# Electron-rich Cations: Preparation and Hydride Reductions of the Cations $[Fe(\eta^5-C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}]^+$, $[Fe(\eta^5-C_5H_5)\{MeC(CH_2PPh_2)_3\}]^+$, and $[Fe(\eta^5-C_5H_5)\{C(CH_2PPh_2)_4\}]^+$ †

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The synthesis of the cations $[Fe(\eta^5-C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}]^+$, $[Fe(\eta^5-C_5H_5)\{MeC(CH_2PPh_2)_3\}]^+$, and $[Fe(\eta^5-C_5H_5)\{C(CH_2PPh_2)_4\}]^+$ as hexafluorophosphate salts is described. These cations are reduced regioselectively by lithium aluminium hydride to give the corresponding iron hydride species by direct attack on iron. The mechanisms of these reductions are discussed.

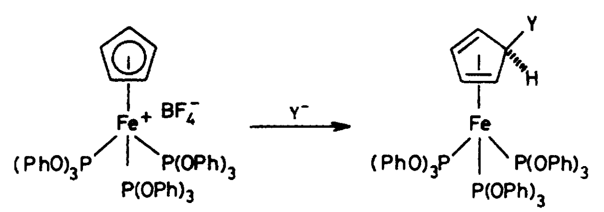
The synthesis and reactivity of $\eta^5$-dienyliron tricarbonyl cations have been extensively studied.[1] In contrast the analogous $\eta^5$-dienyliron tris-phosphine cations have received little attention. We were interested in preparing such cations containing the tris-phosphine ligands triphos $[PhP(CH_2CH_2PPh_2)_2]$, tripod $[MeC(CH_2PPh_2)_3]$, and tetrapod $[C(CH_2PPh_2)_4]$ in order to study the effect of phosphine ligands on the regioselectivity of nucleophilic addition reactions. It was anticipated[2] that on going from the electron-withdrawing tricarbonyl iron group to the electron-donating tris-phosphine-iron group, attack on the dienyl ligand, common in dienyliron tricarbonyl chemistry, would be disfavoured.

Some methods are available for the synthesis of cyclopentadienyliron tris-phosphine cations.[3] These are generally inefficient, however, and the development of new routes to this type of cation was therefore desirable. To our knowledge no examples of nucleophilic additions to cyclopentadienyliron tris-phosphine cations have been reported. Nucleophilic addition to the cyclopentadienyltris(triphenyl phosphite)iron cation (1), however, has been shown to occur on the cyclopentadienyl ring to give the cyclopentadiene complex (2).[4]

We describe here the preparation and reactivity towards hydride of the cations $[Fe(\eta^5-C_5H_5)(triphos)]^+$, $[Fe(\eta^5-C_5H_5)(tripod)]^+$, and $[Fe(\eta^5-C_5H_5)(tetrapod)]^+$. Part of this work has been the subject of preliminary communications.[5]

## Results and Discussion

Treatment of iron(II) dichloride dihydrate successively with triphos and cyclopentadienylthallium gives, after anion exchange, $[Fe(\eta^5-C_5H_5)(triphos)]PF_6$ (3). This route, however, is limited to the tridentate ligand triphos; attempts to employ tripod, for example, resulted only in the isolation of ferrocene. Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2Br]$ with triphos in refluxing toluene leads after anion exchange to (3) in 83% yield. In contrast, reaction of $[Fe(\eta^5-C_5H_5)(CO)_2Br]$ with tripod under these conditions displaces only one carbonyl group and the removal of both carbonyl groups was completed by photolysis in a polar solvent. Treatment of the isobutene cation (4) with the polydentate phosphines triphos, tripod, and tetrapod leads in each case to a mixture of dicarbonyl and monocarbonyl cations of general formulae (5) and (6), which on thermolysis and/or photolysis gives the cations (3), (7), and (8) respectively (Scheme).



(1) (2) Y = H, Ph

This latter method of synthesis has two advantages over previously reported methods. The replacement of carbonyl by phosphine being intramolecular, the reaction is in general more rapid, and furthermore the use of polar solvent (dichloromethane or acetone) results in homogeneous reaction mixtures. These two aspects manifest themselves in the synthesis of cations (3), (7), and (8) in overall yields in excess of 80%.

The triphos cation (3) could exist with either *cis*- or *trans*-fused rings. N.m.r. spectroscopy ($^{31}P$ and $^1H$) indicates that only one isomer is formed, which by analogy with bicyclo[3.3.0]octanes was expected to be the *cis* isomer.[6] In the $^{31}P$ n.m.r. spectrum of (3) the signal due to the central phosphorus atom appears as a double doublet, indicating that the terminal phosphorus atoms are non-equivalent. All three phosphorus atoms are however bound to iron. *X*-Ray data for (3) confirm these points,[7] and indicate that the non-equivalence of the terminal phosphorus atoms is due to the conformations adopted by the phenyl groups.

The reduction of (3) with lithium aluminium hydride in tetrahydrofuran gives a mixture of diastereoisomeric hydrides (9) and (10). The $^1H$ n.m.r. spectrum of the crude product shows two iron hydride double doublet signals in the ratio 1 : 15. In both iron hydrides it is one of the terminal phosphines that is not co-ordinated to the metal since the iron hydride signals show coupling to two non-equivalent phosphorus atoms in the $^1H$ n.m.r. spectrum and the signals due to the unco-ordinated phosphorus atoms appear as doublets in the $^{31}P$ n.m.r. spectrum.

As expected,[2] the hydrides (9) and (10) are formed by direct attack on the metal, and not *via exo*-attack on the cyclopentadienyl ring followed by migration of the *endo*-hydrogen thus produced to the metal.[8] This is demonstrated by the fact that reduction of (3) with lithium aluminium deuteride leads to the iron deuterides analogous to (9) and (10). The infrared spectra of the hydrides (9) and (10) show a weak absorption at 1 875 $cm^{-1}$ characteristic of Fe–H. In contrast this band does not appear in the spectra of the deuterides; another band, however, is present, at 1 325 $cm^{-1}$ ($\nu_{Fe-H}/\nu_{Fe-D} = 1.42$). The $^2H$ n.m.r. spectrum of the crude product from the lithium aluminium deuteride reduction of (3) shows an Fe–D signal

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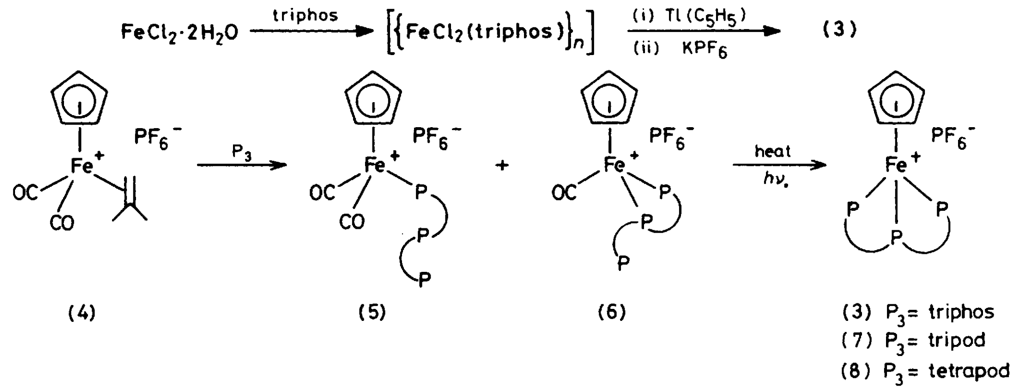
† [Bis(2-diphenylphosphinoethyl)phenylphosphine-*PP'P''*]($\eta^5$-cyclopentadienyl)iron(II), ($\eta^5$-cyclopentadienyl)[1,1,1-tris(diphenylphosphinomethyl)ethane-*PP'P''*]iron(II), and ($\eta^5$-cyclopentadienyl)[tetrakis(diphenylphosphinomethyl)methane-*PP'P''*]iron(II).



Scheme. Preparation of cyclopentadienyliron trisphosphine cations

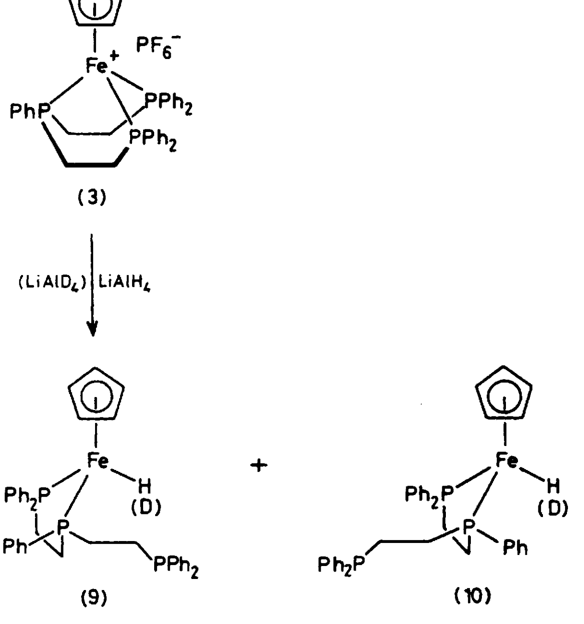
at δ −16.5 and the absence of deuterium bonded to carbon. Two cyclopentadienyl resonances in the $^1H$ n.m.r. spectrum indicated that two diastereoisomers were again present.

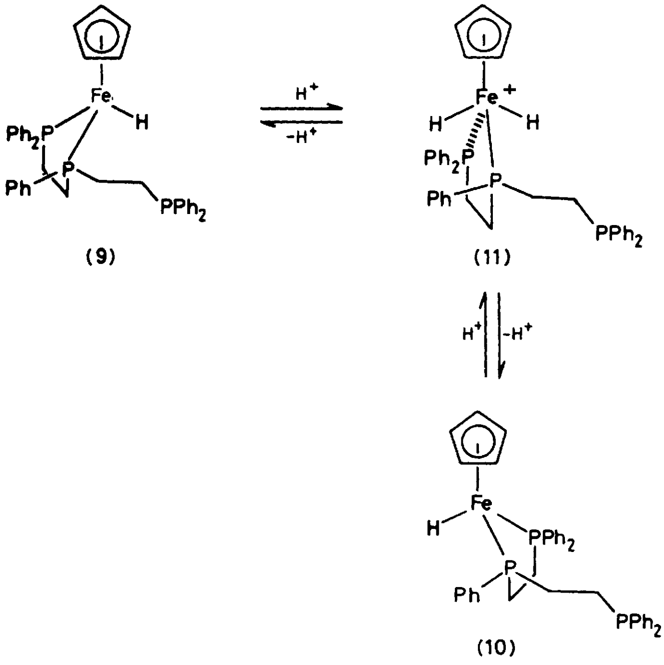
The appearance of a double doublet at δ −16.6 in the $^1H$ n.m.r. spectrum of a solution of a mixture of the iron deuterides corresponding to (9) and (10) in [$^2H_8$]toluene has been previously reported.[5a] The recovered sample showed an i.r. absorption at 2 280 cm$^{-1}$. This observation was originally ascribed by us to scrambling of the cyclopentadienyl hydrogens and the metal deuteride. We have been unable to reproduce this result,* and conclude therefore that such an exchange does not occur. The $^2H$ n.m.r. spectrum of the deuterides eliminates the possibility of this exchange process; even after heating at 90 °C for 3 h no deuterium was detectable on the cyclopentadienyl ligand.

Treatment of benzene solutions of mixtures of (9) and (10) with aqueous toluene-*p*-sulphonic acid causes equilibration of these diastereoisomers to give a 1 : 1.3 mixture. This process presumably involves the *trans* dihydrido-cation (11) as an intermediate. Treatment of the products from lithium aluminium deuteride reduction of (3) with aqueous toluene-*p*-sulphonic acid results in metal H/D exchange and the formation of the equilibrium mixture of the hydrides (9) and (10). Approximately one equivalent of HOD could be detected in the aqueous phase by mass spectrometry. Similarly the hydrides (9) and (10) could be converted into the corresponding deuterides on treatment with $D_3O^+$.

Reduction of the tripod cation (7) with lithium aluminium hydride leads to the diastereoisomeric iron hydrides (12) and (13). Direct attack on the metal is again demonstrated by formation of the corresponding iron deuterides on treatment of (7) with lithium aluminium deuteride. The $^1H$ n.m.r. spectrum of the crude product from the reduction of (7) shows two iron hydride triplet signals at δ −16.0 and −16.1 in the ratio 1 : 2.5. The major isomer could be obtained pure by repeated recrystallisations. The equilibrium mixture of (12) and (13) (1 : 1.8) could be obtained on treatment of mixtures of the deuterides corresponding to (12) and (13) with aqueous acid.

Lithium aluminium hydride reductions of cations (3) and (7) result in mixtures of diastereoisomeric hydrides. This is consistent with the direct attack on the metal being $S_N1$ in character, involving prior dissociation of a phosphine ligand. An $S_N2$ mechanism would be expected to lead, by inversion at iron, only to hydrides (10) and (12) from cations (3) and (7), respectively. The mechanism is not initial formation of (12)





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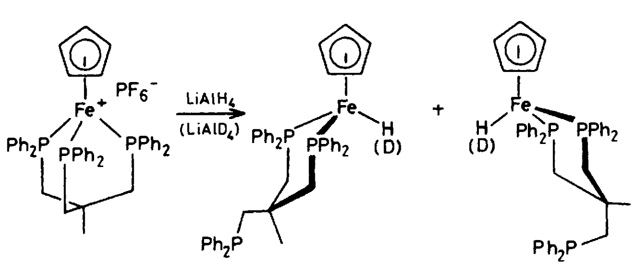
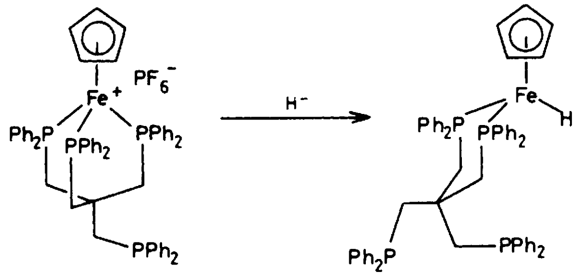
* We attribute the appearance of hydride to adventitious acid present in the initial very dilute solution and to the fact that the recovered sample may have contained residual [$^2H_8$]toluene.



(7) (12) (13)

from (7) followed by equilibration of (12) and (13). This is demonstrated by the stability of the major isomer isolated from the mixture of (12) and (13) by successive recrystallisations. Further evidence for an $S_N1$ mechanism comes from carrying out the reduction of (3) to (9) and (10) in dimethyl sulphoxide. The diastereoisomer ratio in this more polar solvent was 1 : 4 to be compared with the ratio 1 : 15 obtained in tetrahydrofuran. There is also a loss of stereoselectivity on performing the reduction in tetrahydrofuran at elevated temperatures, the ratio being 1 : 5 at 65 °C. We assume, by analogy with classical $S_N1$ reactions, that the minor isomer is (9) (retention) and the major isomer (10) (inversion).

Lithium aluminium hydride reduction of the tetrapod cation (8) similarly produces the iron hydride species (14).



(8) (14)

In contrast to the iron cations (3) and (7) the corresponding ruthenium cations undergo hydride addition *exo* to the cyclopentadienyl ring.[5b] The differences in regioselectivity observed between the iron and ruthenium cations can be attributed to strain in the iron cations which promotes dissociation of a phosphine ligand to generate a 16-electron species prior to nucleophilic attack. The strain effects are different in the iron and ruthenium cations because of their differing atomic sizes ($Fe^{II}$ radius = 1.23 Å; $Ru^{II}$ radius = 1.44 Å)[9] and hence differing metal-to-phosphorus bond lengths.

## Experimental

All reactions and purifications were performed under nitrogen using standard vacuum line and Schlenk-tube techniques.[10] Tetrahydrofuran and toluene were dried over sodium benzophenone ketyl and distilled. Diethyl ether and light petroleum (b.p. 40—60 °C) were dried over sodium wire and distilled. Dichloromethane was dried over calcium hydride and distilled. Infrared spectra were recorded on Perkin-Elmer 137E and 297 instruments. Nuclear magnetic resonance spectra were recorded on Perkin-Elmer R12B (60 MHz $^1H$), Varian EM360L (60 MHz $^1H$), Bruker WH300 (300 MHz $^1H$; 46.07 MHz $^2H$), and Bruker WH90 (36.43 MHz $^{31}P$) spectrometers. Mass spectra were obtained with an A.E.I. MS 50 spectrometer. Elemental analyses were performed by the Central Microanalytical Service of the C.N.R.S. Melting points were determined for samples in capillaries sealed under nitrogen. Chromatography was performed on alumina (Grade II/III) under nitrogen. The ligands triphos [$PhP(CH_2CH_2PPh_2)_2$],[11] tripod [$MeC(CH_2PPh_2)_3$],[12] and tetrapod [$C(CH_2PPh_2)_4$][13] were prepared by the literature methods.

*Preparation of* [$Fe(\eta^5-C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}$]$PF_6$ (3). —*Method* 1. Tetrahydrofuran (100 ml) was added to a mixture of [$\{Fe(\eta^5-C_5H_5)(CO)_2\}_2$] (4.0 g, 11.3 mmol) and sodium amalgam [1.0 g Na (43.5 g atom) in 50.0 g of Hg] and stirred vigorously for 20 h. The resulting suspension was decanted from the amalgam, cooled to −78 °C and a solution of 2-methylallyl chloride (9 ml, 90 mmol) in tetrahydrofuran (10 ml) was added slowly. The resulting mixture was stirred at −78 °C for 1 h and allowed to warm to ambient temperature. The solvent was removed under reduced pressure, the resultant solid extracted with diethyl ether (5 × 15 ml), and the solution concentrated to give a red oil. This was dissolved in tetrahydrofuran (15 ml) and a solution of hexafluorophosphoric acid (5 ml; 75% in $H_2O$) was added dropwise, with stirring, followed by diethyl ether which gave [$Fe(\eta^5-C_5H_5)(CO)_2(\eta^2-C_4H_8)$]$PF_6$ (4) as an orange crystalline solid (6.5 g, 76%).

Compound (4) (0.47 g, 1.3 mmol) and triphos (0.70 g, 1.3 mmol) were dissolved in 1,2-dichloroethane (35 ml) and irradiated, at reflux, with a tungsten filament lamp (350 W) for 9 h. The resulting orange solution was chromatographed on alumina (eluant dichloromethane). Evaporation and crystallisation from dichloromethane–diethyl ether gave (3) (0.95 g, 95%), m.p. 310—313 °C (Found: C, 58.5; H, 4.8; P, 15.3. $C_{39}H_{38}F_6FeP_4$ requires C, 58.5; H, 4.8; P, 15.5%); $^1H$ n.m.r. [$(CD_3)_2CO$] δ 8.1—6.9 (25 H, m, aryl-H), 4.45 (5 H, q, $J_{PH}$ 1.3 Hz, $C_5H_5$), and 3.0—2.0 (8 H, m, $CH_2P$); $^{31}P$ n.m.r. ($CH_2Cl_2$) δ 113.6 (1 P, dd, $J_{PP}$ 38 and 41), and 92.6 (2 P, d, $J_{PP}$ 39 Hz).

*Method* 2. A solution of $FeCl_2 \cdot 2H_2O$ (1.22 g, 7.50 mmol) in ethanol (50 ml) was added to a solution of triphos (4.03 g, 7.55 mmol) in dichloromethane (100 ml) and the mixture was stirred (0.5 h). Cooling (−30 °C) gave white crystals of [$\{FeCl_2(triphos)\}_n$], isolated by filtration, washed successively with ethanol (2 × 15 ml) and ether (3 × 15 ml), and then dried *in vacuo* (yield 4.54 g, 86%).

Tetrahydrofuran (50 ml) was added to a mixture of cyclopentadienylthallium (0.53 g, 2 mmol) and [$\{FeCl_2(triphos)\}_n$] (1.27 g, 1.83 mmol) and the suspension stirred at 20 °C for 24 h. The resulting dark red solution was filtered and the solvent removed under reduced pressure. The product was extracted into acetone (3 × 20 ml) and $KPF_6$ (0.35 g, 1.90 mmol) was added, followed by water (50 ml). Evaporation of the acetone under reduced pressure left an orange solid. Recrystallisation from acetone–water gave (3) (0.56 g, 38%).

*Method* 3. A mixture of [$Fe(\eta^5-C_5H_5)(CO)_2Br$] (1.0 g, 3.90 mmol) and triphos (2.1 g, 3.92 mmol) was heated in refluxing toluene (50 ml) for 4 h. Cooling, filtration, and washing with toluene (2 × 15 ml) left a bright orange mass which was treated with $NH_4PF_6$ (1.2 g, 7.36 mmol) in acetone (40 ml). Evaporation and chromatography (eluant dichloromethane) gave an orange solution which on concentration and addition of diethyl ether gave (3) (2.6 g, 83%).

*Preparation of* [$Fe(\eta^5-C_5H_5)\{MeC(CH_2PPh_2)_3\}$]$PF_6$ (7).—*Method* 1. Compound (7) was prepared as in method 1 for the preparation of (3) from (4). Recrystallisation from dichloromethane–diethyl ether gave (7) containing 0.5 mol equivalents of dichloromethane of crystallisation (yield 91%), m.p. 286—292 °C (Found: C, 59.6; H, 4.9; P, 13.1. $C_{46.5}H_{45}ClF_6FeP_4$ requires C, 59.8; H, 4.8; P, 13.3%); $^1H$ n.m.r. [$(CD_3)_2CO$] δ 7.6—6.7 (30 H, m, aryl-H), 5.05 (5 H, q, $J_{PH}$ 1.2 Hz, $C_5H_5$), 2.7—2.4 (6 H, m, $CH_2P$), and 1.65 (3 H, q, $J_{PH}$ 2.8 Hz, Me); $^{31}P$ n.m.r. ($CH_2Cl_2$) δ 52.0 (s).

*Method* 2. A mixture of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Br]$ (2.2 g, 8.56 mmol) and tripod (5.43 g, 8.70 mmol) was heated in refluxing toluene (100 ml) for 6 h. Cooling, filtration, and washing with toluene (2 × 30 ml) left a bright orange mass. The anion was exchanged with $NH_4PF_6$ (1.8 g, 11.04 mmol) in acetone (50 ml). The solvent was removed under reduced pressure and the dry residue extracted with dichloromethane (3 × 40 ml). The combined extracts were photolysed with a tungsten filament lamp (350 W) for 5 h. Chromatography as before and recrystallisation from dichloromethane–diethyl ether gave orange needles of (7) (5.2 g, 68%).

*Preparation of* $[Fe(\eta^5\text{-}C_5H_5)\{C(CH_2PPh_2)_4\}]PF_6$ (8).—Compound (8) was prepared as in method 1 for the preparation of (3) from (4). Recrystallisation from dichloromethane–diethyl ether gave (8) (yield 82%), m.p. 319—321 °C (Found: C, 64.4; H, 5.1; P, 14.5. $C_{58}H_{53}F_6FeP_5$ requires C, 64.8; H, 5.0; P, 14.4%); $^1H$ n.m.r. $[(CD_3)_2CO]$ $\delta$ 7.9—6.7 (40 H, m, aryl-H), 5.05 (5 H, q, $J_{PH}$ 1.4 Hz, $C_5H_5$), 2.6 (6 H, m), and 3.1 (2 H, m); $^{31}P$ n.m.r. $[(CD_3)_2CO]$ $\delta$ 50.3 (3 P, s, FeP) and 27.2 (1 P, s).

*Preparation of* $[Fe(\eta^5\text{-}C_5H_5)(triphos)H]$ [(9) *and* (10)].—Tetrahydrofuran (25 ml) was added to a mixture of $[Fe(\eta^5\text{-}C_5H_5)(triphos)]PF_6$ (3) (0.35 g, 0.44 mmol) and $LiAlH_4$ (0.06 g, 1.58 mmol) and the suspension stirred for 3 h. The excess of reducing agent was hydrolysed ($H_2O$, 0.5 ml), the solution concentrated to a small volume (*ca.* 5 ml), and light petroleum (50 ml) added. The resulting pale yellow solution was filtered and concentrated to a yellow oil, which was chromatographed [light petroleum–diethyl ether (3 : 1)]. Recrystallisation from light petroleum–diethyl ether (3 : 1) at −30 °C gave a mixture of (9) and (10) (0.13 g, 50%) (Found: C, 71.1; H, 6.0; P, 13.9. $C_{39}H_{39}FeP_3$ requires C, 71.3; H, 6.0; P, 14.2%); $\nu_{max.}$ (Nujol) 1 875w cm$^{-1}$ (Fe–H); $^1H$ n.m.r. ($C_6D_6$) $\delta$ 7.9—7.0 (25 H, m, aryl-H), 4.18 (s, minor isomer) and 4.16 (s) (5 H, $C_5H_5$), 2.57—0.85 (8 H, m, $CH_2P$), and −16.58 (dd, $J_{PH}$ 69.2 and 73.7 Hz) and −16.44 (dd, $J_{PH}$ 69.4 and 73.8 Hz, minor isomer) (1 H, Fe–H); isomer ratio 1 : 15; $^{31}P$ n.m.r. ([$^2H_8$]toluene) $\delta$ 111.5 (1 P, d, $J_{PP}$ 28 Hz, $FePPh_2$), 107.9 (1 P, dd, $J_{PP}$ 28 and 35 Hz, FePPh), and −13.0 (1 P, d, $J_{PP}$ 35 Hz, $PPh_2$); *m/z* 655 (*M* − 1).

In an analogous manner, reactions of cation (3) with $LiAlH_4$ were carried out in tetrahydrofuran at 20 °C (3 h) and 65 °C (30 min) and in dimethyl sulphoxide at 20 °C (2 h). The products were not chromatographed prior to determination of the following diastereoisomer ratios; tetrahydrofuran 20 °C, 1 : 15; 65 °C, 1 : 5; dimethyl sulphoxide 20 °C, 1 : 4.

*Preparation of* $[Fe(\eta^5\text{-}C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}D]$.—This was prepared by the method for the preparation of (9) and (10) using $LiAlD_4$ in place of $LiAlH_4$, followed by $D_2O$ (yield 43%). The product contained less than 1% of the protio-compounds (by $^1H$ n.m.r.) and the ratio of diastereoisomers was 1 : 7; $^2H$ n.m.r. (toluene) $\delta$ −16.5 (m, Fe–D); $^1H$ n.m.r. ([$^2H_8$]toluene) 4.22 (s) and 4.19 (s) (ratio 1 : 7; $C_5H_5$).

*Equilibration of* (9) *and* (10) *with Aqueous Acid.*—The complex $[Fe(\eta^5\text{-}C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}H]$ (0.20 g, 0.3 mmol) was dissolved in benzene (0.5 ml). Aqueous toluene-*p*-sulphonic acid (55 µl; 0.6 mol dm$^{-3}$ in $H_2O$) was added, and the mixture shaken vigorously; the $^1H$ n.m.r. spectrum was then recorded. The ratio of diastereoisomers observed was 1 : 1.3.

*Deuteriation of* (9) *and* (10).—The complex $[Fe(\eta^5\text{-}C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}H]$ (0.20 g, 0.3 mmol) was dissolved in [$^2H_6$]benzene (0.5 ml). Deuteriated toluene-*p*-sulphonic acid (55 µl; 0.6 mol dm$^{-3}$ in $D_2O$) was added, the mixture shaken vigorously, and the $^1H$ n.m.r. spectrum recorded. The signal due to iron hydride was broad and integrated for less than 0.1 H, whereas the ratio of phenyl to cyclopentadienyl protons was constant over 3 days at ambient temperature.

The complex $[Fe(\eta^5\text{-}C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}D]$ (0.20 g, 0.3 mmol) in benzene solution was treated with aqueous toluene-*p*-sulphonic acid (55 µl; 0.6 mol dm$^{-3}$). The $^1H$ n.m.r. spectrum showed the presence of $[Fe(\eta^5\text{-}C_5H_5)\{PhP(CH_2CH_2PPh_2)_2\}H]$, with a diastereoisomer ratio of 1 : 1.3. Mass spectroscopic analysis of the recovered aqueous phase was consistent with the presence of *ca.* 1 equivalent of HOD.

*Preparation of* $[Fe(\eta^5\text{-}C_5H_5)\{MeC(CH_2PPh_2)_3\}H]$ [(12) *and* (13)].—Tetrahydrofuran (20 ml) was added to a mixture of cation (7) (0.30 g, 0.32 mmol) and $LiAlH_4$ (0.05 g, 1.32 mmol), and the resultant suspension stirred for 3 h. The excess of reducing agent was hydrolysed (0.5 ml $H_2O$) and the solvent evaporated off under reduced pressure. Extraction with diethyl ether and chromatography (eluant hexane–diethyl ether, 1 : 1) gave a yellow crystalline solid. Recrystallisation from hexane–diethyl ether (1 : 1) at −30 °C gave (12) and (13) (0.13 g, 54%) (Found: C, 73.9; H, 6.1; P, 12.4. $C_{46}H_{45}FeP_3$ requires C, 74.0; H, 6.0; P, 12.5%); $\nu_{max.}$ (Nujol) 1 850w cm$^{-1}$ (Fe–H); $^1H$ n.m.r. ($C_6D_6$) $\delta$ 8.0—6.8 (30 H, m, aryl-H), 3.93 (s) and 3.88 (s, minor isomer) (5 H, $C_5H_5$), 2.9—1.9 (6 H, m, $CH_2P$), 0.29 (3 H, m, Me), and −16.00 (t, $J_{PH}$ 69.1 Hz, minor isomer) and −16.14 (t, $J_{PH}$ 69.6 Hz) (1 H, Fe–H); $^{31}P$ n.m.r. (toluene) $\delta$ 75.39 (s, minor isomer) and 74.95 (s) (Fe–P), and −27.88 (s, minor isomer) and −30.62 (s); *m/z* 735 (*M* − 1).

The isomer ratio in the crude product before chromatography was 1 : 2.5. The major isomer could be isolated pure by successive recrystallisations from the same solvent mixture.

*Preparation of* $[Fe(\eta^5\text{-}C_5H_5)\{MeC(CH_2PPh_2)_3\}D]$.—This was prepared as for (12) and (13) using $LiAlD_4$ in place of $LiAlH_4$ (yield 60%). The product contained less than 1% protio-compounds (by $^1H$ n.m.r.) and the ratio of diastereoisomers was 2 : 3; $^2H$ n.m.r. (toluene) $\delta$ −16.03 (m, Fe–D); $^1H$ n.m.r. ([$^2H_8$]toluene) $\delta$ 3.84 (s) and 3.91 (s) (ratio 2 : 3, $C_5H_5$).

The complex $[Fe(\eta^5\text{-}C_5H_5)\{MeC(CH_2PPh_2)_3\}D]$ (0.15 g, 0.20 mmol) in benzene solution was treated with aqueous toluene-*p*-sulphonic acid (12 µl; 0.33 mol dm$^{-3}$) as described for (9) and (10). The $^1H$ n.m.r. spectrum showed the presence of $[Fe(\eta^5\text{-}C_5H_5)\{MeC(CH_2PPh_3)_3\}H]$ (diastereoisomer ratio 1 : 1.8).

*Preparation of* $[Fe(\eta^5\text{-}C_5H_5)\{C(CH_2PPh_2)_4\}H]$ (14).—This was prepared from cation (8) by the method described for the preparation of (12) and (13) (yield 28%), m.p. 213—215 °C (Found: C, 74.5; H, 5.8. $C_{58}H_{54}FeP_4$ requires C, 74.8; H, 6.0%); $\nu_{max.}$ (Nujol) 1 850w cm$^{-1}$ (Fe–H); $^1H$ n.m.r. ($C_6D_6$) $\delta$ 7.9—6.8 (40 H, m, aryl-H), 3.9 (5 H, t, $J_{PH}$ 1.3 Hz, $C_5H_5$), 2.7—1.7 (8 H, m, $CH_2P$), and −15.85 (1 H, t, $J_{PH}$ 67 Hz, Fe–H); *m/z* 929 (*M* − 1).

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