

Preliminary communication

THE MONO-, BIS-, AND TRIS-TRIMETHYLPHOSPHINEIRON(II) COMPLEXES $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{PMe}_3)_x(\text{CO})_y(\text{NCMe})_z\}^+\text{PF}_6^-$ ($x + y + z = 3$)

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Summary

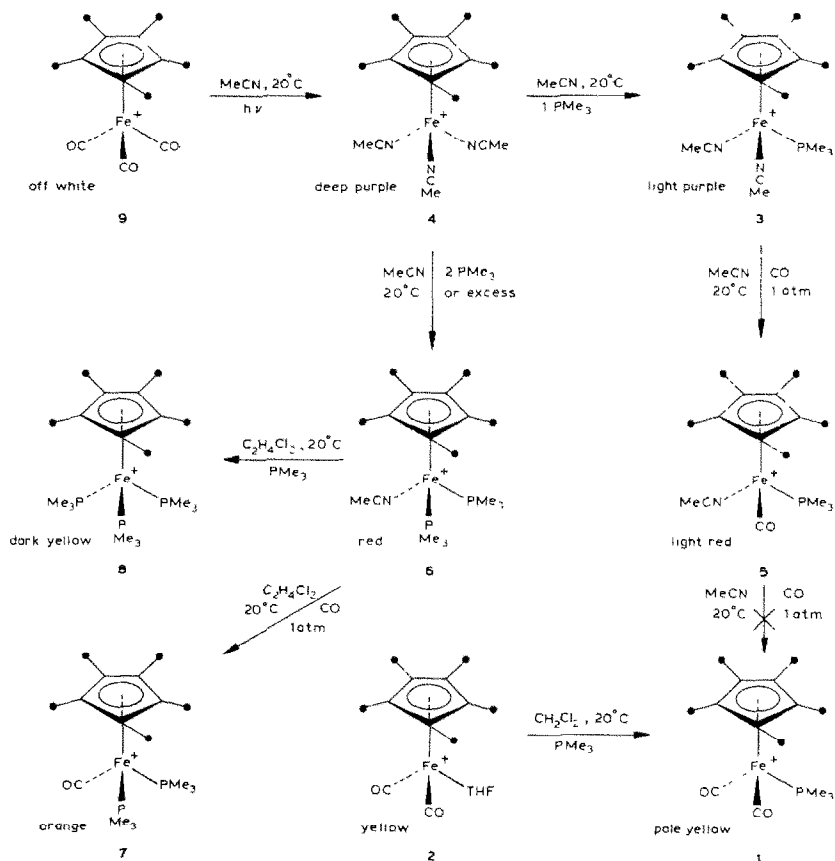
Syntheses are reported for the six trimethylphosphineiron complexes $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{PMe}_3)_x(\text{CO})_y(\text{NCMe})_z\}^+\text{PF}_6^-$ ($x + y + z = 3$).

Trimethylphosphine is an extremely useful ligand because of its small size and high basicity. In particular, it has been used for the design of organometallic complexes intended for activation of small unsaturated molecules and for model reactivity studies [1]. Some time ago, we reported the stepwise hydride reduction of a CO ligand to hydroxymethyl and methyl in $\{\text{Cp}'\text{Fe}(\text{CO})_3\}^+\text{PF}_6^-$, and the formation of $\text{Cp}'\text{Fe}(\text{CO})_2\text{H}$ resulting from the decomposition of the as yet uncharacterized formyl intermediate [2]. In the light of the pioneering results by Green [3] concerning the hydride reduction of $\{\text{Cp}\text{Fe}(\text{CO})_2\text{L}\}^+$, which revealed Cp reduction, we believed that the use of permethylated Cp ($\text{C}_5\text{Me}_5 = \text{Cp}'$) would change the site of reduction to CO. After our report on the modeling of CO reduction in iron complexes using Cp', at least two groups described the use of Cp'Fe or Ru carbonyl complexes for the same purpose [4,5].

As a part of our continuing effort to design model complexes for CO reduction, we now report the syntheses and characterization of trimethylphosphineiron(II) complexes with Cp'. The use of PPh_3 or dppe as ancillary ligands leads to slightly different chemistry, and in particular extensive electron-transfer reactions [6a] which can be avoided using PMe_3 [6b].

$\{\text{Cp}'\text{Fe}(\text{CO})_3\}^+\text{PF}_6^-$ (9), which we reported in 1982 [7], was not used as a starting point, although others have recently used it to make $\{\text{Cp}'\text{Fe}(\text{CO})_2(\text{PMe}_3)\}^+\text{PF}_6^-$ (1). We find that the most convenient synthesis of 1 begins with

$\{\text{Cp}'\text{Fe}(\text{CO})_2(\text{THF})\}^+\text{PF}_6^-$ (**2**) [8a], easily prepared from $\{\text{Cp}'\text{Fe}(\text{CO})_2\}_2$ [8b] and $\text{Cp}_2\text{Fe}^+\text{PF}_6^-$ [9]. The reaction of **2** with PMe_3 in CH_2Cl_2 (20°C , 1 h) gives an 85% yield of the pale yellow complex **1** [10a] after recrystallization from $\text{EtOH}/\text{Me}_2\text{CO}$. The synthesis of complexes bearing more than one PMe_3 ligand requires the use of the air-sensitive purple, crystalline complex $\{\text{Cp}'\text{Fe}(\text{NCMe})_3\}^+\text{PF}_6^-$ (**4**), readily obtained by photolysis in MeCN of **9** [11], or of $\{\text{Cp}'\text{Fe}(\text{CO})_2(\text{NCMe})\}^+\text{PF}_6^-$, which is prepared by oxidation of $\{\text{Cp}'\text{Fe}(\text{CO})_2\}_2$ with $\text{Cp}_2\text{Fe}^+\text{PF}_6^-$ in MeCN [8a]. The reaction of **4** with 1 mol PMe_3 in MeCN immediately gives $\{\text{Cp}'\text{Fe}(\text{PMe}_3)(\text{NCMe})_2\}^+\text{PF}_6^-$ (**3**). Air-sensitive light purple microcrystals of **3** are obtained in 82% yield by crystallization from MeCN/ether . One or both acetonitrile ligands in **3** can be replaced by CO but, interestingly, the reaction of **3** with CO (1 atm) at 20°C in MeCN leads to the selective replacement of only one MeCN ligand; Thus the chiral complex $\{\text{Cp}'\text{Fe}(\text{PMe}_3)(\text{CO})(\text{NCMe})\}^+\text{PF}_6^-$ (**5**) is obtained in 60% yield as air-stable light red crystals. If the reaction between **4** and PMe_3 in MeCN is carried out in the presence of two moles (or excess) of this phosphine, replacement of a second MeCN ligand also occurs within one hour at 20°C but replacement of the last MeCN ligand does not take place in this solvent; air-stable $\{\text{Cp}'\text{Fe}(\text{PMe}_3)_2(\text{NCMe})\}^+\text{PF}_6^-$ (**6**) is isolated in 82% yield as red microcrystals after recrystallization from MeCN/ether ; Complex **6** is an ex-



SCHEME 1

cellent, easily prepared material for use in studies of the coordination of molecules whose activation is of interest. The Cp analogue can also be prepared by photolysis of $\{\text{Cp}(\eta^6\text{-C}_6\text{H}_6)\text{Fe}\}^+\text{PF}_6^-$ in MeCN in the presence of 2 moles or excess PMe_3 (a deficiency, i.e. 1 mol of PMe_3 , also leads to this complex rather than to $\{\text{CpFe}(\text{PMe}_3)(\text{NCMe})_2\}^+$) [12]. Displacement of the last MeCN ligand in 6 occurs smoothly in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ at 20°C in 1 day: the carbonyl complex $\{\text{Cp}'\text{-Fe}(\text{PMe}_3)_2\text{CO}\}^+\text{PF}_6^-$ (7) is obtained from 6 under 1 atm CO as air stable orange microcrystals (70% yield after recrystallization from EtOH/ Me_2CO) and the tris-(trimethylphosphine) complex $\{\text{Cp}'\text{-Fe}(\text{PMe}_3)_3\}^+\text{PF}_6^-$ (8) is obtained from 6 in the presence of 1 mol PMe_3 as air stable dark yellow microcrystals (55% yield after recrystallization from EtOH/ Me_2CO).

The Mössbauer data for the series of complexes $(\text{Cp}'\text{FeL}_3)^+$ (9, L = CO; 4, L = NCMe; 8, L = PMe_3), listed in Table 1, indicate that the replacements of CO by PMe_3 ligands has only small effects on the electronic density at iron (*IS* and *QS*) and on the geometry (*QS*); on the other hand, large changes are found in the tris-acetonitrile complex for the *QS* as well as for the *IS* values. The electron-donating effect of NCMe without back-donation is reflected in a much larger *IS* value, and the much larger *QS* value may indicate a pianostool geometry in which the angles differ from those in 8 and 9.

TABLE 1

MOSSBAUER DATA FOR $\{\text{Cp}'\text{FeL}_3\}^+\text{PF}_6^-$ (L = CO, NCMe, PMe_3), T 293 K.

	<i>IS</i> vs. Fe (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)
9, L = CO	0.08	1.85
4, L = NCMe	0.54	2.37
8, L = PMe_3	0.19	1.86

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