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Preliminary communication

PHOTOCHEMICAL SYNTHESIS, REACTIVITY, AND ELECTROCHEMICAL PROPERTIES OF $[CpFeP_2L]^+$ CATIONS; ($Cp = C_5H_5$, C_5Me_5; $L = CO$ vs. CH_3CN; P = PHOSPHINE OR PHOSPHITE)

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Summary

Photolytic replacement of the arene ligand in the cations $[Cp^\star Fe(p\text{-xylene})]^+$ ($Cp^\star = C_5Me_5$) by $P(OMe)_3$ ligands is only possible when a sensitizer (acetone or anthracene) is present and leads to $Cp^\star Fe^+\{P(OMe_3)\}_3$. Photoextrusion of one phosphite ligand from $[C_5R_5Fe\{P(OMe)_3\}_3]^+$ (R = H, Me) or of the carbonyl from $[C_5R_5Fe(P^\frown P)(CO)]^+$ (R = H, Me; $P^\frown P$ = dppm, dppe) in CH_3CN leads to CH_3CN complexes which are reversibly oxidized.

Cations of the type $[CpFeL^1L^2L^3]^+$ ($Cp = C_5H_5$ or C_5Me_5) * are accessible by photolysis of the cation $[C_5H_5Fe(Arene)]^+$ [1a], or $[C_5Me_5Fe(CO)_3]^+$ [1b], but the photochemical behaviour of the cations $[Cp^\star Fe(Arene)]^+$, $[Cp^\star FeP_2(CO)]^+$ and $[Cp^\star FeL_3]^+$ complexes is not known [2]. We report here several original photochemical synthetic and thermal conversions of these compounds together with related electrochemical behaviour.

We find that: (i) Whereas $[CpFe(Arene)]^+$ cations under irradiation readily undergo arene exchange in the presence of another arene [1] or arene replacement by three identical or different ligands, the analogous species $[Cp^\star Fe(Arene)]^+$ are resistant to photolysis in CH_3CN. However, if the irradiation of these species are carried out in the presence of acetone or anthracene as sensitizer, exchange proceeds well [3]:

$$[Cp^\star Fe(Arene)]^+PF_6^- \xrightarrow[CH_3COCH_3]{P(OMe)_3,\ h\nu} [Cp^\star Fe\{(OMe)_3\}_3][PF_6] \qquad (1)$$

(arene = *p*-xylene: visible light, 1 week; yields: 50–60%)

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* Unless specified otherwise $Cp = C_5H_5$, $Cp^\star = C_5Me_5$. The counter anion is always PF_6^-.

The new complex $[\mathrm{Cp^{\star}Fe\{P(OMe)_3\}_3}][\mathrm{PF_6}]$ can also be obtained thermally by treatment of $[\mathrm{Cp^{\star}Fe(acac)}]$ with $\mathrm{P(OMe)_3}$ in THF and acetic acid [4]:

$$\mathrm{Cp^{\star}Fe(acac)} \xrightarrow[\text{(2) NH}_4\text{PF}_6]{\substack{\text{(1) P(OMe)}_3,\\ \text{THF, CH}_3\text{CO}_2\text{H, 20°C}}} [\mathrm{Cp^{\star}Fe\{P(OMe)_3\}_3}][\mathrm{PF_6}] + \mathrm{acacH} \qquad (2)$$

(ii) Monocarbonyl compounds $[\mathrm{CpFeL_2CO}][\mathrm{PF_6}]$ can be photolyzed in $\mathrm{CH_3CN}$ to give $[\mathrm{CpFeL_2}(\eta^1\text{-}\mathrm{NCCH_3})][\mathrm{PF_6}]$ in acetonitrile. The reverse reaction is found to occur thermally at 20°C:

$$\mathrm{CH_3CN} + [\mathrm{CpFeL_2(CO)}]^+ \xrightleftharpoons[\sim 5\text{ atm CO, 20°C, CH}_2\text{Cl}_2]{h\nu,\ (\lambda \geq 400\text{ nm}),\ \text{CH}_3\text{CN}} [\mathrm{CpFeL_2(NCCH_3)}]^+ + \mathrm{CO} \qquad (3)$$

($\mathrm{L} = \mathrm{P(OMe)_3}$, dppm or dppe)

(iii) $[\mathrm{CpFe\{P(OMe)_3\}_3}]^+$ can be photolyzed in $\mathrm{CH_3CN}$ to give $[\mathrm{CpFe\{P(OMe)_3\}(NCCH_3)}]^+$; the latter reacts in the dark with $\mathrm{P(OMe)_3}$ in $\mathrm{CH_2Cl_2}$ to regenerate the tris(trimethylphosphite) derivative:

$$[\mathrm{CpFe\{P(OMe)\}_3}]^+ \xrightleftharpoons[\text{P(OMe)}_3,\ \text{CH}_2\text{Cl}_2\text{ in the dark}]{h\nu,\ (\lambda \geq 400\text{ nm}),\ \text{CH}_3\text{CN}} [\mathrm{CpFe\{P(OMe)_3\}_2(NCCH_3)}]^+ + \mathrm{P(OMe)_3} \qquad (4)$$

(iv) The piano-stool cationic complexes are reversibly oxidized to dications at potentials ranging from +0.6 to +1.2 V/SCE, [5], but the anodic oxidation of the monocarbonyl compounds is only reversible for the Cp★ (not the parent Cp) species.

$$[\mathrm{CpFeL^1L^2L^3}]^+ \xrightleftharpoons[+1e^-]{-1e^-} [\mathrm{CpFeL^1L^2L^3}]^{2+} \qquad (5)$$

(v) The single carbonyl ligand plays the role of an electron sink in these complexes: comparisons of the multinuclear NMR, electrochemical, electronic spectra, and Mössbauer data [7] (Table 1), all indicate a much higher electron density of the iron moiety when no back-bonding is possible ($\mathrm{CH_3CN}$ complexes).

(vi) The reduction of $[\mathrm{CpFeP_2CO}]^+\ \mathrm{PF_6}^-$ in Na/Hg leads to the known dimers $[\{\mathrm{CpFe(CO)}\}_2\text{-}\mu\text{-}\mathrm{P_2}]$ [6] whereas the permethyl Cp analogues $[\mathrm{Cp^{\star}FeP_2CO}][\mathrm{PF_6}]$ do not dimerize upon reduction; in this latter case, the 19-electron or 17-electron compounds give iron hydrides by H-abstraction from the hydride substrate or the solvent [8]:

$$[\mathrm{CpFeP_2(CO)}]^+ \xrightarrow[\text{THF, Ar}]{\text{Na/Hg, 20°C}} \underset{(19e^-)}{[\mathrm{CpFeP_2(CO)}]} \qquad (6)$$

$$\mathrm{P_2} + [\{\mathrm{CpFe(CO)}\}_2\text{-}\mu\text{-}\mathrm{P_2}] \xleftarrow[\substack{\text{THF}\\ \text{C}_5\text{H}_5\text{ series}}]{\text{slow dimerization}} \underset{(19e^-)}{\mathrm{Cp\dot{F}eP_2(CO)}} \xrightarrow[\substack{\text{THF}\\ \text{C}_5\text{Me}_5\text{ series}}]{\text{D}_2\text{O or LiAlD}_4} [\mathrm{Cp^{\star}Fe}(\eta^1\text{-}\mathrm{P_2})\mathrm{(CO)D}] \qquad (7)$$

(P = diphos, dppm)

TABLE 1

SELECTED DATA FOR $[Fe^{II}CpL_2L']^+$ PF_6^- SALTS, ($Cp = C_5H_5$, C_5Me_5)

Compound	^1H NMR [a] (δ (ppm), Cp signal)	$E_{1/2}$ (oxidation) (V) (SCE) [d] $[Fe^{II}]^{1+} \rightleftarrows [Fe^{III}]^{2+}$
$[CpFe\{P(OMe)_3\}_2(CO)][PF_6]$ [b]	5.00	no oxid. $\leqq +1.50V$
$[CpFe\{P(OMe)_3\}_2(\eta^1\text{-}NCCH_3)][PF_6]$ [c]	4.67	0.87
$[CpFe\{P(OMe)_3\}_3][PF_6]$ [b]	4.87	1.15
$[Cp^{\star}Fe\{P(OMe)_3\}_3][PF_6]$	–	0.834
$[Cp^{\star}Fe\{P(OMe)_3\}_2(CO)][PF_6]$	–	1.5 (irreversible)
$[Cp^{\star}Fe\{P(OMe)_3\}_2(\eta^1\text{-}NCCH_3)][PF_6]$	–	0.585
$[CpFe(diphos)(CO)][PF_6]$ [b]	5.08	no oxid. $\leqq +1.50V$
$[CpFe(diphos)(\eta^1\text{-}NCCH_3)[[PF_6]$ [c]	4.29	0.66
$[CpFe(dppm)(CO)][PF_6]$ [b]	5.3	no oxid. $\leqq +1.50$ V
$[CpFe(dppm)(\eta^1\text{-}NCCH_3)][PF_6]$ [b]	4.62	0.61
$[Cp^{\star}Fe(diphos)(CO)][PF_6]$	–	1.24 [e]
$[Cp^{\star}Fe(diphos)(\eta^1\text{-}NCCH_3)][PF_6]$	–	0.466

[a] Brucker WM250 (^1H, $^{13}C\{^1H\}$) and Varian XL = 100 (^1H). [b] CD_3COCD_3. [c] $CDCl_3$. [d] 0.1 *M* $n\text{-}Bu_4NBF_4$, 10^{-3} *M* in complex (CH_3CN solvent). Pt electrode, *E* vs. SCE. [e] $LiClO_4$ 0.1 *M*.

The findings [7] reported mean that a study can be made of the potential of these systems for photochromism [9] and electrocatalysis [10].

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