Piano-stool Acylcyclopentadienyl Iron Complexes: Photolytic Syntheses and *X*-Ray Crystal Structure of [Fe(η^5-C_5H_4COMe)(dppe)(NCMe)]PF_6†

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Photolysis of monoacyl iron(II) metallocenes, [Fe(η^5-C_5H_4COR)(η^6-arene)]PF_6 (R = Me or Ph), in solvents of low electron donicity, at 273 K, and in the presence of two-electron ligands L [L = $P(OMe)_3$, $NCCH_3$, CO, or dppe ($Ph_2PCH_2CH_2PPh_2$)], leads to exchange of the arene by three L ligands. Thermal ligand exchange of the derived piano-stool cations [Fe(η^5-C_5H_4COR)L^1(L^2)L^3]PF_6, [L^1 = L^2 = $P(OMe)_3$, or L^1–L^2 = dppe; L^3 = NCMe] in the dark and at low CO pressure (5 atm) leads to the corresponding carbonyl derivatives [Fe(η^5-C_5H_4COR)L^1(L^2)(CO)]PF_6. In acetonitrile and under irradiation with visible light, the latter yield the corresponding acetonitrile complexes [Fe(η^5-C_5H_4COR)L^1(L^2)(NCMe)]PF_6. A new series of acyl substituted piano-stool cations [Fe{η^5-$C_5H_3CO(CH_2)_3$}L^1(L^2)L^3]PF_6 is obtained showing chirality at the acetylcyclopentadienyl ring. Diastereotopic phenomena in the racemic series of these asymmetric compounds have been observed by ^1H and ^{31}P n.m.r. spectroscopy. The *X*-ray structure of the acyl derivative [Fe(η^5-C_5H_4COMe)(dppe)(NCMe)]PF_6 has been determined and compared with the unsubstituted cyclopentadienyl piano-stool acetonitrile and carbonyl cationic complexes.

Ligand exchange reactions in chiral complexes are of interest because they enable study of asymmetric induction.[1] We report here a series of such reactions involving acylcyclopentadienyl–iron–arene complexes, some of which are chiral. Many photolytic ligand-exchange reactions of [Fe(cp)(arene)]$^+$ are known when cp is C_5H_5, but none has yet been reported for an acylcyclopentadienyl ring.[2–4] Indeed, the cyclopentadienyl substituents have a strong influence on the thermal stability and on the rate of arene exchange.

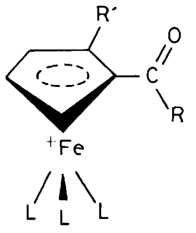
Although [Fe(C_5Me_5)(arene)]$^+$ complexes were believed to be photoinert,[3] we recently showed that this lack of photolability can be overcome in the presence of a sensitizer.[5] By contrast, in complexes for which the cyclopentadienyl ring is substituted by an electron-withdrawing acyl group, photolability is observed. Additionally intermediates are apparently also less stable and so greater care is required in control of the temperature.

Results and Discussion

The known cationic monoacylcyclopentadienyl–iron(II)–arene complexes, [Fe(η^5-C_5H_4COR)(η^6-arene)]PF_6 (**1**; R = Me or Ph), were synthesized from the corresponding monoacylferrocenes[6] under Fischer-type reaction conditions [equation (1)].

$$[Fe(\eta^5\text{-}C_5H_4COR)(cp)] + \text{arene} \xrightarrow{AlCl_3} [Fe(\eta^5\text{-}C_5H_4COR)(\text{arene})]^+ \quad (1)$$

In the study of the photoexchange reactions of these acyl-substituted cationic derivatives we have observed that the presence of acyl substituents provide a greater photolability of the iron(II) complexes as compared with the unsubstituted derivative, or those bearing electron-donating alkyl substituents on the cyclopentadienyl ring. We describe here the photochemical preparation of various symmetric and asymmetric acyl derivatives. Only [**2a**; L = $P(OMe)_3$, R = Me] has been previously prepared, but under different experimental conditions.[7]



L= $P(OMe)_3$, MeCN, CO, or dppe($Ph_2PCH_2CH_2PPh_2$)
R= Me (R′=H) or Ph(R′=H); RR′ = $-(CH_2)_3-$

The complexes [Fe(η^5-C_5H_4COR)(η^6-arene)]PF_6 (**1**; arene = naphthalene, benzene, toluene, xylene, or 1,3,5-trimethylbenzene) have similar photolytic behaviour differing only in their rates of photochemical exchange.[8] The following discussion is restricted to the benzene derivatives. Photolysis in the visible region of dichloromethane solutions of (**1a**; R = Me) and (**1b**; R = Ph) in the presence of an excess of trimethyl phosphite leads to photoexchange of the benzene ligand by three trimethyl phosphite ligands under homogeneous photolytic conditions at 273 K. The piano-stool cations (**2a**; R = Me) and (**2b**; R = Ph), [Fe(η^5-C_5H_4COR){$P(OMe)_3$}$_3$]PF_6, are obtained in high yield (Scheme 1). Under identical conditions (273 K, visible irradiation under homogeneous photolytic conditions), but with acetonitrile as the solvent, irradiation of (**1a**) and (**1b**) leads to [Fe(η^5-C_5H_4COR){$P(OMe)_3$}$_2$(NCMe)]PF_6, (**3a**; R = Me) and (**3b**; R = Ph) respectively. When only 1 equivalent of $P(OMe)_3$ is used (acetonitrile solvent), the

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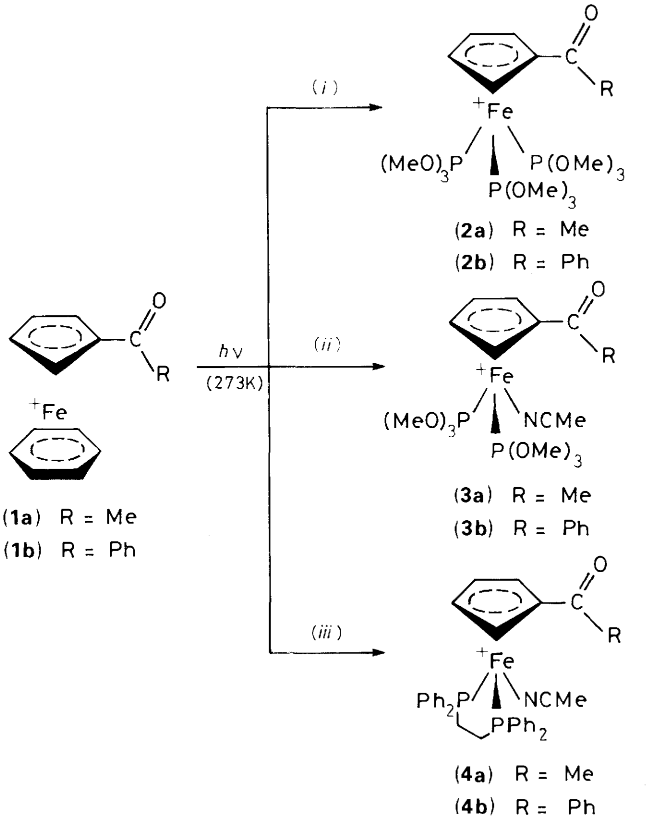
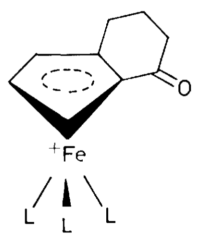
† Acetonitrile(η-acetylcyclopentadienyl)[1,2-bis(diphenylphosphino)-ethane]iron hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

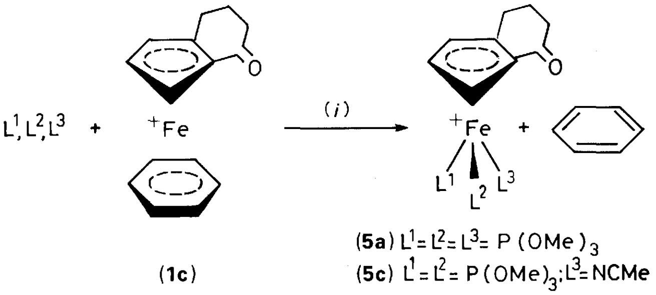
Non-S.I. unit employed: atm ≈ 101 325 Pa.



Scheme 1. (*i*) $P(OMe)_3$, CH_2Cl_2; (*ii*) $P(OMe)_3$, MeCN; (*iii*) dppe, MeCN



L = $P(OMe)_3$ or NCMe



Scheme 2. (*i*) Irradiation at ⩾400 nm, 273 K

expected bis(acetonitrile) derivative $[Fe(\eta^5-C_5H_4COR)\{P(OMe)_3\}(NCMe)_2]PF_6$ is not obtained; instead, total decomposition of the precursor (**1**) is noted. This differs from what happens in the known pentamethylcyclopentadienyl series where the precursor $[Fe(\eta^5-C_5Me_5)(CO)_3]PF_6$, under photolytic conditions of substitution, stabilizes the intermediate species $[Fe(\eta^5-C_5Me_5)(NCMe)_3]^+$ which can then exchange one, two, or three phosphorus ligands in consecutive stages.[3] In a non-substituted series,[2] the intermediate species $[Fe(\eta^5-C_5H_5)(NCMe)_3]^+$ can only be detected by ^1H n.m.r. spectroscopy at 233 K. A stability order for the tris(acetonitrile) complexes is thus: $[Fe(\eta^5-C_5Me_5)(NCMe)_3]^+ \gg [Fe(\eta^5-C_5H_5)(NCMe)_3]^+ \gg [Fe(\eta^5-C_5H_4COR)(NCMe)_3]^+$.

It has been observed that during irradiation, control of the temperature is crucial in the stabilization of the intermediate species $[Fe(\eta^5-C_5H_4COR)(solv)_3]^+$ (R = Me or Ph, solv = solvent molecule). Relatively high temperatures (between 293 and 313 K) bring about decomposition of the precursor (without formation of ferrocene derivatives). On the other hand, irradiation at temperatures lower than 273 K favours the stabilization of the tris(acetonitrile) complexes.

Photolysis of (**1a**) and (**1b**), as above, but in the presence of the bidentate phosphine 1,2-bis(diphenylphosphino)ethane, (dppe), leads to the formation of $[Fe(\eta^5-C_5H_4COR)(dppe)(NCMe)]PF_6$, (**4a**; R = Me) and (**4b**; R = Ph) (Scheme 1). In this reaction, the solvent is a mixture of MeCN (incoming ligand), nitromethane, and benzene. This takes into account the need to photolyse a totally homogeneous medium. The dppe ligand is insoluble in a polar medium such as acetonitrile and nitromethane, but very soluble in benzene. On the other hand, the precursor (**1**) and the products (**3**) and (**4**) show a better solubility and photochemical stability in a solvent of low donor number (DN),[9] and with high dielectric constant, such as nitromethane. The choice of solvent must combine the homogeneity of the medium and the stability of the transient species $\{[Fe(cp)(solv)_n]^+\}^{\ddagger}$.

Table 1 summarizes the solvents used, the proportion of each component in the solvent mixtures, and the yields for several photochemical reactions. In solvents of high DN (⩾14) photochemical decomplexations are observed lowering the yield of product.

The photolability of the cationic chiral metallocene $[Fe\{\eta^5-C_5H_3CO(CH_2)_3\}(C_6H_6)]PF_6$, (**1c**),[10] is similar to those of other acyl derivatives. Photolysis of (**1c**) in the presence of donor ligands L gives a series of asymmetric piano-stool cations which show planar chirality, of interest for studies of static and dynamic stereochemistry in photochemical systems. Chirality of modified cyclopentadienyl rings in piano-stool complexes has already been established by Wojcicki *et al.*[11]

Our initial studies were concerned with exchange of the arene ligand in the racemic series (**1c**) under irradiation with visible light. The results are summarized in Scheme 2. All the reactions were carried out at low temperature (273 K) since higher temperatures led to decomposition of the transient chiral intermediate $\{[Fe\{\eta^5-C_5H_3CO(CH_2)_3\}]^+\}^{\ddagger}$. The new chiral complex $[Fe\{\eta^5C_5H_3CO(CH_2)_3\}\{P(OMe)_3\}_3]PF_6$, (**5a**), prepared using three equivalents of $P(OMe)_3$, has only one signal in its $^{31}P-\{H\}$ n.m.r. spectrum indicating isochronic behaviour for the three $P(OMe)_3$ ligands. In turn, the ^1H and $^1H-\{^{31}P\}$ n.m.r. spectra show a quartet (^2J = 3.6 Hz) and a singlet, respectively. The isochronic behaviour in the temperature range 77—313 K is explained by a rapid rotation (on the n.m.r. time-scale) around the bonds connecting the iron centre to the phosphorus ligand. On the other hand the chiral cation $[Fe\{\eta^5-C_5H_3CO(CH_2)_3\}\{P(OMe)_3\}_2(NCMe)]^+$, (**5c**), prepared using two equivalents of $P(OMe)_3$ does not show a molecular σ plane bisecting the PFeP angle, the two phosphorus atoms being diastereotopic and distinguishable by ^{31}P n.m.r. spectroscopy as two singlets. The same phenomenon is observed for the methyl group of the phosphite ligands with the latter showing two quartets (^2J = 3.5 Hz) and two singlets in the decoupled $^1H-\{^{31}P\}$ n.m.r. spectrum (Figure 1).

Table 1. Experimental conditions of ligand photoexchange

Cationic precursor[a]	Incoming ligand	Solvent[b]	T/K (t/h)	Cationic product	Yield (%)
$[Fe(\eta^5-C_5H_4COMe)(C_6H_6)]^+$	$3P(OMe)_3$	CH_2Cl_2	273 K, (1)	**(2a)**	73
$[Fe(\eta^5-C_5H_4COMe)(C_6H_6)]^+$	$2P(OMe)_3$ + MeCN	CH_2Cl_2–MeCN (2:1)	273 K, (1)	**(3a)**	68
$[Fe(\eta^5-C_5H_4COMe)(C_6H_6)]^+$	dppe + MeCN	$MeNO_2$–MeCN–toluene (2:1:1)	273 K, (1)	**(4a)**	71
$[Fe(\eta^5-C_5H_4COPh)(C_6H_6)]^+$	$3P(OMe)_3$	CH_2Cl_2	273 K, (1)	**(2b)**	77
$[Fe(\eta^5-C_5H_4COPh)(C_6H_6)]^+$	$2P(OMe)_3$ + MeCN	CH_2Cl_2–MeCN (2:1)	273 K, (1)	**(3b)**	63
$[Fe(\eta^5-C_5H_4COPh)(C_6H_6)]^+$	dppe + MeCN	$MeNO_2$–MeCN–toluene (2:1:1)	273 K, (1)	**(4b)**	62
$[Fe\{\eta^5-C_5H_3CO(CH_2)_3\}(C_6H_6)]^+$	$3P(OMe)_3$	$MeNO_2$–CH_2Cl_2 (1:5)	250 K, (2)	**(5a)**	95
$[Fe\{\eta^5-C_5H_3CO(CH_2)_3\}(C_6H_6)]^+$	$2P(OMe)_3$ + MeCN	MeCN	250 K, (2)	**(5c)**	60

[a] All the cationic precursors and cationic products have PF_6^- as counter ion. [b] Volume proportions for solvent mixture are shown in parentheses; either CH_2Cl_2 or $MeNO_2$ can be used as solvent (or cosolvent). [c] All the photoexchange reactions were carried out with a solar lamp or irradiation with visible light and controlled temperature.

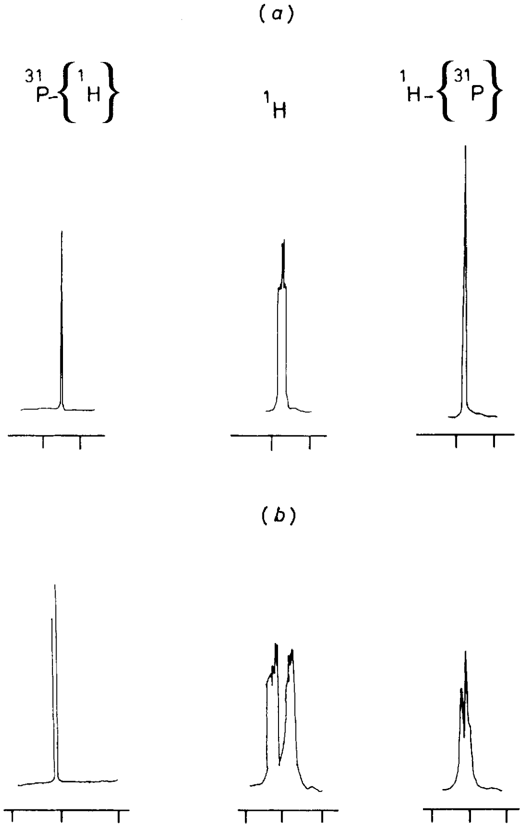
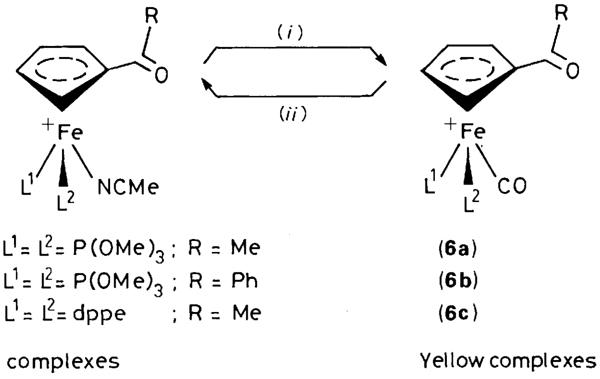


Figure 1. $^{31}P-\{^1H\}$, ^1H, and $^1H-\{^{31}P\}$ N.m.r. spectra in $CDCl_3$ of (*a*) the chiral complex **(5a)** in the 313—77 K temperature range and (*b*) the chiral complex **(5c)** at 313 K



Scheme 3. (*i*) 5 atm CO, in the dark, CH_2Cl_2, room temperature (r.t.); (*ii*) MeCN, irradiation at ⩾400 nm, r.t.

Thermal vs. Photochemical Stability of the Fe–CO *and* Fe–NCMe *Bonds*.—The monoacetonitrile derivatives **(3a)**, **(3b)**, and **(4a)** quantitatively generate the monocarbonyl derivatives in dichloromethane under CO (Carius tube: 5 atm) in the dark; (Scheme 3). The monocarbonyl derivatives are thermally and kinetically stable in the absence of light even in refluxing acetonitrile (315 K). However upon irradiation (273 K, $\lambda \geqslant 400$ nm) substitution of the carbonyl by an acetonitrile ligand readily occurs. It is believed that the photochemical labilization of CO in these cations and in the majority of organometallic carbonyl complexes occurs *via* an excited state having a high degree of a ligand-to-metal charge-transfer (l.m.c.t.) transition.[12]

All of these photolytic syntheses proceed rapidly and without decomposition or side reactions using either u.v. or visible light. The same is true for thermal ligand exchange (replacement of MeCN by CO, in the absence of light) which proceeds under ambient conditions. It should be noted that the thermal reactions are simply the reverse of the photochemical processes.[13]

Description of the Structure and Spectroscopic Correlation of the Cation **(4a)** $[Fe(\eta^5-C_5H_4COMe)(dppe)(NCMe)]PF_6$.—The structure of the cation for the acetyl derivative **(4a)**, $[Fe(\eta^5-C_5H_4COMe)(dppe)(NCMe)]PF_6$, is shown in Figure 2. Final atomic parameters are in Table 2, atomic distances and angles in Table 3. The cation is formed by an iron(II)-d^6 metal centre bonded to the C_5H_4COMe ligand, in a symmetric π manner, to the two phosphorus atoms from the dppe ligand, and to the nitrogen atom of the acetonitrile. The latter two ligands are distributed along a pseudo-three-fold axis around the metal giving angles P(1)–Fe–P(2), N–Fe–P(1), and N–Fe–P(2), of *ca.* 90°. The geometry at the metal centre can thus be regarded as octahedral, if the cyclopentadienyl moiety is regarded as occupying three facial sites.

The mean plane of the lateral acetyl function forms a dihedral angle of 8.9° with the cp (cyclopentadienyl) ring (atomic

Table 2. Atomic positional parameters for [Fe(η^5-C_5H_4COMe)(dppe)(NCMe)]PF_6 (**4a**)

Atom	*x*	*y*	*z*
Fe	0.180 82(4)	0.058 54(4)	0.149 89(2)
P(1)	0.179 46(8)	0.185 80(6)	0.144 88(4)
P(2)	0.304 69(8)	0.061 02(7)	0.099 93(4)
P(3)	0.575 8(1)	0.322 25(8)	0.081 15(5)
F(1)	0.499 4(4)	0.381 8(3)	0.065 5(2)
F(2)	0.638 3(4)	0.385 2(2)	0.104 6(2)
F(3)	0.649 4(3)	0.261 7(3)	0.099 6(2)
F(4)	0.513 0(3)	0.257 2(3)	0.059 1(1)
F(5)	0.513 6(3)	0.311 0(3)	0.127 3(1)
F(6)	0.635 6(3)	0.330 8(3)	0.036 1(1)
O	−0.023 8(3)	0.107 3(2)	0.239 0(1)
N	0.086 0(3)	0.053 0(2)	0.101 7(1)
C(1)	0.121 6(4)	−0.041 5(3)	0.179 3(2)
C(2)	0.225 6(4)	−0.044 2(3)	0.179 9(2)
C(3)	0.262 6(4)	0.017 9(3)	0.205 3(2)
C(4)	0.180 9(4)	0.060 4(3)	0.221 6(2)
C(5)	0.091 8(3)	0.025 0(3)	0.205 0(2)
C(6)	−0.010 1(4)	0.054 1(3)	0.213 1(2)
C(7)	−0.094 4(4)	0.018 2(4)	0.187 6(2)
C(8)	0.067 8(3)	0.224 8(2)	0.116 4(2)
C(9)	−0.025 2(3)	0.211 5(3)	0.135 9(2)
C(10)	−0.110 6(3)	0.237 3(3)	0.114 3(2)
C(11)	−0.103 8(4)	0.274 4(3)	0.072 9(2)
C(12)	−0.014 4(4)	0.286 2(3)	0.005 29(2)
C(13)	0.071 9(4)	0.261 5(3)	0.074 8(2)
C(14)	0.195 9(3)	0.241 9(3)	0.197 5(2)
C(15)	0.284 9(4)	0.238 5(3)	0.219 8(2)
C(16)	0.298 7(4)	0.275 7(4)	0.261 8(2)
C(17)	0.222 3(5)	0.314 9(4)	0.280 8(2)
C(18)	0.133 8(5)	0.319 3(4)	0.258 8(2)
C(19)	0.119 6(4)	0.283 2(3)	0.217 2(2)
C(20)	0.429 7(3)	0.042 6(3)	0.122 2(2)
C(21)	0.461 2(4)	−0.031 9(3)	0.127 3(2)
C(22)	0.551 9(4)	−0.048 4(3)	0.146 2(2)
C(23)	0.615 2(4)	0.009 6(4)	0.159 6(2)
C(24)	0.586 0(4)	0.082 7(3)	0.154 3(2)
C(25)	0.494 2(4)	0.100 3(3)	0.135 5(2)
C(26)	0.300 5(3)	−0.003 6(3)	0.051 1(3)
C(27)	0.241 0(4)	−0.068 9(3)	0.052 0(2)
C(28)	0.244 9(4)	−0.121 2(3)	0.115 6(2)
C(29)	0.305 5(4)	−0.108 4(3)	−0.021 0(2)
C(30)	0.362 1(4)	−0.043 9(4)	−0.022 6(2)
C(31)	0.360 4(4)	0.007 4(3)	0.012 8(2)
C(32)	0.284 6(3)	0.217 1(3)	0.109 2(2)
C(33)	0.309 3(3)	0.156 7(3)	0.073 5(2)
C(34)	0.023 9(3)	0.053 1(3)	0.075 5(2)
C(35)	−0.060 6(4)	0.058 5(4)	0.044 5(2)

Table 3. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations for complex (**4a**)

Fe–P(1)	2.232(1)	N–C(34)	1.128(6)
Fe–P(2)	2.207(1)	C(1)–C(2)	1.395(8)
Fe–N	1.895(4)	C(1)–C(5)	1.438(7)
Fe–C(1)	2.103(5)	C(2)–C(3)	1.403(8)
Fe–C(2)	2.087(5)	C(3)–C(4)	1.408(7)
Fe–C(3)	2.075(5)	C(4)–C(5)	1.430(7)
Fe–C(4)	2.086(5)	C(5)–C(6)	1.477(7)
Fe–C(5)	2.083(5)	C(6)–C(7)	1.490(8)
Fe–N	1.895(4)	C(32)–C(33)	1.520(7)
P(1)–C(32)	1.833(5)	C(34)–C(35)	1.451(7)
P(2)–C(33)	1.843(5)	O–C(6)	1.212(7)
P(1)–Fe–P(2)	86.75(5)	Fe–P(2)–C(33)	108.5(2)
P(1)–Fe–N	89.8(1)	P(1)–C(32)–C(33)	110.3(4)
P(2)–Fe–N	91.0(1)	P(2)–C(33)–C(32)	109.8(3)
Fe–P(1)–C(32)	109.2(2)	N–C(34)–C(35)	174.7(6)

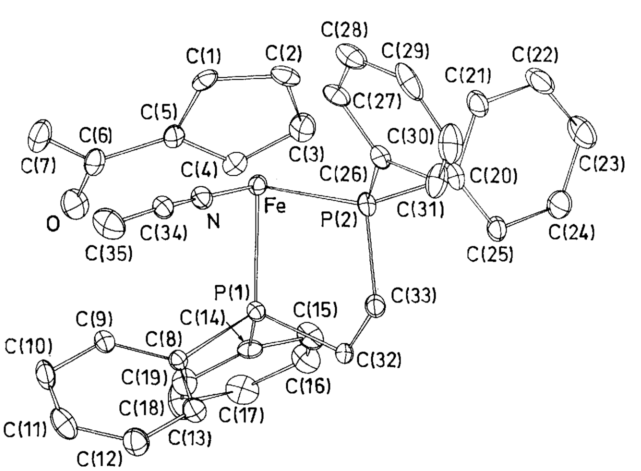


Figure 2. ORTEP drawing of [Fe(η^5-C_5H_4COMe)(dppe)(NCMe)]PF_6 (**4a**), with atom labelling

displacements from the cp ring: C(6) +0.05, C(7) +0.28, and O −0.06 Å).

The cp ring is pentahapto co-ordinated to the iron atom, the out-of-plane displacement Fe–π(cp) being −1.705(1) Å, smaller than the analogous distance found by Pettit and co-workers[14] in [Fe(η^5-C_5H_5)(dppe)(NCMe)]BPh_4 (Table 4 shows a comparison between these structures). It is probable that the electron-withdrawing effect of the acetyl group decreases the electron density about the iron atom and so gives rise to an increased separation between the iron centre and the remaining co-ordinating ligands.

The acetonitrile ligand is virtually linear [N–C(34)–C(35) 174.7(6)°] with the N–C bond strengthened upon co-ordination *via* the N atom. This is illustrated by an increase in the N–C stretching frequency and by the decrease in the N–C bond length with respect to free acetonitrile (Table 4).

The C(32)–P(1)–Fe–P(2)–C(33) chelate ring is not planar but exhibits an envelope conformation; the best unweighted mean plane is through C(32)–P(1)–Fe–P(2), with out-of-plane displacements of −0.042, +0.052, −0.043, and +0.033 Å respectively. The C(33) atom lies 0.569 Å out of this plane and so it must be considered as the flap atom of the envelope conformation. The analogous values for the diphosphine chelate in [Fe(η^5-C_5H_5)(dppe)(NCMe)]BPh_4 are −0.017, +0.022, −0.018, and +0.0141 Å for the atoms on the mean plane, and −0.736 Å for the flap atom.[15]

Intermolecular steric effects are small, and the smallest van der Waals distance is 3.027(8) Å between F(1) and C(34). Similarly, intramolecular contacts are weakened due to a rotation of 55.0° (Figure 3) between the acetonitrile ligand and the acetyl group. This rotation angle is denoted as the dihedral angle between the planes Fe–C(5)–C(6) and Fe–N–Ω, where Ω is the centroid of the cyclopentadienyl ring.

The ^1H n.m.r. spectrum of complex (**4a**) at 250 MHz shows a drastic influence derived from the diamagnetic anisotropic effect of the lateral acetyl function, when compared to related complexes. The acetonitrile ligand also shows a stronger σ-donor influence than ligands such as CO, dppe, and P(OMe)$_3$. Both influences simultaneously produce a greater splitting of the H_α and H_β signals ($\Delta = 1.30$) (Figure 4). The coupling

Table 4. Interatomic distances (Å) and angles (°) and i.r. absorptions (cm^{-1}) for the N–C bond[a]

Compound	Fe–P(1)	Fe–P(2)	Fe–N	Fe–N–C	Fe–Ω	N–C	NC–Me	N≡C–C	$\tilde{\nu}$(CN)	Ref.
$[Fe(\eta^5\text{-}C_5H_4COMe)(dppe)(NCMe)]PF_6$	2.232(1)	2.207(1)	1.895(4)	173.5(4)	1.704(1)	1.128(6)	1.451(7)	174.7(6)	2 265	This work
$[Fe(\eta^5\text{-}C_5H_5)(dppe)(NCMe)]BPh_4$	2.206(2)	2.195(1)	1.881(2)	171.9(5)	1.715(1)	1.139(9)	1.431(1)	176.9(8)	2 270	14
$[Fe(\eta^5\text{-}C_5H_5)(dppe)(CO)]BF_4$	2.211(2)	2.209(2)			1.717(1)					15
MeCN						1.157	1.458	180	2 260	14,*b*

[a] In dichloromethane. [b] B. L. Ross, J. G. Grasselli, W. M. Ritchley, and H. D. Kaesz, *Inorg. Chem.*, 1963, **2**, 1023.

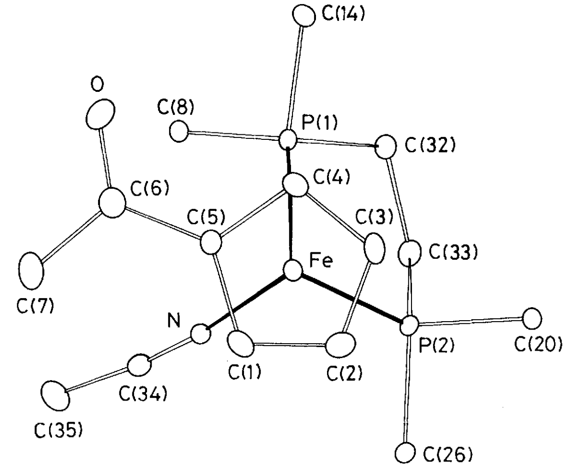


Figure 3. Stereoview of $[Fe(\eta^5\text{-}C_5H_4COMe)(dppe)(NCMe)]PF_6$ (**4a**), showing the tripod projection of FeP_2N on the cyclopentadienyl plane. The eclipse angle is 5°

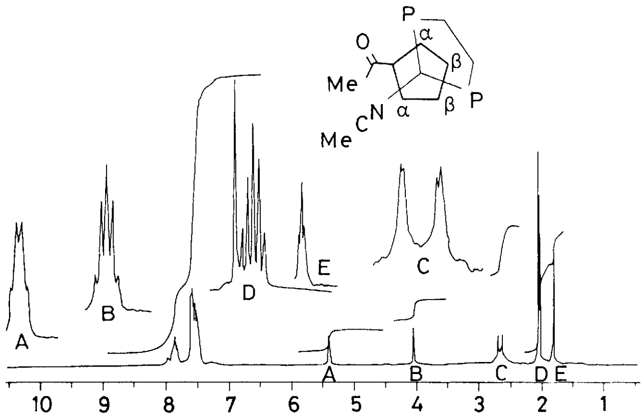


Figure 4. ^1H N.m.r. (250 MHz) spectrum of $[Fe(\eta^5\text{-}C_5H_4COMe)(dppe)(NCMe)]PF_6$ (**4a**), in $[(CD_3)_2CO]$. Signals A and B correspond to H_α and H_β respectively, showing both coupling of H–H and H–P, C corresponds to the non-equivalent protons of the ethylene bridge, *endo* (toward MeCN) and *exo* protons with H–H and P–H coupling, D corresponds to $[(CD_3)_2CO]$ and the methyl group from the acetyl substituent, and E to the methyl group of the acetonitrile ligand

between ^{31}P and H_α and H_β results in two different multiplets. On the other hand, the non-equivalence of the ethylene bridge protons (signal C in Figure 4) is probably understood by the *endo* or *exo* orientation of these, relative to the bound acetonitrile ligand. Both types of protons thus have different shifts with H–H and P–H coupling further splitting the signals. The methyl signal of the acetonitrile ligand is split into a triplet due to interaction with two phosphorus nuclei (J = 1.5 Hz) (Figure 4).

Experimental

All the solvents (spectroscopic grade) were dried and distilled before use, and stored under argon. All manipulations were carried out using standard Schlenk techniques under argon. Photolytic reactions were performed with a tungsten (200 W) or a halogen lamp (500 W) with an Oriel filter (400 nm) in a Pyrex thermostatted cell. I.r. spectra were recorded on a Perkin-Elmer 567 instrument (Nujol or KBr disks), electronic spectra on a Philips Scientific SP-100 u.v.–visible spectrophotometer. Proton and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were recorded on a Brücker WM-250 spectrometer (250 and 62.9 MHz, respectively). Chemical shifts are reported with reference to internal $SiMe_4$. $^{31}P\text{-}\{^1H\}$ N.m.r. spectra were recorded on a Brücker WP-80 instrument at 32.38 MHz, and chemical shifts are referenced to an 85% H_3PO_4 external standard. Elemental analyses were performed at the Centre for Microanalyses of the Centre National de Recherches Scientifiques at Lyon-Villeurbanne. The acylcationic metallocenes $[Fe(\eta^5\text{-}C_5H_4COR)(C_6H_6)]PF_6$ (R = Me or Ph)[16] and the cationic chiral α-oxotetramethylene ferrocenyl derivative $[Fe\{\eta^5\text{-}C_5H_3CO(CH_2)_3\}(C_6H_6)]^+$ were synthesized as described previously.[10]

X-Ray Structural Determination.—Red crystals of $[Fe(\eta^5\text{-}C_5H_4COMe)(dppe)(NCMe)]PF_6$ were obtained by slow vapour diffusion of diethyl ether into a dichloromethane solution of (**4a**). *X*-Ray diffraction data were collected on a four-circle Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo-k_α radiation. The Enraf-Nonius structure determination package and PDP 11/60 computer were used for all data reduction and structure refinement. A summary of crystal data and intensity collection is given in Table 5. The structure was solved in space group *Pbca* by Multan 80, and was refined by full-matrix least-squares calculations based on F_o, weights, based on counting statistics, where $w^{-1} = \sigma_F{}^2 = [\sigma^2(I) + (0.061)^2]/4I$. The atomic scattering factors for both the non-hydrogen atoms and for the hydrogen atoms were taken from ref. 17. The hydrogen atoms were placed at idealized positions with fixed thermal parameters (4.5 Å^2) and not refined. The thermal parameters for all the non-hydrogen atoms were anisotropically refined. The agreement factors are defined as: $R = \Sigma||F_o| - |F_c||/\Sigma F_o$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

The final cycle of least-squares refinement involved 424 variables and 3 066 observed reflections $[F_o{}^2 > 3\sigma(F_o{}^2)]$ and converged to final agreement indices $R = 0.041$ and $R' = 0.051$. The final Fourier difference map revealed no residuals greater than 0.50 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Photolytic Synthesis of Cationic Acyl Piano-stool Complexes $[Fe(\eta^5\text{-}C_5H_4COR)L_3]PF_6$ (**2**)—(**4**) [R = Me or Ph; L = $P(OMe)_3$, NCMe *or* dppe].—In a typical preparative reaction, the acyl-substituted metallocene $[Fe(\eta^5\text{-}C_5H_4COR)(C_6H_6)]PF_6$ (0.5 mmol) and an excess of the incoming ligand L, [12 mmol of $P(OMe)_3$; 0.7 mmol of dppe] are dissolved in a suitable

Table 5. Structure acquisition and refinement details for the *X*-ray crystallographic study of $[Fe(\eta^5\text{-}C_5H_4COMe)(dppe)(NCMe)]PF_6$

Formula	$C_{35}H_{34}F_6FeNOP_3$
M	747.43
Crystal system	Orthorhombic
Space group	*Pbca*
α/Å	13.406(4)
b/Å	17.498(5)
c/Å	29.094(8)
U/Å^3	6 815(7)
D_c/g cm^{-3}	1.455
F(000)	3 072
Z	8
Crystal dimensions (mm)	0.40 × 0.16 × 0.09
T/K	291
λ/Å	0.710 73, graphite monochromatized
Scan type	ω—2θ
Scan width (°)	1.0 + 0.35 tanθ
Aperture/mm	2.0 + 0.5 tanθ
Range of data collected	sin$\theta/\lambda \leqslant$ 0.595 Å^{-1}
Range of *h*, *k*, *l*	0—15, 0—20, 0—34
No. reflections collected	5 984
No. standard reflections	3 $(0,\bar{2},6; \bar{2},3,10; 0,4,\bar{7})$
Average decay	0.70% for 70 h of irradiation
No. of unique reflections	5 484
Largest residual peak in final difference Fourier	0.50 e Å^{-3}
No. of parameters	424
No. of reflection parameters	7.2
Largest shift/error in the last cycle of full matrix refinement	0.02
Goodness of fit	1.218

solvent mixture (20 cm^3) in order to obtain an homogeneous solution. The temperature, duration of photolysis, and solvent proportions in the solvent mixture are summarized in Table 1. The reaction mixture was placed in a Pyrex cell with a cooling jacket in order to thermostat the cell during photolysis. After the required photolysis time thc solvent mixture was removed *in vacuo* and the resulting solid washed with benzene and diethyl ether. This was then recrystallized from dichloromethane–diethyl ether and/or chromatographed on an alumina column.

$[Fe(\eta^5\text{-}C_5H_4COMe)\{P(OMe)_3\}_3]PF_6$ (**2a**). Following the above procedure, this cationic complex was isolated as air-stable, yellow needle-shaped crystals (250 mg, 73%) from $[Fe(\eta^5\text{-}C_5H_4COMe)(C_6H_6)]PF_6$ (193 mg, 0.5 mmol) and an excess of $P(OMe)_3$ (1.49 g, 12 mmol) in dichloromethane. N.m.r. $[(CD_3)_2CO]$: ^1H, δ 5.30 (m, 2 H_α, cp), 4.96 (m, 2 H_β, cp), 3.84 (q, 27 H, CH_3O, $^2J_{PH}$ 10 Hz), and 2.34 (s, 3 H, CH_3CO); $^{13}C\text{-}\{^1H\}$, δ 197.09 (CO), 89.55 (C_q, cp), 86.54 (C_α, cp), 81.80 (C_β, cp), 54.67 (t, CH_3OP), and 28.07 p.p.m. (CH_3CO); ν(CO) 1 670 cm^{-1} (Found: C, 27.45; H, 4.95; Fe, 8.20; P, 17.65. $C_{16}H_{34}F_6FeO_{10}P_4$ requires C, 28.25; H, 5.05; Fe, 8.20; P, 18.20%).

$[Fe(\eta^5\text{-}C_5H_4COPh)\{P(OMe)_3\}_3]PF_6$ (**2b**). Using an exactly analogous procedure to that described for (**2a**), this compound was isolated as yellow crystals (77%). N.m.r. $[(CD_3)_2CO]$: ^1H, δ 7.84—7.56 (m, 5 H, Ph), 5.60 (m, 2H_α, cp), 5.06 (m, 2$H_\beta$cp), 3.76 (q, 2 H, CH_3OP, $^2J_{PH}$ 10 Hz); $^{13}C\text{-}\{^1H\}$ δ 193.70 (CO), 140.43, 132.69, 129.07 (Ph), 88.33 (C_α, cp), 87.62 (C_q, cp), 81.72 (C_β, cp), and 54.49 p.p.m. (d, OCH_3); ν(CO) 1 655 cm^{-1} (Found: C, 33.65; H, 4.85; Fe, 7.60; P, 17.05. $C_{21}H_{36}F_6FeO_{10}P_4$ requires C, 34.00; H, 4.90; Fe, 7.50; P, 16.70%).

$[Fe(\eta^5\text{-}C_5H_4COMe)\{P(OMe)_3\}_2(NCMe)]PF_6$ (**3a**). Following the above general procedure (see also Table 1), complex (**3a**) was isolated as air-stable, orange crystals (101 mg, 68%), from $[Fe(\eta^5\text{-}C_5H_4COMe)(C_6H_6)]PF_6$ (97 mg, 0.25 mmol) and $P(OMe)_3$ (521 mg, 4.2 mmol) in dichloromethane–MeCN (2:1) as solvent. N.m.r.: ^1H ($CDCl_3$), δ 5.28 (m, 2H_α, cp), 4.34 (m, 2H_β, cp), 3.72 (t, 18 H, $POCH_3$, $^2J_{PH}$ 11 Hz), 2.34 (s, 3 H, CH_3CO), and 2.32 (t, 3 H, CH_3CN); $^{13}C\text{-}\{^1H\}$ $[(CD_3)_2CO]$, δ 204.27 (CO), 86.07 (C_α, cp), 76.80 (C_β, cp), 52.87 (t, $POCH_3$), and 3.38 p.p.m. ($\mathit{C}H_3CN$); $^{31}P\text{-}\{^1H\}$, δ 175.84 p.p.m.; ν(CN) 2 260 and ν(CO) 1 675 cm^{-1} (Found: C, 29.20; H, 5.10; Fe, 9.10; P, 14.85. $C_{15}H_{28}F_6FeNO_7P_3$ requires C, 30.15; H, 4.75; Fe, 9.35; P, 15.55%).

$[Fe(\eta^5\text{-}C_5H_4COPh)\{P(OMe)_3\}_2(NCMe)]PF_6$ (**3b**). Using an exactly analogous procedure to that described above, this complex was obtained as orange crystals (103 mg, 63%) from $[Fe(\eta^5\text{-}C_5H_4COPh)(C_6H_6)]PF_6$ (112 mg, 0.25 mmol) and $P(OMe)_3$ (5.21 mg, 4.2 mmol) under the photolytic conditions indicated in Table 1. ^1H N.m.r. ($CDCl_3$), δ 7.8, 7.57, 7.28 (m, 5 H, Ph), 5.20 (m, 2H_α, cp), 4.38 (m, 2H_β, cp), 3.66 (t, 18 H, $POCH_3$), $^2J_{PH}$ 11 Hz), and 2.36 (t, CH_3CN); ν(CN) 2 260 and ν(CO) 1 635 cm^{-1} (Found: C, 36.15; H, 4.10; Fe, 8.25; P, 13.60. $C_{20}H_{20}F_6FeNO_7P_3$ requires C, 36.45; H, 4.60; Fe, 8.45; P, 14.10%).

$[Fe(\eta^5\text{-}C_5H_4COMe)(dppe)(NCMe)]PF_6$ (**4a**). Following the above general procedure and the conditions indicated in Table 1, this cationic complex was isolated as red needle-shaped crystals. The complex $[Fe(\eta^5\text{-}C_5H_4COMe)(C_6H_6)]PF_6$ (193 mg, 0.5 mmol), and dppe (259 mg, 0.65 mmol) in $MeNO_2$–MeCN–toluene (2:1:1) were photolysed at 273 K for 1 h. N.m.r. $[(CD_3)_2CO]$: ^1H, δ 7.58 (m, 20 H, Ph), 5.3 (q, 2H_α, cp), 4.04 (q, H_β, cp), 2.67 (dd, 4 H, CH_2, $^2J_{PH}$ 15, $^3J_{PH}$ 3), 2.08 (s, 3 H, CH_3CO), and 1.82 (t, 3 H, CH_3CN, $^3J_{PH}$ = 1.5 Hz); $^{13}C\text{-}\{^1H\}$, δ 194.43 (CO), 129.31—125.80 (Ph), 127.78 (CN), 83.83 (C_α, cp), 82.49 (C_q, cp), 71.54 (C_β, cp), 28.34 (CH_3CO), 28.12, 28.01 (CH_2), and 3.98 p.p.m. ($\mathit{C}H_3CN$); ν(CN) 2 275 and ν(CO) 1 660 cm^{-1} (Found: C, 56.25; H, 4.60; Fe, 7.30; P, 12.45. $C_{35}H_{34}F_6FeNOP_3$ requires C, 56.25; H, 4.60; Fe, 7.45; P, 12.45%).

$[Fe(\eta^5\text{-}C_5H_4COPh)(dppe)(NCMe)]PF_6$ (**4b**). Using an exactly analogous procedure to that described above for (**4a**), and using the photolytic conditions indicated in Table 1, complex (**4b**) was isolated as a thermally unstable red powder. Yield, 62%. ^1H N.m.r. ($CDCl_3$), δ 7.75—7.50 (m, 25 H, Ph), 5.5 (m, 2H_α, cp), 4.17 (m, 2H_β, cp), 2.66 (dd, 4 H, CH_2, $^2J_{PH}$ = 15, $^3J_{PH}$ = 3 Hz), and 1.68 (t, 3 H, CH_3CN); $^{13}C\text{-}\{^1H\}$, δ 194.01 (CO), 137.10—129.37 (Ph), 133.095 (CN), 89.66 (C_α, cp), 85.47 (C_q, cp), 76.01 (C_β, cp), 28.63, 28.31 (CH_2), and 4.05 p.p.m. ($\mathit{C}H_3CN$); ν(CN) 2 265 and ν(CO) 1 620 cm^{-1} (Found: C, 57.65; H, 4.40; Fe, 7.25; N, 1.55; P, 11.40. $C_{40}H_{36}F_6FeNOP_3$ requires C, 57.65; H, 4.40; Fe, 6.9; N, 1.75; P, 11.50%).

Photolytic Synthesis of the Chiral Cationic Piano-stool Complexes.— $[Fe\{\eta^5\text{-}\overline{C_5H_3CO(C}H_2)_3\}\{P(OMe)_3\}_3]PF_6$ (**5a**). A dichloromethane solution containing the chiral metallocene complex $[Fe\{\overline{C_5H_3CO(C}H_2)_3\}(C_6H_6)]PF_6$ (1 g, 2.42 mmol) and $P(OMe)_3$ (0.9 g, 7.28 mmol) was irradiated under an argon atmosphere at 250 K. Upon exposure to visible light, the solution turned orange. Photolysis was continued for 2 h. After removal of the solvent, the solid was washed with diethyl ether and chromatographed on a short alumina column. Yield, 95%, as orange microcrystals. N.m.r. ($CDCl_3$): ^1H, δ 4.8 (s, 2 H, H_α and H_β), 4.75 (s, 1 H, H_γ), 3.77 (s, 27 H, CH_3O), and 2.32 (m, 6 H, CH_2); $^{13}C\text{-}\{^1H\}$, δ 200.4 (CO), 106.9, 91.2, 83.7, 80.5, 72.2 (cp ring), 54.3 (OCH_3), 38.8, and 21.9 p.p.m. (CH_2); $^{31}P\text{-}\{^1H\}$, δ, 168.5 p.p.m. ($POCH_3$); ν(CO) 1 680 cm^{-1} (Found: C, 38.6; H, 6.60; Fe, 9.8. $C_{18}H_{36}F_6FeOP_4$ requires C, 38.45; H, 6.40; Fe, 9.40%).

$[Fe\{\eta^5\text{-}\overline{C_5H_3CO(C}H_2)_3\}\{P(OMe)_3\}(NCMe)_2]PF_6$ (**5b**). This asymmetric complex was obtained by irradiation at 250 K of $[Fe\{\eta^5\text{-}\overline{C_5H_3CO(C}H_2)_3\}(C_6H_6)]PF_6$ (1 g, 2.42 mmol) with $P(OMe)_3$ (0.3 g, 2.42 mmol) in acetonitrile under an argon atmosphere. Upon exposure to visible light, the solution turned dark red. Photolysis was continued for 2 h. The resulting solution is stable up to 260 K. Decomposition is observed when solvent is removed and/or the temperature increased. Upon monitoring by ^1H n.m.r. spectroscopy (CD_3CN) at 250 K a progressive shift of the signals of $P(OMe)_3$ and the co-ordinated C_6H_6 is observed. All attempts to isolate this compound were unsuccessful.

$[Fe\{\eta^5\text{-}C_5H_3CO(CH_2)_3\}\{P(OMe)_3\}_2(NCMe)]PF_6$ (**5c**). As described above, $[Fe\{\eta^5\text{-}C_5H_3CO(CH_2)_3\}(C_6H_6)]PF_6$ (1 g, 2.42 mmol) and $P(OMe)_3$ (0.6 g, 4.84 mmol) in acetonitrile were photolysed under the same conditions as for complex (**5a**) (273 K, 2 h). The orange solid was chromatographed on alumina and crystallized from acetonitrile. Yield, 60%. N.m.r. ($CDCl_3$): ^1H δ 4.83 (s, 1 H, H_α), 4.16 (d, 2 H, $H_\beta H_\gamma$), 3.76 (d, 18 H, OCH_3), 2.48 (s, 3 H, CH_3CN), and 2.26 (m, 6 H, CH_2); ^{13}C-$\{^1H\}$, δ 200.4 (CO), 134.3, 128.2, 115.6, 84.9, 69.2 (cp ring), 53.7 (OCH_3), 38.8, 21.9 (CH_2), and 4.9 p.p.m. ($\mathit{C}H_3CN$); ^{13}P-$\{^1H\}$, δ 167.6 and 170.1 p.p.m. (POMe); ν(CO) 1 685 cm^{-1} (Found: C, 38.75; H, 5.70; Fe, 10.60. $C_{17}H_{30}F_6FeNOP_3$ requires C, 38.70; H, 5.70; Fe, 10.60%).

Photolytic Two-electron Ligand Exchange in the Acyl Piano-stool Complexes.—In a Carius tube (thickness of walltube = 3.5 mm) with a side branch equipped with a Fischer-Teflon valve and a stirring bar were introduced 0.5 mmol of the acetonitrile derivative (**3a**), (**3b**), or (**4a**), in acetone (20 cm^3). On a vacuum line the red-purple solution was degassed and carbon monoxide introduced at 77 K. A pressure of 5 atm was maintained with a mercury valve. The Carius tube was left in the dark with continuous stirring for 3 d. The solution gradually changed to the yellow colour of the cationic complex (**6a**), (**6b**), or (**6c**). These complexes were purified by recrystallization from acetone–diethyl ether.

Complexes (**6a**), (**6b**), (**7a**), and (**7b**) (0.5 mmol) were photolysed in acetonitrile (20 cm^3) under an argon atmosphere using the same conditions as for complexes (**2**)—(**4**) (irradiation with visible light, 298 K, argon atmosphere, 3—4 h) and isolated and purified as for complexes (**2**)—(**4**).

$[Fe(\eta^5\text{-}C_5H_4COMe)\{P(OMe)_3\}_2(CO)]PF_6$ (**6a**). Following the above general procedure (**6a**) was isolated as air-stable, yellow crystals (70%). ^1H N.m.r. $[(CD_3)_2CO]$, δ 5.20 (m, 2 H, cp), 3.82 (q, 18 H, CH_3OP), and 2.25 (s, 3 H, CH_3CO); ν(C≡O) 1 980 and ν(C=O) 1 670 cm^{-1} (Found: C, 27.90; H, 4.80; Fe, 9.30. $C_{14}H_{25}F_6FeO_8P_3$ requires C, 28.80; H, 4.20; Fe, 9.55%).

$[Fe(\eta^5\text{-}C_5H_4COPh)\{P(OMe)_3\}_2(CO)]PF_6$ (**6b**). Yield 52%. ^1H N.m.r. $[(CD_3)_2CO]$, δ 7.81, 7.48 (m, 5 H, Ph), 5.55 (m, $2H_\alpha$, cp), 5.02 (m, 2 H_β, cp), and 3.73 (q, 18 H, CH_3OP); ν(C≡O) 1 975 and ν(C=O) 1 650 cm^{-1} (Found: C, 34.80; H, 4.60; Fe, 7.85. $C_{19}H_{27}F_6FeO_8P_3$ requires C, 35.3; H, 4.20; Fe, 7.85%).

$[Fe(\eta^5\text{-}C_5H_4COMe)(dppe)(CO)]PF_6$ (**6c**). Yield, 75%. ^1H N.m.r. $[(CD_3)_2CO]$, δ 7.62 (m, 20 H, Ph), 5.42 (q, $2H_\alpha$, cp), 4.12 (q, $2H_\beta$, cp), 2.73 (dd, 4 H, CH_2), and 2.10 (s, 3 H, OCH_3); ν(C≡O) 1 960 and ν(C=O) 1 640 cm^{-1} (Found: C, 55.10; H, 4.95; Fe, 7.1. $C_{34}H_{31}F_6FeO_2P_3$ requires C, 55.60; H, 4.20; Fe, 7.60%).

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