom). Important bond lengths (Å) and angles (deg): **34** basal, Fe−P = 2.24, Fe−diene = 2.14 (outer), 2.07 (inner), Fe−CO(av) = 1.76, CO(ax)−Fe−P = 101, CO(ax)−Fe−CO(bas) = 99, CO(bas)−Fe−P = 90, C3−C2−C101 = 68; **34** axial, Fe−CO(av) = 1.77, P−Fe−CO-(bas) (av) = 99.1, CO−Fe−CO = 89, C103−C102−C101−O101 = 79; **35**, Fe−P = 2.24, Fe−diene = 2.13 (outer), 2.06 (inner), Fe−CO(av) = 1.77, CO(ax)−Fe−P = 100, CO(ax)−Fe−CO(bas) = 102, CO(bas)−Fe−P = 91, C3−C2−C1−O1 = 41.

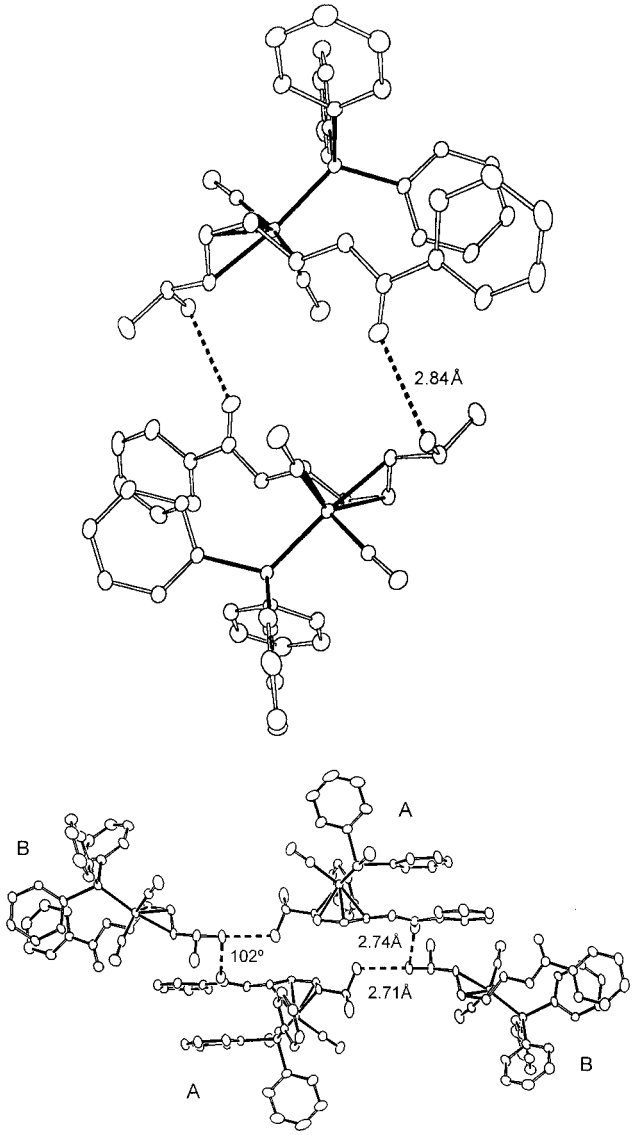


Figure 2. Intermolecular hydrogen-bonded interactions of **35** (top) and **34** (bottom).

nation of **20** using CF_3COOD/CD_2Cl_2 yields a spectrum identical with that of the isolated cation **23**.

In situ protonation of the primary alcohol complex **17** proceeds in a similar fashion to give **44**, which undergoes a first-order solvolysis to give **45** ($k_1 = 3.63 \times 10^{-4}$ s^{-1}).[15] In the case of **16**, solvolysis is sufficiently rapid to preclude observation of **43** on the time scale of the experiment. The methoxy cation **42** is resistant to solvolysis.

A spectrum identical with that of **45** can be obtained by *in situ* protonation of the *E*,*Z* complex **48**, obtained *inter alia* from ring opening of (pyrone)$Fe(CO)_3$ (**46**) (Scheme 5). Adaptation of this route to provide stable salts in the PPh_3 series is frustrated. Though the PPh_3 complex **47** may be easily prepared, it does not undergo ring opening under the same conditions used for **46**.

Finally, it is of interest to compare the results on the *syn*,*anti to syn*,*syn* isomerization of **40** to **39** with the analogous isomerization process of the 1-methyl cations **51** and **52**, which can be generated by *in situ* protonation of the Ψ-*exo* and Ψ-*endo* diastereoisomers **49** and **50** (Scheme 6). In contrast to **40**, **52** is configurationally stable at −20 °C, only isomerizing to **51** with some

(13) Values of the first-order rate constants k_1 and k_2 were obtained from plots of ln [A] against time for disappearance of **38** and **39**, respectively, using the integrated intensity of the methyl doublet as a measure of concentration. Correlation coefficients greater than 0.994 were obtained. Kinetic analysis[14] of a consecutive reaction series indicates that the concentrations of A, B, and C with time can be expressed by

$$[A]_t = [A]_0\, e^{-k_a t}$$

$$[B]_t = [A]_0 k_a \left(\frac{e^{-k_a t} - e^{-k_b t}}{k_b - k_a}\right)$$

$$[C]_t = [A]_0 \left(1 + \frac{k_a\, e^{-k_b t} - k_b\, e^{-k_a t}}{k_b - k_a}\right)$$

Using experimental values of k_1 and k_2, the experimentally observed plots of concentration against time for **39**, **38**, and **40** match almost exactly those predicted by the above equations.

(14) Atkins, P. W. *Physical Chemistry*, 5th ed.; Oxford University Press: Oxford, U.K., 1994; pp 883−884.

(15) The value of k_1 was obtained from a plot of ln [A] against time for the disappearance of **44** using the integrated intensity of the H3 resonances as a measure of concentration (correlation coefficient 0.998).

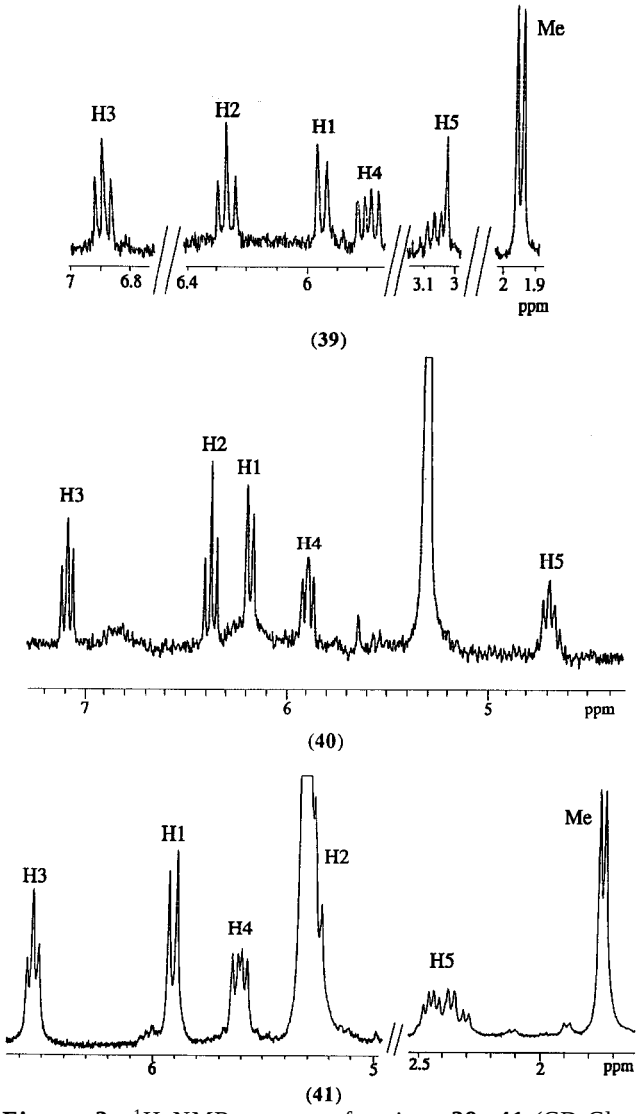
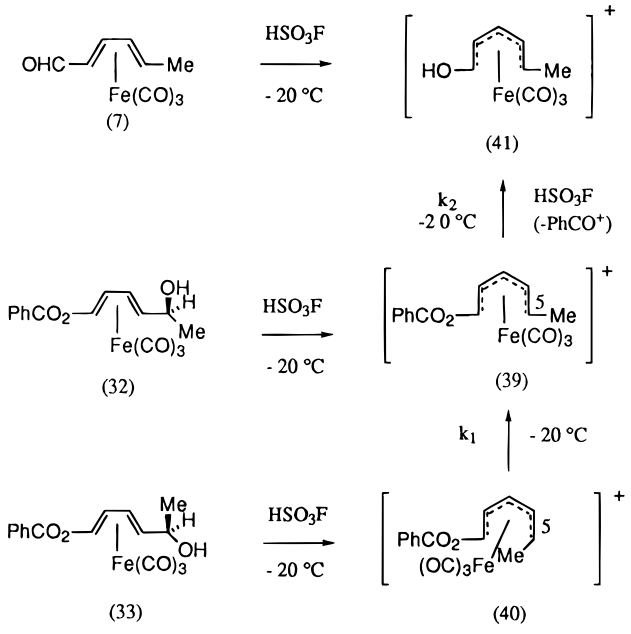


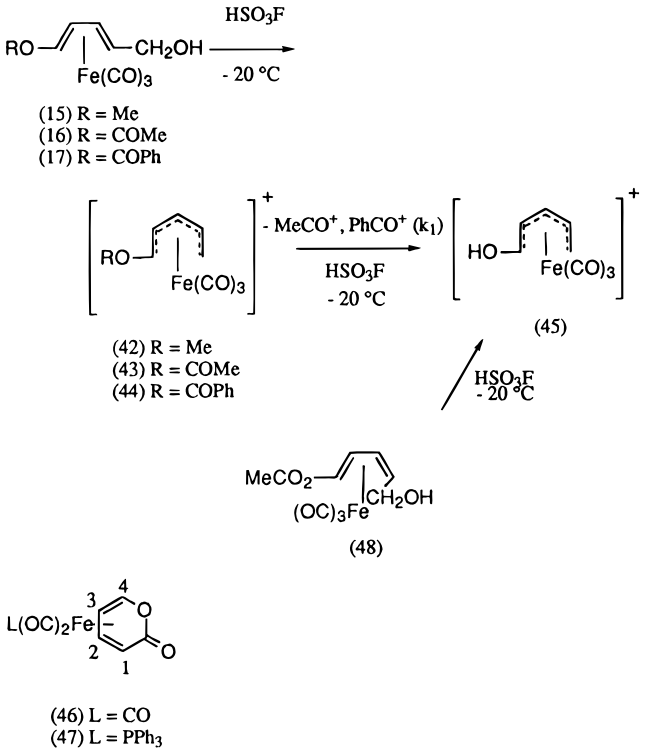
Figure 3. ^{1}H NMR spectra of cations **39**−**41** (CD_2Cl_2−HSO_3F, −20 °C).

Scheme 4

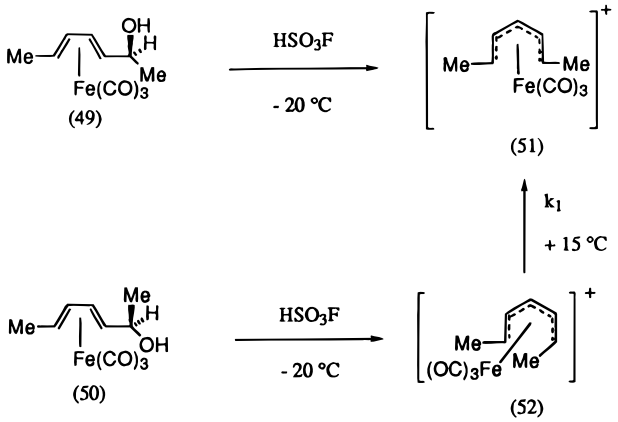


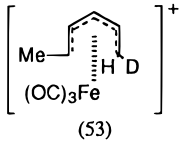
decomposition at +15 °C ($k_1 \approx 9 \times 10^{-5}$ s^{-1}).[16] In other work,[17] we have recently shown that the enantiomerically pure deuterated cation **53** is also configurationally stable, undergoing no deuterium scrambling over a period of hours at room temperature.

Scheme 5



Scheme 6



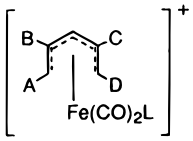


The increased rates of isomerization of **52** and **40** relative to **53** thus indicate a steric acceleration in which the ground-state *cis-syn, anti* cations lie closer in energy to the transition state for the rotational process. The increased rate of isomerization of **40** relative to **52** may reflect an electronic contribution to the lowering of the barrier.

(16) The value of k_1 was obtained from a plot of ln [A] against time for the disappearance of **52** using the integrated intensity of the methyl resonances. Only three data points were obtained before decomposition substantially broadened the spectrum. For previous characterization of these cations, see ref 12b,c.

(17) Howell, J. A. S.; O'Leary, P. J.; Palin, M. G.; Jaouen, G.; Top, S. *Tetrahedron: Asymmetry* **1995**, *7*, 307.

Table 1



entry	ref	nucleophile	L	A	B	C	D	ratio and position of attack
a	18	MeLi	CO	H	H	H	H	1.2:1 B:A
b	18	MeLi	PPh_3	H	H	H	H	>36:1 B:A
c	8	malonate	CO	Me	H	H	H	1.8:1 D:A
d	8	malonate	PPh_3	Me	H	H	H	A only
e	19	malonate	CO	Ph	H	H	H	A only
f	20	malonate	CO	H	Me	H	H	A only
g	21	malonate	CO	Me	Me	H	H	D only
h	21	malonate	CO	Me	H	Me	H	A only
i	21	malonate	CO	Ph	H	Me	H	A only
j	21	malonate	CO	Ph	Me	H	H	1:1 A:C
k	22	malonate	CO	CO_2Me	H	H	H	>20:1 B:D
l	4	$H_2C{=}CHCH_2SiMe_3$	CO	Me	H	OMe	H	A only

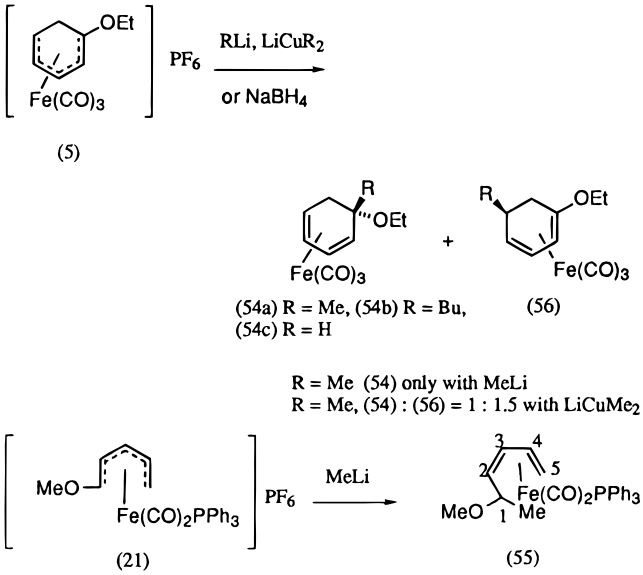
(D) Regioselectivity of Nucleophilic Attack. For acyclic cations, regioselectivity is greatly dependent on the nucleophile, the pentadienyl substituent, and the auxiliary ligands present on the metal. Nevertheless, sufficient data exist in the series given in Table 1, mainly for reaction with malonate, to delineate important stereoelectronic influences.

The relatively poor regiodirecting influence of the terminal methyl substituent is attributed to a relatively weak electron-donating character that favors *ipso* attack which is counterbalanced by a steric effect favoring ω-attack at the other terminal carbon; 2- and 4-alkyl substituents direct attack to the farthest terminus through steric effects. Electron-withdrawing groups direct attack to the internal carbon. The product of internal attack in (entry j) is attributed to the perpendicular orientation of Ph relative to the pentadienyl ligand caused by the 2-methyl substituent; it thus acts as an inductively electron-withdrawing substituent.

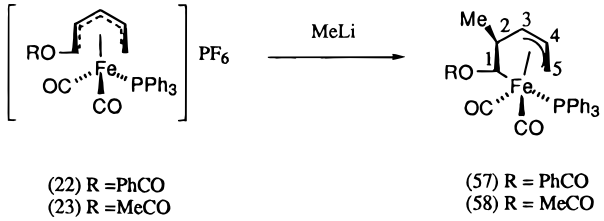
Our results are generally consistent with these observations. Thus, reaction of strong electron donor cyclic and acyclic complexes **5** and **21** with RLi or $NaBH_4$ proceeds exclusively via *ipso* substitution to give **54a**−**c** and **55** (Scheme 7). The regioselectivity is clearly indicated by the multiplicity of the methyl groups (singlet for **54a** and doublet for **55**), while the *E,Z* stereochemistry of **55** is clearly indicated by the deshielded H2 outer diene resonance at 2.45 ppm (J_{2-3} = 4.6 Hz). Lithium dimethylcuprate is less satisfactory. With **21**, substantial dealkylation is observed to generate (pentadienal)$Fe(CO)_2PPh_3$ (**30**:**31** = 8:1), while reaction with **5** proceeds with loss of regioselectivity to give an inseparable 1:1.5 mixture of **54a** and **56**.

Treatment of the acyloxy complexes **22** and **23** proceeds in good yield via internal attack to give the σ,π-allyl complexes **57** and **58** (Scheme 8). Internal attack suggests an electron-withdrawing nature for the acyloxy substituent, which is consistent with the ordering of

Scheme 7



Scheme 8



Hammett σ^+ values (indicative of the extent of resonance between an electron-donor substituent and a cationic reaction center (OMe (−0.78) > Me (−0.31) > Ph (−0.18) > H (0) > CH_3CO_2 (+0.18)).[23]

The configuration of **57** has been confirmed by an X-ray structure determination (Figure 4);[24] *exo* addition of the nucleophile is clearly evident. The structure is essentially octahedral (average non-allyl ∠L−M−L = 92°) with the allyl group occupying two positions with

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(22) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1989**, *30*, 1343.
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(24) The structure of an analogous tricarbonyl complex from the reaction of $P(OMe)_3$ with [(1-carbomethoxypentadienyl)$Fe(CO)_3$]BF_4 has been described: Pinsard, P.; Lellouche, J. P.; Beaucourt, J. P.; Toupet, L.; Schio, L.; Grée, R. *J. Organomet. Chem.* **1989**, *371*, 219.

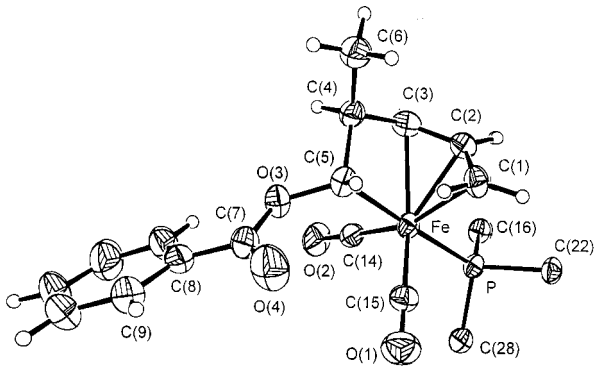
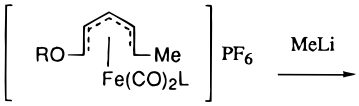
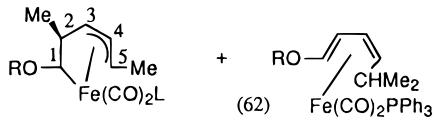


Figure 4. Crystal structure of **57**.

Scheme 9

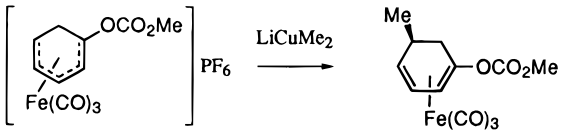


(8) L = CO, R = MeCO
(36) L = PPh_3, R = PhCO



(59) L = CO, R = MeCO
(60) L = PPh_3, R = PhCO
(61) L = CO, R = PhCO

Scheme 10



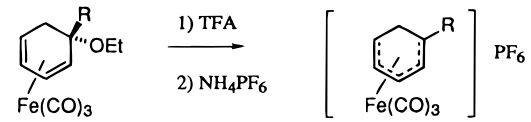
(6) (64)

a bite angle of 62°. The phosphine occupies specifically the position *trans* to the Fe−C σ-bond.

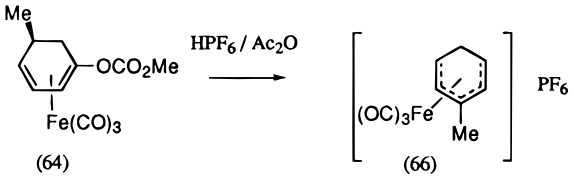
The ^{13}C and ^{31}P NMR spectra of cation **22** are essentially independent of temperature and (on the basis of observed axial and basal ^{13}CO resonances) show that only one basal isomer is populated, assigned as shown above on the basis of minimization of steric interactions between PPh_3 and the acyloxy substituent. It has been observed previously[18] that for the unsubstituted [(pentadienyl)$Fe(CO)_2L]^+$ cation (entries a and b in Table 1), PPh_3 substitution significantly alters regioselectivity toward the internal position. For **22** and **23**, the PPh_3 ligand may thus reinforce the directing effect of the acyloxy substituent.

Reactions of salts **8** and **36** with MeLi provide information on the relative directing power of acyloxy and methyl substituents and the influence of PPh_3 on regioselectivity. The tricarbonyl salt **8** provides only the σ,π-allyl complex **59** as the isolated product, thus indicating the dominance of the directing effect of the acyloxy substituent (Scheme 9). Reaction of the substituted salt **36** yields as isolated products a mixture of **60** and **62** together with a small amount of **61** derived from **60** by phosphine displacement. Though inseparable, the structures of **60** and **62** are clearly confirmed by the NMR spectra. The low yields of the reactions of both **8** and **36** with MeLi should be noted; unstable

Scheme 11



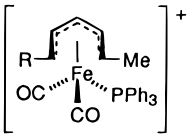
(54 a,b) R = Me, Bu (65 a,b) R = Me, Bu



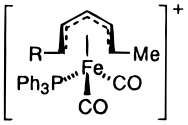
(64) (66)

products derived from nucleophilic attack at other sites (including CO ligands) may be formed but not isolated.

In contrast to **17**, the ^{31}P NMR spectrum of **36** is resolved into two resonances at −60 °C in the ratio 1:1.5, indicating that both basal isomers **36a,b** are substantially populated. It has also recently been shown[8]



(36a) R = $PhCO_2$



(36b) R = $PhCO_2$
(63) R = H

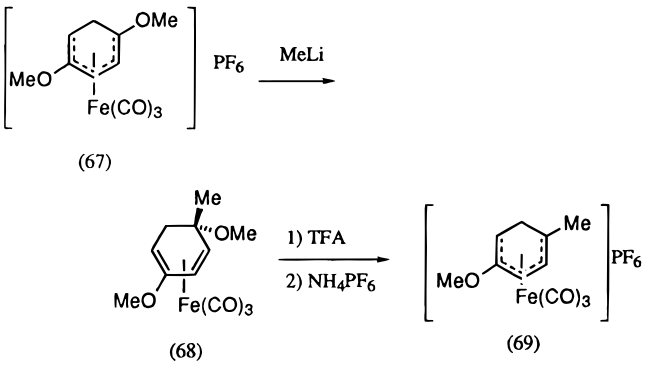
(entries c and d in Table 1) that phosphine substitution to give the [(1-methylpentadienyl)$Fe(CO)_2PPh_3]^+$ cation, assigned structure **63** on the basis of NMR results, selectively augments *ipso* attack at C1. The change in regioselectivity observed between **8** and **36** indicates that PPh_3 selectively activates this *ipso* attack compared to internal attack at C2. A substantial change in regioselectivity is observed for the cyclic acyloxy cation **6**, which reacts with $LiCuMe_2$ exclusively at the unsubstituted terminus to give **64** (Scheme 10). Finally, advantage may be taken of the different regiodirecting powers of alkoxy and acyloxy groups in the cyclic series to provide regioisomeric substituted cyclohexadienyl salts. Thus, whereas protonation of **54a,b** provides access to the 1-substituted salts **65a,b** in good yield, protonation of **64** yields only the 3-substituted complex **66** (Scheme 11). This latter result is in accord with the behavior of similar alkoxy-substituted complexes which are known to rearrange extensively before loss of the alkoxy group.[25] As expected, reaction of the 1,4-dimethoxy cation **67** with MeLi proceeds via *ipso* attack to give **68**, which itself is transformed on protonation into the known 2-methoxy-5-methyl cation **69** (Scheme 12).

Conclusions

The results thus demonstrate the stabilizing effect of PPh_3 substitution on the solvolysis of terminally substituted (acyloxy)- and alkoxypentadienyl complexes. These substituents, introduced using common precursors, provide complementary patterns of regioselectivity in nucleophilic attack (internal (β) vs ipso (α) for acyclic

(25) Owen, D. A.; Stephenson, G. R.; Finch, H.; Swanson, S. *J. Organomet. Chem.* **1989**, *364*, C11.

Scheme 12



complexes, terminal (ω) vs ipso (α) for cyclic complexes) which may have potential applications in synthesis.

Experimental Section

All reactions involving iron complexes were carried out in dry, degassed solvents under nitrogen. NMR spectra were recorded on a JEOL GSX 270 spectrometer; temperatures were measured using the built-in copper/constantan thermocouple. ^{1}H and ^{13}C chemical shifts are measured in ppm relative to tetramethylsilane; ^{31}P chemical shifts are measured in ppm relative to 85% H_3PO_4. Where observed, J_{P-C} values are given in parentheses. All J values are given in Hz. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. Preparative thin-layer chromatography was performed on a Harrison Research 7924 Chromatotron using 2 mm silica gel (type $PF60_{254}$) plates. The substrates **4**,[26] **7**,[11] **9**−**11**,[6] **12**, **14**,[11] **46**, **48**,[27] **49**, and **50**,[11] and **67**[28] were prepared as previously reported.

1. [5-(acetyloxy)-2,4-pentadienal]Fe(CO)$_2$PPh$_3$ (13). Complex **10** (0.5 g, 1.79 mmol) was added to a solution of PPh_3 (0.95 g, 3.58 mmol) in acetone (40 mL), and the mixture was heated to 50 °C; $Me_3NO{\cdot}2H_2O$ (0.6 g, 5.37 mmol) was added and the reaction monitored to completion by infrared spectroscopy (ca. 10 min). Diethyl ether (20 mL) was added and the reaction mixture filtered through Celite. After removal of solvent the crude product was purified by Chromatotron (4:1 petroleum ether (30−40 °C)−ethyl acetate) to give **13** as a yellow solid (0.62 g, 67%). Mp: 127−128 °C. Anal. Found (calcd): C, 62.8 (63.0); H, 4.63 (4.47). Infrared (hexane): 2011, 1951 cm^{-1}. ^{1}H NMR (C_6H_6, +55 °C): 8.96 (d, H1, J_{12} = 4.1), 0.12 (br, H2), 5.23 (dd, H3), 4.78 (br, H4), 4.12 (br, H5), 1.40 (s, $MeCO_2$), 6.9−7.6 (m, Ph). ^{31}P NMR (CD_2Cl_2, −40 °C): 69.7, 62.3 in the ratio of 2.2:1 axial:basal isomers. The latter resonance is further resolved into two (61.9 and 63.5) in the ratio of 1:1.75 at −115 °C due to slowing of the *s-cis*/*s-trans* interconversion.[9]

(pyrone)Fe(CO)$_2$PPh$_3$ (**47**) was prepared in a similar way. Yield: 58%. Mp: 184−185 °C. Anal. Found (calcd): C, 63.4 (63.8); H, 4.07 (4.04). Infrared (CH_2Cl_2): 2003, 1947 cm^{-1}. ^{1}H NMR (C_6D_6, +55 °C): 2.48 (m, H1, J_{1-2} = 5.4), 5.12 (m, H2, J_{2-3} = 6.8), 4.55 (m, H3, J_{3-4} = 5.0), 4.72 (m, H4), 6.9−7.3 (m, Ph). ^{31}P NMR (CD_2Cl_2, +20 °C): 66.7 (br). At −60 °C this is resolved into two resonances at 61.7 and 71.9 ppm in the ratio 1:1.8, assignable to the two possible basal isomers.

2. Synthesis of 16. Complex **10** (1.2 g, 4.28 mmol) was dissolved in methanol (50 mL) and the solution cooled to −10 °C. $NaBH_4$ (0.16 g, 4.28 mmol) was added and the reaction mixture stirred while it was warmed to room temperature. After completion of the reaction, water (50 mL) was added and the product extracted with diethyl ether (3 × 50 mL). After drying over $MgSO_4$, the solvent was removed and the crude product was purified by Chromatotron (4:1 petroleum ether (30−40 °C)−ethyl acetate) to give **16** as a yellow solid (0.93 g, 77%). Mp: 90−92 °C. Anal. Found (calcd): C, 42.9 (42.6); H, 3.79 (3.55). Infrared (CH_2Cl_2): 2055, 1985, 1979 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.5−3.8 (m, CH_2), 0.98 (m, H2), 5.31 (dd, H3, J_{2-3} = 9.0), 5.12 (dd, H4, J_{3-4} = 8.5), 4.05 (d, H5, J_{4-5} = 5.8), 2.02 (s, $MeCO_2$). ^{13}C NMR ($CDCl_3$, −70 °C): 81.7, 84.8 (C3, C4), 57.6 (C2), 63.6 (CH_2), 73.7 (C5), 20.7, 168.9 ($MeCO_2$), 215.0 (CO, axial), 208.6, 208.3 (CO, basal).

Complexes **15**, **17**, and **18**−**20** were prepared similarly.

15: yield 98%; yellow oil. M$^+$ (calculated and found): m/z 253.9874. Infrared (hexane): 2048, 1981, 1974 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.6 (m, CH_2), 0.70 (dd, H2), 5.04 (dd, H3), 5.17 (t, H4), 3.12 (d, H5), 3.41 (s, MeO). ^{13}C NMR (CD_2Cl_2, −70 °C): 56.7 (C1), 101.5, 79.5, 74.1, 63.9 (C2−C5), 60.4 (MeO), 216.9 (CO, axial), 209.4, 209.8 (CO, basal).

17: yield 98%; mp 89−90 °C. Anal. Found (calcd): C, 52.6 (52.3); H, 3.34 (3.49). Infrared (hexane): 2051, 1995, 1981 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.4−3.8 (m, CH_2), 1.10 (m, H2), 5.48 (dd, H3, J_{2-3} = 9.0), 5.18 (dd, H4, J_{3-4} = 8.4), 4.35 (d, H5, J_{4-5} = 5.7), 7.3−8.0 (m, Ph).

18: yield 66%; yellow semisolid. Anal. Found (calcd): C, 64.6 (63.9); H, 5.36 (5.12). Infrared (hexane): 1984, 1926 cm^{-1}. ^{1}H NMR (C_6D_6, +20 °C): 3.30−3.60 (m, br, CH_2, H5), 0.05 (br, H2), 4.58 (br, H3), 4.40 (dd, H4), 2.75 (s, MeO), 6.9−7.7 (m, Ph).

19: yield 95%; mp 148−150 °C. Anal. Found (calcd): C, 62.7 (62.8); H, 4.93 (4.84). Infrared (hexane): 1983, 1927 cm^{-1}. ^{1}H NMR (C_6D_6, +60 °C): 3.30 (m, br, CH_2), −0.06 (m, H2), 4.90 (dd, H3), 4.68 (br, H4), 4.00 (t, br, H5), 1.31 (s, $MeCO_2$).

20: yield 92%; mp 177−179 °C. Anal. Found (calcd): C, 66.7 (66.4); H, 4.59 (4.67). Infrared (hexane): 1983, 1923 cm^{-1}. ^{1}H NMR (C_6D_6, +60 °C): 3.25 (d, CH_2), −0.15 (m, H2), 4.93 (t, br, H3), 4.70 (dd, H4), 4.08 (dd, H5, J_{P-5} = 10.1), 6.8−8.0 (m, Ph).

3. Reaction of 11 with MeMgI. A solution of **11** (1.0 g, 2.9 mmol) in diethyl ether (30 mL) was cooled to −78 °C. MeMgI (3.49 mmol, 1.16 mL of a 3 M solution in diethyl ether) was added dropwise and the resulting solution stirred at −78 °C for 10 min. After it was warmed to room temperature, the reaction mixture was quenched with saturated NH_4Cl solution (30 mL). The aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined ether extracts were dried over $MgSO_4$, and the solvent was removed. Purification of the residue by Chromatotron (4:1 petroleum ether (30−40 °C)−ethyl acetate) provided the two diastereoisomers **33** and **32** in order of elution.

33: yield 0.32 g, 43%; mp 115−116 °C. Anal. Found (calcd): C 53.9 (53.7); H, 4.03 (3.91). Infrared (CH_2Cl_2): 2051, 1981 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.85 (m, CH), 1.06 (dd, H2, J_{2-CH} = 8.8), 5.45 (t, H3, J_{2-3} = 6.1), 5.19 (dd, H4), 4.26 (t, H5), 1.32 (d, Me, J_{CH-Me} = 6.4), 7.4−8.0 (m, Ph).

32: yield 0.14 g, 14%; mp 112−113 °C. Anal. Found (calcd): C 53.5 (53.7); H, 3.99 (3.91). Infrared (CH_2Cl_2): 2043, 1973 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.57 (m, CH), 0.95 (t, H2, J_{2-CH} = 8.8), 5.45 (t, H3, J_{2-3} = 6.1), 5.25 (dd, H4), 4.36 (d, H5), 1.37 (d, Me, J_{CH-Me} = 6.3), 7.4−8.0 (m, Ph).

Reaction with the PPh_3 derivative **14** was carried out in the same way to give the two diastereoisomers **35** and **34** in order of elution.

35: yield 25%; mp 162−164 °C. Anal. Found (calcd): C, 67.3 (66.9); H, 4.91 (4.9). Infrared (hexane): 1977, 1915 cm^{-1}. ^{1}H NMR (C_6D_6, +75 °C): 3.51 (m, br, CH), 0.21 (m, br, H2), 4.59 (dd, H3), 4.79 (br, H4), 4.0 (t, br, H5), 1.10 (d, CH_3, J_{CH-Me} = 7.2), 6.9−8.0 (m, Ph). ^{31}P NMR (CD_2Cl_2, +20°C): 65.2 (br). At −60 °C this is resolved into two resonances at 65.7 and 64.1 in the ratio of 1.4:1.

34: yield 67%; mp 154−155 °C. Anal. Found (calcd): C, 66.9 (66.80); H, 5.00 (4.90). Infrared (hexane): 1975, 1917 cm^{-1}. ^{1}H NMR (C_6D_6, +80 °C): 3.50 (q, br, CH), 0.10 (m, br,

(26) Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882.
(27) DePuy, C. H.; Parton, R. L.; Jones, T. *J. Am. Chem. Soc.* **1977**, *99*, 4070.
(28) Stephenson, G. R.; Finch, H.; Owen, D. A.; Swanson, S. *Tetrahedron* **1993**, *49*, 5649.

H2), 5.05 (dd, H3), 4.73 (br, H4), 4.25 (t, br, H5), 0.99 (d, br, Me, $J_{CH-Me} = 6.7$), 6.9−8.0 (m, Ph). ^{13}C NMR (CD_2Cl_2, −40 °C): 86.7 (8.0), 80.8, 78.0, 71.5 (C3, C4, C5, CH), 57.9 (6.0) (C2), 24.5 (Me), 165.0 (Ph*C*O_2), 127−139 (Ph), 222.4 (6.8) (CO, axial), 214.3 (25.7) (CO, basal). ^{31}P NMR (CD_2Cl_2, +20 °C): 65.8 (br). At −60 °C this is resolved into two resonances at 66.1 and 65.7 ppm in the ratio 3.9:1.

4. Synthesis of 22. Complex **19** (0.19 g, 0.37 mmol) was dissolved in diethyl ether (10 mL) and the solution cooled to 0 °C, with stirring. HPF_6 (0.37 mmol, 69 μL of 60% aqueous HPF_6) was added dropwise with stirring. After standing for 10 min, the yellow precipitate was collected by filtration and washed with cold diethyl ether (0.21 g, 89%). Mp: 113−114 °C dec. Anal. Found (calcd): C, 49.6 (50.2); H, 4.33 (3.73). Infrared (CH_2Cl_2): 2051, 2011 cm^{-1}. ^{13}C NMR (CD_2Cl_2, −40 °C): 61.2 (C5), 86.3, 92.2, 101.2 (3.0), 102.3 (C1−C4), 20.8, 168.0 (MeCO_2), 128−133 (Ph), 204.0 (31.6) (CO, basal), 213.8 (15.2) (CO, axial). ^{31}P NMR (CD_2Cl_2, +20 °C): 60.0.

Complexes **21**, **23**, and **36** were prepared similarly.

21: yield 76%; mp 127−129 °C dec. Anal. Found (calcd): C, 50.2 (50.6); H, 3.87 (3.90). Infrared (CH_2Cl_2): 2040, 1992 cm^{-1}. ^{13}C NMR (CD_2Cl_2, −40 °C): 130.2 (C1), 79.8, 79.8, 99.5 (C2−C4), 62.4, 57.7 (C5, OMe), 128−133 (Ph), 205.4 (32.3) (CO, basal), 221.1 (14.8) (CO, axial). ^{31}P NMR (CD_2Cl_2, +20 °C): 63.6.

23: yield 81%; mp 152−154 °C dec. Anal. Found (calcd): C, 55.0 (54.4); H, 3.60 (3.68). Infrared (CH_2Cl_2): 2045, 2007 cm^{-1}. ^1H NMR (CD_2Cl_2/CF_3CO_2D, −20 °C): 6.13 (d, H1, $J_{1-2} = 8.6$), 5.95 (t, H2, $J_{2-3} \approx J_{3-4} = 8.0$), 6.59, (t, H3), 5.10 (m, H4), 1.11 (m, H5 inner), 2.45 (m, H5 outer), 7.3−8.2 (m, Ph) (all peaks are broadened and J_{4-5} values could not be measured). ^{13}C NMR (CD_2Cl_2, −40 °C): 61.3 (C5), 86.9, 92.5, 100.4, 102.3 (C1−C4), 127−135 (Ph), 163.2 (Ph***C***O_2), 204.2 (33.6) (CO, basal), 213.7 (14.8) (CO, axial). ^{31}P NMR (CD_2Cl_2, +20 °C): 60.1.

36: yield 80%; mp 135−136 °C dec. Anal. Found (calcd): C, 53.2 (55.0); H, 3.73 (3.90). Infrared (CH_2Cl_2) : 2039, 1999 cm^{-1}. ^{13}C NMR (CD_2Cl_2, −65 °C): 84.3, 85.8, 86.9, 90.3, 92.8, 95.4, 95.5, 98.9, 102.1, 104.6 (C1−C5), 14.8, 20.5 (Me), 126−135 (Ph), 163.3, 163.5 (Ph*C*O_2), 205.3 (35.5), 205.4 (35.0) (CO, basal), 215.6 (15.4), 216.3 (13.4) (CO, axial). ^{31}P NMR (CD_2Cl_2, +20 °C): 53.6. At −60 °C this is resolved into two resonances at 54.3 and 55.2 ppm in the ratio of 1:1.5.

5. Synthesis of 8. (sorbaldehyde)$Fe(CO)_3$ (**7**; 1.0 g, 4.24 mmol) in acetic anhydride (4.5 mL) was cooled to −78 °C with stirring. HPF_6 (1.5 mL of a 60% aqueous solution) was added dropwise to yield a dark solution, which later solidified. The mixture was warmed to 0 °C over 1.5 h, and diethyl ether was added in small portions to give a black precipitate. The solvent was decanted and the residue triturated with a 2:1 mixture of diethyl ether−CH_2Cl_2 to give eventually a yellow precipitate, which was separated by filtration (1.4 g, 78%). Anal. Found (calcd): C, 31.0 (31.2); H, 2.7 (2.6). Infrared (CH_2Cl_2): 2111, 2059 cm^{-1}. ^1H NMR (CF_3CO_2D, +20 °C): 3.10 (m, H5, $J_{5-Me} = 5.8$, $J_{4-5} = 12.8$), 5.89, 6.16 (dd, t, H2, 4, $J_{2-3} \approx J_{3-4} = 6.8$), 5.98 (d, H1, $J_{1-2} = 9.6$), 7.10 (t, H3). The material is hygroscopic, decomposing in undried solvents to regenerate **7**.

6. Synthesis of 5. Complex **4** (3.0 g, 12.8 mmol) was added to a solution of Et_3OPF_6 (3.0 g, stabilized with 10% diethyl ether, 10.9 mmol) in dry CH_2Cl_2 (50 mL). After it was stirred for 70 h at room temperature, the solution was poured into diethyl ether (160 mL). The precipitate was collected and dried under vacuum to give **5** as a yellow powder (3.8 g, 85%). Anal. Found (calcd): C, 32.4 (32.4); H, 2.5 (2.7). Infrared (CH_3CN): 2100, 2045 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): 7.20 (t, H3, $J_{2-3} \approx J_{3-4} = 5.5$), 6.43 (t, H4, $J_{4-5} = 5.5$), 4.84 (d, H2), 4.20−4.44 (m, H5, CH_2), 3.45 (dd, H6$_\beta$, $J_{5-6} = 5.5$, $J_{\alpha-\beta} = 18$), 2.95 (d, H6$_\alpha$), 1.44 (t, Me, $J_{CH_2CH_3} = 7$).

7. Synthesis of 6. HPF_6 (2.0 mL, 75% aqueous, 10.3 mmol) was added to acetic anhydride (10 mL) at −15 °C, and the mixture was warmed to room temperature over 1 h. After this mixture was then cooled to 0 °C, a solution of **4** (1.0 g, 4.3 mmol) in dry CH_2Cl_2 (2.0 mL) was added. After the mixture was warmed to room temperature over 2 h, diethyl ether (30 mL) was added. The product **6** was collected as a yellow solid (1.5 g, 88%) by filtration. Infrared (CH_3CN): 2098, 2042 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): 7.01 (t, H3, $J_{2-3} \approx J_{3-4} = 5.5$), 6.28 (t, H4, $J_{4-5} = 5.5$), 4.40 (d, H2), 4.14 (t, H5, $J_{4-5} \approx J_{5-6_\beta} = 5.5$), 3.37 (dd, H6$_\beta$, $J_{\alpha-\beta} = 18$), 2.90 (d, H6$_\alpha$), 2.06 (s, OAc). Satisfactory microanalysis could not be obtained; the structure is confirmed, however, by reduction of **6** to yield the known[29] compound **54c**.

8. Hydrolysis of 23. Sodium bicarbonate (0.08 g) and water (10 mL) were added to a solution of **23** (0.16 g, 0.22 mmol) in the minimum amount of acetone. After it was warmed to 50 °C for 10 min, the yellow solution obtained was extracted with diethyl ether (3 × 20 mL). After drying over $MgSO_4$ and evaporation of the solvent, the residue was purified by Chromatotron (4:1 petroleum ether (30−40 °C)−ethyl acetate) to give, in order of elution, the *E* isomer **30** (35 mg, 70%), identified by comparison with literature data,[9] and the *Z* isomer **31** (5 mg, 10%). Mp: 110−111 °C. Anal. Found (calcd): C, 66.2 (65.8); H, 4.87 (4.60). Infrared (CH_2Cl_2): 1987, 1931 cm^{-1}. ^1H NMR (C_6D_6, +20 °C): 9.21 (d, H1, $J_{1-2} = 3.3$), 2.59 (m, H2, $J_{2-3} \approx J_{2-5} = 5.2$), 4.55 (br, H3, $J_{3-4} = 5.3$), 4.72 (br, H4), 2.5−2.6 (m, 2H5), 6.9−7.6 (m, Ph). ^{31}P NMR (CD_2Cl_2, +20 °C): 68.5. At −100 °C, this is resolved into two resonances at 63.6 and 72.5 ppm in the ratio 1:2.5.

Similar treatment of **36** gave a 1:1 mixture of **37** and **38** which was separated by Chromatotron. Complex **37** was identified by comparison with literature data.[9] **38:** mp 124−125 °C. Anal. Found (calcd): C, 66.8 (66.4); H, 5.05 (4.89). Infrared (CH_2Cl_2): 1971, 1919 cm^{-1}. ^1H NMR (C_6D_6, +20 °C): 9.08 (d, H1, $J_{1-2} = 5.2$), 2.45 (m, H2, 5, $J_{2-3} = 6.0$, $J_{4-5} = 10.8$), 3.90 (m, H3, $J_{3-4} = 6.5$), 4.75 (dd, H5), 1.25 (d, Me, $J_{5-Me} = 6.3$), 6.9−7.6 (m, Ph).

9. Attempted Protonation of 15 and 17. (a) Complex **15** (0.54 g, 2.1 mmol) was dissolved in diethyl ether and the solution cooled to 0 °C. With stirring, HPF_6 (180 μL of a 60% aqueous solution) was added dropwise; no precipitate was observed after 1 h. Saturated $NaHCO_3$ solution (30 mL) was added and the product extracted with diethyl ether (3 × 50 mL). After drying over $MgSO_4$ and evaporation, the residue was purified by Chromatotron using 4:1 petroleum ether (30−40 °C)−ethyl acetate to give, in order of elution, complex **27** (0.23 g, 41%) and an inseparable mixture of **28** and **29** in the ratio of 1:2 (0.21 g, 45%).

27: orange oil. M^+: *m*/*z* 268.0030 (calculated and found). Infrared (hexane): 2065, 2005, 1995 cm^{-1}. ^1H NMR (C_6D_6): 0.40 (m, H2), 2.98, 3.21 (dd, CH_2, $J_{vic} = 10.7$, $J_{1-CH_2} = 5.2$, 4.4), 4.46 (dd, H3), 4.71 (t, H4), 2.72 (d, H5), 2.90, 3.00 (s, 2MeO). ^{13}C NMR (CD_2Cl_2, −70 °C): 101.5, 79.9, 74.0, 73.7 (C3−C5, CH_2), 60.4, 57.8, 53.3 (C2, 2MeO), 216.9 (CO, axial), 209.4, 209.9 (CO, basal).

28/**29:** orange oil. M^+: *m*/*z* 221.9613 (calculated and found). Infrared (hexane): **28**, 2047, 1983, 1975 cm^{-1}; **29**, 2067, 2011, 1995 cm^{-1}. ^1H NMR (C_6D_6): **28**, 8.95 (d, H1, $J_{1-2} = 3.4$), 0.62 (dd, H2), 5.22 (dd, H3), 4.43 (dd, H4), 0.02 (qd, H5i), 1.25 (qd, H5o); **29**, 8.89 (dd, H1, $J_{1-2} = 2.2$, $J_{1-3} = 1.2$), 2.22 (dd, H2, $J_{2-3} = 6.7$), 4.43 (t, H3), 4.55 (m, H4), 1.31 (dd, H5i, $J_{4-5} = 10.0$), 1.58 (m, H5o, $J_{4-5} = 8.0$, $J_{vic} = 2.7$).

(b) Complex **19** when subjected to protonation and $NaHCO_3$ quenching as above, gave only recovered starting material.

10. Attempted Preparation of [(1,5-diacetoxypentadienyl)Fe(CO)$_3$]PF$_6$. Acetoxyaldehyde complex **10** (1.05 g, 3.75 mmol) in ethanoic anhydride (2 mL) was added to a preequilibrated (20 min), precooled (−30 °C) mixture of etha-

(29) *endo*-alkoxy complexes may be formed by acid treatment of the *exo* complex derived from nucleophilic attack on the [(cyclohexadienyl)-$Fe(CO)_3]^+$ cation: (a) Burrows, A. L.; Parker, D. G.; Hine, K.; Johnson, B. F. G.; Lewis, J.; Poe, A.; Vichi, E. J. S. *J. Chem. Soc., Dalton Trans.* **1980**, 1135. (b) Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Parker, D. G. *J. Organomet. Chem.* **1977**, *127*, C22.

noic anhydride (5 mL) and hexafluorophosphoric acid (2 mL). After the mixture was stirred for 1 h, the reaction was monitored by FT-IR and determined to be complete by the presence of bands at 2115 and 2074 cm^{-1}. The reaction solution was pipetted into ether, whereupon a black intractable tar formed.

11. Reaction of 21 with MeLi. A solution of **21** (0.5 g, 0.81 mmol) in CH_2Cl_2 (30 mL) was cooled to −78 °C. MeLi (0.8 mL of a 1 M solution in diethyl ether) was added dropwise with stirring. The solution was warmed to 10 °C and poured into distilled water (50 mL). The product was extracted with diethyl ether (3 × 50 mL) and dried over $MgSO_4$. Removal of solvent and crystallization from petroleum ether gave **55** as orange crystals (0.28 g, 75%). Mp: 121−122 °C. Anal. Found (calcd): C, 66.7 (66.7); H, 5.8 (5.6). Infrared (CH_2Cl_2): 1967, 1911 cm^{-1}. ^1H NMR (C_6D_6, +60 °C): 2.98 (m, H1, $J_{1-2} \approx J_{2-3} = 4.6$, $J_{1-Me} = 6.2$), 2.45 (m, H2), 4.48 (m, H3, $J_{3-4} = 8.0$), 4.80 (m, H4), 1.30 (m, H5outer, J_{4-5}(outer) = 4.5), 1.03 (m, H5 inner, J_{4-5}(inner) = 9.5), 0.95 (d, Me), 3.37 (s, OMe), 6.9−7.6 (m, Ph). ^{13}C NMR ($CDCl_3$, +20 °C): 91.0, 83.6 (C3, C4), 75.8, 61.9, 56.1, 41.6 (C1, C2, C5, OMe), 24.8 (Me), 128−136 (Ph). ^{31}P NMR ($CDCl_3$): 68.5.

Reactions of **22**, **23**, **36**, **8**, **5**, **6**, and **67** with MeLi were performed in a similar fashion. Complexes **61** and **60**/**62** were separated by Chromatotron using 4:1 petroleum ether (30−40 °C)−ethyl acetate, the tricarbonyl complex eluting first.

57: yield 61%, purified by Chromatotron (4:1 petroleum ether (30−40 °C)−ethyl acetate); mp 179−180 °C. Anal. Found (calcd): C, 69.0 (68.8); H, 5.02 (5.03). Infrared (CH_2Cl_2): 1983, 1927 cm^{-1}. ^1H NMR (C_6D_6): 4.30 (m, H1, 3), 3.15 (m, H2, $J_{1-2} \approx J_{2-3} = 6.3$, $J_{2-Me} = 6.9$), 3.60 (m, H4, $J_{3-4} = 6.3$), 1.86 (m, H5 inner, J_{4-5}(inner) = 12.3, J_{P-5}(inner) = 6.9), 2.51 (m, H5 outer, J_{4-5}(outer) = 7.4, J_{P-5}(outer) = 2.9), 0.75 (d, Me, $J_{Me-1} = 6.84$), 6.8−8.5 (m, Ph). ^{13}C NMR (CD_2Cl_2): 96.5, 68.6, 66.8, 66.4 (C1, C3, C4, C5), 44.3 (C2), 23.8 (Me), 166.8 (Ph*C*O_2), 128−134 (Ph), 219.6 (16.8), 219.5 (12.1) (CO). ^{31}P NMR (CD_2Cl_2): 55.3.

58: yield 65%; purified by Chromatotron (4:1 petroleum ether (30−40 °C)−ethyl acetate); mp 179−181 °C. Anal. Found (calcd): C, 64.8 (65.3); H, 5.26 (5.25). Infrared (CH_2Cl_2): 1985, 1927 cm^{-1}. ^1H NMR (C_6D_6): 4.00 (d, H1, $J_{1-2} = 5.8$), 3.06 (m, H2, $J_{2-3} = 6.9$, $J_{2-Me} = 6.9$), 4.26 (t, H3, $J_{3-4} = 6.3$), 3.59 (m, H4), 1.81 (m, H5 inner, J_{4-5}(inner) = 11.2, J_{P-5}(inner) = 6.3), 2.50 (m, H5 outer, J_{4-5}(outer) = 7.9, J_{P-5}(outer) = 3.5), 0.75 (d, Me), 6.8−7.6 (m, Ph).

59: yield 30%; purified by Chromatotron (4:1 petroleum ether (30−40 °C)−ethyl acetate); yellow oil. M^+: *m*/*z* 294.0191 (calculated and found). Infrared (CH_2Cl_2): 2052, 1979 cm^{-1}. ^1H NMR (C_6D_6): 3.54 (d, H1, $J_{1-2} = 6.1$), 2.58 (m, H2, $J_{2-Me} = 7.1$, $J_{2-3} = 4.6$), 2.47 (m, H5, $J_{4-5} = 9.6$, $J_{5-Me} = 5.9$), 3.60 (dd, H4, $J_{3-4} = 5.7$), 3.75 (t, H3), 0.45 (d, Me(2)), 1.35 (d, Me(5)).

61: yield 4%; yellow oil. $(M-CO)^+$: *m*/*z* 328. Infrared (CH_2Cl_2): 2047, 1979 cm^{-1}. ^1H NMR (C_6D_6): 3.86 (d, H1, $J_{1-2} = 6.6$), 2.65 (m, H2, $J_{2-Me} = 7.1$, $J_{2-3} = 4.5$), 2.50 (m, H5, $J_{4-5} = 9.5$, $J_{5-Me} = 6.0$), 3.60 (dd, H4, $J_{3-4} = 5.6$), 3.80, (t, H3), 0.46 (d, Me(2)), 1.33 (d, Me(5)).

60/**62:** yield 59%; yellow semisolid. Infrared (CH_2Cl_2): 1979, 1919 cm^{-1}. ^1H NMR (C_6D_6): **60**, 4.32 (d, H1, $J_{1-2} = 5.9$), 3.10 (m, H2, $J_{2-3} = 6.8$, $J_{2-Me} = 7.2$), 3.70 (t, H3, $J_{3-4} = 6.8$), 3.35 (dd, H4, $J_{4-5} = 9.5$), 2.98 (m, H5, $J_{5-Me} = 5.9$), 0.72 (d, Me(2)), 1.20 (d, Me(5)); **62**, 4.10 (m, H1, $J_{1-2} = 5.8$, $J_{1-P} = 3.4$), 5.46 (t, H2, $J_{2-3} = 5.4$), 5.64 (dd, H3, $J_{3-4} = 6.8$), 1.40 (m, br, CH, $J_{CH-Me} = 6.8$), 0.65, 1.00 (d, 2Me). ^{31}P NMR ($CDCl_3$): **60**, 53.3; **62**, 68.5.

54a: yield 84%; purified by flash chromatography (95:5 hexane−ethyl acetate); yellow oil. Anal. Found (calcd): C, 51.8 (52.0); H, 5.1 (5.2). Infrared (hexane): 2053, 1991, 1973 cm^{-1}. ^1H NMR ($CDCl_3$): 5.36 (m, H3), 5.27 (ddd, H2, $J_{2-3} = 4$), 3.14 (d, H4, $J_{3-4} = 7$), 3.00 (m, H1, $J_{1-2} = 6$), 1.94 (dd, H6$_\beta$, $J_{\alpha-\beta} = 15$, $J_{1-6_\beta} = 4$), 1.62 (dd, H6$_\alpha$, $J_{1-6_\alpha} = 2$), 1.19 (s, Me), 1.20 (t, CH_2CH_3, $J = 7$), 2.43, 3.35 (dd, CH_2CH_3, $J_{gem} = 9$).

54b: yield 89%; purified by flash chromatography (95:5 hexane−ethyl acetate). Anal. Found (calcd): C, 56.3 (56.3); H, 6.55 (6.30). Infrared (hexane): 2052, 1990, 1973 cm^{-1}. ^1H NMR ($CDCl_3$): 5.15−5.43 (m, H2,3), 2.81−3.67 (m, H1,4 and CH_2CH_3), 1.90 (dd, H6$_\beta$, $J_{1-6_\beta} = 4$, $J_{\alpha-\beta} = 15$), 1.55 (dd, H6$_\alpha$, $J_{1-6\alpha} = 2$), 0.6−1.5 (m, Bu^n and CH_2CH_3).

68: yield 46%; purified by flash chromatography (7:3 hexane−CH_2Cl_2); yellow oil. Anal. Found (calcd): C, 49.4 (49.0); H, 4.8 (4.8). Infrared (hexane): 2052, 1988, 1972 cm^{-1}. ^1H NMR ($CDCl_3$): 5.03 (dd, H3, $J_{2-3} = 7.0$), 2.66 (d, H4), 3.22 (m, H1), 1.88 (dd, H6$_\beta$, $J_{\alpha-\beta} = 14.5$, $J_{1-6_\beta} = 3.5$), 1.66 (dd, H6$_\alpha$, $J_{1-6_\alpha} = 2.0$), 1.18 (s, Me), 3.16 (s, 5-OMe), 3.65 (s, 2-OMe).

12. Reaction of 5 and 6 with $LiCuMe_2$. MeLi (2.86 mL, 1.40 M in diethyl ether, 4.0 mmol) was added slowly to a suspension of CuI (380 mg, 2.0 mmol) in dry THF (10 mL) at 0 °C. After the mixture was stirred to obtain a colorless solution, complex **5** (408 mg, 1.0 mmol) was added. After it was stirred for 15 min, the mixture was poured into saturated NH_4Cl solution (10 mL) and diethyl ether (25 mL). After filtration through Celite, the layers were separated and the organic layer washed with water (10 mL) and brine (10 mL) and dried over $MgSO_4$. After removal of solvent, the residue was purified by flash chromatography (97:3 petroleum ether (30−40 °C)−ethyl acetate) to give (in order of elution) complexes **54a** (40 mg, 14%; see section 11) and **56** (62 mg, 22%). Complex **56**: semisolid. Anal. Found (calcd): C, 52.1 (51.8); H, 5.1 (5.1). Infrared (hexane): 2041, 1973, 1967 cm^{-1}. ^1H NMR ($CDCl_3$): 5.38 (dd, H2, $J_{2-3} = 5$), 5.00 (dd, H3, $J_{3-4} = 6.5$), 2.85 (m, H4), 2.25 (m, H5), 2.48 (m, H6$_\beta$, $J_{gem} = 13.5$), 1.35 (m, H6$_\alpha$), 0.95 (d, Me, $J_{5-Me} = 6.5$), 1.22 (t, CH_2CH_3, $J = 7$), 3.35, 3.87 (dq, CH_2CH_3, $J_{gem} = 9$).

Reaction of $LiCuMe_2$ with **6** was performed in the same way. Column chromatography (petroleum ether (30−40 °C) followed by 6:4 petroleum ether−diethyl ether) gave (in order of elution) complexes **64** (62%) and **4** (10%). Complex **64**: yellow oil. Anal. Found (calcd): C, 49.4 (49.3); H, 4.1 (4.1). Infrared (hexane): 2058, 1999, 1970 cm^{-1}. ^1H NMR ($CDCl_3$): 5.43 (d, H2, $J_{2-3} = 4$), 5.07 (m, H3), 3.00 (m, H4), 2.45 (dd, H6$_\beta$, $J_{5-6_\beta} = 11.3$, $J_{\alpha-\beta} = 13.4$), 1.39 (dd, H6$_\alpha$, $J_{5-6_\alpha} = 3.1$), 2.38 (m, H5), 0.98 (d, CH_3, $J_{5-Me} = 6.7$), 2.04 (s, OAc).

13. Reaction of 5 with $NaBH_4$. $NaBH_4$ (300 mg, 7.2 mmol) was added to a stirred solution of **5** (719 mg, 1.76 mmol) in dry CH_3CN (30 mL). After the mixture was stirred for 45 min at room temperature, solvent was removed and the residue extracted with hexane (3 × 30 mL). Purification by flash chromatography (95:5 hexane−diethyl ether) afforded the product **54c**[29] (237 mg, 51%) as a yellow oil. Anal. Found (calcd): C, 50.3 (50.0); H, 4.3 (4.6). Infrared (hexane): 2054, 1992, 1974 cm^{-1}. ^1H NMR ($CDCl_3$): 5.27 (m, H2,3), 3.09 (m, H1), 3.30 (m, H4), 3.41 (m, H5 and CH_2CH_3), 1.95 (ddd, H6$_\beta$, $J_{\alpha-\beta} = 15.5$, $J_{5-6_\beta} = 7.0$, $J_{1-6_\beta} = 2.0$), 1.57 (ddd, H6$_\alpha$, $J_{5-6_\alpha} = 3.5$, $J_{1-6_\alpha} = 2.0$), 1.19 (t, CH_2CH_3, $J = 7.0$).

14. Conversion of 54a into 65a. Complex **54a** (170 mg, 0.62 mmol) was added to trifluoroacetic acid (0.34 mL, 4.41 mmol) and shaken at room temperature for 15 min. The reaction mixture was added to a solution of NH_4PF_6 (170 mg, 1.64 mmol) in water (2 mL), causing immediate formation of a precipitate which was collected by filtration to afford complex **65a**[30] as a yellow powder (202 mg, 85%). Infrared (CH_3CN): 2110, 2060 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): 7.40 (t, H3, $J_{2-3} \approx J_{3-4} = 5.5$), 6.07 (t, H4, $J_{4-5} = 6$), 5.93 (d, H2), 4.55 (t, H5), 3.19 (dd, H6$_\beta$, $J_{\alpha-\beta} = 16$, $J_{5-6_\beta} = 6$), 2.40 (d, H6$_\alpha$), 1.97 (s, Me).

65b: yield 96%; yellow powder. Infrared (CH_3CN): 2110, 2060 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): 7.40 (t, H3, $J_{2-3} = J_{3-4} = 5.5$), 6.18 (t, H4, $J_{4-5} = 6$), 5.89 (d, H2), 4.52 (t, H5), 3.14 (dd, H6$_\beta$, $J_{\alpha-\beta} = 16$, $J_{5-6\beta} = 6$), 2.37 (d, H6$_\alpha$), 0.6−1.7 (m, Bu).

69:[31] yield 85%; yellow powder. Infrared (CH_3CN): 2107, 2056 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): 7.18 (dd, H3, $J_{2-3} = 6$), 5.99

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Table 2. Crystal Data

	34	**35**	**57**
empirical formula	$C_{33}H_{29}FeO_5P$	$C_{33}H_{29}FeO_5P$	$C_{33}H_{29}FeO_4P$
fw	591.37	591.37	576.38
temp, K	293(2)	293(2)	293(2)
wavelength, Å	0.710 69	0.710 69	0.710 69
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
unit cell dimens			
a, Å	9.988(2)	14.0720(10)	11.394(2)
b, Å	20.182(2)	14.8560(10)	15.706(2)
c, Å	14.540(2)	16.0540(10)	16.051(2)
α, deg	90	98.102(10)	90
β, deg	94.030(10)	112.118(10)	90
γ, deg	90	102.579(10)	90
V, Å^3	2923.7(8)	2940.8(3)	2872.2
Z	4	4	4
density (calcd), Mg/m^3	1.344	1.338	1.333
abs coeff, mm^{-1}	0.610	0.607	0.617
F(000)	1228	1232	1200
cryst size, mm	0.28 × 0.34 × 0.41	0.32 × 0.24 × 0.41	0.45 × 0.15 × 0.1
θ range for data collecn, deg	2.02−27.98	2.11−21.99	2.19−31.95
index ranges	$0 \le h \le 13$, $0 \le k \le 26$, $19 \le l \le 19$	$0 \le h \le 14$, $-15 \le k \le 7$, $16 \le l \le 15$	
no. of rflns collected	7620	6932	4832
no. of indep rflns	7032 (R(int) = 0.0787)	6390 (R(int) = 0.0272)	4347 (R(int) = 0.0400)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	7032/0/366	6390/0/725	4347/0/356
goodness of fit[a] on F^2	0.955	0.613	0.779
final R indices ($I > 2\sigma(I)$)[b]	R1 = 0.0730, wR2 = 0.1800	R1 = 0.0721, wR2 = 0.2409	R1 = 0.0463, wR2 = 0.1199
R indices (all data)	R1 = 0.1140, wR2 = 0.2003	R1 = 0.0826, wR2 = 0.2730	R1 = 0.1112, wR2 = 0.1459
largest diff peak and hole, e/Å^3	1.36 and −1.214	0.902 and −0.713	0.408 and −0.338

[a] Goodness of fit = $[\sum w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{parameters})]^{1/2}$. [b] R indices: $R1 = [\sum||F_o| - |F_c||]/\sum|F_o|$ (based on F); $wR2 = [[\sum w(|F_o - F_c|)^2]/[\sum w(|F_o|)^2]]^{1/2}$ (based on F^2). $w = q/[(\sigma F_o)^2 + (a*p)^2 + b*P + d + e*\sin\theta]$.

(d, H2), 4.26 (m, H5), 3.23 (dd, H6$_\beta$, $J_{\alpha-\beta} = 16$, $J_{5-6_\beta} = 5$), 2.55 (d, H6$_\alpha$), 1.90 (s, Me), 3.96 (s, MeO).

15. Conversion of 64 into 66. Aqueous HPF_6 (0.5 mL of 75% solution, 2.7 mmol) was added at room temperature to a stirred solution of **64** (200 mg, 0.68 mmol) in acetic anhydride (2 mL). After 3 h, diethyl ether (10 mL) was added and the product **66** was isolated by filtration as a yellow solid (159 mg, 62%). Infrared (CH_2Cl_2): 2128, 2058 cm^{-1}. ^{1}H NMR (CD_3CN): 5.80 (t, H2/4, $J_{1/5-2/4} = 7.2$), 4.08 (t, H1/5), 3.00 (m, H6$_\beta$, $J_{\alpha-\beta} = 19$, $J_{1/5-6_\beta} = 7.0$), 1.72 (d, H6$_\alpha$), 2.72 (s, Me).

16. *In Situ* NMR Studies. The substrate (10−15 mg) was dissolved in CD_2Cl_2 (1.5 mL) in a 5 mm NMR tube, and the solution was degassed with nitrogen and cooled to −80 °C. After addition of HSO_3F (0.1 mL, triply distilled) by syringe, the solution was mixed by shaking, placed in the NMR spectrometer, and warmed to −20 °C. The mixture remains two phases (yellow-orange CD_2Cl_2 layer over smaller orange HSO_3F layer) but nevertheless provides good-quality spectra. ^{1}H NMR spectral data for cations characterized *in situ* are given below.

39: 5.95 (d, H1, $J_{1-2} = 8.7$), 6.27 (t, H2, $J_{2-3} \approx J_{3-4} = 7.5$), 6.88 (t, H3), 5.79 (dd, H4, $J_{4-5} = 13.7$), 3.06 (m, H5, $J_{5-Me} = 5.9$), 1.93 (d, Me), 7.6−8.3 (m, Ph).

40: 6.18 (d, H1, $J_{1-2} = 8.2$), 6.38 (t, H2, $J_{2-3} \approx J_{3-4} = 6.8$), 7.10 (t, H3), 5.90 (dd, H4, $J_{4-5} = 9.3$), 4.70 (m, H5, $J_{5-Me} = 6.8$), 1.40 (d, Me), 7.6−8.3 (m, Ph).

41: 5.90 (d, H1, $J_{1-2} = 9.8$), 5.23 (t, H2, $J_{2-3} \approx J_{3-4} = 6.9$), 6.52 (t, H3), 5.60 (dd, H4, $J_{4-5} = 11.0$), 2.46 (m, H5, $J_{5-Me} = 6.1$), 1.74 (d, Me).

42: 5.66 (d, H1, $J_{1-2} = 9.8$), 5.19 (dd, H2, $J_{2-3} \approx J_{3-4} = 6.5$), 6.68 (t, H3), 5.93 (m, H4, J_{4-5}(outer) = 9.4, J_{4-5}(inner)= 11.8), 1.51 (dd, H5 inner, $J_{gem} = 4.0$), 3.28 (dd, H5 outer)), 4.06 (s, MeO).

44: 5.98 (d, H1, $J_{1-2} = 8.5$), 6.28 (t, H2, $J_{2-3} \approx J_{3-4} = 7.0$), 7.02 (t, H3), 6.11 (m, H4, J_{4-5}(outer) = 9.5, J_{4-5}(inner) = 13.5), 1.98 (dd, H5 inner, $J_{gem} = 4.0$), 3.85 (dd, H5 outer), 7.8−8.3 (m, Ph).

45: 5.8−6.0 (m, H1,4, $J_{1-2} = 10.3$), 5.25 (dd, H2, $J_{2-3} \approx J_{3-4} = 7.1$), 6.72 (t, H3), 1.50 (dd, H5 inner, J_{4-5}(inner) = 11.7, $J_{gem} = 3.5$), 3.28 (dd, H5 outer, J_{4-5}(outer) = 9.3). ^{1}H NMR of precursor **48** (C_6D_6): 5.09 (d, H1, $J_{1-2} = 6.1$), 4.90 (dd, H2, $J_{2-3} = 5.3$), 4.35 (t, H3, $J_{3-4} = 5.6$), 2.17 (m, H4), 2.61, 3.13 (t, dd, CH_2, $J_{4-CH_2} = 4.9$, 10.2, $J_{vic} = 11.4$), 1.48 (s, CO_2Me).

51: 3.10 (m, H1/5, $J_{1/2-4/5} = 12.2$), 5.65 (dd, H2/4), 6.78 (t, H3, $J_{2/4-3} = 7.0$), 1.75 (d, Me, $J_{1/5-Me} = 5.8$).

52: 3.36 (m, H1, $J_{1-2} = 11.7$, $J_{1-Me} = 6.8$), 5.80 (m, H2,4, $J_{2-3} \approx J_{3-4} = 7.5$), 6.95 (t, H3), 4.25 (m, H5, $J_{4-5} = 9.3$, $J_{5-Me} = 5.9$), 1.22 (d, Me(1)), 1.88 (d, Me(2)).

53: 3.11 (m, H1, $J_{1-2} = 12.6$, $J_{1-Me} = 6.4$), 5.77 (dd, H2), 6.01 (dd, H4), 6.87 (t, H3, $J_{2-3} \approx J_{3-4} = 7.0$), 2.03 (d, H5, $J_{4-5} = 12.8$), 1.85 (d, Me).

17. Crystallography. The structures were solved by direct methods (SHELXS-86)[33] and refined by full-matrix least squares (SHELXL-93).[34] Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All calculations were performed on a VAX 6610 computer. The ORTEX program[35] was used to obtain the drawings. Crystal data are given in Table 2.

Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for complexes **34**, **35**, and **57** (26 pages). Ordering information is given on any current masthead page.

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