NEW CYCLOPENTADIENYLIRON TRIMETHYLPHOSPHINE COMPLEXES

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Summary

Preparations of $[Fe(C_5H_5)(CO)_{3-n}(PMe_3)_n]X$ complexes (n = 1, 2, 3) are described. Irradiation of $[Fe(C_5H_5)(CO)(PMe_3)_2]BF_4$ in acetonitrile gave $[Fe(C_5H_5)(PMe_3)_2(MeCN)]BF_4$ which is a precursor to $Fe(C_5H_5)(PMe_3)_2X$ (X = I, CN) and $[Fe(C_5H_5)(PMe_3)_2(PPh_3)]BF_4$. Reactions of $Fe(C_5H_5)(CO)_2X$ compounds (X = SPh, SiMe_3, SnMe_3, SnPh_3) with PMe_3 gave mono- and disubstituted products, $Fe(C_5H_5)(CO)_{2-n}(PMe_3)_nX$. The reaction of $Fe(C_5H_5)(CO)_2Me$ with PMe_3 gave $Fe(C_5H_5)(CO)(PMe_3)COMe$ or $Fe(C_5H_5)(PMe_3)_2Me$, depending on conditions. One electron oxidations of $Fe(C_5H_5)(PMe_3)_2SPh$, $Fe(C_5H_5)$-$(PMe_3)_2SnPh_3$ and $[Fe(C_5H_5)(PMe_3)_3]PF_6$ produced 17 electron products which were isolable.

Introduction

The use of trimethylphosphine as a ligand in organometallic chemistry began very slowly, in contrast to the use of other phosphine ligands. No doubt this was due in part to difficulties in obtaining and handling this volatile, air sensitive compound. Recently the use of trimethylphosphine as a ligand has received more attention and some interesting work has resulted [1].

When coordinated to metals, trialkylphosphines act as good donors of electronic charge. Trimethylphosphine is the least sterically demanding ligand in this group, and multiple substitution of PMe_3 is often encountered. As a consequence, the use of PMe_3 for the synthesis of electron-rich complexes appears ideal. Electron-rich complexes are a subject of primary interest in our current research program [2].

The compounds described here are cyclopentadienyliron carbonyl species, formally derived from $[Fe(C_5H_5)(CO)_3]^+$ or $Fe(C_5H_5)(CO)_2X$ (X = halide, R, H, and metalloidal groups) by PMe_3 substitution. References to several compounds in this category have appeared previously. The compound $Fe(C_5H_5)(CO)$-$(PMe_3)H$ was prepared via a substitution reaction of $Fe(C_5H_5)(CO)_2H$, and Fe-

$(C_5H_5)(CO)(PMe_3)Cl$ was obtained from this compound by reaction with CCl_4 [3]. Prepared from $Fe(C_5H_5)(CO)_2I$ by direct substitution was $Fe(C_5H_5)(CO)$-$(PMe_3)I$, and from this compound $Fe(C_5H_5)(CO)(PMe_3)CN$ was obtained [4]. Finally, ultraviolet photolysis of $Fe(C_5H_5)(CO)_2Me$ with PMe_3 was recently reported to give $Fe(C_5H_5)(CO)(PMe_3)Me$ [1b].

Experimental

Various starting materials were prepared by the literature methods: Fe-$(C_5H_5)(CO)_2X$ (X = Br, Cl [5], SPh [6], $SnMe_3$, $SiMe_3$ [7], $SnPh_3$ [8], $SnCl_3$ [9], Me [10]), $[Fe(C_5H_5)(CO)_2(THF)]BF_4 \cdot 1/2 \ CH_2Cl_2$ [11], and PMe_3 [12]. Other reagents were commercial samples. Chromatographic separations were carried out using Merck alumina, neutral grade. Solvents used were reagent grade. Petroleum ether refers to the commercial solvent Skelly B, a hydrocarbon mixture bp 60—80°C containing primarily hexanes. All reactions were carried out under N_2.

Most of the photolyses were carried out on solutions in Pyrex flasks using a GE 100-PSP44-4 sunlamp. On a few occasions, noted in the text, irradiation was carried out with a 450 watt Hanovia mercury discharge lamp contained in a water-cooled quartz immersion well of 500 ml photochemical reactor.

Cyclic voltammetric data were obtained in CH_2Cl_2 at 25°C using a 3-electrode configuration (stationary Pt bead working electrode, Pt spiral counter electrode, and SCE (aqueous KCl) reference electrode). Voltage and current functions were controlled using a PAR system, Model 169. Tetrabutylammonium perchlorate (0.1 M) was the base electrolyte. Substrate concentrations were $\sim 5 \times 10^{-3} \ M$. Data are given in Table 1.

Proton NMR spectra were run on a JEOL NM-MH-100 spectrometer; chemical shifts are reported as δ values in ppm and were measured vs internal TMS. Infrared data were recorded on a Beckman Acculab-7 spectrometer using KBr

TABLE 1

CYCLIC VOLTAMMETRIC DATA ON CERTAIN COMPOUNDS REPORTED HERE [a]

Process	$1/2[E_{pc} + E_{pa}]$ (V, vs SCE)	$E_{pc} - E_{pa}$ (V)
A $Fe(C_5H_5)(PMe_3)_2X \rightleftharpoons [Fe(C_5H_5)(PMe_3)_2X]^+ + e^-$		
X = Me	−0.47	0.300
SPh	−0.37 [b]	0.100
$SnMe_3$	−0.20	0.300
$SnPh_3$	−0.02	0.060
I	+0.025 [c]	0.310
CN	+0.42	0.330
B $Fe(C_5H_5)(CO)(PMe_3)X \rightleftharpoons [Fe(C_5H_5)(CO)(PMe_3)X]^+ + e^-$		
X = SPh	0.32	0.520
I	0.685	0.410
C $[Fe(C_5H_5)(CO)(PMe_3)_2]^+ \rightleftharpoons [Fe(C_5H_5)(CO)(PMe_3)_2]^{2+} + e^-$	+1.30	
D $[Fe(C_5H_5)(PMe_3)_3]^+ \rightleftharpoons [Fe(C_5H_5)(PMe_3)_3]^{2+} + e^-$	+0.71	0.170

[a] CH_2Cl_2 solutions, see Experimental Section for details. [b] Shows a second 1e oxidation, $E_{1/2} = 1.06$ V, $E_{pc} - E_{pa} = 0.11$ V. [c] Shows a second 1e oxidation $E_{1/2} = 1.25$ V, $E_{pc} - E_{pa} = 0.24$ V.

discs except as noted. Magnetic susceptibility data was obtained using a Faraday Balance. Analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee.

For some compounds analysis was accomplished by parent peak match (AEI-MS 902 high resolution mass spectrometer). Purity of these compounds was ascertained by NMR and infrared data (no spurious NMR resonances or infrared absorptions seen) and by constancy of m.p. values when the compound melted without decomposition.

[Fe(C₅H₅)(PMe₃)₃]Br. A solution of ~3.0 ml (29 mmol) of PMe_3 and 1.0 g (3.9 mmol) of $Fe(C_5H_5)(CO)_2Br$ in 100 ml MeCN was irradiated for 6.5 h (at reflux), changing from purple to yellow in this time. After being allowed to cool, the solution was filtered. The solvent was evaporated in vacuo to ~10 ml; additional of ~25 ml diethyl ether caused yellow crystals to precipitate. This product was recrystallized from CH_2Cl_2/petroleum ether, yield 1.47 g (87%); mp >250°C.

Anal. Found: C, 38.97; H, 7.77; P, 21.34. Calcd. for $C_{14}H_{34}BrFeP_3$: C, 39.01; H, 7.45; P, 21.55%. NMR (DMSO-d_6): δ 1.45 m (27 H, PMe_3), 4.40 q (5 H, C_5H_5, J(P—H) = 1.9 Hz).

The PF_6^- salt of this cation was prepared by a metathesis reaction. A sample of $[Fe(C_5H_5)(PMe_3)_3]Br$ (3.8 g, 8.9 mmol) was dissolved in 50 ml H_2O and 3.0 g (18 mmol) of NH_4PF_6 added. This addition produced a yellow precipitate which was separated by filtration. The solid was redissolved in 25 ml CH_2Cl_2. After drying over $MgSO_4$ the solvent volume was reduced to 10 ml on a rotary evaporator; addition of 50 ml of diethyl ether caused precipitation of the crystalline product, 3.56 g (93%); mp 181°C d.

[Fe(C₅H₅)(CO)(PMe₃)₂]BF₄. A 12.0 ml sample of PMe_3 (118 mmol) was added to a solution of 14.6 g (39.2 mmol) $[Fe(C_5H_5)(CO)_2(THF)]BF_4 \cdot$ 1/2 CH_2Cl_2 in 750 ml acetone. The color of the solution immediately changed from red to yellow. The solution was heated at reflux for 35.5 h and allowed to cool. The volume of solvent was reduced to ~10 ml and 25 ml petroleum ether added, precipitating the yellow crystalline product, 13.5 g (88%); mp >300°C.

Anal. Found: C, 37.20; H, 6.12; P, 16.17. Calcd. for $C_{12}H_{23}BF_4FeOP_2$: C, 37.16; H, 5.98; P, 15.97%. IR: ν(CO) at 1960s cm^{-1}. NMR (DMSO-d_6): δ 1.55 m (18 H, PMe_3), 5.02 t (5 H, C_5H_5, J(P—H) = 1.9 Hz).

A PF_6^- salt of this complex was obtained by another route. A sample of PMe_3 (1.0 ml, 9.8 mmol) was added to a solution of 2.54 g (8.33 mmol) of $Fe(C_5H_5)(CO)(PMe_3)Br$ (vide infra) in 100 ml toluene. The solution was heated at reflux for 45 min, a yellow precipitate forming during this time. The precipitate was separated by filtration, dissolved in 50 ml water, and NH_4PF_6 (3.0 g in 25 ml H_2O) was added; a yellow precipitate formed. This was separated, then dissolved in 25 ml CH_2Cl_2. Addition of 75 ml of diethyl ether caused precipitation of the product; 2.50 g (67%); mp >300°C.

The iodide salt of this complex was obtained in excellent yield from $[Fe(C_5H_5)(CO)_2(PMe_3)]I$ (vide infra) and PMe_3. A solution of 1.84 g (4.83 mmol) $[Fe(C_5H_5)(CO)_2(PMe_3)]I$ and 0.50 ml (4.9 mmol) PMe_3 in 100 ml MeCN was heated at reflux for 2 h. An infrared spectrum taken at this time showed complete conversion of the starting material. The solvent was removed in vacuo and the residue recrystallized from CH_2Cl_2/petroleum ether giving 1.81 g (87%)

of the product, $[Fe(C_5H_5)(CO)(PMe_3)_2]I$, m.p. 302—340°C, identified by infrared and NMR spectra.

$[Fe(C_5H_5)(CO)_2(PMe_3)]BF_4$. A 0.16 ml (1.56 mmol) sample of PMe_3 was added to a solution of 0.50 g (1.34 mmol) of $[Fe(C_5H_5)(CO)_2(THF)]BF_4 \cdot 1/2\ CH_2Cl_2$ in 200 ml acetone at —23°C. A color change (red to yellow) occurred within a few seconds. After allowing the solution to warm to room temperature, the solvent volume was reduced to ~5 ml; addition of ~50 ml petroleum ether gave the yellow crystalline product which was recrystallized from acetone/petroleum ether; 0.27 g (59%); m.p. >250°C.

Anal. Found: C, 35.09; H, 4.40; P, 8.89. Calcd. for $C_{10}H_{14}BF_4FePO_2$: C, 35.34; H, 4.15; P, 9.11%. IR: ν(CO) 2030s and 1990s cm^{-1}. NMR (DMSO-d_6): δ 1.73 d (9 H, PMe_3, J(P—H) = 12 Hz); 5.64 d (5 H, C_5H_5, J(P—H) = 1.8 Hz).

$[Fe(C_5H_5)(PMe_3)_2(MeCN)]BF_4$. A solution of 0.50 g (1.29 mmol) of $[Fe(C_5H_5)(CO)(PMe_3)_2]BF_4$ in 100 ml MeCN was irradiated (at reflux) for 3.5 h. The color changed gradually from yellow to red. The solvent was removed, and the solid residue extracted with 25 ml CH_2Cl_2. Solvent was removed in vacuo; addition of 10 ml diethyl ether precipitated 0.48 g (94%) of the orange product, mp 168—175°C (d). A satisfactory analysis was not obtained for this complex. An analytically pure PF_6^- salt (mp >300°C d) was prepared in 96% yield in a similar reaction from $[Fe(C_5H_5)(CO)(PMe_3)_2]PF_6$.

Anal. Found: C, 33.80; H, 5.65; P, 20.50. Calcd. for $C_{13}H_{26}F_6FeNP_3$: C, 34.01; H, 5.71; P, 20.24%. IR: ν(CN) 2260 m cm^{-1}. NMR (DMSO-d_6): δ 1.55 m (18 H, PMe_3); 2.05 s (3 H, CH_3CN); 4.60 t (5 H, C_5H_5, J(P—H) = 1.5 Hz).

$[Fe(C_5H_5)(PMe_3)_2(PPh_3)]BF_4$. A 1.0 g (3.8 mmol) sample of PPh_3 was added to a solution of 0.46 g (1.2 mmol) of $[Fe(C_5H_5)(PMe_3)_2(MeCN)]BF_4$ in 100 ml THF. The solution was stirred for 18 h at room temperature. The product, which precipitated as an orange solid, was collected by filtration and recrystallized from CH_2Cl_2/THF; 0.48 g (67%); m.p. 185—190°C.

Anal. Found: C, 55.62; H, 6.34; P, 14.79. Calcd. for $C_{29}H_{38}BF_4FeP_3$: C, 55.98; H, 6.16; P, 14.93%. NMR (CD$_2$Cl$_2$): δ 1.37 m (18 H, PMe_3); 4.25 q (5 H, C_5H_5, J(P—H) = 1.8 Hz); 7.42 m (15 H, PPh_3). An NMR spectrum in DMSO-d_6 showed these resonances plus resonances at 1.52 m and 4.54 t which are believed to be due to $[Fe(C_5H_5)(PMe_3)_2(DMSO$-$d_6)]BF_4$ (vide infra). It is presumed that an equilibrium is established between PPh_3 and DMSO-d_6 complexes in this system.

$[Fe(C_5H_5)(PMe_3)_2(DMSO)]PF_6$. A few drops of DMSO were added to a mixture of 0.66 g (1.7 mmol) $Fe(C_5H_5)(PMe_3)_2I$ and 0.5 g (3 mmol) NH_4PF_6 in 100 ml CH_2Cl_2. The yellow solid which formed was stirred with 20 ml of H_2O. This solid was then collected by filtration and washed with water. The product was extracted from this solid with CH_2Cl_2, and this solution dried over anhydrous $MgSO_4$. After filtration, the solution volume was reduced in vacuo to ~5 ml, and 25 ml Et_2O was added, precipitating yellow crystals of the product; 0.61 g (74%); m.p. 283—286°C(d).

Anal. Found: C, 31.25; H, 5.93; P, 18.38. Calcd. for $C_{13}H_{29}F_6FeOP_3S$: C, 31.49; H, 5.89; P, 18.73%. NMR (DMSO-d_6): δ 4.54 t (5 H, C_5H_5, J(P—H) = 2 Hz); 3.23 s (6 H, DMSO), 1.52 m (18 H, PMe_3).

Reaction of $Fe(C_5H_5)(CO)_2SnCl_3$ and PMe_3. Two experiments utilizing different conditions were carried out, each giving complexes of the form $[Fe(C_5H_5)(CO)_{3-n}(PMe_3)_n]^+$.

In the first reaction, 1.0 ml (9.8 mmol) of PMe$_3$ was added to a solution of 0.50 g (1.2 mmol) Fe(C$_5$H$_5$)(CO)$_2$SnCl$_3$ in 100 ml acetonitrile, and this solution was irradiated for 3 h. Evaporation of the solvent left a solid residue which was extracted with acetone; to this acetone solution 1.0 g (6 mmol) NH$_4$PF$_6$ was added. After stirring for 1 h the solvent was removed in vacuo and the residue remaining extracted with 10 ml CH$_2$Cl$_2$. Filtration of this solution followed by addition of 25 ml petroleum ether precipitated 0.58 g (95%) of [Fe(C$_5$H$_5$)-(PMe$_3$)$_3$]PF$_6$.

In a second reaction, 0.50 ml (4.9 mmol) of PMe$_3$ was added to a solution of 0.29 g (0.72 mmol) Fe(C$_5$H$_5$)(CO)$_2$SnCl$_3$ in 100 ml of toluene. A white precipitate formed immediately. The precipitate was separated by filtration, redissolved in 15 ml water, and 1.0 g (6 mmol) of NH$_4$PF$_6$ was added. This caused the immediate formation of a white precipitate. This precipitate was separated by filtration and dissolved in acetone. The solution was dried over anhydrous MgSO$_4$. After filtration, the volume of solution was reduced in vacuo to ~5 ml and ~25 ml petroleum ether added, causing precipitation of 0.16 g (57%) of [Fe(C$_5$H$_5$)(CO)$_2$(PMe$_3$)]PF$_6$ whose identity was verified by IR and NMR.

Fe(C$_5$H$_5$)(CO)(PMe$_3$)Br. A solution containing PMe$_3$ (0.35 ml, 3.43 mmol) and 0.77 g (3.0 mmol) Fe(C$_5$H$_5$)(CO)$_2$Br was irradiated in 100 ml toluene (reflux temperature) for 4.5 h. The color of the solution changed from purple to green. The solution was allowed to cool. Filtration separated a yellow solid which was identified by IR data as [Fe(C$_5$H$_5$)(CO)$_2$(PMe$_3$)]Br. Evaporation of the filtrate left a green oil. This was dissolved in ~10 ml CH$_2$Cl$_2$; addition of ~50 ml petroleum ether followed by slow evaporation gave green crystals. This process was repeated to obtain a pure sample of the product, 0.57 g (62%); m.p. 111—117°C.

Anal. Found: C, 35.55; H, 4.78; P, 10.36. MW, 302 (osmometric in CHCl$_3$). Calcd. for C$_9$H$_{14}$BrFeOP: C, 35.45; H, 4.63; P, 10.16%; MW, 304.9. IR (CHCl$_3$): ν(CO) 1955s cm^{-1}. NMR (C$_6$D$_6$): δ 1.15 d (9 H, PMe$_3$, J(P—H) = 10.5 Hz); 4.12 d (5 H, C$_5$H$_5$, J(P—H) = 1.5 Hz).

Fe(C$_5$H$_5$)(CO)(PMe$_3$)I. A sample of 0.33 ml (3.2 mmol) of PMe$_3$ was added to 0.50 g (1.64 mmol) Fe(C$_5$H$_5$)(CO)$_2$I in 75 ml heptane. The solution was heated at reflux temperature for 1 h. During this time a large amount of yellow solid formed. After the solution had cooled this solid was separated by filtration and crystallized from MeOH/THF; 0.21 g was obtained (representing about 30% yield overall based on Fe). An NMR spectrum indicated that this was a mixture of 79% [Fe(C$_5$H$_5$)(CO)$_2$(PMe$_3$)]I, 5% [Fe(C$_5$H$_5$)(CO)(PMe$_3$)$_2$]I and 16% [Fe(C$_5$H$_5$)(PMe$_3$)$_3$]I. The green filtrate (from the original filtration) was evaporated in vacuo leaving a green crystalline solid. This substance, the product, was recrystallized from CH$_2$Cl$_2$/petroleum ether, 0.22 g (38%); m.p. 143—150°C d.

Anal. Found: C, 30.57; H, 4.27; P, 9.07; MW 372 (osmometric in CHCl$_3$). Calcd. for C$_9$H$_{14}$FeIOP: C, 30.72; H, 4.01; P, 8.80%; MW 351.9. IR (CH$_2$Cl$_2$): ν(CO) 1950 cm^{-1}. NMR (C$_6$D$_6$): δ 1.16 d (9 H, PMe$_3$, J(P—H) = 0.6 Hz), 4.10 d (5 H, C$_5$H$_5$, J(P—H) = 1.5 Hz).

In another reaction, a mixture of 5.00 g (16.5 mmol) Fe(C$_5$H$_5$)(CO)$_2$I and 1.7 ml (16.5 mmol) PMe$_3$ in 500 ml toluene was irradiated for 2 h. A yellow precipitate was separated by filtration from a green filtrate. This precipitate

was recrystallized from CH_2Cl_2/petroleum ether, giving a light yellow powder, 1.87 g (30%); identified as $[Fe(C_5H_5)(CO)_2(PMe_3)]I$, m.p. 204—206°C d, by IR (ν(CO)) and NMR data. Solvent was removed from the green filtrate in vacuo and the solid residue remaining was recrystallized twice from Et_2O/petroleum ether to give 3.2 g (55%) of $Fe(C_5H_5)(CO)(PMe_3)I$.

Photolysis of $[Fe(C_5H_5)(CO)_2(PMe_3)]I$. A solution of 2.05 g (5.40 mmol) of this compound in 300 ml acetone was irradiated for 4 h. The resulting dark green solution was filtered, solvent evaporated in vacuo, and the residue crystallized from Et_2O/petroleum ether to give 1.23 g (65%) of $Fe(C_5H_5)(CO)(PMe_3)I$.

Photolysis of $[Fe(C_5H_5)(CO)(PMe_3)_2]I$. Irradiation of 1.89 g (4.2 mmol) of this compound in 300 ml acetone was carried out for 3.5 h. Filtration and solvent evaporation in vacuo left a mixture of a yellow solid and a dark colored solid. The latter extracted into 50 ml THF; evaporation of the solution in vacuo and recrystallization of the residue remaining yielded $Fe(C_5H_5)(CO)$-$(PMe_3)I$ (0.37 g, 25%). The yellow solid remaining after the THF extractions was recrystallized twice from CH_2Cl_2/Et_2O; 0.88 g of solid were obtained. An NMR of this substance showed that it was a 1 : 2 mixture of $[Fe(C_5H_5)(CO)$-$(PMe_3)_2]I$ (15% recovery) and $[Fe(C_5H_5)(PMe_3)_3]I$ (29% yield).

$Fe(C_5H_5)(CO)(PMe_3)SPh$. A solution of 1.00 g (3.5 mmol) $Fe(C_5H_5)(CO)_2$-SPh and 1.0 mol (9.8 mmol) PMe_3 in 100 ml toluene was heated at reflux for 1.3 h. The mixture was allowed to cool and then filtered, and the solvent was removed from the filtrate in vacuo to give a solid residue. This solid was extracted with 50 ml CH_2Cl_2 and this solvent was partially evaporated in vacuo; upon addition of petroleum ether the product, a purple powder, precipitated, 0.57 g (49%); m.p. 103—106°C.

Anal, by mass spectrometric peak match. Found: 334.0243. Calcd. for $^{12}C_{15}{}^1H_{19}{}^{56}Fe^{16}O^{31}P^{32}S$: 334.0243. IR (KBr): ν(CO) 1922s cm^{-1}. NMR (CS_2): δ 1.42 d (9 H, PMe_3, J(P—H) = 10 Hz); 4.42 d (5 H, C_5H_5, J(P—H) = 1.8 Hz); 6.75 m (3 H, m, p-SC_6H_5); 7.22 m (2 H, o-SC_6H_5).

$Fe(C_5H_5)(CO)(PMe_3)COMe$. A solution of 2.0 g (10.4 mmol) $Fe(C_5H_5)(CO)_2$-Me and 2.0 ml (19.6 mmol) PMe_3 in 10 ml toluene was heated at reflux for 15 h. After cooling, the solution was filtered. Evaporation of the solvent, in vacuo, left an orange oil. Chromatography on alumina gave a single orange band which eluted rapidly with 30% petroleum ether/70% Et_2O. Evaporation in vacuo gave the crude solid product which was purified by sublimation at 80—90°C/0.03 mmHg; the product is a waxy orange solid, 1.6 g (78%) m.p. 71—73°C.

Anal, by mass spectrometric peak match: Found: 268.0309. Calcd. for $^{12}C_{11}{}^1H_{17}{}^{56}Fe^{16}O_2{}^{31}P$: 268.0311. IR: ν(CO) 1878vs and 1585s cm^{-1}. NMR (C_6D_6): δ 0.98 d (9 H, PMe_3, J(P—H) = 10 Hz); 2.65 s (3 H, Me); 4.12 s (5 H, C_5H_5).

$Fe(C_5H_5)(CO)(PMe_3)SnPh_3$. A mixture of 2.00 g (3.8 mmol) $Fe(C_5H_5)(CO)_2$-$SnPh_3$ and 0.39 ml (3.8 mmol) PMe_3 in 300 ml toluene was irradiated for 3.0 h. After being allowed to cool, the mixture was filtered. The solvent was evaporated in vacuo; chromatography of the residue on alumina (CH_2Cl_2 eluent) gave a single bright yellow band which was collected. Evaporation of the solvent in vacuo produced a residue. This was crystallized by dissolving it in 20 ml of Et_2O, and adding 50 ml petroleum ether, and cooling; yield 1.02 g (47%); m.p. 151—153°C.

Anal. Found: C, 56.17; H, 4.97; P, 5.54. Calcd. for $C_{27}H_{29}FeOPSn$: C, 56.40; H, 5.08; P, 5.39%. IR: $\nu(CO)$ 1880vs cm^{-1}. NMR (CDCl$_3$); δ 1.24 d (9 H, PMe$_3$, J(P—H) = 10 Hz); 4.45 d (5 H, C$_5H_5$, J(P—H) = 2 Hz); 7.20 m (9 H) and 7.50 m (6 H, C$_6H_5$).

[Fe(C$_5$H$_5$)(CO)(PMe$_3$)]H. A mixture of Fe(C$_5$H$_5$)(CO)(PMe$_3$)Br (6.6 mmol) and LiAlH$_4$ (1.0 g, 26.4 mmol) in 50 ml THF was stirred for 16 h. The solution was then cooled to 0°C and 25 ml EtOH was added slowly. After the solution had returned to room temperature, solvent was evaporated in vacuo and the solid residue was sublimed at 60—70°C/0.1 mmHg to give 1.04 g (70%) of the known yellow crystalline product; m.p. 71.5—73°C. The identity of the product was confirmed by NMR and IR data [3].

Fe(C$_5$H$_5$)(CO)(PMe$_3$)Me. This known compound [1b] was prepared from Fe-(C$_5$H$_5$)(CO)(PMe$_3$)Br (3.16 g, 10.4 mmol) and MeLi (prepared from 1.50 g Li and 6.7 ml MeI in 70 ml Et$_2$O). After stirring for 0.5 h, 125 ml of water was added to the reaction mixture. The ether layer was separated, dried, and solvent evaporated in vacuo. Sublimation of the residue at 50—60°C/0.03 mmHg gave 2.07 g (83%) of the product, identified by comparison of NMR data with data on the known compound and by m.p. (lit. mp. 45°C [1b]).

Fe(C$_5$H$_5$)(PMe$_3$)$_2$Me. A solution of 1.5 g (6.3 mmol) Fe(C$_5$H$_5$)(CO)$_2$Me and 1.0 ml (9.8 mmol) PMe$_3$ in 125 ml petroleum ether was irradiated for 6.5 h. The solution was filtered, solvent evaporated in vacuo, and the residue sublimed at 70—80°C/0.05 mmHg to give 1.45 g (81%) of the deep red crystalline product. The product is rapidly destroyed by contact with air; m.p. 93—100°C.

Anal., by mass spectrometric peak match: Found: 288.0854. Calcd. for $^{12}C_{12}{}^1H_{26}{}^{31}P_2Fe$: 288.0853. NMR (CS$_2$): δ —0.82 t (3 H, CH_3, J(P—H) = 6 Hz); 1.20 t (18 H, PMe$_3$, J(P—H) = 3 Hz); 3.56 t (5 H, C$_5H_5$, J(P—H) = 6 Hz).

Fe(C$_5$H$_5$)(PMe$_3$)$_2$SiMe$_3$. A total of 1.0 g (4.0 mmol) Fe(C$_5$H$_5$)(PMe$_3$)$_2$SiMe$_3$ and 2.0 ml (19 mmol) PMe$_3$ in 310 ml of petroleum ether was irradiated (quartz reactor) at 25°C for 5 h. The reaction mixture was filtered and the solvent was evaporated to leave an orange oily residue. The residue was chromatographed on a 3 × 30 cm alumina column which had been packed in petroleum ether. Elution with 90% petroleum ether/10% diethyl ether gave a yellow band. The solvent was evaporated and the solid residue which remained was sublimed (67°C/0.03 mmHg) to yield 0.24 g (17%) of orange crystals; m.p. 240—242°C (d).

Anal., by mass spectrometric peak match: Found: 346.1099. Calcd. for $^{12}C_{11}{}^1H_{32}{}^{56}Fe^{31}P_2{}^{28}Si$: 346.1090. NMR (CS$_2$): δ 0.08 s (9 H, SiMe$_3$); 1.28 m (18 H, PMe$_3$); 3.80 t (5 H, C$_5H_5$, J(P—H) = 2 Hz).

Fe(C$_5$H$_5$)(PMe$_3$)$_2$SnPh$_3$. A solution of 7.0 g (13 mmol) Fe(C$_5$H$_5$)(CO)$_2$SnPh$_3$ and 3.0 ml (29 mmol) PMe$_3$ in 500 ml MeCN was irradiated at 81°C (reflux temperature) for 6 h. The solvent was evaporated in vacuo and the orange solid residue which remained was extracted with 50 ml of CHCl$_3$. The solvent was evaporated to 10 ml, and 50 ml of petroleum ether was added to precipitate an orange powder, which was recrystallized from CHCl$_3$/petroleum ether; yield 3.81 g, 66% m.p. 210—215°C.

Anal. Found: C, 55.83; H, 6.15; P, 9.86%; MW (osmometric in CHCl$_3$), 571. Calcd. for $C_{29}H_{38}FeP_2Sn$: C, 55.90; H, 6.15; P, 9.94%, MW 623.1. NMR (C$_6$D$_6$): δ 0.98 m (18 H, PMe$_3$); 3.96 t (5 H, C$_5H_5$, J(P—H) = 2 Hz); 7.22 m (9 H) and 7.84 m (6 H C$_6H_5$).

Fe(C$_5$H$_5$)(PMe$_3$)$_2$SnMe$_3$. A solution of 0.51 ml (2.7 mmol) Fe(C$_5$H$_5$)(CO)$_2$-SnMe$_3$ and 1.0 ml (9.8 mmol) PMe$_3$ in 100 ml of pentane was irradiated at 36°C for 10.5 h. The reaction mixture was filtered and the solvent was evaporated leaving a solid residue. This was sublimed at 80°C/0.1 mmHg for 1 h to remove a white impurity. The remainder of the material was sublimed at 120°C/0.1 mmHg to give 0.96 g (81%) of yellow-orange crystals; m.p. 261—265°C (d). The compound is noticeably decomposed after a few days in air, but may be stored for long periods of time, without decomposition, under nitrogen.

Anal. by mass spectrometric peak mass: Found: 436.0337. Calcd. for ^{12}C$_{14}$^{1}H$_{32}$^{56}Fe^{31}P$_2$^{118}Sn: 436.0342. NMR (C$_6$D$_6$): δ 0.42 s (9 H, SnMe$_3$); 1.00 t (18 H, PMe$_3$, J(P—H) = 4 Hz); δ 3.75 (5 H, C$_5$H$_5$, J(P—H) = 2 Hz).

Fe(C$_5$H$_5$)(PMe$_3$)$_2$I. A solution of 0.50 g (1.3 mmol) [Fe(C$_5$H$_5$)(PMe$_3$)$_2$-(MeCN)]BF$_4$ and 2.0 g (5.0 mmol) Bu$_4$NI in 100 ml of THF was heated at reflux for 2 h, during which time the solution changed from red to black. The solvent was evaporated in vacuo and the residue remaining was extracted with toluene. The toluene was evaporated, and the residue remaining was then extracted with Et$_2$O. Addition of petroleum ether followed by complete evaporation of the solvent mixture gave black crystals of the product, 0.33 g (66%); m.p. 128—130°C (d).

Anal. Found: C, 33.16; H, 5.80; P, 15.49; MW 384 (osmometric in CHCl$_3$). Calcd. for C$_{11}$H$_{23}$FeP$_2$I: C, 33.03; H, 5.80; P, 15.49%, MW 400. NMR (CS$_2$): δ 1.57 t (18 H, PMe$_3$, J(PH) = 4 Hz); 3.77 t (5 H, C$_5$H$_5$, J(P—H) = 2 Hz). (An NMR spectrum of a sample dissolved in DMSO-d_6 or MeCN-d_3 (= L) contained only resonances associated with the solvated species, [Fe(C$_5$H$_5$)(PMe$_3$)$_2$L]$^+$).

Fe(C$_5$H$_5$)(PMe$_3$)$_2$CN. To a solution of 0.77 g (1.9 mmol) [Fe(C$_5$H$_5$)(PMe$_3$)$_2$-(MeCN)]BF$_4$ in 75 ml of methanol was added 0.12 g (1.9 mmol) KCN. The resulting solution was stirred at room temperature for 17 h. The solvent was evaporated in vacuo leaving a solid residue which was extracted with 100 ml of diethyl ether. Evaporation of solvent gave a yellow solid residue which was sublimed at 120°C/0.02 mmHg to give 0.17 g (30%) of yellow crystals; m.p. 178—180°C.

Anal., by mass spectrometric peak match: Found: 299.0628. Calcd. for ^{12}C$_{12}$^{1}H$_{23}$^{56}Fe^{14}N^{31}P$_2$: 299.0650. ν(CN) 2042s cm^{-1}. NMR (C$_6$D$_6$): δ 1.08 m (18, PMe$_3$); 3.95 t (5 H, C$_5$H$_5$, J(P—H) = 2 Hz).

[Fe(C$_5$H$_5$)(PMe$_3$)$_2$SnPh$_3$]BF$_4$. Silver tetrafluoroborate (0.82 g, 4.2 mmol) was added to a solution of 2.61 g (4.2 mmol) of Fe(C$_5$H$_5$)(PMe$_3$)$_2$SnPh$_3$. Silver metal and solid product precipitated immediately. The mixture was filtered through diatomaceous earth. Acetone (~1 liter) was used to extract the material retained on the filter until the extracts were no longer yellow. The solvent was evaporated and the residue that remained was crystallized from CH$_2$Cl$_2$/Et$_2$O, giving 2.29 g (77%) of a yellow powder; m.p. 183—183.5°C (d).

Anal. Found: C, 48.97; H, 5.33; P, 8.78. Calcd. for C$_{29}$H$_{36}$BF$_4$FeP$_2$Sn: C, 49.07; H, 5.40; P, 8.73%. μ_{eff} = 2.05 BM.

[Fe(C$_5$H$_5$)(PMe$_3$)$_2$SPh]BF$_4$. A solution of 0.52 g (1.6 mmol) Fe(C$_5$H$_5$)(CO)-(PMe$_3$)SPh and 0.50 ml (4.9 mmol) PMe$_3$ in 50 ml of THF was irradiated at 67°C for 13.5 h. Filtration and evaporation of solvent gave a dark oil which could not be crystallized. The oil was dissolved in 50 ml of acetone and 0.29 g

(1.5 mmol) of AgBF$_4$ was added, causing the solution to immediately become purple and silver metal to precipitate. The reaction mixture was filtered through diatomaceous earth, and the diatomaceous earth was washed with acetone until the washings were no longer purple. The acetone solution of the product was evaporated to 5 ml and 50 ml of diethyl ether was added, precipitating deep purple crystals. The crystals were dissolved in 10 ml of CH$_2$Cl$_2$, and reprecipitated upon addition of 50 ml of diethyl ether, 0.21 g (29%); m.p. 157—159°C (d).

Anal. Found: C, 43.56; H, 6.03; P, 13.44. Calcd. for C$_{17}$H$_{28}$BF$_4$FeP$_2$S: C, 43.53; H, 6.02; P, 13.21%. μ_{eff} = 1.88 BM.

[Fe(C$_5$H$_5$)(PMe$_3$)$_3$](PF$_6$)$_2$. A 0.374 g (2.14 mmol) sample of NOPF$_6$ was added to a solution of 1.05 g (2.14 mmol) of [Fe(C$_5$H$_5$)(PMe$_3$)$_3$]PF$_6$ in 50 ml acetone. Gas evolution began immediately and the color changed from orange to red. After 1.0 h the solvent was evaporated to ~10 ml; Et$_2$O addition caused the precipitation of an orange powder. This was dissolved in 25 ml MeCN, and the solution was filtered. The product was precipitated from this solution upon addition of 50 ml diethyl ether, yield 0.93 g (68%); m.p. 180°C (d).

Anal. Found: C, 26.58; H, 5.28; P, 24.00. Calcd. for C$_{14}$H$_{32}$F$_{12}$FeP$_5$: C, 26.31; H, 5.05; P, 24.23%. μ_{eff} = 2.12 BM.

Discussion

The most common route to complexes of the type [Fe(C$_5$H$_5$)(CO)$_{3-n}$-(PR$_3$)$_n$]X (n = 1, 2, 3, X = halides) is by the reaction of Fe(C$_5$H$_5$)(CO)$_2$X (X = halide) with a given ligand. Previously, we reported such reactions with PPh$_3$ and dpe (1,2-bis(diphenylphosphino)ethane) and also with isocyanides [13—15]. In the latter instance substitution of both carbonyls and the halide ion may occur, giving [Fe(C$_5$H$_5$)L$_3$]X. By controlling the reaction conditions the intermediate products in this reaction, [Fe(C$_5$H$_5$)(CO)$_{3-n}$(L)$_n$]X (n = 1, 2, 3) and Fe(C$_5$H$_5$)(CO)$_{2-n}$(L)$_n$X (n = 1, 2), can be obtained. In reactions with phosphines the extent of the reaction is usually restricted because of the steric demand of the phosphine ligands. With PPh$_3$ the final products of direct substitution reactions are [Fe(C$_5$H$_5$)(CO)$_2$L]X and Fe(C$_5$H$_5$)(CO)(L)X. With dpe it is possible to obtain either [Fe(C$_5$H$_5$)(CO)(dpe)]X or Fe(C$_5$H$_5$)(dpe)X depending on conditions.

Reactions of Fe(C$_5$H$_5$)(CO)$_2$I with PMe$_3$ described in this work were run using both thermal and photolytic conditions in non-polar solvents with comparable results. A yellow precipitate and a green solution formed, from which green and yellow solids can be obtained. The green product is the known [3] compound Fe(C$_5$H$_5$)(CO)(PMe$_3$)I, while the yellow product is predominantly [Fe(C$_5$H$_5$)(CO)$_2$(PMe$_3$)]I, along with much smaller amounts of [Fe(C$_5$H$_5$)-(CO)(PMe$_3$)$_2$]I and [Fe(C$_5$H$_5$)(PMe$_3$)$_3$]I. Subsequently, it was shown that [Fe(C$_5$H$_5$)(CO)$_2$(PMe$_3$)]I can be converted to Fe(C$_5$H$_5$)(CO)(PMe$_3$)I on photolysis and to [Fe(C$_5$H$_5$)(CO)(PMe$_3$)$_2$]I on heating with PMe$_3$ in acetonitrile solution, both reactions proceeding quickly and in high yield. In addition, photolysis of [Fe(C$_5$H$_5$)(CO)(PMe$_3$)$_2$]I in acetone gives approximately equal quantities of Fe(C$_5$H$_5$)(CO)(PMe$_3$)I and [Fe(C$_5$H$_5$)(PMe$_3$)$_3$]I. The use of acetone as a solvent in these reactions allows the ionic species to remain in solution. Isola-

tion of $[Fe(C_5H_5)(CO)_2(PMe_3)]I$ as the primary product in the reaction of Fe-$(C_5H_5)(CO)_2I$ and PMe_3 in toluene or heptane is believed to be a consequence of solvent choice. In less polar media the ionic product $[Fe(C_5H_5)(CO)_2$-$(PMe_3)]I$ precipitates and is thus precluded from further reaction at an appreciable rate.

The photolytic reaction of $Fe(C_5H_5)(CO)_2Br$ and PMe_3 (1 : 1) in a non-polar solvent gives $Fe(C_5H_5)(CO)(PMe_3)Br$ in good yield ($\sim$60%), along with insoluble $[Fe(C_5H_5)(CO)_2(PMe_3)]Br$ in lesser amounts. When a polar solvent, MeCN, and an excess of PMe_3 is used for this reaction the trisubstituted compound, $[Fe(C_5H_5)(PMe_3)_3]Br$, forms as the only product. Photolysis in MeCN of $[Fe(C_5H_5)(CO)(PMe_3)_2]BF_4$, a likely intermediate in this reaction, gives isolable species $[Fe(C_5H_5)(PMe_3)_2(MeCN)]BF_4$. The acetonitrile ligand in this complex is readily displaced by other ligands, and in the presence of PMe_3 the rapid formation of $[Fe(C_5H_5)(PMe_3)_3]BF_4$ is observed.

Another related example, the $Fe(C_5H_5)(CO)_2SnCl_3$-PMe_3 system, is noteworthy. When these reagents are mixed in toluene an immediate reaction occurs to yield $[Fe(C_5H_5)(CO)_2(PMe_3)]^+$. If the same reagents are photolyzed in acetonitrile then the trisubstituted complex $[Fe(C_5H_5)(PMe_3)_3]^+$ is obtained in almost quantitative yield. Both complexes were isolated as PF_6^- salts.

The scheme below (Scheme 1) summarizes the basic chemistry of this system. Each of the individual steps have been established independently.

The initial failure to obtain a compound $Fe(C_5H_5)(PMe_3)_2X$ was an enigma. Analogous species $Fe(C_5H_5)(CNR)_2X$ had easily been made in our laboratories earlier [15], as had the compounds $Fe(C_5H_5)(dpe)X$ [14]. In addition a compound of a chelating alkylphosphine, $Fe(C_5H_5)(dmpe)I$ (dmpe = $Me_2PCH_2CH_2$-PMe_2) is known, although its synthesis by displacement of the phosphite ligands in $Fe(C_5H_5)(P(OPh)_3)_2I$ is circuitous and apparently somewhat difficult to accomplish [16]. We put substantial effort into preparing a $Fe(C_5H_5)$-$(PMe_3)_2X$ (X = halide) species, but such compounds proved very difficult to make. However, after testing a number of possible routes it was found that the

SCHEME 1

STEPWISE REACTION OF $Fe(C_5H_5)(CO)_2X$ AND PMe_3

X = Br , I ; L = PMe₃
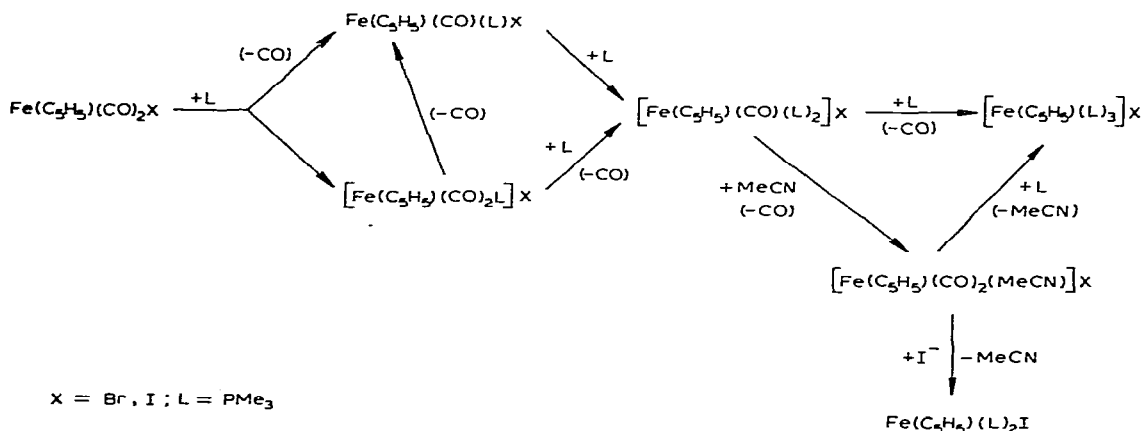
reaction of [Fe(C$_5$H$_5$)(PMe$_3$)$_2$(MeCN)]BF$_4$ and I$^-$ in THF did give the desired product, Fe(C$_5$H$_5$)(PMe$_3$)$_2$I, in good yield, vis:

$$[Fe(C_5H_5)(PMe_3)_2(MeCN)]BF_4 + I^- \xrightarrow{THF} Fe(C_5H_5)(PMe_3)_2I + BF_4^- + MeCN$$
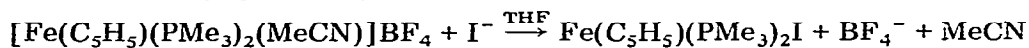
The same reaction with bromide ion was unsuccessful, bromide ion apparently not being capable of displacing acetonitrile under these conditions. This is in accord with the idea that there is a strong tendency toward halide displacement in electron rich compounds by other ligand groups [17]. In these systems (FeC$_5$H$_5$)(PMe$_3$)$_2$X-MeCN) there is a close balance between preference for X$^-$ and MeCN in the metal coordinate sphere.

When Fe(C$_5$H$_5$)(PMe$_3$)$_2$I is dissolved in MeCN the complex [Fe(C$_5$H$_5$)-(PMe$_3$)$_2$(MeCN)]I is formed. Presumably the high concentration of the solvent drives the equilibrium to form this species.

The complex [Fe(C$_5$H$_5$)(PMe$_3$)$_2$(MeCN)]BF$_4$ was used as a precursor to a triphenylphosphine complex, [Fe(C$_5$H$_5$)(PMe$_3$)$_2$(PPh$_3$)]BF$_4$. The PPh$_3$ ligand is also easily displaced. In an NMR spectrum of this compound in DMSO-d_6 resonances for cationic PPh$_3$ and DMSO complexes may be identified. The latter complex can be prepared independently from Fe(C$_5$H$_5$)(PMe$_3$)$_2$I and DMSO.

The species [Fe(C$_5$H$_5$)(CO)$_2$(PMe$_3$)]BF$_4$ and [Fe(C$_5$H$_5$)(CO)(PMe$_3$)$_2$]BF$_4$ are also obtained specifically by another route. Starting with [Fe(C$_5$H$_5$)(CO)$_2$-(THF)]BF$_4$ the former complex is made by displacement of THF with PMe$_3$ at $-23°$C. The starting material is well known as a precursor for similar complexes [11]. If additional PMe$_3$ is used ($>2 : 1$ molar ratio) and the solution refluxed (acetone, 35 h), the only product obtained is the disubstituted species. One can follow this reaction by IR, stopping when the monosubstituted product has been consumed. Apparently a thermal reaction to the trisubstituted species does not occur, although this reaction was found to occur under photolytic conditions.

Reactions involving CO displacement by PMe$_3$ were carried out for various other Fe(C$_5$H$_5$)(CO)$_2$X species (X = SiMe$_3$, SnMe$_3$, SnPh$_3$, SPh), with either mono- or disubstituted products being formed. Heating Fe(C$_5$H$_5$)(CO)$_2$Me and Me$_3$P in toluene gives only Fe(C$_5$H$_5$)(CO)(PMe$_3$)COMe. Photolysis with excess PMe$_3$ gives red, crystalline, air sensitive Fe(C$_5$H$_5$)(PMe$_3$)$_2$Me. Earlier, this reaction was reported to give only Fe(C$_5$H$_5$)(CO)(PMe$_3$)Me [4]. One possible reason for the failure to obtain the disubstituted product in this earlier work is the short reaction time employed.

Spectroscopic data on Fe(C$_5$H$_5$)(L)(PMe$_3$)X (L = CO, PMe$_3$) compounds support their formulation. Noteworthy is the fact that the number of phosphines substituted can be quickly discerned from the appearance of the cyclopentadienyl proton resonances as either a doublet (monosubstitution) or a triplet (disubstitution), the splittings resulting from coupling of the cyclopentadienyl protons to ^{31}P. The chemical shift of the cyclopentadienyl protons in Fe(C$_5$H$_5$)-(PMe$_3$)$_2$X derivatives always appears at $<\delta$ 4.00 ppm whereas the values for Fe(C$_5$H$_5$)(CO)(PMe$_3$)X species are in the range of δ 4.10—4.50 ppm. Similarly, the chemical shift and multiplicity of the cyclopentadienyl protons in [Fe(C$_5$H$_5$)(CO)$_{3-n}$(PMe$_3$)$_n$]X (n = 1, 2, 3) occur in a regular progression. For n = 1 this resonance is a doublet at δ 5.64 ppm; for n = 2 and n = 3 one sees, respectively, a triplet at δ 5.02 ppm and a quartet at δ 4.40 ppm.

Because of our general interest in oxidative chemistry of electron-rich complexes we recorded cyclic voltammograms for a number of these compounds. Data on 1-electron oxidation processes are noted in Table 1. It comes as no surprise that compounds of the formula $Fe(C_5H_5)(PMe_3)_2X$ have low $E_{1/2}$ values indicating a substantial ease of oxidation. Somewhat higher $E_{1/2}$ values are found for $Fe(C_5H_5)(CO)(PMe_3)X$ species. Chemical oxidations were carried out on several of the compounds identified as likely to be susceptible to electron loss. Isolated 17e complexes include $[Fe(C_5H_5)(PMe_3)_2X]^+$ (X = SPh, SnPh$_3$), analogous to other complexes $[Fe(C_5H_5)(dpe)X]^+$ reported earlier [18]. Also isolated was the 17e complex $[Fe(C_5H_5)(PMe_3)_3](PF_6)_2$. This is the first example of an $[Fe(C_5H_5)(L)_3]^{2+}$ species that we have encountered.

Acknowledgement

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