Organometallics **1995,** *14,* 3839−3847 3839

Stabilization of 16-Electron Paramagnetic Organoiron Species *versus* Coordination of Dinitrogen. X-ray Crystal Structures of [Fe(η^5-C_5H_5)(N_2)(dippe)][BPh_4], [Fe(η^5-C_5Me_5)(dippe)][BPh_4], and [Fe(η^5-C_5H_5)Cl(dippe)][BPh_4] (dippe = 1,2-Bis(diisopropylphosphino)ethane)

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Received February 27, 1995⊗

The purple compound [CpFeCl(dippe)] (Cp = C_5H_5; dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with dinitrogen and Na[BPh_4] in EtOH or MeOH, to furnish the novel half-sandwich end-on dinitrogen complex [CpFe(N_2)(dippe)][BPh_4] (**1**). This compound is diamagnetic and dissociates dinitrogen reversibly in thf or acetone solution, to yield the paramagnetic complex [CpFe(dippe)][BPh_4] (**2**). **1** and **2** are in equilibrium in acetone solution under dinitrogen. Thermodynamic parameters for such equilibrium have been estimated. The related complex [Cp*FeCl(dippe)] (Cp* = C_5Me_5) dissolves in MeOH or EtOH to yield only [Cp*Fe(dippe)]$^+$, and no dinitrogen uptake is observed. The X-ray crystal structure of [Cp*Fe(dippe)][BPh_4] (**3**) has been determined. The complexes **1**−**3** react with a variety of neutral donors L (L = CNBu^t, CO, MeCN) furnishing the corresponding adducts [CpFe(L)(dippe)][BPh_4] or [Cp*Fe(L)(dippe)][BPh_4], as expected. The insertion of $SnCl_2$ into the Fe−Cl bond only occurs in [FeCpCl(dippe)], yielding [CpFe($SnCl_3$)(dippe)]. Both [CpFeCl(dippe)] and [Cp*FeCl(dippe)] are readily oxidized by atmospheric oxygen in alcoholic solution to the corresponding Fe^{III} derivatives, [CpFeCl(dippe)]$^+$ and [Cp*FeCl(dippe)]$^+$, respectively. The X-ray crystal structure has been determined for [CpFeCl(dippe)][BPh_4].

Introduction

It is well established that iron plays an important role in biological[1] as well as in nonbiological[2] nitrogen fixation. Its relevance has been enhanced recently, following an X-ray structural determination of the molybdenum-containing component of the enzyme nitrogenase[3] and the discovery of a nitrogenase that contains iron but no molybdenum or vanadium.[1] Despite these facts, relatively few dinitrogen complexes of iron are known. With very few exceptions, those reported contain tertiary phosphine as coligands. The methods for the preparation include abstraction of loosely bound ligands, displacement of dihydrogen in adducts of the type Fe(η^2-H_2)L_n, direct addition of dinitrogen to a coordinatively unsaturated metal complex, and reduction of a suitable precursor complex under dinitrogen. Thus, sodium tetraphenylborate abstracts chloride from both *trans*-[FeHCl(depe)$_2$] and *trans*-[$FeCl_2$(dmpe)$_2$] (depe = 1,2-bis(diethylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane) to yield the corresponding adducts *trans*-[FeH(N_2)(depe)$_2$][BPh_4][4] and *trans*-[FeCl(N_2)(dmpe)$_2$][BPh_4].[5] The labile dihydrogen ligand in the complexes [FeH_2(H_2)($PEtPh_2$)$_3$] and [FeH(H_2)(dmpe)$_2$][BPh_4] is displaced by dinitrogen furnishing [FeH_2(N_2)($PEtPh_2$)$_3$][6] and *trans*-[FeH(N_2)(dmpe)$_2$][BPh_4],[7] respectively. The five-coordinate, coordinatively unsaturated hydrides [FeH(dppe)$_2$][BPh_4] and [FeH(pp$_3$)][BPh_4] (pp$_3$ = P($CH_2CH_2PPh_2$)$_3$) add dinitrogen yielding the hydrido dinitrogen complexes *trans*-[FeH(N_2)(dppe)$_2$][BPh_4][8] and *cis*-[FeH(N_2)(pp$_3$)][BPh_4].[9] More recently, it has been reported that the reduction of [$FeCl_2$(depe)$_2$] with sodium naphthalenide in tetrahydrofuran under dinitrogen affords the iron(0) dinitrogen complex [Fe(N_2)(depe)$_2$], which has been structurally characterized.[10] Besides these systems, there are some reports on the synthesis of half-sandwich bridging N_2 complexes of the type [{CpFe($R_2PCH_2CH_2PR_2$)}$_2$(μ-N_2)]$^{2+}$ (Cp = C_5H_5; R = Ph, Me).[11,12] These complexes are poorly characterized, and not much is known about their structure and properties. No half-

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⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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0276-7333/95/2314-3839$09.00/0

sandwich complex of iron containing a terminal $\mathrm{N_2}$ ligand is known. On the other hand, dinitrogen has shown in most cases to be unreactive toward direct protonation by acids, although there are some examples of dinitrogen reduction to ammonia and/or hydrazine mediated by dinitrogen complexes of iron.[7,13-15] Continuing our studies on the effects of bulky phosphine ligands on the binding and activation of small molecules, we have now shown that the complexes [CpFeCl(dippe)] and [Cp*FeCl(dippe)][16] have labile chloride ligands, which can be easily abstracted by $\mathrm{Na[BPh_4]}$ in alcoholic solution to yield paramagnetic, coordinatively unsaturated species. In the case of the Cp derivative, this species reacts further with dinitrogen yielding the end-on dinitrogen complex $\mathrm{[CpFe(N_2)(dippe)][BPh_4]}$. In this work we describe the synthesis, characterization, and reactivity of such compounds, including the structural aspects as well as the study of their behavior in solution.

Experimental Section

All synthetic operations were performed under a dry dinitrogen atmosphere following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40−60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane,[17] $\mathrm{[Fe(C_5H_5)Cl(dippe)]}$,[16] and $\mathrm{[Fe(C_5Me_5)Cl(dippe)]}$[16] were prepared according to the literature. 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 $\mathrm{SiMe_4}$ ($^1\mathrm{H}$ and $^{13}\mathrm{C}\{^1\mathrm{H}\}$), 85% $\mathrm{H_3PO_4}$ ($^{31}\mathrm{P}\{^1\mathrm{H}\}$), or $\mathrm{Sn^nBu_4}$ ($^{119}\mathrm{Sn}$). Magnetic moments were measured in solution using the Evans method.[18] Microanalyses were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía or by Butterworth Laboratories, Middlesex, U.K.

$\mathbf{[Fe(C_5H_5)(N_2)(dippe)][BPh_4]}$ (1). To a solution of $\mathrm{[FeCl(C_5H_5)(dippe)]}$ (0.2 g, *ca.* 0.5 mmol) in MeOH (20 mL) under dinitrogen, an excess of $\mathrm{Na[BPh_4]}$ (0.34 g, 1 mmol) dissolved in MeOH (10 mL) was added. The resulting mixture was stirred at room temperature for 1 h. During this time, a mustard-yellow precipitate is formed. It was filtered out, washed with ethanol and petroleum ether, and dried *in vacuo*. This product was recrystallized from THF/ethanol as amber-brown crystals suitable for X-ray diffraction. Yield: 0.21 g, 58%. Anal. Calcd for $\mathrm{C_{43}H_{57}N_2BFeP_2}$: C, 70.06; H, 7.80; N, 3.83. Found: C, 70.1; H, 7.58; N, 3.4. IR: $\nu(\mathrm{N{\equiv}N})$ 2112 $\mathrm{cm^{-1}}$. NMR: $^1\mathrm{H}$ (acetone-d_6), δ 5.061 (s, $\mathrm{C_5\mathit{H}_5}$)); $^{31}\mathrm{P}\{^1\mathrm{H}\}$, 98.37 (s). This compound coexists in acetone solution under dinitrogen with paramagnetic $\mathrm{[Fe(C_5H_5)(dippe)_2][BPh_4]}$ (**2**) as an equilibrium mixture.

$\mathbf{[Fe(C_5H_5)(dippe)][BPh_4]}$ (2). This compound can be obtained by following a procedure analogous to that for **1**, using an argon atmosphere instead of dinitrogen, although in rather poor yield (25%). The following method has shown to be more efficient: $\mathrm{[Fe(C_5H_5)(N_2)(dippe)][BPh_4]}$ (**1**) (0.36 g, *ca.* 0.5 mmol) was dissolved in acetone (20 mL) under argon. An effervescence was observed, corresponding to the evolution of dinitrogen. Once the effervescence ceased, the mixture was stirred under argon at room temperature for 10 min. Then, the solution was concentrated to *ca.* 3−4 mL. Addition of petroleum ether afforded a brown precipitate, which was filtered out, washed with petroleum ether, and dried *in vacuo*. Yield: quantitative. Anal. Calcd for $\mathrm{C_{43}H_{57}BFeP_2}$: C, 73.5; H, 8.12. Found: C, 73.3; H, 8.26. μ_{eff} 3.6 μ_{B} (acetone-d_6, 293 K). NMR (acetone-d_6): $^1\mathrm{H}$, δ −37.2, −8.1, −0.8, 3.21, 17.3, 38.0 ppm.

$\mathbf{[Fe(C_5Me_5)(dippe)][BPh_4]}$ (3). A solution of $\mathrm{[FeCl(C_5Me_5)(dippe)]}$ (0.49 g, 1 mmol) in deoxygenated MeOH (20 mL) under dinitrogen or argon was treated with an excess of $\mathrm{Na[BPh_4]}$ (0.5 g) in MeOH (10 mL). A yellow-brown crystalline precipitate was immediately formed. The mixture was stirred for 15 min. Then, it was filtered out, washed with ethanol and petroleum ether, and dried *in vacuo*. It was recrystallized from hot acetone or an acetone/EtOH mixture. Yield: 0.46 g, 60%. Anal. Calcd for $\mathrm{C_{48}H_{67}BFeP_2}$: C, 72.7; H, 8.46. Found: C, 72.4; H, 8.31. μ_{eff} 3.8 μ_{B} (acetone-d_6, 293 K). NMR (acetone-d_6): $^1\mathrm{H}$, δ −42.60, −14.32, 3.80, 6.94, 7.47, 48.85.

$\mathbf{[Fe(C_5H_5)(CNBu^t)(dippe)][BPh_4]}$ (4). To a solution of $\mathrm{[Fe(C_5H_5)Cl(dippe)]}$ (0.2 g, *ca.* 0.5 mmol) in MeOH (20 mL) a slight excess of $\mathrm{CNBu^t}$ (0.2 mL) was added. The purple solution changed immediately to yellow. It was stirred for 15 min at room temperature. Then $\mathrm{Na[BPh_4]}$ (0.34 g) dissolved in ethanol (10 mL) was added. A yellow, crystalline precipitate was obtained. It was filtered out, washed with ethanol and petroleum ether, and dried *in vacuo*. The product was recrystallized from acetone/EtOH. Yield: 0.27 g 69%. This product can also be obtained by treatment of acetone solutions of **1** or **2** with $\mathrm{CNBu^t}$, followed by addition of EtOH, concentration, and cooling to −20 °C. Anal. Calcd for $\mathrm{C_{48}H_{66}BFeNP_2}$: C, 73.4; H, 8.41; N, 1.8. Found: C, 72.8; H, 8.75; N, 1.8. IR: $\nu(\mathrm{C{\equiv}N})$ 2084 $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$, δ 1.489 (s, $\mathrm{CNC(C\mathit{H}_3)_3}$), 4.861 (t, $J(\mathrm{H,P}) = 1.2$ Hz, $\mathrm{C_5\mathit{H}_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$, 108.55 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$, 19.168, 19.355, 19.440, 19.746 (s, $\mathrm{P(CH(\mathit{C}H_3)_2)_2}$), 23.554 (t, $J(\mathrm{C,P}) = 18.0$ Hz, $\mathrm{P\mathit{C}H_2}$), 29.079 (t, $J(\mathrm{C,P}) = 12.8$ Hz, $\mathrm{P(\mathit{C}H(CH_3)_2)_2}$), 29.674 (t, $J(\mathrm{C,P}) = 9.2$ Hz, $\mathrm{P(\mathit{C}H(CH_3)_2)_2}$), 30.592 (s, $\mathrm{C(\mathit{C}H_3)_3}$), 58.556 (s, $\mathrm{\mathit{C}(CH_3)_3}$), 78.377 (s, $\mathrm{\mathit{C}_5H_5}$), 164.853 (t, $J(\mathrm{C,P}) = 16.2$ Hz, $\mathrm{\mathit{C}NBu^t}$).

$\mathbf{[Fe(C_5Me_5)(CNBu^t)(dippe)][BPh_4]}$ (5). This compound was obtained in a fashion analogous to that for **4**, starting from either [Cp*FeCl(dippe)] in MeOH or compound **3** in acetone. Yield: 74%. Anal. Calcd for $\mathrm{C_{53}H_{76}BFeNP_2}$: C, 74.4; H, 8.90; N, 1.6. Found: C, 75.4; H, 9.13; N, 1.42. IR: $\nu(\mathrm{C{\equiv}N})$ 2087 $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$, δ 1.537 (s, $\mathrm{CNC(C\mathit{H}_3)_3}$), 2.052 (s, $\mathrm{C_5\mathit{Me}_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$, 91.22 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$, 10.652 (s, $\mathrm{C_5(\mathit{C}H_3)_5}$), 18.837, 18.845, 19.644, 20.766 (s, $\mathrm{P(CH(\mathit{C}H_3)_2)_2}$), 19.049 (t, $J(\mathrm{C,P}) = 19.9$ Hz, $\mathrm{P\mathit{C}H_2}$), 24.506 (t, $J(\mathrm{C,P}) = 6.6$ Hz, $\mathrm{P(\mathit{C}H(CH_3)_2)_2}$), 27.719 (t, $J(\mathrm{C,P}) = 12.7$ Hz, $\mathrm{P(\mathit{C}H(CH_3)_2)_2}$), 30.049 (s, $\mathrm{C(\mathit{C}H_3)_3}$), 57.57 (s, $\mathrm{\mathit{C}(CH_3)_3}$), 89.77 (s, $\mathrm{\mathit{C}_5Me_5}$), 170.23 (m, $\mathrm{\mathit{C}NBu^t}$).

$\mathbf{[Fe(C_5H_5)(CO)(dippe)][BPh_4]}$ (6). CO was bubbled through a solution of [CpFeCl(dippe)] (0.2 g, *ca.* 0.5 mmol) in EtOH (20 mL). The solution changed its color from purple to yellow. An excess of $\mathrm{Na[BPh_4]}$ (0.34 g) dissolved in EtOH (10 mL) was added, producing a yellow crystalline precipitate. It was filtered out, washed with EtOH and petroleum ether, and dried *in vacuo*. Yellow crystals were obtained upon recrystallization from acetone/EtOH. Yield: 0.28 g, 77%. Anal. Calcd for $\mathrm{C_{44}H_{57}BFeOP_2}$: C, 72.3; H, 7.81. Found: C, 72.6; H, 7.88. IR: $\nu(\mathrm{C{\equiv}O})$ 1943 $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$, δ 5.29 (s, $\mathrm{C_5\mathit{H}_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$, 106.5 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$, 18.406, 18.500, 18.727, 19.176 (s, $\mathrm{P(CH(\mathit{C}H_3)_2)_2}$), 22.613 (t, $J(\mathrm{C,P}) = 18.4$ Hz, $\mathrm{P\mathit{C}H_2}$), 28.151 (t, $J(\mathrm{C,P}) = 14.0$ Hz, $\mathrm{P(CH(\mathit{C}H_3)_2)_2}$), 29.176 (t, $J(\mathrm{C,P}) = 9.0$ Hz, $\mathrm{P(CH(\mathit{C}H_3)_2)_2}$), 83.118 (s, $\mathrm{\mathit{C}_5H_5}$), 215.951 (t, $J(\mathrm{C,P}) = 25.4$ Hz, $\mathit{C}\mathrm{O}$).

$\mathbf{[Fe(C_5Me_5)(CO)(dippe)][BPh_4]}$ (7). This compound was obtained in a fashion analogous to that for **6**, starting from

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either [Cp*FeCl(dippe)] in MeOH or compound **3** in acetone. Yield: 69%. Anal. Calcd for $C_{49}H_{67}BFeOP_2$: C, 73.0; H, 8.48. Found: C, 73.2; H, 8.60. IR: $\nu(C{\equiv}O)$ 1928 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 2.040 (t, J = 2 Hz, C_5Me_5); $^{31}P\{^1H\}$, 90.05 (s); $^{13}C\{^1H\}$, 18.306, 18.500, 18.657, 19.479 (s, $P(CH(CH_3)_2)_2$), 21.764 (t, $J(C,P)$ = 16.6 Hz, PCH_2), 28.455 (t, $J(C,P)$ = 15.4 Hz, $P(CH(CH_3)_2)_2$), 29.176 (t, $J(C,P)$ = 8.5 Hz, $P(CH(CH_3)_2)_2$), 89.708 (s, C_5H_5) (the signal corresponding to *C*O is not observed).

[Fe(C_5H_5)(MeCN)(dippe)][BPh_4] (8). To a solution of [CpFeCl(dippe)] (0.2 g, *ca.* 0.5 mmol) in 20 mL of methanol was added an excess of MeCN (2 mL). The color changed from purple to deep red. The solution was stirred for 15 min at room temperature. Then, the addition of an excess of Na[BPh_4] dissolved in 10 mL of MeOH produced a crystalline, red precipitate, which was filtered out, washed with ethanol and diethyl ether, and dried *in vacuo*. This compound was recrystallized from acetone/EtOH. Yield: 0.28 g, 76%. Anal. Calcd for $C_{45}H_{60}BFeNP_2$: C, 72.7; H, 8.08; N, 1.88. Found: C, 72.3; H, 8.20; N, 1.6. IR: $\nu(C{\equiv}N)$ 2256 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 2.278 (s, CH_3CN), 4.597 (t, C_5H_5, $J(P,H)$ = 1.2 Hz); $^{31}P\{^1H\}$, 101.3 (s); $^{13}C\{^1H\}$, 3.77 (s, CH_3CN), 19.219, 19.508, 19.916 (s, $P(CH(CH_3)_2)_2$), 22.823 (t, $J(C,P)$ = 17.3 Hz, PCH_2), 26.784 (t, $J(C,P)$ = 9.9 Hz, $P(CH(CH_3)_2)_2$), 28.722 (t, $J(C,P)$ = 9.9 Hz, $P(CH(CH_3)_2)_2$), 75.79 (s, C_5H_5), 134.8 (s, MeCN).

[Fe(C_5Me_5)(MeCN)(dippe)][BPh_4] (9). To a solution of **3** (0.39 g, *ca.* 0.5 mmol) in 20 mL of acetone, MeCN (2 mL) was added, and the mixture was stirred for 15 min at room temperature. A red solution was obtained. EtOH (15 mL) was added. Concentration and cooling to −20 °C afforded red crystals, which were filtered out, washed with petroleum ether, and dried *in vacuo*. Yield: 0.26 g, 65%. Anal. Calcd for $C_{50}H_{70}BFeNP_2$: C, 73.8; H, 8.61; N, 1.72. Found: C, 73.7; H, 8.63; N, 1.5. IR: $\nu(C{\equiv}N)$ 2238 cm^{-1}. This product is paramagnetic. μ_{eff} 4.0 μ_B.

[Fe(C_5H_5)(P(OPh)$_3$)(dippe)][BPh_4] (10). To a solution of [CpFeCl(dippe)] (0.2 g, *ca.* 0.5 mmol) in 20 mL of MeOH an excess of $P(OPh)_3$ (3 mL) was added. A yellow-brown solution was obtained. The mixture was stirred for 15 min at room temperature. Then, an excess of Na[BPh_4] (0.34 g) in 10 mL of MeOH was added, and a yellow precipitate was obtained. The precipitate was fitered out, washed with EtOH and diethyl ether, and dried *in vacuo*. The product was recrystallized from acetone/EtOH. Yield: 0.37 g, 73%. Anal. Calcd for $C_{61}H_{72}BFeO_3P_3$: C, 72.3; H, 7.11. Found: C, 73.2; H, 7.46. NMR ($CDCl_3$): ^1H, δ 4.838 (s C_5H_5), 7.025, 7.126, 7.232 (m, $P(OC_6H_5)_3$); $^{31}P\{^1H\}$, AX_2 spin system, 158.9 (t, P_A), 103.9 (d, P_X, $J(P_A,P_X)$ = 81.8 Hz); $^{13}C\{^1H\}$, 20.273, 20.426 (s br, $P(CH(CH_3)_2)_2$), 21.803 (dt, $J(C,P_X)$ = 18.6 Hz, $J(C,P_A)$ = 2.3 Hz, PCH_2), 32.513 (dt, $J(C,P_X)$ = 8.2 Hz, $J(C,P_A)$ = 3.7 Hz, $P(CH(CH_3)_2)_2$), 34.111 (dt, $J(C,P_X)$ = 12.2 Hz, $J(C,P_A)$ = 3.7 Hz, $P(CH(CH_3)_2)_2$), 76.58 (s, C_5H_5), 121.076 (d, $J(C,P)$ = 3.6 Hz, $P(OC_6H_5)_3$), 130.123 (s, $P(OC_6H_5)_3$), 151.87 (d, $J(C,P)$ = 17.1 Hz, $P(OC_6H_5)_3$).

[Fe(C_5H_5)($SnCl_3$)(dippe)] (11). To a solution of [CpFeCl(dippe)] (0.2 g, *ca.* 0.5 mmol) in 20 mL of dichloromethane, a slight excess of solid anhydrous $SnCl_2$ (0.4 g) was added. The mixture was stirred overnight at room temperature. A magenta solution was obtained. The solution was filtered, in order to remove unreacted $SnCl_2$. The filtered solution was concentrated to a small volume (*ca.* 2 mL). Addition of petroleum ether (15 mL) produced a microcrystalline precipitate, which was filtered out, washed with petroleum ether, and dried *in vacuo*. Yield: 0.19 g, 64%. Anal. Calcd for $C_{19}H_{37}Cl_3FeP_2Sn$: C, 37.5; H, 6.08. Found: C, 37.7; H, 5.95. NMR ($CDCl_3$): ^1H, δ 4.616 (t, $J(H,P)$ = 1.6 Hz, C_5H_5); $^{31}P\{^1H\}$, 101.0 (s, with $^{119}Sn/^{117}Sn$ satellites, $J(P,^{119}Sn)$ = 565 Hz, $J(P,^{117}Sn)$ = 540 Hz); $^{13}C\{^1H\}$, 19.540, 19.650, 19.727, 20.17 (s, $P(CH(CH_3)_2)_2$), 23.130 (t, $J(C,P)$ = 19.4 Hz, PCH_2), 29.491 (t, $J(C,P)$ = 11.0 Hz, $P(CH(CH_3)_2)_2$), 32.106 (t, $J(C,P)$ =15.0 Hz, $P(CH(CH_3)_2)_2$), 75.11 (s, C_5H_5); ^{119}Sn, 48.7 (t, $J(^{119}Sn,P)$ = 565 Hz, reference Sn^nBu_4).

[FeCl(C_5H_5)(dippe)][BPh_4] (12). A solution of [CpFeCl(dippe)] (0.2 g, *ca.* 0.5 mmol) in 20 mL of MeOH was stirred in the air for 15 min at room temperature. The solution changed its color to dark red. Addition of an excess of Na[BPh_4] (0.34 g) in 10 mL of MeOH afforded a dark red, crystalline precipitate. It was filtered out, washed with EtOH and petroleum ether, and dried *in vacuo*. The product was recrystallized from a mixture dichloromethane/ethanol. Yield: 0.25 g, 67%. Anal. Calcd for $C_{43}H_{57}BClFeP_2$: C, 70.0; H, 7.73. Found: C, 70.2; H, 7.52. μ_{eff} 2.4 μ_B.

[FeCl(C_5Me_5)(dippe)][BPh_4] (15). This compound was obtained in the form of brown crystals, by following a procedure identical to that outlined above for compound **14**, starting from [FeCp*Cl(dippe)] in MeOH. Yield: 64%. Anal. Calcd for $C_{48}H_{67}BClFeP_2$: C, 71.3; H, 8.30. Found: C, 71.5; H, 8.47. μ_{eff} 2.3 μ_B.

Experimental Determination of K_{eq}, for the Equilibrium between [CpFe(N_2)(dippe)]$^+$ and [CpFe(dippe)]$^+$, and of Its Dependence with Temperature. K_{eq} was determined by following the procedure outlined in ref 18b, by measuring the effective magnetic moment μ_{eff} for an acetone-d_6 solution of **1** of known concentration under dinitrogen. In such solution, μ_{eff} range from zero (if only [CpFe(N_2)(dippe)]$^+$ is present) to 3.6 μ_B (if only [CpFe(dippe)]$^+$ is present). Intermediate values of the magnetic moment indicate a mixture of [CpFe(N)$_2$(dippe)]$^+$ and [CpFe(dippe)]$^+$. The percentage of diamagnetic dinitrogen complex present can be calculated from the solution μ_{eff} and the value of 3.6 μ_B for pure [CpFe(dippe)]$^+$, according to the equation

$$\%\ \text{diamagnetic species} = 100 \times [1 - (\mu_{eff}/3.6)^2]$$

The equilibrium constant for the process is

$$K_{eq} = \frac{\%\ \text{paramagnetic}}{\%\ \text{diamagnetic}}$$

The concentration of N_2 in solution is assumed to be constant (equal to the solubility of N_2 in acetone), since the experiment was conducted under a dinitrogen atmosphere in a N_2-saturated solvent. For this reason, it is included in the value of the calculated K_{eq}. By measurement of μ_{eff} for the solution at different temperatures, the corresponding values of K_{eq} can be determined. A plot of ln K_{eq} *versus* $1/T$ allowed the calculation of ΔH° and ΔS° for the process.

Experimental Data for the X-ray Crystal Structure Determinations. A summary of crystallographic data for compounds **1**, **3**, and **12** is given in Table 1. X-ray measurements were made on crystals of the appropriate size, which were 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) corrections were applied. Decay was negligible during data collection for compound **3**, but deterioration corrections were applied in the case of compounds **1** (7.20%) and **12** (0.90%). Reflections having $I > 3\sigma(I)$ 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[19] software system and ORTEP[20] for plotting. All the structures were solved by the Patterson method and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. Hydrogen atoms were included at idealized positions and not refined. Maximum and minimum peaks in the final difference Fourier maps were +0.87 and −0.78 e Å^{-3}

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(19) *TEXSAN: Single-Crystal Structure Analysis Software*, version 5.0; Molecular Structure Corp.: The Woodlands, TX, 1989.

(20) Johnson, C. K. *ORTEP, A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table 1. Summary of Data for the Crystal Structure Analyses of 1, 3, and 12

compd	**1**	**3**	**12**
formula	$C_{43}H_{57}BFeN_2P_2$	$C_{48}H_{67}BFeP_2$	$C_{43}H_{57}BClFeP_2$
fw	730.54	772.66	737.98
cryst size (mm)	0.29 × 0.17 × 0.34	0.30 × 0.35 × 0.15	0.15 × 0.20 × 0.25
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
cell params	$a = 15.180(6)$ Å	$a = 14.378(9)$ Å	$a = 15.202(8)$ Å
	$b = 12.791(4)$ Å	$b = 21.374(6)$ Å	$b = 12.858(5)$ Å
	$c = 20.582(4)$ Å	$c = 14.481(9)$ Å	$c = 20.290(4)$ Å
	$\beta = 92.30(2)°$	$\beta = 100.84(5)°$	$\beta = 92.90(2)°$
V	3993(2) Å^3	4371(7) Å^3	3961(3) Å^3
Z	4	4	4
ϱ_{calcd}	1.215 g cm^{-3}	1.174 g cm^{-3}	1.240 g cm^{-3}
T	290 K	290 K	290 K
λ(Mo Kα)	0.710 69 Å	0.710 69 Å	0.716 09 Å
μ(Mo Kα)	4.86 cm^{-1}	4.45 cm^{-1}	5.60 cm^{-1}
F(000)	1560	1664	1572
scan speed (ω)	4° min^{-1}	16° min^{-1}	16° min^{-1}
2θ interval	$5° < 2\theta < 45°$	$5° < 2\theta < 45°$	$5° < 2\theta < 45°$
unique reflcns	5540 ($R_{int} = 0.166$)	5938 ($R_{int} = 0.162$)	5486 ($R_{int} = 0.289$)
obsd reflcns ($I > 3\sigma_I$)	2121	3069	1995
R^a	0.074	0.052	0.060
R_w ($w = \sigma_F^{-2}$)^b	0.074	0.061	0.069
gof	2.15	1.82	1.89

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

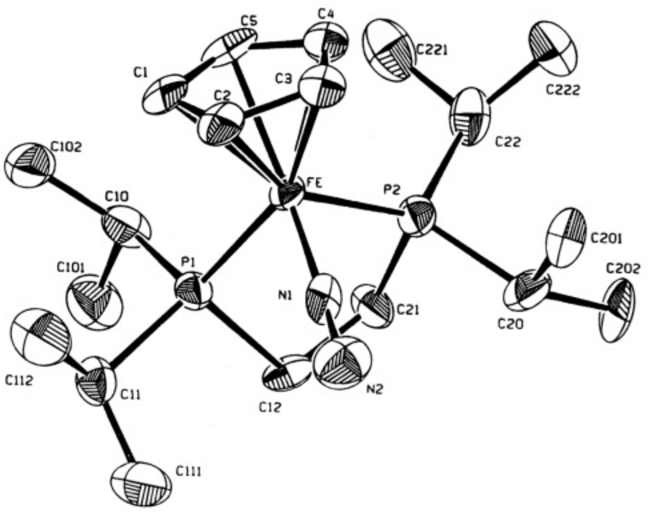

Figure 1. ORTEP drawing of the cation $[CpFe(N_2)(dippe)]^+$. Hydrogen atoms are omitted.

for **1**, +0.50 and −0.61 e Å^{-3} for **3**, and +0.92 and −0.40 e Å^{-3} for **12**. Atomic coordinates and selected bond lengths and angles for each compound are listed in Tables 2−7.

Results and Discussion

The purple compound [CpFeCl(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane)[16] reacts with dinitrogen and Na[BPh$_4$], in ethanol or methanol, to furnish the novel half-sandwich, end-on dinitrogen complex $[CpFe(N_2)(dippe)][BPh_4]$ (**1**) (eq 1) as a mustard-yellow

$$[CpFeCl(dippe)] + Na[BPh_4] \xrightarrow[-NaCl]{N_2} [CpFe(N_2)(dippe)][BPh_4] \quad (1)$$

crystalline material, in 70−80% yield. **1** exhibits one strong $\nu(N_2)$ band at 2112 cm^{-1} in the IR spectrum, i.e. in the range observed for other iron−dinitrogen complexes. The X-ray crystal structure of **1** has been determined; a view of the cationic complex is displayed in Figure 1. Final atomic coordinates are given in Table 2, and selected bond lengths and angles are in Table 3. It shows a "three-legged piano stool" structure, analogous to that found for other complexes that contain the cyclopentadienyl bis(phosphine) auxiliary fragments. The dinitrogen ligand is bound in the end-on manner, with a Fe−N(1)−N(2) angle of 173(1)°. The Fe−N(1) distance of 1.76(1) Å is similar to that in $[FeH_2(N_2)(PEtPh_2)_3]$ (1.786(7) Å).[6b] The N−N separation of 1.13(1) Å is longer than the corresponding for the free N_2 molecule (1.098 Å), as expected, and fully comparable with the values reported for other iron−dinitrogen complexes such as $[FeH(N_2)(dmpe)_2][BPh_4]$ (1.13(3) Å),[7] $[FeH_2(N_2)(PEtPh_2)_3]$ (1.136(7) Å),[6b] and $[Fe(N_2)(depe)_2]$ (1.139(13) Å).[10] The Fe−P separations are similar, although slightly longer than those observed in other half-sandwich iron−phosphine complexes. The cyclopentadienyl ligand is planar and pentahapto bonded. Compound **1** is diamagnetic, air stable in the solid state, and does not lose N_2 by pumping *in vacuo*. However, it is very labile in thf or acetone solution, where it dissociates dinitrogen reversibly, according to eq 2.

$$\underset{\mathbf{1}}{[CpFe(N_2)(dippe)]^+} \rightleftarrows \underset{\mathbf{2}}{[CpFe(dippe)]^+} + N_2 \quad (2)$$

Under argon, complex **1** is completely dissociated to the paramagnetic, 16-electron complex $[CpFe(dippe)][BPh_4]$ (**2**), which can be isolated upon concentration and precipitation with petroleum ether. **2** has an effective magnetic moment of 3.6 μ_B in acetone solution (Evans' method), corresponding to an intermediate-spin d^6 electronic configuration with two unpaired electrons, although greater than the calculated value of 2.83 μ_B expected for an intermediate-spin Fe^{II} cation. This fact has also been observed for half-sandwich Fe^{III} complexes, and it has been attributed to the existence of an important orbital contribution to the magnetic moment.[21,22] For Fe^{II}, few organometallic complexes that contain unpaired electrons are known. An example of a 16-electron, paramagnetic Fe^{II} organometallic complex

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[21] Roger, C.; Hamon, P.; Toupet, L.; Raaba, H.; Saillard, J.-Y.; Lapinte, C. *Organometallics* **1991**, *10*, 1045.

[22] Blake, J. R.; Wittenbrink, R. J.; Clayton, T. W., Jr.; Chiang, H. Y. *J. Am. Chem. Soc.* **1990**, *112*, 6539.

Table 2. Positional Parameters and B(eq) Values (Å^2) for [Fe(N_2)(Cp)(dippe)][BPh_4]

atom	x	y	z	B(eq)
Fe	0.3207(1)	0.1705(2)	0.16885(9)	3.3(1)
P(1)	0.2895(2)	0.3411(3)	0.1544(2)	3.5(2)
P(2)	0.1823(2)	0.1549(3)	0.2054(2)	4.1(2)
N(1)	0.3665(8)	0.194(1)	0.2472(6)	4.1(7)
N(2)	0.404(1)	0.206(1)	0.2953(7)	7(1)
C(1)	0.401(1)	0.155(1)	0.0867(8)	5(1)
C(2)	0.442(1)	0.107(1)	0.1399(8)	4.6(9)
C(3)	0.386(1)	0.024(1)	0.1595(8)	4.9(9)
C(4)	0.312(1)	0.028(1)	0.1207(8)	4.3(8)
C(5)	0.319(1)	0.111(2)	0.0753(7)	5(1)
C(10)	0.234(1)	0.380(1)	0.0765(7)	5.0(8)
C(11)	0.376(1)	0.443(1)	0.1694(8)	4.9(8)
C(12)	0.207(1)	0.369(1)	0.2144(7)	5.6(9)
C(20)	0.182(1)	0.118(1)	0.2933(7)	6(1)
C(21)	0.135(1)	0.286(1)	0.2082(8)	6(1)
C(22)	0.093(1)	0.084(1)	0.1631(8)	6(1)
C(101)	0.192(1)	0.487(1)	0.0809(8)	7(1)
C(102)	0.296(1)	0.381(1)	0.0183(7)	7(1)
C(111)	0.385(1)	0.478(1)	0.2400(9)	7(1)
C(112)	0.466(1)	0.407(1)	0.148(1)	8(1)
C(201)	0.233(1)	0.018(2)	0.3053(8)	8(1)
C(202)	0.088(1)	0.110(2)	0.3204(9)	10(1)
C(221)	0.087(1)	0.105(1)	0.091(1)	7(1)
C(222)	0.089(1)	−0.035(1)	0.1745(9)	8(1)
C(501)	0.6694(9)	0.216(1)	0.0401(6)	3.7(8)
C(502)	0.647(1)	0.326(1)	0.0395(8)	5(1)
C(503)	0.579(1)	0.359(1)	−0.003(1)	6(1)
C(504)	0.534(1)	0.296(2)	−0.0449(9)	6(1)
C(505)	0.554(1)	0.193(2)	−0.0470(8)	6(1)
C(506)	0.622(1)	0.158(1)	−0.0034(8)	4.9(8)
C(601)	0.745(1)	0.200(1)	0.1649(7)	3.6(7)
C(602)	0.668(1)	0.244(1)	0.1901(7)	4.7(8)
C(603)	0.662(1)	0.257(1)	0.2579(9)	5(1)
C(604)	0.731(2)	0.237(1)	0.2994(8)	6(1)
C(605)	0.809(1)	0.194(1)	0.2758(9)	6(1)
C(606)	0.814(1)	0.180(1)	0.2075(8)	4.9(8)
C(701)	0.766(1)	0.052(1)	0.0840(6)	3.8(7)
C(702)	0.843(1)	−0.000(1)	0.0723(8)	6(1)
C(703)	0.855(1)	−0.107(2)	0.0738(8)	7(1)
C(704)	0.786(2)	−0.171(1)	0.0871(7)	7(1)
C(705)	0.706(1)	−0.125(1)	0.0993(8)	6(1)
C(706)	0.698(1)	−0.018(1)	0.0988(6)	4.1(7)
C(801)	0.840(1)	0.238(1)	0.0572(6)	3.6(7)
C(802)	0.890(1)	0.313(1)	0.0892(7)	4.6(8)
C(803)	0.960(1)	0.367(1)	0.0611(8)	4.5(8)
C(804)	0.979(1)	0.343(2)	−0.0039(9)	6(1)
C(805)	0.930(1)	0.272(1)	−0.0367(7)	5(1)
C(806)	0.860(1)	0.218(1)	−0.0085(7)	4.9(8)
B	0.752(1)	0.179(1)	0.0854(7)	3.7(8)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex [Fe(Cp)(N_2)(dippe)][BPh_4]

Bond Distances			
Fe−P(1)	2.251(4)	Fe−C(3)	2.13(1)
Fe−P(2)	2.269(4)	Fe−C(4)	2.07(1)
Fe−N(1)	1.76(1)	Fe−C(5)	2.07(1)
Fe−C(1)	2.13(1)	N(1)−N(2)	1.13(1)
Fe−C(2)	2.12(1)		
Angles			
P(1)−Fe−P(2)	86.3(1)	P(2)−Fe−C(3)	113.0(5)
P(1)−Fe−N(1)	91.5(4)	P(2)−Ce−C(4)	92.1(4)
P(1)−Fe−C(1)	96.4(5)	P(2)−Fe−C(5)	107.3(5)
P(1)−Fe−C(2)	121.0(5)	N(1)−Fe−C(1)	121.9(7)
P(1)−Fe−C(3)	159.6(4)	N(1)−Fe−C(2)	90.6(6)
P(1)−Fe−C(4)	141.1(6)	N(1)−Fe−C(3)	93.9(6)
P(1)−Fe−C(5)	103.9(5)	N(1)−Fe−C(4)	127.4(7)
P(2)−Fe−N(1)	92.8(4)	N(1)−Fe−C(5)	155.2(6)
P(2)−Fe−C(1)	145.1(6)	Fe−N(1)−N(2)	173(1)
P(2)−Fe−C(2)	152.3(5)		

is [Fe(η^5-pentadienyl)(PEt_3)$_2$][PF_6],[22] which has been subjected to X-ray structure analysis. A magnetic moment of 2.85 μ_B for this compound indicates the presence of two unpaired electrons. It has been already mentioned that the dinitrogen adduct [CpFe(N_2)(dippe)]$^+$ co-exists with the 16-electron complex [CpFe(dippe)]$^+$ as an equilibrium mixture in acetone or thf under dinitrogen. Thus, the ^1H NMR spectrum of **1** in acetone-d_6 under N_2 (Figure 2) displays signals corresponding to the diamagnetic cation [CpFe(N_2)(dippe)]$^+$ in the range 0−10 ppm. The C_5H_5 resonance appears as one singlet at 5.06 ppm, whereas the phosphine protons appear as a series of overlapping multiplets. Besides these resonances, broad, paramagnetically shifted signals corresponding to the protons of the 16-electron cation [CpFe(dippe)]$^+$ are observed in the range −40 to +40 ppm. The $^{31}P\{^1H\}$ NMR spectrum consists of one singlet at 98.4 ppm, due to the equivalent phosphorus atoms of the dinitrogen complex. No signal is observed for [CpFe(dippe)]$^+$. Due to the occurrence of the equilibrium shown in eq 2 and to the presence of both diamagnetic and paramagnetic species, it was not possible to obtain the $^{13}C\{^1H\}$ spectrum of compound **1**. The equilibrium constant K_{eq} for the process shown in eq 2 and its dependance with temperature have been determined by measuring the magnetic moment of acetone solutions of **1** under dinitrogen at different temperatures. This yielded a value of K_{eq} = 2.1 at 20 °C. A van't Hoff plot (Figure 3) allowed the calculation of ΔH° and ΔS° for the process, the corresponding values being 18.2 ± 0.5 kJ mol^{-1} and 68 ± 2 J mol^{-1} K^{-1}, respectively. These data suggest that the reaction in eq 2 is entropy driven and therefore that at high temperatures the equilibrium favors the formation of the paramagnetic 16-electron complex, whereas the addition of N_2 to **3** may be favored by lowering the temperature.

At variance with the behavior found for [CpFeCl(dippe)], which forms [CpFe(N_2)(dippe)]$^+$, the related complex [Cp*FeCl(dippe)] (Cp* = C_5Me_5)[16] dissolves in methanol or ethanol under dinitrogen yielding orange solutions from which only [Cp*Fe(dippe)][BPh_4] (**3**) can be isolated upon addition of Na[BPh_4]. No dinitrogen uptake is observed. Compound **3** does not add N_2 at room temperature even under pressure (5 atm). It seems that the stronger donor properties of the C_5Me_5 ligand, as well as its higher steric demands, preferentially stabilize the 16-electron complex to the detriment of the 18-electron dinitrogen adduct [Cp*Fe(N_2)(dippe)]$^+$, which does not seem to be a stable species. Compound **3** is paramagnetic and has an effective magnetic moment similar to that of **2** (3.8 μ_B, Evans' method). The X-ray crystal structure of **3** has been determined and a view of the complex cation [Cp*Fe(dippe)]$^+$ is shown in Figure 3. Final atomic coordinates are given in Table 4, and selected bond lengths and angles are in Table 5. The iron atom is in a formally five-coordinate environment. The Cp* ring is pentahapto bonded, and the dippe ligand coordinates perpendicularly to the Cp* plane (dihedral angle between the least-squares Cp* plane and that defined by Fe−P(1)−P(2), 92.6°). The Fe−P separations found for this compound are longer than those in **1**, due possibly to the steric interactions of the phosphine isopropyl groups with the ring methyl substituents. These Fe−P bond lengths are also longer than in the Cp* complex [Cp*FeH_2(dippe)][BPh_4],[16] although in this case iron is formally in the oxidation state +4, being smaller in size. The C_5 ring of the Cp* ligand is planar, with the methyl substituents above this plane, displaced away from the iron atom. The X-ray

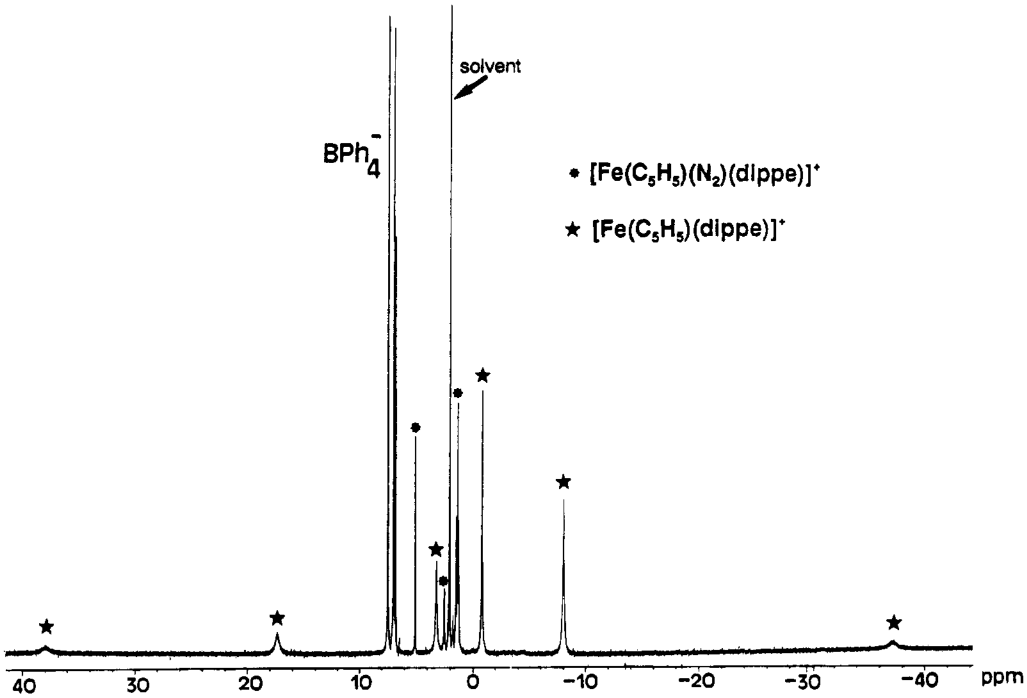

Figure 2. ^{1}H NMR spectrum of **1** in acetone-d_6 under dinitrogen in the range −40 to +40 ppm, showing peaks corresponding to both [CpFe(N$_2$)(dippe)]$^+$ (*) and [CpFe(dippe)]$^+$ (★).

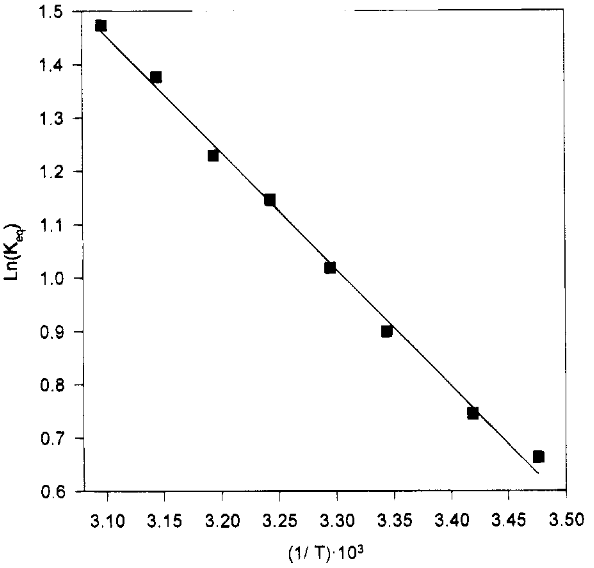

Figure 3. Plot of ln K_{eq} *versus* $1/T$ (K^{-1}) for the equilibrium in acetone-d_6 solution between [CpFe(N$_2$)(dippe)]$^+$ and [CpFe(dippe)]$^+$ (eq 2) under dinitrogen.

crystal structure of **3** does not show any indications of stabilization by means of an intra- or intermolecular agostic interaction. This structure is closely related to that of the complex [Fe(η^5-pentadienyl)(PEt$_3$)$_2$][PF$_6$],[22] which constitutes another example of a 16-electron paramagnetic organometallic compound of iron, in which there is no significant agostic interaction.

No ammonia or hydrazine was detected upon reaction of the dinitrogen adduct **1** with HBF$_4$. Furthermore, the complex decomposed, and the only species identified was the phosphonium salt [^{i}Pr$_2$PCH$_2$CH$_2$PH^{i}Pr$_2$][BF$_4$].

The complexes **1**–**3** react with a variety of neutral donors L furnishing the corresponding adducts [CpFe(L)(dippe)][BPh$_4$] or [Cp*Fe(L)(dippe)][BPh$_4$] as expected. Thus, the reaction with CNBu^t afforded the complexes [CpFe(CNBu^t)(dippe)][BPh$_4$] (**4**) and [Cp*Fe(CNBu^t)(dippe)][BPh$_4$] (**5**), respectively. In analogous fashion, the reaction with CO yielded [CpFe(CO)(dippe)][BPh$_4$] (**6**) and [Cp*Fe(CO)(dippe)][BPh$_4$] (**7**). All these compounds can be also obtained directly from [CpFeCl(dippe)] or [Cp*FeCl(dippe)] in MeOH, by addition of L and subsequent precipitation with Na[BPh$_4$]. Complexes **4**–**7** are crystalline, air-stable materials, which display one strong ν(C≡N) or ν(C≡O) band in their respective IR spectra. The ν(C≡N) band appears at essentially the same wavenumber for both **4** and **5**, indicating that the isocyanide is acting mainly as a σ-donor. However, the ν(C≡O) band in the Cp* derivative **7** is at lower frequency than in the Cp complex **6**, as result of increased back-bonding, due possibly to the fact that the stronger donor properties of the Cp* ligand provides a metal site which is more electron-rich. The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of these compounds are consistent with a "three-legged piano stool" structure, as has been found for **1** and for other half-

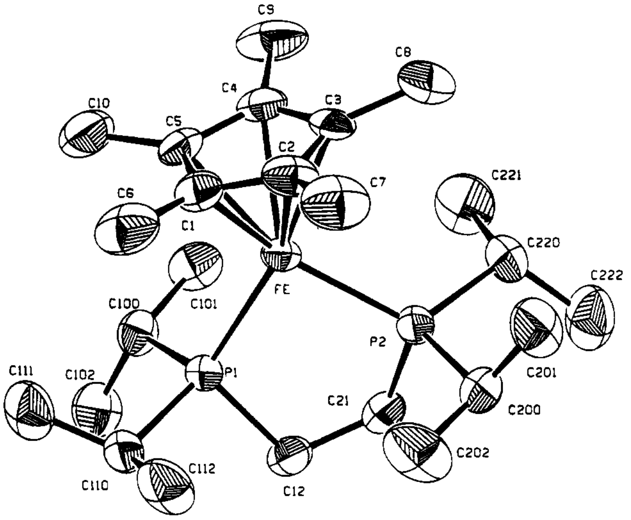

Figure 4. ORTEP drawing of the cation [Cp*Fe(dippe)]$^+$. Hydrogen atoms are omitted.

Table 4. Positional Parameters and B(eq) Values (Å^2) for [Fe(Cp*)(dippe)][BPh$_4$]

atom	x	y	z	B(eq)
Fe	0.31508(7)	0.05103(5)	0.25061(7)	2.51(4)
P(1)	0.4403(1)	0.0907(1)	0.1924(1)	2.59(8)
P(2)	0.3130(1)	0.1438(1)	0.3295(1)	2.73(9)
C(1)	0.3139(5)	−0.0487(4)	0.2457(6)	3.5(3)
C(2)	0.2665(6)	−0.0305(4)	0.3163(6)	4.0(4)
C(3)	0.1864(5)	0.0061(4)	0.2764(5)	3.5(4)
C(4)	0.1832(5)	0.0081(4)	0.1775(5)	3.5(4)
C(5)	0.2621(5)	−0.0245(3)	0.1576(5)	3.1(3)
C(6)	0.3927(6)	−0.0965(4)	0.2562(7)	5.7(5)
C(7)	0.2918(6)	−0.0517(5)	0.4174(6)	6.1(5)
C(8)	0.1098(6)	0.0279(4)	0.3249(7)	6.0(5)
C(9)	0.1027(6)	0.0349(4)	0.1056(7)	5.8(5)
C(10)	0.2804(6)	−0.0.415(4)	0.0627(6)	5.7(5)
C(12)	0.4702(5)	0.1680(4)	0.2463(5)	3.7(4)
C(21)	0.3874(5)	0.1991(4)	0.2800(5)	3.5(4)
C(100)	0.4093(5)	0.1060(3)	0.0645(5)	3.1(3)
C(101)	0.3118(5)	0.1373(4)	0.0392(5)	4.1(4)
C(102)	0.4838(6)	0.1420(4)	0.0237(5)	4.7(4)
C(110)	0.5591(5)	0.0532(4)	0.2089(5)	3.6(4)
C(111)	0.5645(6)	−0.0003(4)	0.1425(6)	5.3(5)
C(112)	0.5936(6)	0.0328(5)	0.3113(6)	5.6(5)
C(200)	0.3650(5)	0.1416(4)	0.4570(5)	3.9(4)
C(201)	0.2985(6)	0.1133(5)	0.5145(5)	5.7(5)
C(202)	0.4602(6)	0.1080(5)	0.4750(6)	6.9(6)
C(220)	0.2022(5)	0.1886(4)	0.3252(5)	3.9(4)
C(221)	0.1522(6)	0.1978(5)	0.2235(7)	6.3(5)
C(222)	0.2146(6)	0.2506(4)	0.3799(6)	5.9(5)
C(601)	0.6161(5)	0.4288(3)	0.2114(5)	3.0(3)
C(602)	0.6073(5)	0.4627(3)	0.1278(5)	3.1(4)
C(603)	0.6247(5)	0.5265(4)	0.1237(6)	3.9(4)
C(604)	0.6525(6)	0.5593(4)	0.2057(7)	4.4(4)
C(605)	0.6635(6)	0.5282(4)	0.2900(6)	5.0(5)
C(606)	0.6462(5)	0.4643(4)	0.2925(5)	3.8(4)
C(701)	0.6944(5)	0.3140(4)	0.2085(5)	2.9(3)
C(702)	0.6954(5)	0.2542(4)	0.1695(6)	3.8(4)
C(703)	0.7771(7)	0.2207(4)	0.1676(6)	4.8(5)
C(704)	0.8630(6)	0.2461(5)	0.2052(6)	5.1(5)
C(705)	0.8869(5)	0.3042(5)	0.2453(6)	5.0(5)
C(706)	0.7849(5)	0.3378(4)	0.2479(5)	3.8(4)
C(801)	0.5636(5)	0.3358(3)	0.3141(5)	2.9(3)
C(802)	0.6051(5)	0.2882(3)	0.3752(5)	3.2(3)
C(803)	0.5754(6)	0.2743(4)	0.4580(5)	4.3(4)
C(804)	0.5026(7)	0.3072(5)	0.4852(6)	4.9(5)
C(805)	0.4595(6)	0.3538(4)	0.4261(7)	4.7(5)
C(806)	0.4902(6)	0.3679(4)	0.3451(6)	4.0(4)
C(901)	0.5123(5)	0.3333(3)	0.1227(5)	2.7(3)
C(902)	0.4167(5)	0.3254(3)	0.1290(5)	3.3(4)
C(903)	0.3489(5)	0.3105(4)	0.0479(7)	4.1(4)
C(904)	0.3730(6)	0.3041(4)	−0.0377(6)	4.3(4)
C(905)	0.4663(6)	0.3122(4)	−0.0465(5)	4.3(4)
C(906)	0.5330(5)	0.3261(4)	0.0331(5)	3.8(4)
B	0.5960(6)	0.3530(4)	0.2148(6)	2.8(4)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex [Fe(Cp*)(dippe)][BPh$_4$]

	Bond Distances		
Fe−P(1)	2.290(2)	Fe−C(3)	2.178(7)
Fe−P(2)	2.292(2)	Fe−C(4)	2.192(7)
Fe−C(1)	2.133(8)	Fe−C(5)	2.149(7)
Fe−C(2)	2.162(8)		
	Angles		
P(1)−Fe−P(2)	87.01(8)	P(2)−Fe−C(1)	151.7(2)
P(1)−Fe−C(1)	111.1(2)	P(2)−Fe−C(2)	116.2(2)
P(1)−Fe−C(2)	143.3(2)	P(2)−Fe−C(3)	101.8(2)
P(1)−Fe−C(3)	168.1(2)	P(2)−Fe−C(4)	120.8(2)
P(1)−Fe−C(4)	130.3(2)	P(2)−Fe−C(5)	157.9(2)
P(1)−Fe−C(5)	105.0(2)		

sandwich isocyanide and carbonyl derivatives of iron and ruthenium.[23-25] **1−3** also react with acetonitrile to yield the adducts [CpFe(MeCN)(dippe)][BPh$_4$] (**8**) and [Cp*Fe(MeCN)(dippe)][BPh$_4$] (**9**), as deep red crystals. Both compounds exhibit one medium band near 2250 cm^{-1} in their IR spectra, attributable to ν(C≡N) of the coordinated acetonitrile. The ^{1}H NMR spectrum of **8** shows one singlet at 4.596 ppm, corresponding to the protons of the cyclopentadienyl ligand, and one singlet at 2.278 ppm, due to the acetonitrile protons. The ^{31}P{^{1}H} NMR spectrum consists of one singlet. These data, together with the ^{13}C{^{1}H} NMR spectrum, support a "three-legged" piano-stool structure for this compound, as it has been suggested for the parent compounds [CpFe(MeCN)(dppe)][BF$_4$] and [Cp*Fe(MeCN)(dppe)][BF$_4$].[27] Whereas the NMR spectral properties of **8** are typical of a diamagnetic species, the Cp* derivative **9** is paramagnetic in solution. It is well established that acetonitrile is a labile ligand, and sometimes their adducts exist in solution as equilibrium mixtures with free acetonitrile and the corresponding coordinatively unsaturated metal complex, as in the case of [RuH(MeCN)(dippe)$_2$][BPh$_4$].[26] This might suggest that the paramagnetism of **9** arises from the existence of a dissociation process, similar to that found for the dinitrogen complex **1**, giving rise to the paramagnetic, 16-electron species [Cp*Fe(dippe)]$^+$, according to eq 3.

$$[\mathrm{Cp^*Fe(MeCN)(dippe)}]^+ \rightleftarrows [\mathrm{Cp^*Fe(dippe)}]^+ + \mathrm{MeCN} \quad (3)$$

Two facts are against this: (1) The ^{1}H NMR spectrum of **9** in acetone-d_6 consists of very broad features, different from the characteristic resonances of the cation [Cp*Fe(dippe)]$^+$, which are readily observable despite its paramagnetism. (2) The equilibrium shown in eq 3 would be shifted to the left in the presence of an excess of MeCN. However, the ^{1}H NMR spectrum of **9** recorded in acetonitrile-d_3 indicates the presence of paramagnetic species. Furthermore, **9** in acetonitrile-d_3 solution has an effective magnetic moment of 4.0 μ_B, and therefore this compound can be regarded as a paramagnetic, formally six-coordinate, 18-electron Fe^{II} organometallic complex. The effective magnetic moment of **9** is greater than the value of 3.18 μ_B found for the unique paramagnetic, six-coordinate, 18-electron organometallic complex reported to date, [Cp*Fe(Me$_2$CO)(dppe)][CF$_3$SO$_3$].[28] This compound is assumed to have two unpaired electrons, corresponding to a spin-intermediate $S = 1$ state, although the magnetic behavior could also result from the effective coexistence of $S = 0$ and $S = 2$ species. This may also happen in our case. It is interesting the fact that the Cp adduct **8** is diamagnetic whereas **9** is paramagnetic. This has also been observed in the dppe−acetone system, since [CpFe(Me$_2$CO)(dppe)][PF$_6$][11] seems to be diamagnetic, at variance with [Cp*Fe(Me$_2$CO)(dppe)][CF$_3$SO$_3$] which is paramagnetic, as it has been already mentioned. The complexes [CpFe(MeCN)(dppe)][BF$_4$] and [Cp*Fe(MeCN)(dppe)][BF$_4$][27] are also diamagnetic. The reasons for these differences in magnetic behavior remain unclear.

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Table 6. Positional Parameters and *B*(eq) Values (Å^2) for [Fe(Cp)(Cl)(dippe)][BPh$_4$]

atom	*x*	*y*	*z*	*B*(eq)
Fe(1)	0.3268(1)	0.1717(1)	0.17163(9)	2.87(9)
Cl	0.3920(3)	0.2122(3)	0.2699(2)	5.9(2)
P(1)	0.2922(3)	0.3423(3)	0.1555(2)	2.8(2)
P(2)	0.1876(2)	0.1575(3)	0.2086(2)	3.3(2)
C(1)	0.393(1)	0.028(1)	0.1613(7)	4.5(9)
C(2)	0.447(1)	0.106(1)	0.1410(7)	4.3(8)
C(3)	0.403(1)	0.155(1)	0.0872(7)	4.5(8)
C(4)	0.320(1)	0.106(1)	0.0785(7)	5(1)
C(5)	0.316(1)	0.025(1)	0.1251(8)	4.6(9)
C(12)	0.2132(9)	0.369(1)	0.2174(7)	3.9(7)
C(21)	0.141(1)	0.290(1)	0.2121(7)	4.7(8)
C(100)	0.235(1)	0.380(1)	0.0752(7)	4.2(8)
C(101)	0.189(1)	0.486(1)	0.0794(8)	6(1)
C(102)	0.294(1)	0.379(1)	0.0178(8)	6(1)
C(110)	0.3801(9)	0.442(1)	0.1669(6)	3.5(7)
C(111)	0.388(1)	0.487(1)	0.2370(7)	5.0(8)
C(112)	0.469(1)	0.405(1)	0.1462(8)	6(1)
C(200)	0.095(1)	0.085(1)	0.1655(7)	4.5(8)
C(201)	0.094(1)	−0.030(1)	0.1753(8)	7(1)
C(202)	0.087(1)	0.115(1)	0.0921(8)	7(1)
C(220)	0.191(1)	0.114(1)	0.2962(7)	4.5(8)
C(221)	0.244(1)	0.014(1)	0.3078(7)	6(1)
C(222)	0.102(1)	0.106(1)	0.3259(8)	7(1)
C(501)	0.768(1)	0.051(1)	0.0810(5)	2.7(6)
C(502)	0.846(1)	0.005(1)	0.0672(6)	3.6(8)
C(503)	0.859(1)	−0.104(1)	0.0705(7)	5(1)
C(504)	0.791(1)	−0.164(1)	0.0864(7)	5(1)
C(505)	0.710(1)	−0.125(1)	0.1007(7)	5(1)
C(506)	0.701(1)	−0.017(1)	0.0975(6)	4.2(8)
C(601)	0.6664(8)	0.215(1)	0.0357(6)	3.1(7)
C(602)	0.644(1)	0.321(1)	0.0315(7)	4.6(8)
C(603)	0.575(1)	0.359(1)	−0.0106(8)	5(1)
C(604)	0.530(1)	0.292(2)	−0.0514(7)	6(1)
C(605)	0.549(1)	0.187(1)	−0.0483(7)	6(1)
C(606)	0.617(1)	0.151(1)	−0.0063(7)	4.4(8)
C(701)	0.8377(9)	0.239(1)	0.0522(7)	3.3(7)
C(702)	0.8901(9)	0.314(1)	0.0867(6)	3.4(7)
C(703)	0.957(1)	0.366(1)	0.0599(7)	4.1(8)
C(704)	0.9798(8)	0.344(1)	−0.0031(7)	4.0(7)
C(705)	0.930(1)	0.273(1)	−0.0401(7)	4.0(8)
C(706)	0.862(1)	0.225(1)	−0.0127(6)	3.4(7)
C(801)	0.745(1)	0.204(1)	0.1621(7)	3.2(7)
C(802)	0.6685(9)	0.246(1)	0.1872(6)	3.2(7)
C(803)	0.661(1)	0.260(1)	0.2540(9)	5(1)
C(804)	0.729(1)	0.235(1)	0.2988(7)	5(1)
C(805)	0.804(1)	0.196(1)	0.2762(7)	5(1)
C(806)	0.8117(9)	0.179(1)	0.2096(7)	4.4(8)
B	0.754(1)	0.177(1)	0.0838(8)	3.4(8)

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex [Fe(Cp)Cl(dippe)][BPh$_4$]

Bond Distances			
Fe(1)−Cl	2.241(5)	Fe(1)−C(2)	2.13(1)
Fe(1)−P(1)	2.276(4)	Fe(1)−C(3)	2.13(1)
Fe(1)−P(2)	2.283(6)	Fe(1)−C(4)	2.07(1)
Fe(1)−C(1)	2.12(1)	Fe(1)−C(5)	2.11(1)
Angles			
Cl−Fe(1)−P(1)	89.5(2)	P(1)−Fe(1)−C(2)	122.3(5)
Cl−Fe(1)−P(2)	95.7(2)	P(1)−Fe(1)−C(3)	96.5(4)
Cl−Fe(1)−C(1)	95.8(5)	P(1)−Fe(1)−C(4)	105.3(5)
Cl−Fe(1)−C(2)	90.4(4)	P(1)−Fe(1)−C(5)	141.7(5)
Cl−Fe(1)−C(3)	120.4(5)	P(2)−Fe(1)−C(1)	114.3(5)
Cl−Fe(1)−C(4)	155.0(5)	P(2)−Fe(1)−C(2)	152.1(5)
Cl−Fe(1)−C(5)	128.8(5)	P(2)−Fe(1)−C(3)	143.8(5)
P(1)−Fe(1)−P(2)	85.1(2)	P(2)−Fe(1)−C(4)	105.3(5)
P(1)−Fe(1)−C(1)	159.1(5)	P(2)−Fe(1)−C(5)	91.3(4)

The reaction of complexes **1**−**3** with neutral donor molecules is controlled by the steric effects of the incoming ligand. Bulky molecules do not coordinate to the 16-electron complex **3**, which due to the presence of five methyl substituents at the cyclopentadienyl ring is more sterically demanding than compounds **1** and **2**. For instance, P(OPh)$_3$, which has a large cone angle, does not react at all with acetone or thf solutions of **3**, even under reflux. However, it reacts cleanly with **1**, **2**, or [CpFeCl(dippe)] in MeOH yielding [CpFe(P(OPh)$_3$)(dippe)][BPh$_4$], isolable as tetraphenylborate salt **10**. This is a yellow, crystalline, air-stable compound. Its ^{31}P{^{1}H} NMR spectrum corresponds to an AX$_2$ spin system and consists of one doublet at 103.9 ppm attributable to the two equivalent phosphorus atoms of the dippe ligand, coupled to one phosphorus atom of P(OPh)$_3$, which appears as a triplet at 158.9 ppm, J(P$_A$,P$_X$) = 81.8 Hz. The structure assumed for **10** is again the basic "three-legged piano stool", entirely unexceptional. Further differences between the reactivity of [CpFeCl(dippe)] and [Cp*FeCl(dippe)] can be found in their reaction with SnCl$_2$. Both compounds react with anhydrous SnCl$_2$ in CH$_2$Cl$_2$, but no characterizable product has been isolated in the case of the Cp* derivative. However, the reaction of [CpFeCl(dippe)] with SnCl$_2$ yielded the magenta trichlorostannyl complex [CpFe(SnCl$_3$)(dippe)] (**11**). This compound is formed by insertion of SnCl$_2$ into the Fe−Cl bond, a process which is well-known and has been thoroughly studied,[29,30] due to the ability of the trichlorostannyl ligand to promote or modify the catalytic activity of transition metal complexes.[31] The ^{31}P{^{1}H} NMR spectrum of **11** consists of one singlet, plus small satellites due to coupling of the phosphorus atoms to the NMR active ^{117}Sn and ^{119}Sn nuclei, with coupling constants J(P,^{117}Sn) = 540 Hz and J(P,^{119}Sn) = 565 Hz, respectively. Consistent with this, the ^{119}Sn NMR spectrum of **11** displays one triplet due to coupling of the ^{119}Sn nucleus with two equivalent phosphorus atoms of the phosphine ligand. Acetone or tetrahydrofuran solutions of **1**−**3** are very air-sensitive, turning dark brown when exposed to atmospheric oxygen. No product has been isolated from the reaction of any of these compounds with air. However, exposure to air of [CpFeCl(dippe)] or [Cp*FeCl(dippe)] in methanol produced red-brown solutions, from which crystalline materials were isolated upon addition of Na[BPh$_4$]. These materials were identified as the Fe^{III}, 17-electron derivatives [CpFeCl(dippe)][BPh$_4$] (**12**) and [Cp*FeCl(dippe)][BPh$_4$] (**13**). There is a growing interest in the chemistry of 17-electron organometallic complexes due to their relationship with the electron-transfer processes[32] and because their physical properties, such as conductivity, magnetism, and optical effects.[33] Half-sandwich Fe^{III} complexes have been prepared by oxidation of the corresponding Fe^{II} precursors, using different oxidizing agents, such as [Cp$_2$Fe][PF$_6$],[16,21,34] [Ph$_3$C][PF$_6$],[35] or atmospheric oxygen,[21] as it happens in our case. Dark

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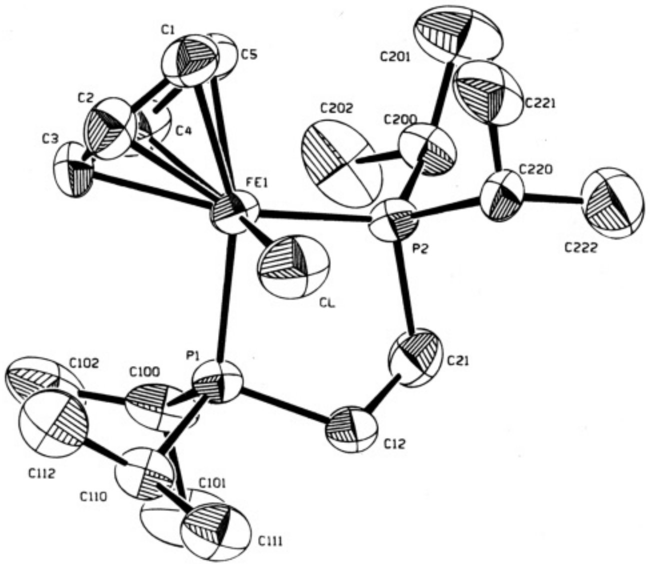

Figure 5. ORTEP drawing of the cation $[CpFeCl(dippe)]^+$. Hydrogen atoms are omitted.

red **12** and brown **13** are both paramagnetic, as expected, having effective moment values of 2.40 and 2.30 μ_B, respectively, corresponding to one unpaired electron, and consistent with data reported in the literature for other half-sandwich Fe^{III} complexes, i.e. $[Cp^*Fe(CH_3)(dppe)][PF_6]$ (2.39 μ_B),[21] $[Cp^*Fe(CH_2OCH_3)(dppe)][PF_6]$ (2.29 μ_B),[36] or $[CpFeH(dippe)][BPh_4]$ (2.40 μ_B).[16] The X-ray crystal structure of **12** was determined. Atomic coordinates and bond lengths and angles are listed in Tables 6 and 7. The molecular structure of the cation $[CpFeCl(dippe)]^+$ is shown in Figure 5. The structure consists of monomeric complex cations, with the expected "three-legged piano stool" arrangement, similar to that found for the related Fe^{II} complex $[Cp^*FeCl(dppe)]$.[21] The Fe−Cl distance of 2.241(5) Å is slightly shorter than the corresponding to the Fe^{II} derivative $[Cp^*FeCl(dppe)]$ (2.346(1) Å). This difference arises from the fact that Fe^{III} is smaller in size than the Fe^{II} cation rather than from the steric effects of the Cp* ligand. The C5 ring of the cyclopentadienyl group is planar and is pentahapto bonded to the iron atom, with Fe−C separations in the range of those reported in the literature. All other bond lengths and angles, including the dippe ligand and the $[BPh_4]^-$ anion, are also in the range expected, being unexceptional.

It interesting to note that **1**−**3** react quantitatively with H_2 to yield the hydrides $[CpFeH_2(dippe)][BPh_4]$ or $[Cp^*FeH_2(dippe)][BPh_4]$. These compounds had been previously characterized as organoiron(IV) dihydrides, rather than iron(II) dihydrogen complexes, as inferred from NMR T_1 measurements and the X-ray crystal structure of the Cp* complex.[16] However, the value of 2112 cm^{-1} found for $\nu(N_2)$ in **1** suggests that, at least in this case, the dihydrogen adduct $[CpFe(H_2)(dippe)][BPh_4]$ should be stable, according to the criterion for the stability of the metal−dihydrogen bond proposed by Morris,[36] based upon the value of $\nu(N_2)$ for the associated dinitrogen complex, and no homolytic splitting of dihydrogen should occur.

Acknowledgment. Suggestions from Prof. E. Carmona (Univ. de Sevilla) and Prof. G. J. Leigh (Univ. of Sussex), as well as financial support from the Ministerio de Educación y Ciencia of Spain (DGICYT, Project PB91-0741, Programa de Promoción General del Conocimiento), are gratefully acknowledged.

Supporting Information Available: Tables of X-ray crystallographic data, including atomic coordinates, isotropic thermal parameters, anisotropic thermal parameters, and interatomic distances and angles (39 pages). Ordering information is given on any current masthead page.

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