# Iron(O) Arene and Iron(II) Hydride Complexes from the Hydrogenation or Thermolysis of High-spin Iron(II) Alkyls†

**Ann R. Hermes, Timothy H. Warren and Gregory S. Girolami** *

*School of Chemical Sciences, The University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois 61801, USA*

The reactions of hydrogen with the 14-electron high-spin iron(II) dialkyls of stoichiometry [$FeR_2$(dippe)] [dippe = 1,2-bis(diisopropylphosphino)ethane] have been studied. The *p*-methylbenzyl complex in diethyl ether yielded the zerovalent *p*-xylene complex [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)], where the arene ligand has been formed by addition of a hydrogen atom to the α-carbon of the *p*-methylbenzyl group. Hydrogenation of [Fe($CH_2C_6H_4Me$-*p*)$_2$(dippe)] in toluene gave a mixture of several products: the iron(O) arene complexes [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)] and [Fe($\eta^6$-$C_6H_5Me$)(dippe)], the iron(II) monohydride [Fe($\eta^5$-$C_6H_5Me_2$-1,4)H(dippe)], where the 1,4-dimethylcyclohexadienyl ligand arises from addition of two hydrogen atoms to a *p*-methylbenzyl group, and the iron(II) dihydride [$FeH_2$(dippe)$_2$]. Further experiments suggest that these products do not interconvert under the reaction conditions, but instead are probably formed from a common intermediate. Several of the products formed in the hydrogenolysis reactions can be independently prepared. Reaction of [$FeBr_2$(dippe)] with $MgEt_2$ or $MgBu^t_2$ in an arene solvent provides an alternative route to [Fe($\eta^6$-arene)(dippe)] species, the complexes [Fe($\eta^6$-$C_6H_6$)(dippe)] and [Fe($\eta^6$-$C_6H_5Me$)(dippe)] being prepared in this fashion. Presumably, the alkyl complexes '$FeEt_2$(dippe)' and '$FeBu^t_2$(dippe)' are generated, but they rapidly undergo β elimination to give unstable iron(II) hydrides; these intermediates then reductively eliminate $H_2$ to yield an iron(O) centre which is trapped by the arene solvent. The iron(II) dihydride [$FeH_2$(dippe)$_2$] has been prepared independently by sodium-amalgam reduction of $FeBr_2$ in the presence of an excess of dippe and 4 atm of $H_2$. The NMR spectra of all the new complexes are described.

Most organotransition-metal complexes are diamagnetic and possess electron counts of 16 or 18; by contrast, the reactivities of organotransition-metal compounds that are paramagnetic or possess very low electron counts ($\leqslant 14$) are relatively poorly understood. We have described the preparation of an unusual series of co-ordinatively and electronically unsaturated iron(II) alkyls of stoichiometry $FeR_2$(dippe), where dippe is the bulky chelating phosphine 1,2-bis(diisopropylphosphino)ethane.[1] These 14-electron high-spin organoiron species are highly reactive; for example, we have shown previously that they are easily carbonylated to give acyl intermediates which subsequently eliminate ketones.[2]

We now describe the reactions of the four-co-ordinate alkyls [$FeR_2$(dippe)] with $H_2$. Hydrogenation of the *p*-methylbenzyl complex [Fe($CH_2C_6H_4Me$-*p*)$_2$(dippe)] gives several products: among these are an iron(0) $\eta^6$-*p*-xylene complex, an iron(II) 1,4-dimethylcyclohexadienyl hydride complex, and an iron(II) dihydride. In the first two products the co-ordinated arene is derived from the *p*-methylbenzyl groups which were originally σ-bonded to the high-spin iron(II) centre. We also describe a more versatile route to zerovalent iron arene complexes *via* thermolysis of β-unstable iron(II) alkyls in arene solvents.

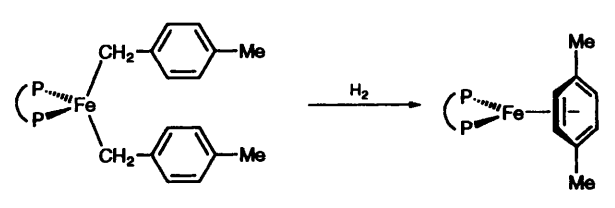
## Results

*Reaction of* 14-*Electron Iron*(II) *Dialkyls with Dihydrogen*.—We have previously described a series of 14-electron iron(II) alkyls of stoichiometry [$FeR_2$(dippe)], where the R group is neopentyl, (trimethylsilyl)methyl, benzyl, or *p*-methylbenzyl.[1] Not all of these complexes react readily with hydrogen. For example, treatment of the (trimethylsilyl)methyl complex [Fe($CH_2SiMe_3$)$_2$(dippe)] with 8 atm of dihydrogen in pentane does not result in any visible colour change, and ultimately the starting material is recovered in good yield.

In contrast, treatment of the *p*-methylbenzyl complex [Fe($CH_2C_6H_4Me$-*p*)$_2$(dippe)] in diethyl ether with molecular hydrogen at 6 atm yields a red-orange diamagnetic product (Scheme 1) which may be crystallized from pentane (Table 1). This product has been identified as the 18-electron iron(0) *p*-xylene complex [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)]. The $^1H$ and $^{13}C$ NMR data clearly reveal the presence of a π-bound arene ligand: the aromatic hydrogen atoms resonate at δ 4.34 and the ring carbon atoms appear at δ 72.8 (for the tertiary carbons) and 93.3 (for the quaternary carbons). These values are similar to those of other [Fe(arene)$L_2$] complexes;[3–8] for example [Fe($\eta^6$-$C_6H_6$)($PMe_3$)$_2$] exhibits $^1H$ and $^{13}C$ NMR resonances for the π-complexed benzene ring at δ 4.71 and 74.5, respectively.[8]

The hydrogenation of transition-metal complexes that contain benzyl ligands has not previously resulted in the formation of products with π-bound arene rings; the only similar reaction that has been reported is the hydrogenation of Zr($CH_2Ph$)$_4$ (1 atm $H_2$, 50 °C) to give free toluene which is subsequently hydrogenated to methylcyclohexane.[9] No organometallic product was identified in this study.

If the hydrogenation of the *p*-methylbenzyl complex [Fe($CH_2C_6H_4Me$-*p*)$_2$(dippe)] is carried out in toluene instead



Scheme 1 $\widehat{\mathrm{P\,P}}$ = dippe

---

† *Non-SI unit employed:* atm = 101 325 Pa.

**Table 1** Physical and analytical data for the iron(0) arene compounds

| | | | Analysis (%)* | |
|---|---|---|---|---|
| Compound | Colour | M.p./°C | C | H |
| [Fe($\eta^6$-$C_6H_6$)(dippe)] | Red | 75–79 | 58.2 (60.6) | 9.85 (9.65) |
| [Fe($\eta^6$-$C_6H_5Me$)(dippe)] | Red | 93–97 | 61.5 (61.5) | 9.85 (9.85) |
| [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)] | Red-orange | | 61.9 (62.3) | 9.90 (10.0) |

* Calculated values in parentheses.

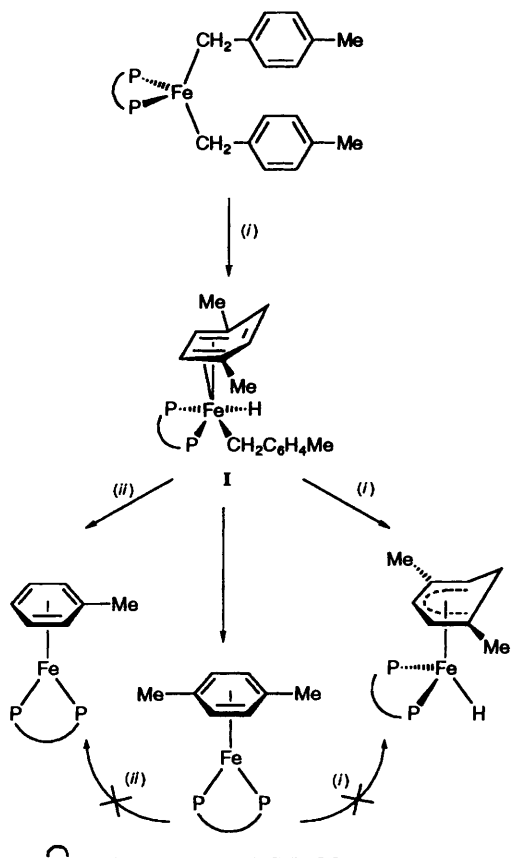
of diethyl ether a mixture of several products is obtained; fortunately, these products can be separated by fractional crystallization from toluene. The first crop of red crystals (which is the major product) is the same arene complex, [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)], described above; interestingly, however, small amounts of the arene-exchange product [Fe($\eta^6$-$C_6H_5Me$)(dippe)] are also observed by $^1H$ NMR spectroscopy. This latter toluene complex can also be prepared by another route (see below).

More interesting are the other two products, which can be isolated by further concentration and cooling of the supernatant. The second and third crops consist of a yellow-brown crystalline material which is an iron hydride as shown by the presence of a hydride resonance at $\delta$ −22.7 (t, $J_{PH}$ = 78 Hz). This material has been identified as the 1,4-dimethylcyclohexadienyl complex [Fe($\eta^5$-$C_6H_5Me_2$-1,4)H(dippe)], although the samples are contaminated with about 5% of another hydride species (see Experimental section). The IR spectrum exhibits a band at 2720 $cm^{-1}$ assignable to the *exo* C–H stretch of the dimethylcyclohexadienyl ring,[10–12] and a band at 1930 $cm^{-1}$ which may be assigned to the Fe–H stretching mode. The $^1H$ NMR chemical shifts resemble those of other iron cyclohexadienyl complexes,[13–17] and the two methyl substituents are located at the 1 and 4 positions (the ring carbon bearing two hydrogen atoms being located at the 6 position). The related complex [Fe($\eta^5$-$C_6H_7$)H{P(OMe)$_3$}$_2$] has been prepared by co-condensation of iron vapour with benzene and trimethyl phosphite,[7] and [Fe($\eta^5$-$C_6H_7$)H(dippe)] and [Fe($\eta^5$-$C_6H_7$)H(dippp)] [dippp = 1,3-bis(diisopropylphosphino)propane] have been examined by $^{31}P$ and $^{57}Fe$ NMR spectroscopy but no synthetic details are available.[18]

The last crops of material obtained from the toluene solution consist of a single product with a hydride resonance at $\delta$ −17.4 which is a broad pseudo-quintet at room temperature. This material has been identified as the iron(II) dihydride [$FeH_2$(dippe)$_2$] by comparison with an authentic sample (see below).

The different distributions of products seen when [Fe($CH_2C_6H_4Me$-*p*)$_2$(dippe)] is hydrogenated in diethyl ether *vs.* toluene may be more apparent than real: it is possible that the 1,4-dimethylcyclohexadienyl complex and the iron(II) dihydride are also generated in diethyl ether but simply were not isolated from the reaction solutions. Alternatively, the higher solubility of $H_2$ in toluene *vs.* diethyl ether may have been responsible for the formation of the hydride products in sufficient yield to allow their isolation.

*Chemical Interrelationships of the Hydrogenation Products.*—It is of interest to establish whether the different products formed in the hydrogenation of [Fe($CH_2C_6H_4Me$-*p*)$_2$(dippe)] are generated independently or are formed sequentially, one from another. We have carried out two experiments to help answer this question. First, hydrogenation of isolated samples of the arene complex [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)] does *not* yield the 1,4-dimethylcyclohexadienyl complex or [$FeH_2$(dippe)$_2$] even at a pressure of 10 atm; instead, the zerovalent arene complex is recovered in good yield. Similarly, refluxing the *p*-xylene complex [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)] in toluene does *not* afford the toluene complex [Fe($\eta^6$-$C_6H_5Me$)(dippe)]; the *p*-xylene complex is again recovered in good yield.



**Scheme 2** P P = dippe. (*i*) $H_2$; (*ii*) $C_6H_5Me$

These observations clearly show that [Fe($\eta^5$-$C_6H_5Me_2$-1,4)H(dippe)], [$FeH_2$(dippe)$_2$], and [Fe($\eta^6$-$C_6H_5Me$)(dippe)] cannot be formed under our reaction conditions by means of secondary reactions from [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)]. Instead, we suggest that [Fe($CH_2C_6H_4Me$-*p*)$_2$(dippe)] reacts with 1 equivalent of $H_2$ to generate an intermediate, **I**, which can react in several ways to give the various products. One possible structure for **I** that explains the several observed products is the hydride–alkyl–$\eta^4$-*p*-xylene complex [FeH($CH_2C_6H_4Me$-*p*)($\eta^4$-$C_6H_4Me_2$-1,4)(dippe)], which would be formed by addition of $H_2$ across the Fe–C bond of one of the *p*-methylbenzyl groups and rearrangement of the resulting *p*-xylene ligand to the $\eta^4$ form. In theory, this intermediate can react *via* one of four pathways (Scheme 2): (1) reductive elimination of the hydride and alkyl groups to give [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)]; (2) arene exchange with toluene to give an $\eta^4$-toluene complex which reductively eliminates the hydride and alkyl groups to give [Fe($\eta^6$-$C_6H_5Me$)(dippe)]; (3) transfer of the hydride ligand to the $\eta^4$-*p*-xylene ligand to give an $\eta^5$-1,4-dimethylcyclohexadienyl complex followed by hydrogenolysis of the remaining *p*-methylbenzyl group; this would yield the observed product [Fe($\eta^5$-$C_6H_5Me_2$-1,4)H(dippe)]; (4) arene exchange with toluene followed by hydrogen transfer and hydrogenolysis to given an $\eta^5$-methylcyclohexadienyl hydride complex; and (5) complete hydrogenolysis to an iron dihydride species.

The products of all but the fourth pathway have been isolated as described above. The fourth possible product, [Fe($\eta^5$-$C_6H_6$Me)H(dippe)], has not been isolated in a pure state but may be responsible for a weak hydride signal at δ −19.8 (t, $J_{PH}$ = 75 Hz) which was observed as a minor impurity in samples of the 1,4-dimethylcyclohexadienyl hydride product.

Although the proposal of **I** as a common intermediate in the formation of the various products is consistent with the observations, it is also possible that hydrogenation of [Fe($CH_2C_6H_4$Me-*p*)$_2$(dippe)] diverges along different reaction pathways right from the start.

*Decomposition of High-spin Iron*(II) *'β-Unstable' Alkyls.*—In the reactions described above the iron(0) arene products presumably arise *via* hydrogenolysis of the iron(II) alkyls to iron(II) hydride intermediates which subsequently reductively eliminate $H_2$. If this presumption is correct, then iron(0) arene complexes should be preparable by the thermal decomposition of 'β-unstable' iron(II) alkyls in arene solvents.

Alkylation of [$FeBr_2$(dippe)] with $MgEt_2$ or $MgBu^t_2$ in diethyl ether gives yellow solutions at −78 °C which darken considerably upon warming above 0 °C. Evidently, the [Fe-$R_2$(dippe)] alkyls are unstable for R = Et or $Bu^t$, and we have been unable to isolate any organometallic products from these solutions. Alkylation of [$FeBr_2$(dippe)] with $MgEt_2$ or $MgBu^t_2$ in benzene or toluene, however, gives red solutions from which the corresponding zerovalent arene complexes [Fe($\eta^6$-arene)-(dippe)] may be isolated in reasonable yields. Presumably, the arene molecules are able to trap intermediates formed when the 'β-unstable' alkyls [$FeR_2$(dppe)] decompose.

The NMR data for the iron(0) benzene and toluene complexes are given in Table 2. The 18-electron, diamagnetic arene complexes are easily identified by their $^1H$ and $^{13}C$ NMR spectra. Similar π-arene species, such as [Fe($\eta^6$-$C_6H_6$)($PF_3$)$_2$], [Fe($\eta^6$-$C_6H_5$Me)($PF_3$)$_2$], [Fe($\eta^6$-$C_6H_5$Me){P(OMe)$_3$}$_2$] and [Fe($\eta^6$-$C_6H_6$)($PMe_3$)$_2$], have been previously prepared *via* metal-atom vapour techniques.[3–8]

*Independent Preparation of* [$FeH_2$(dippe)$_2$].—The iron(II) dihydride [$FeH_2$(dippe)$_2$], which was obtained as the last crop of material from the hydrogenation of [Fe($CH_2C_6H_4$Me-*p*)$_2$-(dippe)], can be prepared independently by sodium-amalgam reduction of $FeBr_2$ in the presence of an excess of dippe and an atmosphere of $H_2$ [equation (1)]. The hydride

$$\mathrm{FeBr_2 + 2\,Na\text{–}Hg + H_2 + 2\,dippe \longrightarrow [FeH_2(dippe)_2] + 2\,NaBr + Hg} \quad (1)$$

resonance of [$FeH_2$(dippe)$_2$] appears as a pseudo-quintet at δ −17.4; the separation between the outer lines of the five-line pattern (which is equal to the sum of the four independent $J_{PH}$ coupling constants) is 155 Hz (Fig. 1). The temperature-dependent $^1H$ and $^{31}P$-{$^1H$} NMR spectra of this dihydride are virtually identical to those seen for other $FeH_2L_4$ species, which have been intensively investigated.[19–21] Jesson and co-workers[19,21] have shown that these molecules are dynamic, and that the NMR line shapes are consistent with a 'tetrahedral jump' exchange mechanism; undoubtedly a similar mechanism is responsible for the fluxionality of [$FeH_2$-(dippe)$_2$].

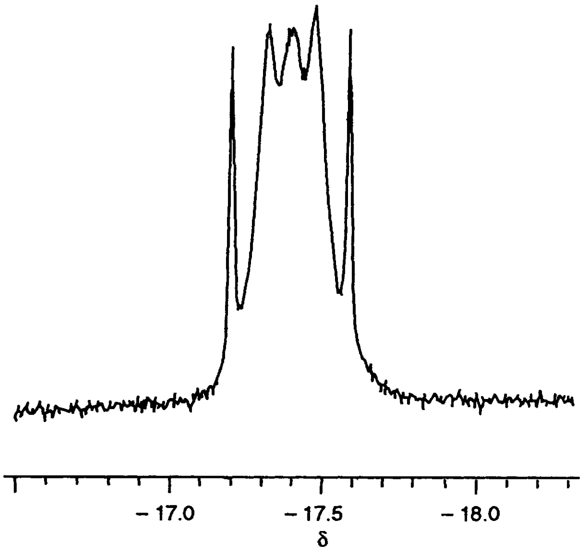


**Fig. 1** The 300 MHz $^1H$ NMR spectrum of [$FeH_2$(dippe)$_2$] in $C_6D_5CD_3$ at 25 °C. Only the hydride region is shown

**Table 2** Proton and $^{13}C$-{$^1H$} NMR data for iron(0) arene complexes[a]

| Compound | $^1H$ | Assignment | $^{13}C$-{$^1H$} |
|---|---|---|---|
| [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)] | 2.47 (s) | Ring Me | 22.5 (s) |
| | 4.34 (s) | $C_6H_4$ | 72.8 (s) |
| | | *ipso*-C | 93.3 (s) |
| | *b* | $PCH_2$ | 22.3 't', *N* = 43.0 |
| | 1.69 (m), $J_{HH}$ = 7.5 | *CH*Me$_2$ | 29.0 't', *N* = 11.0 |
| | 1.03 (dd), $J_{PH}$ = 12.0, $J_{HH}$ = 7.4 | CH*Me*$_2$ | 19.6 (s) |
| | 1.03 (dd), $J_{PH}$ = 13.5, $J_{HH}$ = 7.5 | CH*Me*$_2$ | 19.0 (s) |
| [Fe($\eta^6$-$C_6H_6$)(dippe)] | 4.80 (s) | $C_6H_6$ | 75.8 (s) |
| | *b* | $PCH_2$ | 22.4 't', *N* = 43.5 |
| | 1.65 (m), $J_{HH}$ = 7.5 | *CH*Me$_2$ | 29.2 't', *N* = 11.9 |
| | 0.96 (dd), $J_{PH}$ = 11.9, $J_{HH}$ = 7.4 | CH*Me*$_2$ | 19.1 (s) |
| | 1.03 (dd), $J_{PH}$ = 13.6, $J_{HH}$ = 7.6 | CH*Me*$_2$ | 19.7 (s) |
| [Fe($\eta^6$-$C_6H_5$Me)(dippe)] | 2.35 (s) | Ring Me | 22.5 (s) |
| | 4.43 (m) | *o*-CH | 72.8 (s) |
| | 4.45 (m) | *m*-CH | 75.8 (s) |
| | 5.51 (t), $J_{HH}$ = 5.1 | *p*-CH | 78.2(d),$J_{PC}$ = 6.5 |
| | | *ipso*-C | 90.8 (s) |
| | 0.92 (d), $J_{PH}$ = 9.6 | $PCH_2$ | 22.3 't', *N* = 42.6 |
| | 1.70 (m), $J_{HH}$ = 7.5 | *CH*Me$_2$ | 29.0 't', *N* = 10.1 |
| | 0.96 (dd), $J_{PH}$ = 11.9, $J_{HH}$ = 7.3 | CH*Me*$_2$ | 19.6 (s) |
| | 1.05 (dd), $J_{PH}$ = 13.6, $J_{HH}$ = 7.6 | CH*Me*$_2$ | 19.0 (s) |

[a] Coupling constants in Hz; $N = {}^1J_{PC} + {}^2J_{PC}$ for $PCH_2$ carbons; $N = {}^1J_{PC} + {}^4J_{PC}$ for *C*HMe$_2$ carbons. [b] Obscured by other peaks.

## Experimental

All operations were carried out in vacuum or under argon. Solvents were distilled from sodium (toluene) or sodium–benzophenone (pentane, diethyl ether, benzene) immediately before use. Iron(II) bromide,[22] 1,2-bis(diisopropylphosphino)ethane,[23] and the iron alkyls [$FeR_2$(dippe)][1] were prepared as described elsewhere.

Microanalyses were performed by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B instrument as Nujol mulls between KBr salt plates. The $^1H$ and $^{13}C$ NMR data were obtained on a General Electric QE-300 spectrometer at 300 and 75.4 MHz respectively, the $^{31}P$ NMR data at 101.265 MHz on a locally constructed intrument. Chemical shifts are reported in δ units relative to $SiMe_4$ ($^1H$, $^{13}C$) or 85% $H_3PO_4$ ($^{31}P$). Melting points were measured on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

*[1,2-Bis(diisopropylphosphino)ethane](η⁶-*p*-xylene)iron*(0).—A solution of the complex [$Fe(CH_2C_6H_4Me$-*p*$)_2$(dippe)] (0.4 g, 0.76 mmol) in diethyl ether (40 $cm^3$) was treated with $H_2$ (6 atm). After having been stirred for 24 h the solution was yellow-brown. It was filtered, concentrated to *ca.* 15 $cm^3$ and cooled to −78 °C to give red-orange prisms. Yield: 0.16 g (50%). IR ($cm^{-1}$): 3032m, 1405w, 1355m, 1300w, 1235m, 1225m, 1172w, 1149m, 1102m, 1090m, 1080w, 1017s, 950w, 916m, 874s, 840m, 821m, 802s, 774s, 680s, 665(sh), 620s, 605s and 585(sh).

*[1,2-Bis(diisopropylphosphino)ethane](η⁵-1,4-Dimethylcyclohexadienyl)hydridoiron*(II).—A solution of the complex [$Fe(CH_2C_6H_4Me$-*p*$)_2$(dippe)] (0.83 g, 1.57 mmol) in toluene (40 $cm^3$) was treated with $H_2$ (6 atm). After having been stirred for 48 h the initially deep red solution was a lighter orange-red. The solution was filtered, concentrated to *ca.* 15 $cm^3$ and cooled to −78 °C. The first crop of crystals obtained (0.28 g) were red and were identified as a 70%:30% mixture of [Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe)] and [Fe($\eta^6$-$C_6H_5Me$)(dippe)] by $^1H$ NMR spectroscopy. Further concentration of the supernatant resulted in the isolation of yellow-brown crystals of the product. Yield: 0.13 g (22%). $^1H$ NMR ($C_6D_6$, 25 °C): δ 5.61 (d, $J_{HH}$ = 5, $H^3$ of ring), 4.04 (d, $J_{HH}$ = 5, $H^2$ of ring), 2.45 (m, $PCH_2$ + PC*H*$Me_2$), 2.11 (s, 4-Me of ring), 1.53 (s, 1-Me of ring), 0.96 (m, PCH*Me*$_2$) 0.84 (m, PCH*Me*$_2$) and −22.7 (t, $J_{PH}$ = 78 Hz, FeH). IR ($cm^{-1}$): 3041m, 3008m, 2720m, 1930m, 1510m, 1300w, 1240m, 1225w, 1150m, 1102s, 1092(sh), 1070w, 1020s, 958w, 920w, 880s, 853w, 840m, 805w, 774s, 675s, 660m, 635s and 610s. A minor impurity (*ca.* 5%) is present in samples of the dimethylcyclohexadienyl complex which gives a weak hydride signal at δ −19.8 (t, $J_{PH}$ = 75 Hz); this species could be the methylcyclohexadienyl complex, [Fe($\eta^5$-$C_6H_6Me$)H(dippe)], derived from the toluene solvent. Further concentration and cooling of the supernatant from this reaction yields a fourth crop of yellow-brown powder (0.06 g) which was identified as [$FeH_2(dippe)_2$] by comparison with an authentic sample (see below).

*(η⁶-Benzene)[1,2-bis(diisopropylphosphino)ethane]iron*(0).—To a suspension of $FeBr_2$ (0.78 g, 3.6 mmol) in benzene (25 $cm^3$) was added dippe (1.0 $cm^3$, 3.5 mmol). The $FeBr_2$ dissolved over 20 min to give a pale orange solution of [$FeBr_2$(dippe)]. The solution was cooled to −10 °C, and di(*tert*-butyl)magnesium (12 $cm^3$ of a 0.29 mol $dm^{-3}$ solution in diethyl ether, 3.5 mmol) was added. The solution immediately turned red, and the mixture was stirred for 2 h at 25 °C. After the solvent was removed under vacuum, the residue was extracted with pentane (40 $cm^3$). The filtered extract was concentrated to *ca.* 3 $cm^3$ and cooled to −78 °C. The resulting red prisms were collected and recrystallized from pentane. Yield: 0.49 g (32%). IR ($cm^{-1}$): 3030m, 1596w, 1420w, 1355m, 1300w, 1260w, 1240m, 1187w, 1151w, 1140w, 1095w, 1078m, 1013s, 980w, 966s, 912m, 873s, 850m, 818w, 770s, 681s, 667s, 610s(br), 590s, 488m, 460m, 432m, 404m, 389m and 376m.

*[1,2-Bis(diisopropylphosphino)ethane](η⁶-toluene)iron*(0).—The complex [$FeBr_2$(dippe)] was prepared *in situ* in toluene (30 $cm^3$) as above by reaction of $FeBr_2$ (0.59 g, 2.9 mmol) and dippe (0.8 $cm^3$, 2.8 mmol). The resulting solution was cooled to −78 °C and treated with di(*tert*-butyl)magnesium (10 $cm^3$ of a 0.29 mol $dm^{-3}$ solution in diethyl ether, 2.9 mmol). Upon being warmed to 25 °C the solution turned red. After 2 h, the solvent was removed under vacuum and the residue was extracted with ether (30 $cm^3$). The filtered extract was cooled to −78 °C to give red rosette-shaped crystals. Recrystallization from pentane afforded an analytically pure sample. Yield: 0.39 g (33%). $^{31}P$-{$^1H$} NMR ($C_6D_6$, 25 °C): δ 109.1 [s, $^1J$(Fe–P) = 106 Hz]. IR ($cm^{-1}$): 3030m, 1810w, 1787w, 1763w, 1734w, 1690w, 1635w, 1620w, 1575w, 1553w, 1500w, 1412w, 1355m, 1299w, 1287w, 1257m, 1238s, 1224(sh), 1195w, 1150w, 1144w, 1091m, 1060s, 1044m, 1010s, 979s, 950w, 916m, 900m, 875s, 850s, 842s, 785s, 777s, 768s, 680s, 660s, 615s, 589s, 488s, 460s, 430m, 388s and 346m.

*Bis[1,2-bis(diisopropylphosphino)ethane]dihydridoiron*(II).—To a suspension of $FeBr_2$ (0.62 g, 2.9 mmol) in diethyl ether (40 $cm^3$) was added 1,2-bis(diisopropylphosphino)ethane (1.68 $cm^3$, 5.8 mmol). The solution turned yellow and then a dark orange precipitate appeared. The suspension was transferred to a Fisher–Porter bottle that had been previously charged with sodium amalgam prepared from sodium (1.56 g, 6.8 mmol) and mercury (10 $cm^3$). The bottle was then pressurized with $H_2$ (4 atm) and the suspension stirred for 30 min. The bottle was vented, and the resulting dark blue-green solution was taken to dryness under vacuum. The residue was extracted with pentane (20 $cm^3$), the extract was filtered and the filtrate concentrated to *ca.* 5 $cm^3$ and cooled to −20 °C to afford a brown precipitate. Yield: 0.15 g (9%) (Found: C, 58.0; H, 12.1. Calc. for $C_{28}H_{66}FeP_4$: C, 57.7; H, 11.3%). NMR ($C_6D_5CD_3$, 25 °C): $^1H$, δ −17.4 (br, pseudo-quintet, $\Sigma J_{PH}$ = 155 Hz, FeH); $^{31}P$-{$^1H$}, δ 115.0(br s) and 91.5(br s). IR ($cm^{-1}$): 1890m, 1868m, 1840m, 1250m, 1070m(br), 1020s, 953w, 917w, 872s, 803m, 785s, 737m, 673s, 655s, 632s, 610s, 600s, 550w, 492m, 480m, 460w, 396m, 384m, 372w and 352w.

## Acknowledgements

We thank the National Science Foundation (Grant CHE 89-17586) and the Office of Naval Research under their Young Investigator Award Program for support of this research. We thank the Exxon Education Foundation for a fellowship (to A. R. H.); G. S. G. is the recipient of an A. P. Sloan Foundation Research Fellowship (1988–1990) and a Henry and Camille Dreyfus Teacher-Scholar Grant (1988–1993).

## References

1 A. R. Hermes and G. S. Girolami, *Organometallics*, 1987, **6**, 763.
2 A. R. Hermes and G. S. Girolami, *Organometallics*, 1988, **7**, 394.
3 D. L. Williams-Smith, L. R. Wolf and P. S. Skell, *J. Am. Chem. Soc.*, 1972, **94**, 4042.
4 R. Middleton, J. R. Hull, S. R. Simpson, C. H. Tomlinson and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 1973, 120.
5 S. R. Weber and H. H. Brintzinger, *J. Organomet. Chem.*, 1977, **127**, 45.
6 S. D. Ittel, F. A. Van-Catledge and J. P. Jesson, *J. Am. Chem. Soc.*, 1979, **101**, 3874.
7 S. D. Ittel and C. A. Tolman, *Organometallics*, 1982, **1**, 1432.
8 M. L. H. Green and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1987, 411.
9 U. Zucchini, E. Albizzati and U. Giannini, *J. Organomet. Chem.*, 1971, **26**, 357.
10 I. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc. C*, 1969, 2024.
11 F. Calderazzo, *Inorg. Chem.*, 1966, **5**, 429.

12 M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 1969, **8**, 1950.
13 A. J. Deeming, *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, ch. 31.3.4.9.
14 L. K. Beard, jun., M. P. Silvon and P. S. Skell, *J. Organomet. Chem.*, 1981, **209**, 245.
15 S. D. Ittel, *J. Organomet. Chem.*, 1980, **195**, 331.
16 I. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc. C*, 1968, 2257.
17 I. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc. C*, 1968, 2261.
18 R. Benn, H. Brennecke, A. Frings, H. Lehmkuhl, G. Mehler, A. Rufińska and T. Wildt, *J. Am. Chem. Soc.*, 1988, **110**, 5661.
19 P. Meakin, E. L. Muetterties, F. N. Tebbe and J. P. Jesson, *J. Am. Chem. Soc.*, 1971, **93**, 4701.
20 D. H. Gerlach, W. G. Peet and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 4545.
21 P. Meakin, E. L. Muetterties and J. P. Jesson, *J. Am. Chem. Soc.*, 1973, **95**, 75.
22 G. Winter, *Inorg. Synth.*, 1973, **14**, 101.
23 M. D. Fryzuk, T. Jones and F. W. B. Einstein, *Organometallics*, 1984, **3**, 185.

*Received 2nd August* 1994; *Paper* 4/04740K