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Half-Sandwich Halide, Alkyl, Hydride, and Related Complexes of Iron Containing the Bulky Diphosphine 1,2-Bis(diisopropylphosphino)ethane. Crystal Structure of [$FeH_2(C_5Me_5)$(dippe)][BPh_4]

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The four-coordinate iron phosphine complex [$FeCl_2$(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with LiC_5H_5 or LiC_5Me_5 in thf, yielding the corresponding half-sandwich derivatives [$FeCl(C_5H_5)$(dippe)] (**1**) or [$FeCl(C_5Me_5)$(dippe)] (**2**), respectively. These complexes react with Grignard reagents RMgCl to give [$FeR(C_5H_5)$(dippe)] (R = Me (**3**) or CH_2SiMe_3 (**4**)) or [$FeR(C_5Me_5)$(dippe)] (R = Me (**5**)). If ^iPrMgCl is used, the monohydrides [$FeH(C_5H_5)$(dippe)] (**6**) and [$FeH(C_5Me_5)$(dippe)] (**7**) are obtained, presumably through a β-elimination reaction. These hydrides are also prepared by reaction between the corresponding chloro complexes and Li[$HBEt_3$] in thf. The monohydrides **6** and **7** undergo a one-electron oxidation by reaction with [$Fe(C_5H_5)_2$][PF_6], yielding the 17-electron hydrides [$FeH(C_5H_5)$(dippe)]$^+$ and [$FeH(C_5Me_5)$(dippe)]$^+$, isolable as tetraphenylborate salts, [$FeH(C_5H_5)$(dippe)][BPh_4] (**8**) and [$FeH(C_5Me_5)$(dippe)][BPh_4] (**9**). The reaction of **1** or **2** with dihydrogen in methanol, followed by addition of Na[BPh_4] yielded the dihydrides [$FeH_2(C_5H_5)$(dippe)][BPh_4] (**10**) and [$FeH_2(C_5Me_5)$(dippe)][BPh_4] (**11**), respectively. No equilibrium dihydride $\rightleftharpoons$ dihydrogen has been detected in these complexes, and therefore, they must be regarded as organoiron(IV) species. The crystal structure of **11** has been determined. Crystal data: monoclinic system, space group $P2_1/n$, cell parameters $a = 14.277(4)$ Å, $b = 21.388(6)$ Å, $c = 14.619(6)$ Å, $\beta = 101.07(3)°$, and $Z = 4$. It suggests a transoid arrangement of hydride ligands, consistent with the formulation as an iron(IV) dihydride. The vinylidene complexes [Fe=C=$CHPh(C_5H_5)$(dippe)][BPh_4] (**12**) and [Fe=C=$CHPh(C_5Me_5)$(dippe)][BPh_4] (**13**) were also prepared and characterized. Deprotonation of these vinylidene complexes yielded the alkynyl derivatives [Fe(C≡CPh)(C_5H_5)(dippe)] (**14**) and [Fe(C≡CPh)(C_5H_5)(dippe)] (**15**). All the compounds were characterized by NMR, IR, and microanalysis.

Introduction

The chemistry of the cyclopentadienyl or pentamethylcyclopentadienyl bis(phosphine) auxiliary has attracted very much attention in recent years,[1] due to the potential of these systems for the development of new organic synthetic methods and their ability to bind and activate a range of small molecules, including dihydrogen[2] and dioxygen,[3] among others. However, the chemistry of the iron homologues is still rather underdeveloped when compared to ruthenium. Half-sandwich phosphine derivatives of iron have been prepared by several methods, including reduction of iron−phosphine complexes in the presence of cyclopentadiene,[4] photochemically-induced displacement of carbonyl ligands in [$FeCl(C_5H_5)(CO)_2$] by phosphines,[5] or reaction of suitable precursors such as [$Fe(\eta^6\text{-}C_6H_6)(PMe_3)_2$] with cyclopentadiene or pentamethylcyclopentadiene.[6] The reaction of [$Fe(acac)_2]_2$ (acac = η^2-acetylacetonate) with LiC_5Me_5 in the presence of PMe_3 or dmpe (1,2-bis(dimethylphosphino)ethane) yields [$Fe(C_5Me_5)$(L)(acac)] (L = PMe_3 or η^1-dmpe),[7] which are transformed into the corresponding half-sandwich chloro complexes [$FeCl(C_5Me_5)L_2$] (L = PMe_3, L_2 = η^2-dmpe) upon treatment with $SiMe_3Cl$ *in situ*. A variety of cyclopentadienyl bis(phosphine) iron complexes of the type [$FeCpClL_2$] (Cp = C_5H_5, C_5H_4Me, or C_5Me_5; L = PMe_nPh_{3-n}, $n = 0-3$) have also been obtained by starting from precursor complexes such as [$FeCl_2(PMe_3)_2$] or [FeCpCl(COD)] (COD = 1,5-cyclooctadiene).[8] In order to establish the influence of bulky phosphine ligands in the reactivity of these iron-based systems, we have started from the four-coordinate complex [$FeCl_2$(dippe)][9] for the synthesis of the corresponding [FeCl(L)(dippe)] (L = C_5H_5 or C_5Me_5) complexes, by reaction with LiC_5H_5 or LiC_5Me_5 in thf. In an analogous fashion, the reaction of [$FeCl_2$(dppe)] with LiC_5Me_5 had been previously used as a convenient method for the preparation of the corresponding [FeCl-

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(C_5Me_5)(dppe)] complex.[10] These materials exhibit a rich chemistry, which parallels that found for other iron and ruthenium complexes with different phosphine ligands. Here we present some of the results of our research on the chemistry of these half-sandwich derivatives, which include the synthesis and characterization of alkyl and hydride complexes, as well as vinylidene and alkynyl derivatives.

Experimental Section

All synthetic operations were performed under a dry dinitrogen atmosphere following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethyl ether, and petroleum ether were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane[11] and [$FeCl_2$(dippe)][9] were prepared according to the literature. Dicyclopentadiene was purchased from Merck and cracked before use. Pentamethylcyclopentadiene, phenylacetylene, and solutions of Li[$HBEt_3$] and Grignard reagents were supplied by Aldrich and used without further purification. IR spectra were recorded in Nujol mulls on a Perkin-Elmer 881 spectrophotometer. NMR spectra were taken on Varian Unity 400-MHz or Varian Gemini 200-MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). Magnetic moments were measured in solution using the Evans method.[12] Microanalyses were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía or by Mr. Colin Macdonald at the AFRC-Nitrogen Fixation Laboratory, University of Sussex, Brighton, U.K.

[FeCl(C_5H_5)(dippe)] (1). [$FeCl_2$(dippe)] (2.33 g, 6 mmol) in thf (20 cm^3) was treated with a thf solution of LiC_5H_5 (made from an excess of freshly cracked cyclopentadiene and the stoichiometric amount of 1.6 M Li^nBu, 3.8 cm^3, 6 mmol, in 15 cm^3 of thf) at room temperature. The color changed immediately, and a purple solution was obtained. It was stirred for 30 min at room temperature. Then, the solvent was removed *in vacuo*, and the residue was extracted with the minimum amount of petroleum ether. The filtered solution was chromatographied on a silica gel column. Elution with petroleum ether yielded an orange band, from which ferrocene was isolated upon removal of the solvent. Once ferrocene was removed, the column was eluted with diethyl ether. In this way, a purple band containing **1** moved down. Removal of the solvent of this fraction yielded purple-black crystals of **1**, pure enough for synthetic purposes. The pure product was obtained upon recrystallization from concentrated petroleum ether solutions at −20 °C. Yield: 1.15 g, 46%. Anal. Calcd for $C_{19}H_{37}ClFeP_2$: C, 54.5; H, 8.84. Found: C, 54.2; H, 8.93. NMR (C_6D_6), δ: ^1H 4.205 (s, FeC_5H_5); $^{31}P\{^1H\}$ 99.6 (s); $^{13}C\{^1H\}$ 19.71, 19.76, 19.93, 21.15 (s, $P(CH(CH_3)_2)_2$), 22.38 (t, J(C,P) = 17.6 Hz, PCH_2), 25.99 (t, J(C,P) = 9.8 Hz, $P(CH(CH_3)_2)_2$), 29.46 (t, J(C,P) = 7.8 Hz, $P(CH(CH_3)_2)_2$), 73.3 (s, C_5H_5).

[FeCl(C_5Me_5)(dippe)] (2). [$FeCl_2$(dippe)] (0.38 g, 1 mmol) in thf (20 cm^3) was treated with a thf suspension of LiC_5Me_5 (made from pentamethylcyclopentadiene, 0.15 cm^3, *ca.* 1 mmol, and the corresponding amount of 1.6 M Li^nBu, 0.65 cm^3, *ca.* 1 mmol, in 15 cm^3 of thf) at room temperature. As for **1**, a purple solution was obtained. It was stirred for 30 min at room temperature. Then, the solvent was removed *in vacuo*. The residue was extracted with several portions of diethyl ether and then centrifuged. Concentration and cooling to −20 °C afforded dark blue crystals of **2**, which can be recrystallized from diethyl ether/petroleum ether. Yield: 0.3 g, 61%. Anal. Calcd for $C_{24}H_{47}ClFeP_2$: C, 58.9; H, 9.62. Found: C, 58.1; H, 9.64. NMR, δ: ^1H (C_6D_6, 293 K) 1.592 (s, $FeC_5(CH_3)_5$); $^{31}P\{^1H\}$ ($C_6D_5CD_3$, 293 K) 89.8 (s, br, $\Delta\nu_{1/2}$ = 112 Hz), (243 K) 87.2 (s, $\Delta\nu_{1/2}$ = 11 Hz).

[Fe(CH_3)(C_5H_5)(dippe)] (3). **1** (0.2 g, 0.5 mmol) in Et_2O (20 cm^3) at −79 °C was treated with MeMgCl (0.18 cm^3 of a 3 M solution in thf, 0.54 mmol). The reaction mixture was allowed to reach room temperature. A red solution was obtained. It was stirred at room temperature for 1 h. Then, the solvent was removed *in vacuo*. The residue was extracted with petroleum ether and then centrifuged. Concentration and cooling to −20 °C yielded dark red crystals. Yield: 0.14 g, 70%. Anal. Calcd for $C_{20}H_{40}FeP_2$: C, 60.3; H, 10.3. Found: C, 60.3; H, 10.1. NMR (C_6D_6), δ: ^1H −0.530 (s, br, $FeCH_3$), 4.232 (t, J(H,P) = 1.2 Hz, FeC_5H_5); $^{31}P\{^1H\}$ 114.8 (s); $^{13}C\{^1H\}$ −23.9 (t, J(C,P) = 25 Hz, $FeCH_3$), 19.78, 19.89, 20.19, 20.59 (s, $P(CH(CH_3)_2)_2$), 22.73 (t, J(C,P) = 17.6 Hz, PCH_2), 27.75 (t, J(C,P) = 10 Hz, $P(CH(CH_3)_2)_2$), 29.99 (t, J(C,P) = 8.3 Hz, $P(CH(CH_3)_2)_2$), 72.9 (s, FeC_5H_5).

[Fe(CH_2SiMe_3)(C_5H_5)(dippe)] (4). **1** (0.2 g, 0.5 mmol) in Et_2O (20 cm^3) at −79 °C was treated with Me_3SiCH_2MgCl (0.3 cm^3 of a 1.9 M solution in Et_2O, *ca.* 0.5 mmol). The mixture was warmed to room temperature and then stirred for 30 min. The solvent was removed *in vacuo*. The residue was extracted with petroleum ether, and the resulting red solution was centrifuged. Concentration and cooling to −20 °C yielded dark red crystals, very soluble in nonpolar solvents. Yield: 0.16 g, 66%. Anal. Calcd for $C_{23}H_{48}FeP_2Si$: C, 58.6; H, 10.2. Found: C, 58.1; H, 9.98. NMR (C_6D_6), δ: ^1H −2.118 (t, J(H,P) = 6.9 Hz, $FeCH_2Si(CH_3)_3$), 0.365 (s, $FeCH_2Si(CH_3)_3$), 4.277 (s, FeC_5H_5); $^{31}P\{^1H\}$ 108.8 (s); $^{13}C\{^1H\}$ −32.1 (t, J(C,P) = 20.1 Hz, $FeCH_2Si(CH_3)_3$), 5.3 (s, $FeCH_2Si(CH_3)_3$), 19.90, 19.94, 20.01, 20.85 (s, $P(CH(CH_3)_2)_2$), 21.78 (t, J(C,P) = 17.1 Hz, PCH_2), 26.99 (t, J(C,P) = 7.1 Hz, $P(CH(CH_3)_2)_2$), 31.15 (t, J(C,P) = 5.5 Hz, $P(CH(CH_3)_2)_2$), 73.4 (s, FeC_5H_5).

[Fe(CH_3)(C_5Me_5)(dippe)] (5). It was obtained following a procedure identical to that for **3**, starting from **2** (0.75 g, 1.5 mmol) and 0.75 cm^3 of 3 M MeMgCl (*ca.* 2 mmol). Yield: 0.59 g, 84%. Anal. Calcd for $C_{25}H_{50}FeP_2$: C, 64.1; H, 10.7. Found: C, 63.9; H, 10.9. NMR (C_6D_6), δ: ^1H −0.802 (t, br, J(H,P) ≈ 5 Hz, $FeCH_3$), 1.680 (s, $FeC_5(CH_3)_5$); $^{31}P\{^1H\}$ 100.6 (s); $^{13}C\{^1H\}$ −11.1 (t, J(C,P) = 25.4 Hz, $FeCH_3$), 11.1 (s, $FeC_5(CH_3)_5$), 19.62, 19.96, 21.33, 21.55 (s, $P(CH(CH_3)_2)_2$), 24.83 (br, PCH_2), 25.51 (t, J(C,P) = 4.5 Hz, $P(CH(CH_3)_2)_2$), 26.10 (br, $P(CH(CH_3)_2)_2$), 80.8 (s, $FeC_5(CH_3)_5$).

[FeH(C_5H_5)(dippe)] (6). **1** (0.4 g, *ca.* 1 mmol) in thf (20 cm^3) was treated with Li[$HBEt_3$] ("Super-hydride", 1 cm^3 of a 1 M thf solution, 1 mmol). The purple solution changed its color to yellow. The mixture was stirred at room temperature for 30 min. Then, it was taken to dryness. The residue was extracted with petroleum ether and then centrifuged. Successive concentration and cooling to −20 °C afforded several crops of yellow-orange crystals of **6**. Yield: 0.26 g, 68%. **6** can also be synthesized using ^iPrMgCl instead of Li[$HBEt_3$] as a source of hydride, in similar yields. The deuterated compound [FeD(C_5H_5)(dippe)] was prepared using Li[$DBEt_3$] instead of Li[$HBEt_3$]. Anal. Calcd for $C_{19}H_{38}FeP_2$: C, 59.4; H, 9.89. Found: C, 59.0; H, 9.80. IR: ν(FeH) 1911 cm^{-1}; ν(FeD) 1384 cm^{-1}. NMR (C_6D_6), δ: ^1H −17.13 (t, J(H,P) = 71.3 Hz, FeH), 4.262 (s, FeC_5H_5); $^{31}P\{^1H\}$ 130.1 (s); $^{13}C\{^1H\}$ 18.73, 18.93, 19.11, 20.22 (s, $P(CH(CH_3)_2)_2$), 22.53 (t, J(C,P) = 17.5 Hz, PCH_2), 28.53 (t, J(C,P) = 14 Hz, $P(CH(CH_3)_2)_2$), 29.06 (t, J(C,P) = 6 Hz, $P(CH(CH_3)_2)_2$), 73.35 (s, C_5H_5).

[FeH(C_5Me_5)(dippe)] (7). It was obtained following a procedure identical to that for **6**, starting from **2** (0.5 g, *ca.* 1 mmol). As for **6**, ^iPrMgCl can also be used as a source of hydride. The deuterated compound [FeD(C_5Me_5)(dippe)] was prepared using Li[$DBEt_3$] instead of Li[$HBEt_3$]. Yield: 62%. Anal. Calcd for $C_{24}H_{48}FeP_2$: C, 63.4; H, 10.6. Found: C, 62.8; H, 10.3. IR: ν(FeH) 1901 cm^{-1}; ν(FeD) 1376 cm^{-1}. NMR (C_6D_6), δ: ^1H −17.38 (t, J(H,P) = 72.3 Hz, FeH), 1.933 (s, FeC_5-

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$(\mathrm{C}\mathit{H}_3)_5$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 119.3 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 13.42 (s, $\mathrm{FeC_5(}\mathit{C}\mathrm{H_3)_5}$), 17.76, 18.58, 19.80, 20.95 (s, $\mathrm{P(CH(}\mathit{C}\mathrm{H_3)_2)_2}$), 22.62 (t, J(C,P) = 18 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 25.51 (br, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 29.30 (t, J(C,P) = 14.7 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 83.76 (s, $\mathrm{Fe}\mathit{C}_5\mathrm{(CH_3)_5}$).

[FeH($\mathbf{C_5H_5}$)(dippe)][BPh$_4$] (8). To a solution of **6** (0.19 g, 0.5 mmol) in $\mathrm{CH_2Cl_2}$ (15 cm^3) was added $\mathrm{[Fe(C_5H_5)_2][PF_6]}$ (0.15 g, 0.45 mmol). The yellow solution turned orange. The solvent was removed *in vacuo*, and the residue was washed with two portions of petroleum ether, in order to remove ferrocene and unreacted **6**. The orange residue was then dissolved in ethanol, and solid Na[BPh$_4$] (0.2 g, excess) was added. The resulting orange solid was filtered, washed with ethanol and petroleum ether, and dried *in vacuo*. It was recrystallized from acetone/EtOH. The deuterated compound was obtained by starting from [FeD($\mathrm{C_5H_5}$)(dippe)]. Yield: 0.28 g, 89%. Anal. Calcd for $\mathrm{C_{43}H_{58}BFeP_2}$: C, 73.4; H, 8.25. Found: C, 73.2; H, 8.36%; IR: ν(FeH) 1939 cm^{-1}; ν(FeD) 1397 cm^{-1}. $\mu_{\mathrm{eff}} = 2.40$ μ_{B} (acetone-d_6, 293 K).

[FeH($\mathbf{C_5Me_5}$)(dippe)][BPh$_4$] (9). It was obtained following a procedure identical to that for **8**, starting from **7** (0.23 g, 0.5 mmol). Red crystals were obtained upon recrystallization from acetone/EtOH. The deuterated compound was obtained by starting from [FeD($\mathrm{C_5Me_5}$)(dippe)]. Yield: quantitative. Anal. Calcd for $\mathrm{C_{48}H_{68}BFeP_2}$: C, 74.5; H, 8.80. Found: C, 74.5; H, 8.91. IR: ν(FeH) 1915 cm^{-1}; ν(FeD) 1306 cm^{-1}. $\mu_{\mathrm{eff}} = 2.65\ \mu_{\mathrm{B}}$ (acetone-d_6, 293 K).

[FeH$_2$($\mathbf{C_5H_5}$)(dippe)][BPh$_4$] (10). Dihydrogen was bubbled through a solution of **1** (0.4 g, 1 mmol) in MeOH, until a pale yellow solution was obtained. Then, Na[BPh$_4$] (0.38 g, 1.1 mmol) in MeOH was added, and a yellow precipitate was formed. It was filtered, washed with ethanol and petroleum ether, and dried *in vacuo*. The compound was recrystallized from acetone/EtOH. Yield: 0.56 g, 79%. Anal. Calcd for $\mathrm{C_{43}H_{59}BFeP_2}$: C, 73.3; H, 8.38. Found: C, 72.9; H, 8.37. NMR (acetone-d_6), δ: ^{1}H −9.627 (t, J(H,P) = 61 Hz, $\mathrm{Fe}\mathit{H}_2$, T_1(400 MHz, 213 K) = 300 ms), 5.188 (s, $\mathrm{FeC_5}\mathit{H}_5$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 117.2 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 18.66, 19.06 (s, $\mathrm{P(CH(}\mathit{C}\mathrm{H_3)_2)_2}$), 22.22 (t, J(C,P) = 13.5 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 29.04 (t, J(C,P) = 13.1 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 81.64 (s, $\mathit{C}_5\mathrm{H_5}$).

[FeH$_2$($\mathbf{C_5Me_5}$)(dippe)][BPh$_4$] (11). An experimental procedure identical to that for **10** was followed for the preparation of this compound, starting from **2** (0.5 g, 1 mmol). Yield: 0.54 g, 70%. Anal. Calcd for $\mathrm{C_{48}H_{69}BFeP_2}$: C, 74.4; H, 8.92. Found: C, 74.5; H, 8.91. NMR (acetone-d_6), δ: ^{1}H −8.490 (t, J(H,P) = 66.6 Hz, $\mathrm{Fe}\mathit{H}_2$, T_1(400 MHz, 203 K) = 510 ms), 1.974 (s, $\mathrm{FeC_5(C}\mathit{H}_3)_5$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 108.5 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 11.84 (s, $\mathrm{FeC_5(}\mathit{C}\mathrm{H_3)_5}$), 18.70, 19.15 (s, $\mathrm{P(CH(}\mathit{C}\mathrm{H_3)_2)_2}$), 22.42 (t, J(C,P) = 18.8 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 27.64 (t, J(C,P) = 12.7 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 95.03 (s, $\mathrm{Fe}\mathit{C}_5\mathrm{(CH_3)_5}$).

[Fe=C=CHPh($\mathbf{C_5H_5}$)(dippe)][BPh$_4$] (12). To a solution of **1** (0.2 g, *ca.* 0.5 mmol) in thf was added another solution containing LiC≡CPh (made from phenylacetylene, 0.1 cm^3, and Li^{n}Bu, 0.32 cm^3 of a 1.6 M solution, 0.5 mmol) in thf. The purple color of the initial solution changed to brown and then red. The mixture was stirred at room temperature for 30 min. The solvent was removed *in vacuo*. The residue was extracted with diethyl ether and filtered through Celite. To the solution was added $\mathrm{HBF_4{\cdot}Et_2O}$ (0.1 cm^3, excess). The resulting oily mixture was taken to dryness, and the residue was dissolved in ethanol. Addition of solid Na[BPh$_4$] (0.2 g, 0.58 mmol) yielded a yellow-brown precipitate, which was filtered out, washed with ethanol and petroleum ether, and dried *in vacuo*. For the recrystallization, it was dissolved in the minimum amount of $\mathrm{CH_2Cl_2}$. Addition of ethanol and cooling to −20 °C afforded golden-brown plates of **12**. Yield: 0.35 g, 88%. Anal. Calcd for $\mathrm{C_{51}H_{63}BFeP_2}$: C, 76.1; H, 7.84. Found: C, 76.2; H, 7.89. IR: ν(C=C) 1616 cm^{-1}. NMR ($\mathrm{CDCl_3}$), δ: ^{1}H 5.833 (t, J(H,P) = 4.4 Hz, $\mathrm{Fe{=}C{=}C}\mathit{H}\mathrm{Ph}$), 4.971 (s, $\mathrm{FeC_5}\mathit{H}_5$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 104.6 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 19.31, 19.58, 19.64, 19.82 (s, $\mathrm{P(CH(}\mathit{C}\mathrm{H_3)_2)_2}$), 23.08 (t, J(C,P) = 18.3 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 31.07 (t, J(C,P) = 7.5 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 32.46 (t, J(C,P) = 14.1 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 129.1 (s, $\mathrm{Fe{=}C{=}}\mathit{C}\mathrm{HPh}$), 357.6 (t, J(C,P) = 31.2 Hz, $\mathrm{Fe{=}}\mathit{C}\mathrm{{=}CHPh}$), 86.7 (s, $\mathrm{Fe}\mathit{C}_5\mathrm{H_5}$).

Table 1. Summary of Data for the Crystal Structure Analysis of [FeH$_2$($\mathbf{C_5Me_5}$)(dippe)][BPh$_4$]

formula	$\mathrm{C_{48}H_{69}BFeP_2}$
fw	774.68
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cell params	
a (Å)	14.277(4)
b (Å)	21.388(6)
c (Å)	14.619(6)
β (deg)	101.07(3)
vol (Å^3)	4381(3)
Z	4
ϱ_{calcd} (g cm^{-3})	1.174
T (K)	290
λ(Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	4.447
F(000)	1672
scan speed (ω) (deg min^{-1})	16
2θ interval (deg)	$5 < 2\theta < 45$
no. of unique reflns	5958 ($R_{\mathrm{int}} = 0.117$)
no. of obsd reflns ($I > 3\sigma_I$)	3130
R	0.050
R_{w} ($w = \sigma_F^{-2}$)	0.058

[Fe=C=CHPh($\mathbf{C_5Me_5}$)(dippe)][BPh$_4$] (13). It was prepared by following an experimental procedure identical to that for **12**, starting from **2** (0.49 g, 1 mmol). The pure product was obtained upon recrystallization from thf/EtOH as brown crystals. Yield: 0.75 g, 85%. Anal. Calcd for $\mathrm{C_{56}H_{73}BFeP_2}$: C, 76.9; H, 8.35. Found: C, 76.6; H, 8.36. IR: ν(C=C) 1594 cm^{-1}. NMR ($\mathrm{CDCl_3}$), δ: ^{1}H 5.435 (t, J(H,P) = 5.8 Hz, $\mathrm{Fe{=}C{=}C}\mathit{H}\mathrm{Ph}$), 1.658 (s, $\mathrm{FeC_5(C}\mathit{H}_3)_5$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 89.9 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 11.1 (s, $\mathrm{FeC_5(}\mathit{C}\mathrm{H_3)_5}$), 18.89, 19.05, 20.20, 20.63 (s, $\mathrm{P(CH(}\mathit{C}\mathrm{H_3)_2)_2}$), 20.62 (t, J(C,P) = 17.5 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 24.93 (t, J(C,P) = 5.5 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 32.38 (t, J(C,P) = 14.2 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 99.6 (s, $\mathrm{Fe}\mathit{C}_5\mathrm{(CH_3)_5}$), 126.1 (s, $\mathrm{Fe{=}C{=}}\mathit{C}\mathrm{HPh}$), 352.4 (t, J(C,P) = 32 Hz, $\mathrm{Fe{=}}\mathit{C}\mathrm{{=}CHPh}$).

[Fe(C≡CPh)($\mathbf{C_5H_5}$)(dippe)] (14). **12** (0.4 g, 0.5 mmol) in thf was treated with an excess of solid KO^{t}Bu (0.1 g, 0.9 mmol). The solution turned red-orange. It was stirred at room temperature for 1 h. Then, the solvent was removed *in vacuo*. The residue was extracted with petroleum ether, and the red solution was filtered through Celite. Concentration and cooling to −20 °C afforded nice red crystals. Yield: 0.15 g, 63%. Anal. Calcd for $\mathrm{C_{27}H_{42}FeP_2}$: C, 66.9; H, 8.67. Found: C, 66.8; H, 8.70. IR: ν(C≡C) 2050 cm^{-1}; reinforced ν(C=C) in the phenyl ring 1579 cm^{-1}. NMR ($\mathrm{C_6D_6}$), δ: ^{1}H 4.232 (s, $\mathrm{FeC_5}\mathit{H}_5$), 6.640, 6.880, 7.141 (several multiplets, $\mathrm{FeC{\equiv}CC_6}\mathit{H}_5$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 111.1 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 19.64, 19.78, 19.98, 20.77 (s, $\mathrm{P(CH(}\mathit{C}\mathrm{H_3)_2)_2}$), 23.63 (t, J(C,P) = 18.3 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 28.41 (t, J(C,P) = 13 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 29.88 (t, J(C,P) = 6.5 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 126.9 (t, J(C,P) = 43 Hz, $\mathrm{Fe}\mathit{C}\mathrm{{\equiv}CPh}$), 131.4 (s, $\mathrm{FeC{\equiv}}\mathit{C}\mathrm{Ph}$), 76.6 (s, $\mathrm{Fe}\mathit{C}_5\mathrm{H_5}$).

[Fe(C≡CPh)($\mathbf{C_5Me_5}$)(dippe)] (15). This compound was obtained in a fashion analogous to that for **14**, by deprotonation of **13** using KO^{t}Bu. Yield: 73%. Anal. Calcd for $\mathrm{C_{32}H_{52}FeP_2}$: C, 69.3; H, 9.38. Found: C, 68.9; H, 9.49. IR: ν(C≡C) 2050 cm^{-1}; reinforced ν(C=C) in the phenyl ring 1587 cm^{-1}. NMR ($\mathrm{C_6D_6}$), δ: ^{1}H 1.490 (s, $\mathrm{FeC_5(C}\mathit{H}_3)_5$), 6.650, 6.900, 7.190 (several multiplets, $\mathrm{FeC{\equiv}CC_6}\mathit{H}_5$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 96.8 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 11.5 (s, $\mathrm{FeC_5(}\mathit{C}\mathrm{H_3)_5}$), 19.11, 19.64, 20.87, 21.81 (s, $\mathrm{P(CH(}\mathit{C}\mathrm{H_3)_2)_2}$), 19.59 (t, J(C,P) = 17.6 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 24.45 (br, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 27.17 (t, J(C,P) = 12.2 Hz, $\mathrm{P(}\mathit{C}\mathrm{H(CH_3)_2)_2}$), 86.1 (s, $\mathrm{Fe}\mathit{C}_5\mathrm{(CH_3)_5}$), 132.0 (s, $\mathrm{FeC{\equiv}}\mathit{C}\mathrm{Ph}$), $\mathrm{Fe}\mathit{C}\mathrm{{\equiv}CPh}$ not observed.

Experimental Data for the X-ray Crystal Structure Determination of 11. A summary of crystallographic data for compound **11** is given in Table 1. X-ray measurements were made on a prismatic orange crystal of approximate dimensions 0.35 × 0.35 × 0.55 mm. It was mounted onto a glass fiber, and transferred to an AFC6S-Rigaku automatic diffractometer, using Mo Kα graphite-monochromated radiation. Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the ω-scan method. Lorentz, polarization, and absorption (ψ-scan method, absorption correction factor in the range 0.92–1.00) corrections were applied. Decay was negligible during data collection (less than 0.7%). From 5958 unique reflections, a set of 3130 reflections with $I > 3\sigma(I)$ were used for structure resolution. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[13] software system and ORTEP[14] for plotting. The structure was solved by the Patterson method, and anisotropically refined by full-matrix least-squares methods for all nonhydrogen atoms. The two hydride atoms were located on a regular difference Fourier map at the final stages of refinement and allowed to refine in the last three cycles with thermal parameters fixed to 1.2 times the isotropic equivalent value for the Fe atom. The other hydrogen atoms were included at idealized positions and not refined. Refinement concluded with $R = 0.050$ and $R_w = 0.058$ ($w = \sigma_F^{-2}$). Maximum and minimum peaks in the final difference Fourier map were +0.39 and −0.32 e Å^{-3}. Atomic coordinates and selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Table 2. Atomic Fractional Coordinates for $[FeH_2(C_5Me_5)(dippe)][BPh_4]$

atom	*x*	*y*	*z*
Fe	0.18676(7)	0.05502(5)	0.25021(7)
P1	0.1893(1)	0.1428(1)	0.1700(1)
P2	0.0675(1)	0.0911(1)	0.3116(1)
C1	0.3124(5)	0.0107(4)	0.2223(5)
C2	0.3169(5)	0.0145(3)	0.3214(5)
C3	0.2376(5)	−0.0204(4)	0.3416(5)
C4	0.1853(6)	−0.0433(4)	0.2561(6)
C5	0.2311(5)	−0.0237(4)	0.1842(5)
C6	0.3906(6)	0.0308(5)	0.1735(7)
C7	0.3975(6)	0.0383(4)	0.3927(6)
C8	0.2203(6)	−0.0363(4)	0.4370(6)
C9	0.1064(7)	−0.0917(4)	0.2446(7)
C10	0.2041(7)	−0.0474(4)	0.0829(6)
C12	0.1138(5)	0.1978(3)	0.2175(5)
C21	0.0359(5)	0.1680(4)	0.2589(5)
C51	0.3073(5)	0.1843(4)	0.7902(4)
C52	0.2166(5)	0.1610(4)	0.7524(5)
C53	0.1342(6)	0.1958(5)	0.7536(6)
C54	0.1383(6)	0.2541(5)	0.7935(6)
C55	0.2254(7)	0.2792(4)	0.8302(6)
C56	0.3074(5)	0.2443(4)	0.8275(6)
C61	0.4904(5)	0.1653(3)	0.8761(5)
C62	0.5870(5)	0.1731(3)	0.8731(5)
C63	0.6566(5)	0.1874(3)	0.9522(7)
C64	0.6301(6)	0.1954(4)	1.0372(6)
C65	0.5375(6)	0.1879(4)	1.0435(5)
C66	0.4702(5)	0.1743(4)	0.9652(5)
C71	0.4395(5)	0.1632(3)	0.6858(5)
C72	0.3970(5)	0.2096(3)	0.6251(5)
C73	0.4261(6)	0.2237(4)	0.5410(5)
C74	0.5008(7)	0.1909(5)	0.5168(5)
C75	0.5430(6)	0.1445(4)	0.5748(6)
C76	0.5137(6)	0.1306(4)	0.6572(6)
C81	0.3850(5)	0.0705(3)	0.7893(5)
C82	0.3948(5)	0.0361(3)	0.8722(5)
C83	0.3749(5)	−0.0263(4)	0.8759(6)
C84	0.3455(6)	−0.0608(4)	0.7953(7)
C85	0.3354(6)	−0.0283(4)	0.7109(6)
C86	0.3550(5)	0.0350(4)	0.7081(5)
C100	0.3019(5)	0.1872(4)	0.1777(5)
C101	0.2900(6)	0.2489(4)	0.1215(6)
C102	0.3489(6)	0.2015(5)	0.2793(7)
C110	0.1405(5)	0.1448(4)	0.0422(5)
C111	0.0400(6)	0.1189(5)	0.0169(5)
C112	0.2060(7)	0.1127(5)	−0.0138(5)
C200	0.0903(5)	0.1050(3)	0.4401(4)
C201	0.0088(6)	0.1391(4)	0.4749(5)
C202	0.1845(6)	0.1394(4)	0.4745(5)
C220	−0.0533(5)	0.0552(4)	0.2908(5)
C221	−0.0882(5)	0.0361(4)	0.1875(6)
C222	−0.0618(6)	−0.0014(4)	0.3535(6)
B	0.4064(6)	0.1466(4)	0.7863(6)
H1	0.104(4)	0.050(3)	0.180(4)
H2	0.220(4)	0.103(3)	0.308(4)

Results and Discussion

The 14-electron, four-coordinate complex $[FeCl_2(dippe)]$, which is known to react with bulky alkylmagnesium reagents to yield paramagnetic monoalkyl species [FeRCl(dippe)] (R = mesityl or neopentyl),[15] reacts with LiC_5H_5 in thf yielding purple solutions from which a mixture of orange and purple crystals was obtained. These two materials were easily separated by chromatography on a silica gel column. The orange product, which was collected first, when the column was eluted with petroleum ether, was identified as ferrocene. The purple product was eluted with diethyl ether. Microanalysis indicated a formula $[FeCl(C_5H_5)(dippe)]$ (**1**) for this compound. In a similar fashion, the reaction of $[FeCl_2(dippe)]$ with LiC_5Me_5 in thf yielded dark blue crystals of $[FeCl(C_5Me_5)(dippe)]$ (**2**), as inferred from microanalysis. No decamethylferrocene was detected as a byproduct of this reaction. **1** and **2** are air-sensitive crystalline materials, soluble in nonpolar solvents. In these compounds, a pentahapto coordination of the rings rather than monohapto is expected, since an 18-electron configuration is achieved in this way. According to this, the ^{1}H NMR spectrum of **1** displays one singlet at 4.205 ppm attributable to the protons of the η^5-cyclopentadienyl ligand, apart from a series of overlapping multiplets due to the protons of the phosphine ligands. One sharp singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum, indicative of the equivalence of the phosphorus atoms. These spectral data are consistent with a "three-legged piano stool" structure for **1**, as has been found for other complexes of the type $[MCl(C_5H_5)L_2]$ and $[MCl(C_5Me_5)L_2]$ (M = Fe or Ru; L_2 = one diphosphine or two monodentate phosphine ligands).[10,16] Furthermore, the $^{13}C\{^1H\}$ NMR spectrum supports this structural assignment, and seven individual resonances for the carbon atoms of the phosphine ligand are observed. The resonances of the carbon atoms directly attached to phosphorus appear as virtually coupled triplets, whereas the resonance for the carbons of the cyclopentadienyl ligand appear as a singlet at 73.3 ppm. A similar pattern has been observed in the $^{13}C\{^1H\}$ NMR of related complexes such as $[RuCl(C_5H_5)(dcpe)]$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane).[16] Whereas the spectral properties of **1** are typical of diamagnetic species, complex **2** seems to behave differently. The ^{1}H NMR spectrum of **2** displays broadened signals. One of these signals, centered at 1.592 ppm is attributed to the methyl protons of the C_5Me_5 ligand. The $^{31}P\{^1H\}$ NMR spectrum of **2** at 293 K consists of one broad resonance centered at 89.8 ppm, with a half-width of 112 Hz. This signal shifts considerably as the temperature is raised, increasing its width. At 348 K, the signal merges into the baseline and the spectrum becomes featureless, whereas cooling at 293 K restores the initial

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[13] Molecular Structure Corporation. TEXSAN, Single-Crystal Structure Analysis Software, version 5.0, 1989.

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $[FeH_2(C_5Me_5)(dippe)][BPh_4]$

	Distances		
Fe—P1	2.219(2)	Fe—C4	2.105(8)
Fe—P2	2.211(2)	Fe—C5	2.099(8)
Fe—C1	2.137(7)	Fe—H1	1.41(5)
Fe—C2	2.132(7)	Fe—H2	1.35(6)
Fe—C3	2.130(7)		
	Angles		
C3—Fe—C4	39.0(3)	P1—Fe—C4	150.3(2)
C3—Fe—C5	65.5(3)	P1—Fe—C5	113.5(2)
C3—Fe—H1	123(2)	P1—Fe—H1	77(2)
C3—Fe—H2	98(2)	P1—Fe—H2	70(2)
C4—Fe—C5	39.0(3)	P2—Fe—C1	166.6(2)
C4—Fe—H1	87(2)	P2—Fe—C2	127.6(2)
C4—Fe—H2	137(2)	P2—Fe—C3	101.9(2)
C4—Fe—H1	84(2)	P2—Fe—C4	108.5(2)
C5—Fe—H2	142(2)	P2—Fe—C5	142.3(2)
H1—Fe—H2	131(3)	P2—Fe—H1	74(2)
P1—Fe—P2	90.67(8)	P2—Fe—H2	72(2)
P1—Fe—C1	100.1(2)	C1—Fe—C2	39.4(3)
P1—Fe—C2	120.1(2)	C1—Fe—C3	65.6(3)
P1—Fe—C3	159.1(2)	C1—Fe—C4	65.2(3)

spectrum. If the temperature is lowered, the broad resonance sharpens, and stabilizes its position at 87.2 ppm, with a half-width of 11 Hz, at 243 K. At this temperature, the sample is essentially diamagnetic ($\mu_{eff} < 0.5\ \mu_B$), but the magnetic moment increases up to 2.0 μ_B at 348 K. At higher temperatures there is a significant decomposition of the sample. Due to this particular behavior, good $^{13}C\{^1H\}$ NMR spectra could not be obtained. The temperature dependence of μ_{eff} for **2** in solution can be rationalized in terms of equilibria between diamagnetic and paramagnetic species. The temperature dependence of the chemical shift of the $^{31}P\{^1H\}$ signal, as well as the observed broadening/sharpening of the resonance, is explained in the same terms. A similar behavior has been observed for the complexes $[FeCl_2(depe)_2]$ (depe = 1,2-bis(diethylphosphino)ethane) and $[FeCl_2(dnppe)_2]$ (dnppe = 1,2-bis(di-*n*-propylphosphino)ethane).[17] For these compounds, the total or partial loss of one phosphine ligand seems to be the process responsible for the diamagnetic–paramagnetic equilibria, although it is not possible to assign structures to the paramagnetic species. In our case, the nature of the paramagnetic species also remains unclear. The opening of the phosphine chelate ring might give rise to 16-electron paramagnetic species of the type $[FeCl(C_5Me_5)(\eta^1\text{-dippe})]$, although a magnetic spin-state crossover, similar to that found in the complexes $[FeX_2(dppen)_2]$ (X = Cl, Br; dppen = 1,2-bis(diphenylphosphino)ethylene),[18] or even the presence of small amounts of Fe^{III} impurities which might give spin exchange with **2** in solution, are all possibilities that cannot be disregarded.

1 and **2** are good starting materials for the preparation of [FeXL(dippe)] (L = C_5H_5 or C_5Me_5; X = monoanionic ligand) derivatives by metathetical exchange. Alkyl complexes of the type $[Fe(R)CpL_2]$ (Cp = C_5H_5 or C_5Me_5; R = alkyl; L_2 = one diphosphine or two monodentate phosphine ligands) are among the most important class of half-sandwich phosphine derivatives.[6–8,10] They have been usually prepared by reaction of the corresponding halo complexes with Grignard reagents,[7,10] although photochemical displacement of CO by phosphine ligands in alkyl precursors such as $[Fe(CH_3)(C_5Me_5)(CO)_2]$ has also been used.[19] We have studied the alkylation reactions of **1** and **2** using Grignard reagents. **1** reacts with RMgCl (R = Me or CH_2SiMe_3), yielding the corresponding alkyls $[FeR(C_5H_5)(dippe)]$ (R = Me (**3**) or CH_2SiMe_3 (**4**)). **2** also reacts with MeMgCl to yield $[FeMe(C_5Me_5)(dippe)]$ (**5**). However, attempts to obtain $[FeCH_2SiMe_3(C_5Me_5)(dippe)]$ were unsuccessful due to decomposition. These alkyl complexes are deep red, air-sensitive crystalline solids, very soluble in nonpolar solvents. All their ^1H NMR spectra exhibit, apart from the C_5H_5 or C_5Me_5 and phosphine resonances, one typical high-field signal attributable to the protons on the carbon atom directly attached to iron. These signals appear as a triplet for **4**, or as broad unresolved resonances for **3** and **5**. The ^1H NMR spectrum of **4** also displays one singlet at 0.365 ppm due to the $Si(CH_3)_3$ protons. Consistent with this, the iron-bound carbon atom of the alkyl groups appears as a high-field triplet on the respective $^{13}C\{^1H\}$ NMR spectra of compounds **3**–**5**. The splitting pattern observed for these signals is obviously due to coupling to two equivalent phosphorus atoms. One singlet is present on the $^{31}P\{^1H\}$ NMR spectra of these compounds. The spectral data are consistent with a "three-legged piano stool" structure for the alkyl complexes, similar to that suggested for **1** and **2**. Attempts to produce acyl complexes by CO insertion into the iron–alkyl bond failed, although monohapto and dihapto acyl complexes of iron, with dippe have been previously obtained by reaction of the monoalkyl derivatives [FeRX(dippe)] (R = mesityl or neopentyl) with CO.[20]

The reaction of **1** and **2** with ^iPrMgCl did not produce the expected alkyl derivatives. Yellow or yellow-orange crystals were isolated from these reactions, which displayed one medium-strong band near 1900 cm^{-1} on their respective IR spectra, assigned to iron–hydride stretching. The presence of a hydride ligand in these complexes was confirmed by one high-field triplet on the ^1H NMR spectra. These spectral data, together with the microanalyses, are consistent with the formation of the monohydride complexes $[FeH(C_5H_5)(dippe)]$ (**6**) and $[FeH(C_5Me_5)(dippe)]$ (**7**), presumably through a β-elimination reaction from the corresponding alkyl complex. A similar behavior has been observed for both $[FeCl(C_5Me_5)(PMe_3)_2]$ and $[RuCl(C_5Me_5)(PMe_3)_2]$, which react with ^iPrMgCl to yield the corresponding monohydride complexes $[FeH(C_5Me_5)(PMe_3)_2]$[7] and $[RuH(C_5Me_5)(PMe_3)_2]$,[21] respectively. The hydrides **6** and **7** are also accessible from **1** and **2**, respectively, by reaction with $Li[HBEt_3]$. These neutral monohydrides react quantitatively with ferrocenium hexafluorophosphate in dichloromethane, affording orange or red solutions, from which the 17-electron iron hydride cations $[FeH(C_5H_5)(dippe)]^+$ and $[FeH(C_5Me_5)(dippe)]^+$ were isolated as $[PF_6]^-$ salts, and then more conveniently transformed into the corresponding tetraphenylborate salts $[FeH(C_5H_5)(dippe)][BPh_4]$ (**8**) and $[FeH(C_5Me_5)(dippe)][BPh_4]$ (**9**). The reaction of neutral 18-electron half-sandwich complexes with ferrocenium salts has been widely used

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for the preparation of 17-electron radical cations, which include halide, alkyl, and hydride complexes such as $[FeCl(C_5Me_5)(dppe)]^+$,[10] $[Fe(CH_3)(C_5Me_5)(dppe)]^+$,[10] and $[FeH(C_5Me_5)(dppe)]^+$,[22] as well as the Fe^{III} alkynyl derivatives. $[Fe(C{\equiv}CR)(C_5Me_5)(dppm)]^+$ (dppm = 1,1-bis(diphenylphosphino)methane).[23] Compounds **8** and **9** are paramagnetic, as expected for 17-electron radicals, having magnetic moments of 2.40 and 2.65 μ_B, respectively (Evans' method). These values are similar to those found in solution for other Fe^{III} half-sandwich phosphine complexes, i.e. $[FeH(C_5Me_5)(dppe)][PF_6]$ (2.40 μ_B)[22] or $[FeCH_3(C_5Me_5)(dppe)][PF_6]$ (2.39 μ_B),[10] and greater than the calculated value of 1.73 μ_B expected for a low-spin Fe^{III} cation. This has been attributed to the existence of an orbital contribution.[10] **8** and **9** exhibit bands on their IR spectra at 1939 and 1915 cm^{-1}, respectively, indicative of terminal hydride ligands, as demonstrated by deuterium-labeling. These materials are homologues of the recently reported and structurally characterized iron(III) hydride $[FeH(C_5Me_5)(dppe)][PF_6]$.[22] The X-ray crystal structure of $[FeH(C_5Me_5)(dppe)][PF_6]$ has shown a three-legged piano stool geometry for the iron(III) complex cation. This is also assumed to be the basic structure for our iron(III) hydrides **8** and **9**. The remarkable character of these materials is due to the fact that 17-electron metal hydrides, resulting from the oxidation of the corresponding 18-electron neutral complexes, are usually short-lived species, with several pathways of decomposition, as revealed by recent studies on the redox properties of the cyclopentadienylbis(phosphine)ruthenium hydride system.[24]

Following the work with iron hydrides, we became interested in the study of the interaction of dihydrogen with **1** and **2**. Thus, when dihydrogen was bubbled through a methanolic solution of **1** or **2**, yellow solutions were obtained, from which crystalline solids precipitated upon addition of solid $Na[BPh_4]$. Analytical data for these materials are consistent with the formulation as $[FeH_2(C_5H_5)(dippe)][BPh_4]$ (**10**) or $[FeH_2(C_5Me_5)(dippe)][BPh_4]$ (**11**), respectively. **10** and **11** are yellow crystalline materials, which darken with time even when stored under dinitrogen or argon. The IR spectra do not show bands clearly attributable to ν(FeH). However, the hydridic protons appear on the ^1H NMR spectra in acetone-d_6 as triplets centered at −9.627 and −8.490 ppm for **10** and **11**, respectively, due to coupling with two equivalent phosphorus atoms (one singlet is observed on the respective $^{31}P\{^1H\}$ NMR spectra). Partial decomposition to paramagnetic species is observed when the spectra are recorded in $CDCl_3$. These data suggest the equivalence of the hydride ligands and the two phosphorus atoms. The possibility of formulating **10** and/or **11** either as organoiron(IV) dihydrides, or iron(II) dihydrogen complexes must be taken into account. The large coupling constant J(H,P) seems to point to a dihydride rather than a dihydrogen structure, in which the signal for the dihydrogen protons usually appears as a broad, unresolved resonance. However, there are some reports in which coupling of the dihydrogen protons with phosphorus atoms has been detected,[25] and therefore no definitive conclusions about the nature of the hydrogen ligands in these complexes can be made, solely on the basis of the observed coupling with phosphorus. However, the T_1 (longitudinal relaxation time) measurements made for **10** and **11** support a "classical" dihydride estructure, since the minimum values for T_1 are 300 and 510 ms, respectively (400 MHz, acetone-d_6). According to these data, compounds **10** and **11** must have four-legged piano stool structures, but it still remains unclear whether the hydride ligands adopt a cisoid disposition (C_s symmetry) or a transoid disposition (C_{2v} symmetry). The $^{13}C\{^1H\}$ NMR spectra of **10** and **11** are simpler than those of the other complexes described in this work, consisting of only four signals for the phosphine carbon atoms apart from the resonances due to the C_5H_5 or C_5Me_5 ligands. This pattern indicates a change from the C_s symmetry of the three-legged piano stool structure of previous compounds to a C_{2v} symmetry.[16] In this symmetry, with two orthogonal mirror planes (assuming free rotation of the C_5H_5 or C_5Me_5 ligands), all four isopropyl groups are equivalent, giving rise to three separate resonances for the carbon atoms of the isopropyl groups plus one for the backbone carbon atoms of the ethane group. This is in support of a structure with a transoid disposition of hydride ligands. The X-ray crystal structure of **11** has been determined, confirming its formulation as a "classical" organoiron(IV) dihydride. A view of the cation $[FeH_2(C_5Me_5)(dippe)]^+$ is shown in Figure 1. The final atomic coordinates are given in Table 2, and selected bond lengths and angles are in Table 3. This crystal structure represents, as far as we are aware, the first structural report of an organoiron(IV) dihydride

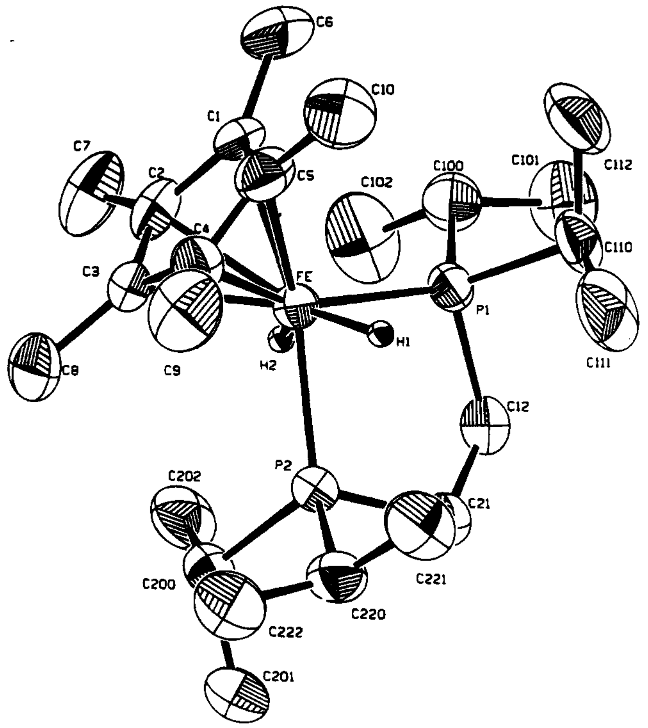

Figure 1. ORTEP drawing of the cation $[FeH_2(C_5Me_5)(dippe)]^+$. Hydrogen atoms, except hydrides, have been omitted.

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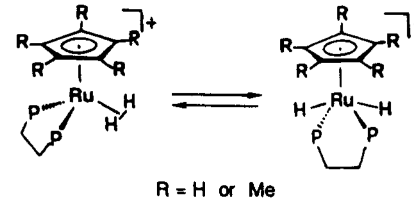
complex. The crystal structure of the related ruthenium(IV) dihydride $[RuH_2(\eta^5\text{-indenyl})(dppm)][BF_4]$ is known.[26] The coordination around iron can be described as a four-legged piano stool structure. The two hydride atoms are in transoid positions, with an H1—Fe—H2 angle of 131(3)°. The iron—hydride bond distances Fe—H1 1.41(5) Å and Fe—H2 1.35(6) Å are in the normal range previously observed in other iron hydride complexes.[4,22] The Fe—P separations (2.219(2) and 2.211(2) Å) are similar to those observed in the complex $[FeD(C_5Me_5)(dppe)][PF_6]$.[22] The C5 ring of the C_5Me_5 group is planar. As in the complex $[FeD(C_5Me_5)(dppe)]^+$, the plane defined by the C_5Me_5 centroid, the hydrides, and the iron atom is nearly normal to the C5 ring. All the other bond lengths and angles found in the ligands and tetraphenylborate anion are in the usual range.

Iron(IV) is relatively uncommon. This oxidation state is of relative importance in coordination compounds containing dithiocarbamate[27] and related ligands, such as dithiolenes,[28] although several organometallic complexes of Fe^{IV} are also known, i.e. $[Fe(norbornyl)_4]$[29] and $[FeH(C_5H_5)(SiCl_3)_2(CO)]$.[30] As far as iron polyhydrides are concerned, for a long time $[FeH_4(PEtPh_2)_2]$[31] was considered a rare example of an Fe^{IV} tetrahydride, but it is now known to be an Fe^{II} dihydride dihydrogen complex, as inferred from T_1 measurements[32] and structural studies by neutron diffraction.[33] The unstable trihydride complex $[FeH_3(C_5Me_5)(PMe_3)]$, which also contains Fe^{IV}, was obtained only in benzene or tetrahydrofuran solution, where it seems to exist as an equilibrium mixture with the Fe^{II} hydride dihydrogen complex $[FeH(H_2)(C_5Me_5)(PMe_3)]$.[7] While ruthenium dihydride or dihydrogen complexes of the type $[RuH_2(Cp)L_2]^+$ (Cp = C_5H_5 or C_5Me_5; L_2 = one diphosphine or two monodentate phosphine ligands) are relatively common,[34] the first stable organoiron(IV) dihydride has only been recently isolated and reported.[22] This was obtained by protonation of $[FeH(C_5Me_5)(dppe)]$ with HBF_4 in Et_2O at −80 °C. In this case, the dihydrogen complex $[Fe(C_5Me_5)(H_2)(dppe)]^+$ is formed first, and it rearranges irreversibly into the iron(IV) dihydride form as the temperature is raised. It is interesting to note that the homologue complex $[FeH_2(C_5Me_5)(dmpe)][BF_4]$, which was also obtained by protonation of the corresponding monohydride, was found to be extremely unstable in solution.[7] It has been found for ruthenium complexes that steric interactions between the phosphine ligands and the C_5H_5 or C_5Me_5 ring are very important in determining the position of the equilibria in eq 1. Thus, bulky phosphines and C_5Me_5 *versus* C_5H_5 favor the transoid dihydride form.[35] This is fully consistent with our results for the iron complexes **10** and **11**. Furthermore, the reduced size of iron compared to ruthenium makes these steric interactions even stronger. This fact, together with the strong electron-donating capabilities of the dippe ligand, which provides an electron-rich metal center at iron capable of homolytic splitting of dihydrogen, may explain why the corresponding dihydrogen complexes have never been detected in our case. For the analogous complex with the poorer σ-donor, but better π-acceptor, phosphine ligand dppe, the stabilization of coordinated dihydrogen is still possible, but only at low temperatures. The dihydrides **10** and **11** are quite stable toward reductive elimination of dihydrogen, and do not react with CO to give the corresponding $[Fe(C_5H_5)(CO)(dippe)]^+$ or $[Fe(C_5Me_5)(CO)(dippe)]^+$ derivatives. However, these and other cationic complexes containing neutral donor ligands, including dinitrogen, have been prepared by other methods and will be reported elsewhere.[36]



(1)

Alkynyl and vinylidene complexes are also among the most important half-sandwich bis(phosphine) derivatives of iron and ruthenium.[1,23,37] Attempts to prepare $[Fe(C{\equiv}CPh)(C_5H_5)(dippe)]$ and $[Fe(C{\equiv}CPh)(C_5Me_5)(dippe)]$ by direct reaction of **1** or **2** with $LiC{\equiv}CPh$ failed. Oily substances were obtained from such reactions. However, the reaction of these oils, which should contain the impure alkynyl complexes, with HBF_4, followed by treatment with $NaBPh_4$ in ethanol, yielded yellow-brown crystalline materials. These were characterized as the vinylidene complexes $[Fe{=}C{=}CHPh(C_5H_5)(dippe)][BPh_4]$ (**12**) and $[Fe{=}C{=}CHPh(C_5Me_5)(dippe)][BPh_4]$ (**13**), respectively, which are formed upon electrophilic attack of H^+ on the β-carbon of the corresponding σ-alkynyl complex present in the reaction mixture. The IR spectra of **12** and **13** display one strong band near 1600 cm^{-1}, assigned to ν(C=C) in the vinylidene ligand. The ^1H NMR spectra show the signal corresponding to the proton on the β-carbon of the vinylidene ligands, which appear as a triplet due to coupling with two equivalent phosphorus atoms. This pattern has also been observed for other transition metal phosphine−vinylidene complexes.[37,38] The most characteristic feature of $^{13}C\{^1H\}$ NMR spectra of vinylidene complexes is the extremely low-field resonance for the carbon atom of the vinylidene fragment directly attached to iron. For **12** and **13** these signals appear at 357.6 and 352.4 ppm, respectively, as triplets due to coupling with two phosphorus atoms. The signal for the β-carbon of the vinylidene appear as a singlet near 126 ppm for both compounds. The structure for **12** and **13** is expected to be a three-legged piano stool. Deprotonation of vinylidene complexes is an efficient method for the preparation of alkynyl derivatives.[1,23] Thus, **12**

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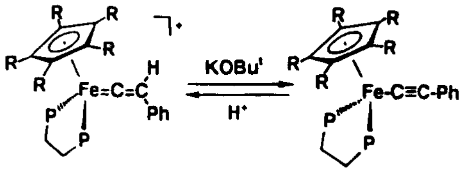
and **13** are cleanly deprotonated by KO^{t}Bu, affording red crystals of [Fe(C≡CPh)(C$_5$H$_5$)(dippe)] (**14**) and [Fe(C≡CPh)(C$_5$H$_5$)(dippe)] (**15**) respectively, according to eq 2. These materials exhibit one strong ν(C≡C) band at 2050 cm^{-1} on their respective IR spectra, as expected. The ^{1}H NMR spectra show signals in the aromatic region due to the protons in the phenyl ring of the alkynyl ligands, whereas the ^{31}P{^{1}H} NMR spectra consist of one singlet in both cases. The carbon atoms of the alkynyl ligands are difficult to observe on the ^{13}C{^{1}H} NMR spectra. The carbon atom of the alkynyl directly bound to iron appears as a triplet at 126.9 ppm for **14**, but it has not been detected in the case of **15**. One singlet near 132 ppm for both **14** and **15**, respectively, has been assigned to the β-carbon resonances. All attempts to isolate alkynyl or vinylidene complexes, derived from 1-alkynes other than phenylacetylene, such as HC≡CCOOMe or HC≡CSiMe$_3$, have been so far unsuccessful.



(2)

R = H or Me

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Supplementary Material Available: Tables of X-ray crystallographic data, including atomic coordinates, interatomic distances and angles, and anisotropic thermal parameters (27 pages). Ordering information is given on any current masthead page.

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