

Preliminary communication

PHOTOCHEMICAL SYNTHESIS, REACTIVITY, AND ELECTROCHEMICAL PROPERTIES OF $[\text{Cp}^*\text{FeP}_2\text{L}]^+$ CATIONS; ($\text{Cp} = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$; $\text{L} = \text{CO}$ vs. CH_3CN ; $\text{P} = \text{PHOSPHINE OR PHOSPHITE}$)

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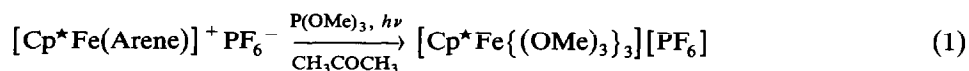
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Summary

Photolytic replacement of the arene ligand in the cations $[\text{Cp}^*\text{Fe}(p\text{-xylene})]^+$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) by $\text{P}(\text{OMe})_3$ ligands is only possible when a sensitizer (acetone or anthracene) is present and leads to $\text{Cp}^*\text{Fe}^+\{\text{P}(\text{OMe})_3\}_3$. Photoextrusion of one phosphite ligand from $[\text{C}_5\text{R}_5\text{Fe}\{\text{P}(\text{OMe})_3\}_3]^+$ ($\text{R} = \text{H}, \text{Me}$) or of the carbonyl from $[\text{C}_5\text{R}_5\text{Fe}(\text{P} \wedge \text{P})(\text{CO})]^+$ ($\text{R} = \text{H}, \text{Me}$; $\text{P} \wedge \text{P} = \text{dppm}, \text{dppe}$) in CH_3CN leads to CH_3CN complexes which are reversibly oxidized.

Cations of the type $[\text{CpFeL}^1\text{L}^2\text{L}^3]^+$ ($\text{Cp} = \text{C}_5\text{H}_5$ or C_5Me_5) * are accessible by photolysis of the cation $[\text{C}_5\text{H}_5\text{Fe}(\text{Arene})]^+$ [1a], or $[\text{C}_5\text{Me}_5\text{Fe}(\text{CO})_3]^+$ [1b], but the photochemical behaviour of the cations $[\text{Cp}^*\text{Fe}(\text{Arene})]^+$, $[\text{Cp}^*\text{FeP}_2(\text{CO})]^+$ and $[\text{Cp}^*\text{FeL}_3]^+$ complexes is not known [2]. We report here several original photochemical synthetic and thermal conversions of these compounds together with related electrochemical behaviour.

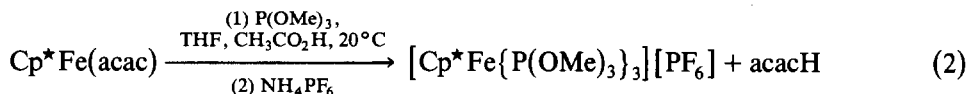
We find that: (i) Whereas $[\text{CpFe}(\text{Arene})]^+$ cations under irradiation readily undergo arene exchange in the presence of another arene [1] or arene replacement by three identical or different ligands, the analogous species $[\text{Cp}^*\text{Fe}(\text{Arene})]^+$ are resistant to photolysis 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]:



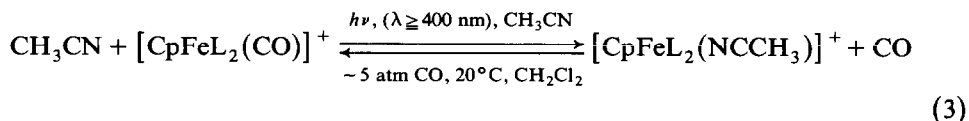
(arene = *p*-xylene: visible light, 1 week; yields: 50–60%)

* Unless specified otherwise $\text{Cp} = \text{C}_5\text{H}_5$, $\text{Cp}^* = \text{C}_5\text{Me}_5$. The counter anion is always PF_6^- .

The new complex $[\text{Cp}^*\text{Fe}\{\text{P}(\text{OMe})_3\}_3][\text{PF}_6]$ can also be obtained thermally by treatment of $[\text{Cp}^*\text{Fe}(\text{acac})]$ with $\text{P}(\text{OMe})_3$ in THF and acetic acid [4]:

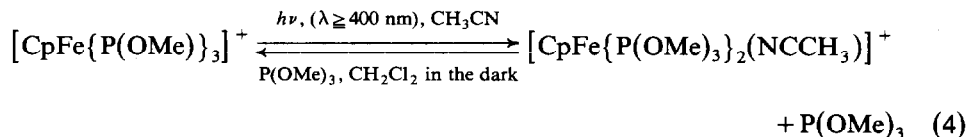


(ii) Monocarbonyl compounds $[\text{CpFeL}_2\text{CO}][\text{PF}_6]$ can be photolyzed in CH_3CN to give $[\text{CpFeL}_2(\eta^1\text{-NCCH}_3)][\text{PF}_6]$ in acetonitrile. The reverse reaction is found to occur thermally at 20°C :



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

(iii) $[\text{CpFe}\{\text{P}(\text{OMe})_3\}_3]^+$ can be photolyzed in CH_3CN to give $[\text{CpFe}\{\text{P}(\text{OMe})_3\}_2(\text{NCCH}_3)]^+$; the latter reacts in the dark with $\text{P}(\text{OMe})_3$ in CH_2Cl_2 to regenerate the tris(trimethylphosphite) derivative:

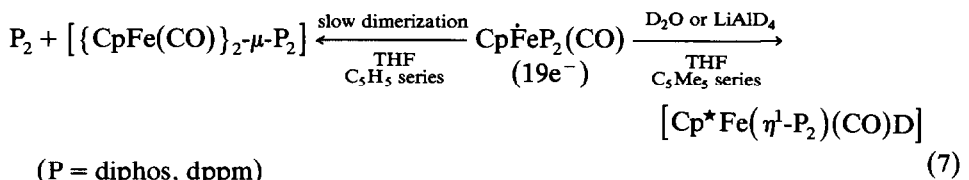
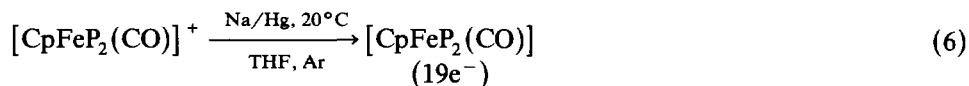


(iv) The piano-stool cationic complexes are reversibly oxidized to dications at potentials ranging from +0.6 to +1.2 V/SCE, [5], but the anodic oxidation of the monocarbonyl compounds is only reversible for the Cp^* (not the parent Cp) species.



(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 (CH_3CN complexes).

(vi) The reduction of $[\text{CpFeP}_2\text{CO}]^+ \text{PF}_6^-$ in Na/Hg leads to the known dimers $[\{\text{CpFe}(\text{CO})\}_2\text{-}\mu\text{-P}_2]$ [6] whereas the permethyl Cp analogues $[\text{Cp}^*\text{FeP}_2\text{CO}][\text{PF}_6]$ 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]:



(P = diphos, dppm)

TABLE 1

SELECTED DATA FOR $[\text{Fe}^{\text{II}}\text{CpL}_2\text{L}']^+ \text{PF}_6^-$ 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⁺ \rightleftharpoons [Fe^{III}] ²⁺ |
|---|---|---|
| $[\text{CpFe}\{\text{P}(\text{OMe})_3\}_2(\text{CO})][\text{PF}_6]^{-b}$ | 5.00 | no oxid. $\leq +1.50\text{V}$ |
| $[\text{CpFe}\{\text{P}(\text{OMe})_3\}_2(\eta^1\text{-NCCH}_3)][\text{PF}_6]^{-c}$ | 4.67 | 0.87 |
| $[\text{CpFe}\{\text{P}(\text{OMe})_3\}_3][\text{PF}_6]^{-b}$ | 4.87 | 1.15 |
| $[\text{Cp}^*\text{Fe}\{\text{P}(\text{OMe})_3\}_3][\text{PF}_6]$ | – | 0.834 |
| $[\text{Cp}^*\text{Fe}\{\text{P}(\text{OMe})_3\}_2(\text{CO})][\text{PF}_6]$ | – | 1.5 (irreversible) |
| $[\text{Cp}^*\text{Fe}\{\text{P}(\text{OMe})_3\}_2(\eta^1\text{-NCCH}_3)][\text{PF}_6]$ | – | 0.585 |
| $[\text{CpFe}(\text{diphos})(\text{CO})][\text{PF}_6]^{-b}$ | 5.08 | no oxid. $\leq +1.50\text{V}$ |
| $[\text{CpFe}(\text{diphos})(\eta^1\text{-NCCH}_3)][\text{PF}_6]^{-c}$ | 4.29 | 0.66 |
| $[\text{CpFe}(\text{dppm})(\text{CO})][\text{PF}_6]^{-b}$ | 5.3 | no oxid. $\leq +1.50\text{V}$ |
| $[\text{CpFe}(\text{dppm})(\eta^1\text{-NCCH}_3)][\text{PF}_6]^{-b}$ | 4.62 | 0.61 |
| $[\text{Cp}^*\text{Fe}(\text{diphos})(\text{CO})][\text{PF}_6]$ | – | 1.24 ^e |
| $[\text{Cp}^*\text{Fe}(\text{diphos})(\eta^1\text{-NCCH}_3)][\text{PF}_6]$ | – | 0.466 |

^a Bruker WM250 (^1H , $^{13}\text{C}\{^1\text{H}\}$) and Varian XL=100 (^1H). ^b CD_3COCD_3 . ^c CDCl_3 . ^d 0.1 M n-Bu₄NBF₄, 10⁻³ M in complex (CH₃CN solvent). Pt electrode, E vs. SCE. ^e LiClO₄ 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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References and Notes

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