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Synthesis and Properties of Iron(II) Hydride Complexes Containing the Tripodal Tetraphosphine Ligand $P(CH_2CH_2PMe_2)_3$

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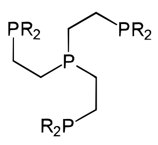
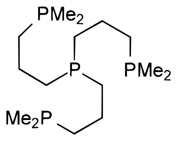
The preparation and characterization of iron(II) hydride complexes containing the tripodal tetraphosphine ligand tris[2-(dimethylphosphino)ethyl]phosphine, $P(CH_2CH_2PMe_2)_3$ (PP_3), **1**, are reported. Dissolution of the chloro hydride complex $FeHCl(PP_3)$, **2**, in methanol affords an equilibrium mixture of **2** and the methoxy hydrido complex $FeH(OMe)(PP_3)$, **3**. Reaction of a methanol solution containing **2** and **3** with anionic or neutral ligands affords the corresponding hydrido complexes: reaction with NaBr affords $FeHBr(PP_3)$, **4**; reaction with NaI affords $FeHI(PP_3)$, **5**; reaction with NaN_3 affords $FeHN_3(PP_3)$, **6**; reaction with CO affords $[FeH(CO)(PP_3)]^+$, **7**; reaction with N_2 affords $[FeH(N_2)(PP_3)]^+$, **8**; and reaction with PPh_3 affords $[FeHPPh_3(PP_3)]^+$, **9**. In some cases, further reaction of the product iron hydride complexes is observed. Reaction of $FeHN_3(PP_3)$, **6**, with NaN_3 for an extended period affords $Fe(N_3)_2(PP_3)$, **10**. On standing in solution, $[FeH(N_2)(PP_3)]^+$, **8**, is converted to the dinitrogen-bridged complex $[FeH(PP_3)N{\equiv}NFeH(PP_3)]^{2+}$, **11**. The carbonyl hydride complex **7** and the dinitrogen hydride complex **8** can be deprotonated to give the neutral iron(0) complexes $Fe(CO)(PP_3)$, **12**, and $Fe(N_2)(PP_3)$, **13**, respectively. The air-sensitive complexes **4**−**13** were characterized, by multinuclear NMR, IR, Raman, and mass spectroscopy and by elemental analysis.

Introduction

Complexes containing tripodal tetradentate phosphine ligands such as $P(CH_2CH_2PPh_2)_3$, **14**, act as catalysts for a variety of organic transformations, many of which are not observed with analogous complexes containing mono- and bidentate ligands.[1] The polydentate architecture provides stability and constrains the arrangement of donors in the coordination sphere. In octahedral complexes, tripodal tetradentate phosphine ligands enforce a *cis* geometry of the two remaining ligands. Ruthenium and iron complexes of the related ligand $P(CH_2CH_2CH_2PMe_2)_3$, **15**, undergo C−H insertion reactions with alkene and arene substrates.[2] The η^2-dihydrogen−η^1-hydride complexes $[M(P4)H(H_2)]^+$ (M = Fe, Ru, P4 = $P(CH_2CH_2PPh_2)_3$,[3] $P(CH_2CH_2CH_2PMe_2)_3$,[4] $P(CH_2CH_2PCy_2)_3$; Cy = cyclohexyl[5]) show an interaction between the *cis* hydride and dihydrogen ligands which has led to the speculation that these are complexes of the ligand "H_3".



1 R=Me
14 R=Ph
16 R=Cyclohexyl



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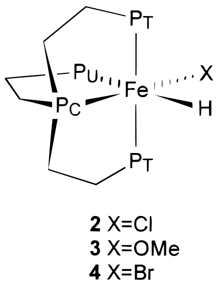
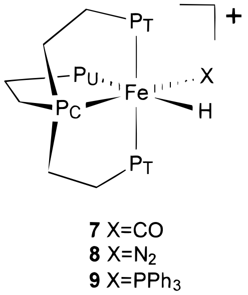
Very few complexes containing the related "hybrid" of ligands **14** and **15**, *i.e.* $P(CH_2CH_2PMe_2)_3$ (PP_3), **1**,[6] have been reported, despite the fact that the synthesis of **1** was reported in 1975.[7] The long and low-yielding original synthesis of **1** probably accounts for the subsequent lack of interest in this ligand. We have reported[8] a new, efficient, and high-yielding synthesis of PP_3, **1**, which has facilitated the investigation of iron hydride complexes of PP_3, **1**. The syntheses and properties of a series of iron(II) chloride, hydride, and methyl complexes containing **1** have also been reported.[9]

In this paper we report the synthesis of the iron(II) hydride complexes, $FeHX(PP_3)$ (X = Br, **4**; X = I, **5**; X = N_3, **6**; X = CO, **7**; X = N_2, **8**; X = PPh_3, **9**) by substitution of the chloro ligand of $FeHCl(PP_3)$, **2**. Also reported are the bis(azide) complex $Fe(N_3)_2(PP_3)$, **10**, formed on extended reaction of **6**



2 X=Cl
3 X=OMe
4 X=Br
5 X=I
6 X=N3



7 X=CO
8 X=N2
9 X=PPh3

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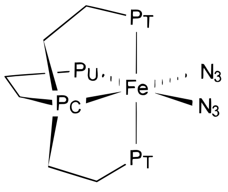

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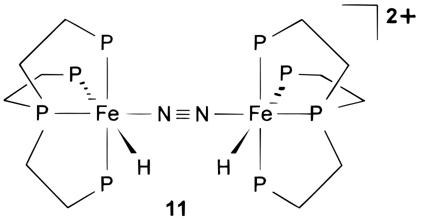
with NaN_3, and the bridging dinitrogen complex $[FeH(PP_3)N{\equiv}NFeH(PP_3)]^{2+}$, **11**. Deprotonation of **7** and **8** affords the five-coordinate carbonyl and dinitrogen complexes **12** and **13**, respectively.



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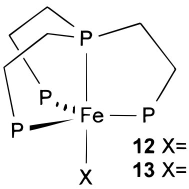


12 X=CO
13 X=N_2

Experimental Section

All synthetic manipulations involving air-sensitive materials were carried out under an inert atmosphere of argon in an argon-filled drybox or under a nitrogen atmosphere using standard Schlenk techniques. THF, benzene, and hexane were dried over sodium before distillation from sodium and benzophenone under nitrogen. Ethanol and methanol were distilled from magnesium under nitrogen. The iron(II) dichloride complex $FeCl_2(PP_3)$ and the iron(II) chloro hydrido complex $FeHCl(PP_3)$, **2**, were prepared using previously reported methods.[9]

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AMX400 and AMX600 spectrometers at the temperatures quoted. ^{1}H and ^{13}C chemical shifts were internally referenced to residual solvent resonances. ^{31}P spectra were referenced to external neat trimethyl phosphite at 140.85 ppm. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR. Raman spectra were recorded on a Bruker RFS100 FT-Raman spectrometer using 180° backscattering. Mass spectra were recorded on a MAT TSQ-46 (Finnegan, San Jose, CA) spectrometer equipped with a desorption probe, with a source temperature of 140 °C and an electron energy of 100 eV. Chemical ionization (CI) was used, with methane (>99.999%) as the ionization gas. Elemental analyses were carried out on all compounds, which showed reasonable air stability for short periods, by the Joint Elemental Analysis Facility, The University of Sydney. Melting points were recorded on a Gallenkamp heating stage and are uncorrected.

$FeHBr(PP_3)$, 4. Sodium bromide (20 mg, 190 μmol) was added to a solution of $FeHCl(PP_3)$, **2** (18 mg, 46 μmol), in ethanol (2 mL). The solution was heated at 60 °C and the reaction followed by ^{31}P NMR spectroscopy. After 10 min, all of the chloro hydrido complex had been converted to $FeHBr(PP_3)$, **4**. The mixture was filtered. The filtrate was evaporated to dryness *in vacuo*, and the residue was extracted into benzene. Removal of the benzene solvent *in vacuo* afforded $FeHBr(PP_3)$, **4**, as a yellow solid, which was recrystallized from hexane/benzene (18 mg, 90%); mp 187.5−188.5 °C.

^{31}P{^{1}H} NMR spectrum (162 MHz, benzene-d_6, 300 K), δ: 189.7 (dt, 1P, $\mathbf{P_C}$, $^2J_{P(C)-P(T)}$ = 30.5 Hz, $^2J_{P(C)-P(U)}$ = 24.0 Hz); 59.9 (dd, 2P, $\mathbf{P_T}$, $^2J_{P(T)-P(U)}$ = 21.8 Hz); 58.1 (dt, 1P, $\mathbf{P_U}$). ^{1}H{^{31}P} NMR spectrum (400 MHz, benzene-d_6, 300 K), δ: −11.89 (s, 1H, Fe−**H**); 1.24, 1.29, 1.41, 1.79 (4 × m, 4 × 2H, $-P_C\mathbf{HH}C\mathbf{HH}P_T-$); 1.10, 1.26 (2 × m, 2 × 2H, $-P_CC\mathbf{H_2}C\mathbf{H_2}P_U-$); 1.52, 2.05 (2 × s, 2 × 6H, 2 × $-P_T(C\mathbf{H_3})$); 1.57 (s, 6H, $-P_U(C\mathbf{H_3})_2$). ^{13}C{^{1}H} NMR spectrum (101 MHz, benzene-d_6, 300 K), δ: 26.6 (dt, $-P_T(CH_3)$, $^1J_{P(T)-C}$ = 16.7 Hz, $^3J_{P(U)-C}$ = 7.2 Hz); 18.9 (t, $-P_T(\mathbf{C}H_3)$, $^1J_{P(T)-C}$ = 2.9 Hz); 19.7 (dt, $-P_U(\mathbf{C}H_3)_2$, $^1J_{P(U)-C}$ = 12.4 Hz, $^3J_{P(T)-C}$ = 3.0 Hz); 27.2 (ddt, $-P_TCH_2\mathbf{C}H_2P_C-$, $^1J_{P(C)-C}$ = 23.4 Hz, $^2J_{P(T)-C}$ = 9.1 Hz, $^3J_{P(U)-C}$ = 1.4 Hz); 34.3 (dt, $-P_T\mathbf{C}H_2CH_2P_C-$, $^1J_{P(T)-C}$ = 15.3 Hz, $^2J_{P(C)-C}$ = 15.3 Hz); 27.7 (ddt, $-P_UCH_2\mathbf{C}H_2P_C-$, $^1J_{P(C)-C}$ = 20.5 Hz, $^2J_{P(U)-C}$ = 17.6 Hz, $^3J_{P(T)-C}$ = 1.9 Hz); 33.5 (dd, $-P_U\mathbf{C}H_2CH_2P_C-$, $^1J_{P(U)-C}$ = 25.7 Hz, $^2J_{P(C)-C}$ = 15.3 Hz). MS (CI, CH_4), *m/z* > 300: 436 ($FeH^{81}Br(PP_3)$, 86), 435 ($Fe^{81}Br(PP_3)$, 100), 434 ($FeH^{79}Br(PP_3)$, 90), 433 ($Fe^{79}Br(PP_3)$, 100), 427 (14), 425 (23), 421 (11), 419 (12), 399 (15), 383 (11), 382 (12), 371 (16), 365 (22), 353 (13) 331 ($(PP_3)O_2$, 20), 329 (22), 327 (24), 315 ($(PP_3)O$, 20). Anal. Calcd for $C_{12}H_{31}BrFeP_4$: C, 33.13; H, 7.18. Found: C, 33.2; H, 6.6.

$FeHI(PP_3)$, 5. Potassium iodide (40 mg, 270 μmol) was added to a solution of $FeHCl(PP_3)$, **2** (33 mg, 85 μmol), in ethanol (2 mL), resulting in a rapid darkening of the solution from bright to dark yellow. The solution was filtered, the filtrate evaporated to dryness *in vacuo*, and the residue extracted into benzene. Removal of the benzene *in vacuo* afforded $FeHI(PP_3)$, **5**, as a dark yellow solid, which was recrystallized from hexane/benzene (35 mg, 85%); mp > 300 °C dec.

^{31}P{^{1}H} NMR spectrum (162 MHz, benzene-d_6, 300 K), δ: 195.4 (dt, 1P, $\mathbf{P_C}$, $^2J_{P(C)-P(T)}$ = 32.7 Hz, $^2J_{P(C)-P(U)}$ = 26.2 Hz); 58.6 (dd, 2P, $\mathbf{P_T}$, $^2J_{P(T)-P(U)}$ = 22.9 Hz); 56.1 (dt, 1P, $\mathbf{P_U}$). ^{1}H{^{31}P} NMR spectrum (400 MHz, benzene-d_6, 300 K), δ: −12.69 (s, 1H, Fe−**H**)); 1.21, 1.21, 1.48, 1.81 (4 × m, 4 × 2H, $-P_CC\mathbf{HH}C\mathbf{HH}P_T-$); 1.09, 1.21 (2 × m, 2 × 2H, $-P_CC\mathbf{H_2}C\mathbf{H_2}P_U-$); 1.57, 2.07 (2 × s, 2 × 6H, 2 × $-P_T(C\mathbf{H_3})$); 1.57 (s, 6H, $-P_U(C\mathbf{H_3})_2$). ^{13}C{^{1}H} NMR spectrum (101 MHz, benzene, 300 K), δ: 28.8 (dt, $-P_T(\mathbf{C}H_3)$, $^1J_{P(T)-C}$ = 18.1 Hz, $^3J_{P(U)-C}$ = 7.2 Hz); 19.5 (t, $-P_T(\mathbf{C}H_3)$, $^1J_{P(T)-C}$ = 4.3 Hz); 20.8 (dt, $-P_U(\mathbf{C}H_3)_2$, $^1J_{P(U)-C}$ = 14.3 Hz, $^3J_{P(T)-C}$ = 2.9 Hz); 27.5 (ddt, $-P_TCH_2\mathbf{C}H_2P_C-$, $^1J_{P(C)-C}$ = 24.3 Hz, $^2J_{P(T)-C}$ = 9.1 Hz, $^3J_{P(U)-C}$ = 1.9 Hz); 33.8 (dt, $-P_T\mathbf{C}H_2CH_2P_C-$, $^1J_{P(T)-C}$ = 14.8 Hz, $^2J_{P(C)-C}$ = 14.8 Hz); 27.3 (dt, $-P_UCH_2\mathbf{C}H_2P_C-$, $^1J_{P(C)-C}$ = 20.0 Hz, $^2J_{P(U)-C}$ = 18.1 Hz); 33.6 (dd, $-P_U\mathbf{C}H_2CH_2P_C-$, $^1J_{P(U)-C}$ = 26.7 Hz, $^2J_{P(C)-C}$ = 15.3 Hz). MS (CI, CH_4), *m/z* > 250: 483 (M + 1, 16), 482 (M, 100), 481 (M − 1, 88), 467 (M − Me, 9), 353 (8). Anal. Calcd for $C_{12}H_{31}FeIP_4$: C, 29.90; H, 6.48. Found: C, 30.5; H, 6.6.

$FeHN_3(PP_3)$, 6. Sodium azide (20 mg, 310 μmol) was added to a solution of $FeHCl(PP_3)$, **2** (32 mg, 82 μmol), in ethanol (2 mL). The solution was heated at 60 °C and the reaction followed by ^{31}P NMR spectroscopy; after 10 min, all of the chloro hydrido complex **2** had been converted to $FeHN_3(PP_3)$, **6**. The solution was filtered, the filtrate evaporated to dryness *in vacuo*, and the residue extracted into benzene. Removal of the benzene solvent *in vacuo* afforded $FeHN_3(PP_3)$, **6**, as a yellow solid, which was recrystallized from hexane/benzene (26 mg, 80%); mp 140.5-141.0 °C.

^{31}P{^{1}H} NMR spectrum (162 MHz, toluene-d_8, 300 K), δ: 179.8 (dt, 1P, $\mathbf{P_C}$, $^2J_{P(C)-P(T)}$ = 26.9 Hz, $^2J_{P(C)-P(U)}$ = 18.2 Hz); 61.4 (dd, 2P, $\mathbf{P_T}$, $^2J_{P(T)-P(U)}$ = 21.1 Hz); 59.4 (dt, 1P, $\mathbf{P_U}$). ^{1}H{^{31}P} NMR spectrum (600 MHz, toluene-d_8, 303 K), δ: −12.04 (s, 1H, Fe−**H**); 1.27, 1.60 (2 × m, 2 × 2H, $-P_CCH_2C\mathbf{HH}P_T-$); 1.20, 1.23 (2 × m, 2 × 2H, $-P_CC\mathbf{HH}CH_2P_T-$); 1.03 (m, 2H, $-P_CC\mathbf{H_2}CH_2P_U-$); 1.17 (m, 2H, $-P_CCH_2C\mathbf{H_2}P_U-$); 1.39, 1.83 (2 × s, 2 × 6H, 2 × $-P_T(C\mathbf{H_3})$); 1.50 (s, 6H, $-P_U(C\mathbf{H_3})_2$). ^{13}C{^{1}H} NMR spectrum (101 MHz, benzene, 300 K), δ: 24.8 (dt, $-P_T(\mathbf{C}H_3)$, $^1J_{P(T)-C}$ = 14.8 Hz, $^3J_{P(U)-C}$ = 6.7 Hz); 19.6 (br s, $-P_T(\mathbf{C}H_3)$); 20.0 (dt, $-P_U(\mathbf{C}H_3)_2$, $^1J_{P(U)-C}$ = 9.5 Hz, $^3J_{P(T)-C}$ = 3.3 Hz); 26.7 (ddt, $-P_TCH_2\mathbf{C}H_2P_C-$, $^1J_{P(C)-C}$ = 22.9 Hz, $^2J_{P(T)-C}$ = 9.1 Hz, $^3J_{P(U)-C}$ = 1.9 Hz); 34.7 (dt, $-P_T\mathbf{C}H_2CH_2P_C-$, $^1J_{P(T)-C}$ = 16.7 Hz, $^2J_{P(C)-C}$ = 16.7 Hz); 27.5 (dt, $-P_UCH_2\mathbf{C}H_2P_C-$, $^1J_{P(C)-C}$ = 20.5 Hz, $^2J_{P(U)-C}$ = 16.7 Hz); 33.7 (dd, $-P_U\mathbf{C}H_2CH_2P_C-$, $^1J_{P(U)-C}$ = 27.7 Hz, $^2J_{P(C)-C}$ = 16.2 Hz). IR ν_{max} (Nujol): 2027 cm^{-1} ($-N_3$).

$Fe(N_3)_2(PP_3)$, 10. Sodium azide (20 mg, 310 μmol) was added to a solution of $FeCl_2(PP_3)$, **17** (33 mg, 78 μmol), in ethanol (3 mL) and the reaction mixture stirred overnight. The solution was filtered and the solvent removed *in vacuo*. The residue was extracted into acetone (10 mL) and the resulting solution filtered. Removal of the benzene solvent *in vacuo* afforded the dark orange bis(azide) complex $Fe(N_3)_2(PP_3)$, **10** (30 mg, 88%); mp 208−211 °C dec.

In an alternative preparation, excess sodium azide was added to a solution of $FeHCl(PP_3)$, **2**, in methanol. The solution was heated at 60 °C and the reaction followed by ^{31}P NMR spectroscopy. Initially, the azide hydride complex FeHN$_3$(PP$_3$), **6**, was formed, which reacted with further azide to afford the dark orange bis(azide) complex Fe(N$_3$)$_2$(PP$_3$), **10**, over the period of 1 h.

^{31}P{^{1}H} NMR spectrum (162 MHz, CD$_3$OD, 233 K), δ: 169.0 (dt, 1P, $\mathbf{P_C}$, $^2J_{\mathrm{P(C)-P(T)}} = 27.5$ Hz, $^2J_{\mathrm{P(C)-P(U)}} = 30.5$ Hz); 53.7 (dd, 2P, $\mathbf{P_T}$, $^2J_{\mathrm{P(T)-P(U)}} = 44.3$ Hz); 79.9 (dt, 1P, $\mathbf{P_U}$). ^{1}H{^{31}P} NMR spectrum (400 MHz, methanol-d_4, 233 K), δ: 1.88, 1.95, 2.36, 2.36 (4 × m, 4 × 2H, $-\mathrm{P_CC\mathbf{HH}C\mathbf{HH}P_T}-$); 1.59, 1.81 (2 × m, 2 × 2H, $-\mathrm{P_CC\mathbf{H_2}C\mathbf{H_2}P_U}-$); 1.55, 1.70 (2 × s, 2 × 6H, 2 × $-\mathrm{P_T(C\mathbf{H_3})}$); 1.40 (s, 6H, $-\mathrm{P_U(C\mathbf{H_3})_2}$). ^{13}C{^{1}H} NMR spectrum (101 MHz, CD$_3$OD, 233 K), δ: 15.5, 17.8 (2 × m, $-\mathrm{P_T(\mathbf{C}H_3)}$); 18.4 (m, $-\mathrm{P_U(\mathbf{C}H_3)_2}$); 24.9, 26.0, 32.0, 33.9 (4 × m, $-\mathrm{P\mathbf{C}H_2CH_2P}-$). IR $\nu_{\max}$ (Nujol): 2023, 2029 cm^{-1} ($-$N$_3$).

[FeH(CO)(PP$_3$)]$^+$, 7. A solution containing FeHCl(PP$_3$), **2** (19 mg, 49 μmol), and sodium tetraphenylborate (20 mg, 58 μmol) in ethanol (4 mL) was placed under an atmosphere of carbon monoxide. Within a few minutes, a white precipitate began to form. After 30 min of standing, the precipitate was isolated by filtration, washed with ethanol (10 mL), and dried *in vacuo* to afford [FeH(CO)(PP$_3$)]$^+$, **7** (BPh$_4$ salt) (22 mg, 64%); mp 294−296 °C dec.

Alternatively, a solution of the chloride salt of **7** was formed as above, without the addition of sodium tetraphenylborate.

^{31}P{^{1}H} NMR spectrum (BPh$_4$ salt, 162 MHz, acetone-d_6, 300 K), δ: 174.3 (dt, 1P, $\mathbf{P_C}$, $^2J_{\mathrm{P(C)-P(T)}} = 33.1$ Hz, $^2J_{\mathrm{P(C)-P(U)}} = 36.6$ Hz); 67.2 (dd, 2P, $\mathbf{P_T}$, $^2J_{\mathrm{P(T)-P(U)}} = 17.8$ Hz); 67.9 (dt, 1P, $\mathbf{P_U}$). ^{1}H{^{31}P} NMR spectrum (BPh$_4$ salt, 600 MHz, acetone-d_6, 303 K), δ: −13.56 (s, 1H, Fe−**H**); 2.19, 2.40 (2 × m, 2 × 2H, $-\mathrm{P_CCH_2C\mathbf{HH}P_T}-$); 2.29, 2.53 (2 × m, 2 × 2H, $-\mathrm{P_CC\mathbf{HH}CH_2P_T}-$); 2.28 (m, 2H, $-\mathrm{P_CC\mathbf{H_2}CH_2P_U}-$); 2.05 (m, 2H, $-\mathrm{P_CCH_2C\mathbf{H_2}P_U}-$); 1.72, 1.76 (2 × s, 2 × 6H, 2 × $-\mathrm{P_T(C\mathbf{H_3})}$); 1.69 (s, 6H, $-\mathrm{P_U(C\mathbf{H_3})_2}$); 7.46 (br, 8H, B$\mathbf{Ph_{ortho}}$); 7.08 (t, 8H, $^3J_{\mathrm{H-H}} = 7.1$ Hz, B$\mathbf{Ph_{meta}}$); 6.93 (t, 4H, B$\mathbf{Ph_{para}}$). ^{13}C{^{1}H} NMR spectrum (BPh$_4$ salt, 101 MHz, acetone-d_6, 300 K, carbonyl resonance only), δ: 218.9 (ddt, 1C, **C**O, $^2J_{\mathrm{P(C)-C}} = 31.5$ Hz, $^2J_{\mathrm{P(T)-C}} = 20.0$ Hz, $^2J_{\mathrm{P(U)-C}} = 17.2$ Hz). ^{13}C{^{1}H} NMR spectrum (chloride salt, 101 MHz, methanol, 300 K), δ: 25.7 (m, $-\mathrm{P_T(\mathbf{C}H_3)}$); 18.9 (t, $-\mathrm{P_T(\mathbf{C}H_3)}$, $^1J_{\mathrm{P(T)-C}} = 9.4$ Hz); 19.6 (dt, $-\mathrm{P_U(\mathbf{C}H_3)_2}$, $^1J_{\mathrm{P(U)-C}} = 23.5$ Hz, $^3J_{\mathrm{P(T)-C}} = 2.9$ Hz); 25.8 (m, $-\mathrm{P_TCH_2\mathbf{C}H_2P_C}-$); 34.7 (dt, $-\mathrm{P_T\mathbf{C}H_2CH_2P_C}-$, $^1J_{\mathrm{P(T)-C}} = 15.3$ Hz, $^2J_{\mathrm{P(C)-C}} = 17.6$ Hz); 25.6 (m, $-\mathrm{P_UCH_2\mathbf{C}H_2P_C}-$); 33.7 (dd, $-\mathrm{P_U\mathbf{C}H_2CH_2P_C}-$, $^1J_{\mathrm{P(U)-C}} = 29.3$ Hz, $^2J_{\mathrm{P(C)-C}} = 15.3$ Hz). MS (+CI, CH$_4$), *m/z* >150: 384 (M + 1, 7), 383 (M, 50), 382 (FePP$_3$CO, 53), 183 (10), 165 (100), 155 (42). IR $\nu_{\max}$ (Nujol, BPh$_4$ salt): 1936 cm^{-1} ($-$CO).

[FeH(N$_2$)(PP$_3$)]$^+$, 8. A solution containing FeHCl(PP$_3$), **2** (67 mg, 170 μmol), and sodium tetraphenylborate (60 mg, 180 μmol) in ethanol (4 mL), under argon, was flushed with dinitrogen. Within a few minutes, a white precipitate began to form. After 30 min of standing under a nitrogen atmosphere, this precipitate was isolated by filtration, washed with ethanol (10 mL), and dried *in vacuo* to afford [FeH(N$_2$)(PP$_3$)]$^+$, **8** (BPh$_4$ salt) (82 mg, 68%); mp 225−230 °C dec.

^{31}P{^{1}H} NMR spectrum (BPh$_4$ salt, 162 MHz, acetone-d_6, 300 K), δ: 172.3 (dt, 1P, $\mathbf{P_C}$, $^2J_{\mathrm{P(C)-P(T)}} = 30.5$ Hz, $^2J_{\mathrm{P(C)-P(U)}} = 27.1$ Hz); 63.2 (dd, 2P, $\mathbf{P_T}$, $^2J_{\mathrm{P(T)-P(U)}} = 17.0$ Hz); 61.4 (dt, 1P, $\mathbf{P_U}$). ^{1}H{^{31}P} NMR spectrum (BPh$_4$ salt, 400 MHz, acetone-d_6, 243 K), δ: −12.66 (s, 1H, Fe−**H**); 1.9−2.3 (6 × m, 6 × 2H, $-\mathrm{PC\mathbf{HH}C\mathbf{HH}P}-$); 1.70, 1.76 (2 × s, 2 × 6H, 2 × $-\mathrm{P_T(C\mathbf{H_3})}$); 1.68 (s, 6H, $-\mathrm{P_U(C\mathbf{H_3})_2}$); 7.46 (br, 8H, B$\mathbf{Ph_{ortho}}$); 7.08 (t, 8H, $^3J_{\mathrm{H-H}} = 7.1$ Hz, B$\mathbf{Ph_{meta}}$); 6.93 (t, 4H, B$\mathbf{Ph_{para}}$). ^{13}C{^{1}H} NMR spectrum (BPh$_4$ salt, 101 MHz, acetone-d_6, 243 K), δ: 23.5 (t, $-\mathrm{P_T(\mathbf{C}H_3)}$, $^1J_{\mathrm{P(T)-C}} = 15.3$ Hz); 18.0 (t, $-\mathrm{P_T(\mathbf{C}H_3)}$, $^1J_{\mathrm{P(T)-C}} = 6.5$ Hz); 18.6 (d, $-\mathrm{P_U(\mathbf{C}H_3)_2}$, $^1J_{\mathrm{P(U)-C}} = 19.6$ Hz); 26.2 (m, $-\mathrm{P_TCH_2\mathbf{C}H_2P_C}-$); 33.2 (dt, $-\mathrm{P_T\mathbf{C}H_2CH_2P_C}-$, $^1J_{\mathrm{P(T)-C}} = 18.9$ Hz, $^2J_{\mathrm{P(C)-C}} = 12.4$ Hz); 25.9 (m, $-\mathrm{P_UCH_2\mathbf{C}H_2P_C}-$); 32.3 (m, $-\mathrm{P_UCH_2CH_2P_C}-$) 122.5 (BPh$_4$), 126.3 (BPh$_4$), 137.0 (BPh$_4$), 164.8 (BPh$_4$). IR $\nu_{\max}$ (Nujol, BPh$_4$ salt): 2117 cm^{-1} ($-$N$_2$).

[FeH(PP$_3$)N≡NFeH(PP$_3$)]$^{2+}$, 11. FeN$_2$(PP$_3$) **13** (15 mg, 39 μmol) was dissolved in ethanol (0.5 mL), initially affording [FeH(N$_2$)(PP$_3$)]$^+$, **8**. On 16 h of standing, the major product was the dinitrogen-bridged dimer [FeH(PP$_3$)N≡NFeH(PP$_3$)]$^{2+}$, **11**. Sodium tetraphenylborate (20 mg, 58 μmol) was added, forming a pale yellow precipitate, which was collected by filtration and washed with ethanol (2 mL). The precipitate was partially extracted with acetone (1 mL), and ^{31}P NMR indicated that this extract contained mainly [FeH(N$_2$)(PP$_3$)]$^+$, **8**, and other byproducts as well as some [FeH(PP$_3$)N≡NFeH(PP$_3$)]$^{2+}$, **11**. Extraction of the residue into acetone (5 mL) and removal of solvent *in vacuo* afforded [FeH(PP$_3$)N≡NFeH(PP$_3$)]$^{2+}$, **11** (BPh$_4$ salt) (10 mg, 37%), as a pale yellow solid.

^{31}P{^{1}H} NMR spectrum (BPh$_4$ salt, 162 MHz, acetone-d_6, 300 K), δ: 172.7 (dt, 1P, $\mathbf{P_C}$, $^2J_{\mathrm{P(C)-P(T)}} = 30.5$ Hz, $^2J_{\mathrm{P(C)-P(U)}} = 25.4$ Hz); 62.2 (dd, 2P, $\mathbf{P_T}$, $^2J_{\mathrm{P(T)-P(U)}} = 17.0$ Hz); 59.6 (dt, 1P, $\mathbf{P_U}$). ^{1}H{^{31}P} NMR spectrum (methoxide salt, 400 MHz, methanol-d_4, 300 K), δ: −12.51 (s, 1H, Fe−**H**); 1.95−2.3 (6 × m, 6 × 2H, $-\mathrm{PC\mathbf{HH}C\mathbf{HH}P}-$); 1.75, 1.90 (2 × s, 2 × 6H, 2 × $-\mathrm{P_T(C\mathbf{H_3})}$); 1.75 (s, 6H, $-\mathrm{P_U(C\mathbf{H_3})_2}$). ^{13}C{^{1}H} NMR spectrum (methoxide salt, 101 MHz, methanol-d_4, 300 K), δ: 25.5 (t, $-\mathrm{P_T(\mathbf{C}H_3)}$, $^1J_{\mathrm{P(T)-C}} = 18.4$ Hz); 20.2 (t, $-\mathrm{P_T(\mathbf{C}H_3)}$, $^1J_{\mathrm{P(T)-C}} = 6.3$ Hz); 20.7 (d, $-\mathrm{P_U(\mathbf{C}H_3)_2}$, $^1J_{\mathrm{P(U)-C}} = 18.0$ Hz); 26.9 (dt, $-\mathrm{P_TCH_2\mathbf{C}H_2P_C}-$, $^1J_{\mathrm{P(C)-C}} = 29.2$ Hz, $^2J_{\mathrm{P(T)-C}} = 9.0$ Hz); 34.6 (dt, $-\mathrm{P_T\mathbf{C}H_2CH_2P_C}-$, $^1J_{\mathrm{P(T)-C}} = 18.0$ Hz, $^2J_{\mathrm{P(C)-C}} = 13.9$ Hz); 27.4 (dd, $-\mathrm{P_UCH_2\mathbf{C}H_2P_C}-$, $^1J_{\mathrm{P(C)-C}} = 25.6$ Hz, $^2J_{\mathrm{P(U)-C}} = 18.8$ Hz); 33.4 (dd, $-\mathrm{P_U\mathbf{C}H_2CH_2P_C}-$, $^1J_{\mathrm{P(U)-C}} = 31.4$ Hz, $^2J_{\mathrm{P(C)-C}} = 12.1$ Hz). Raman $\nu_{\max}$ (solid state, BPh$_4$ salt): 2054, 2064 cm^{-1} ($-$N$_2$). Anal. Calcd for C$_{72}$H$_{102}$B$_2$Fe$_2$N$_2$P$_8$: C, 62.82; H, 7.47; N, 2.03. Found: C, 62.4; H, 7.3; N, 1.9.

[FeH(PPh$_3$)(PP$_3$)]$^+$, 9. Triphenylphosphine (30 mg, 120 μmol) was added to a solution of FeHCl(PP$_3$), **2** (25 mg, 64 μmol), in methanol (2 mL). The mixture was heated at 60 °C for 10 min, resulting in a color change from bright to pale yellow. A solution of sodium tetraphenylborate (40 mg, 120 μmol) in methanol (2 mL) was added, resulting in the formation of a pale yellow precipitate, which was isolated by filtration, washed with methanol (10 mL), and dried *in vacuo* to afford [FeH(PPh$_3$)(PP$_3$)]$^+$, **9** (BPh$_4$ salt) (46 mg, 77%); mp 199−201 °C dec.

Alternatively, a solution of the chloride salt of **9** was formed as above, without the addition of sodium tetraphenylborate.

^{31}P{^{1}H} NMR spectrum (BPh$_4$ salt, 162 MHz, acetone-d_6, 300 K), δ: 173.4 (ddt, 1P, $\mathbf{P_C}$, $^2J_{\mathrm{P(C)-P(T)}} = 35.8$ Hz, $^2J_{\mathrm{P(C)-P(U)}} = 21.2$ Hz, $^2J_{\mathrm{P(C)-PPh_3}} = 70.3$ Hz); 52.3 (ddd, 2P, $\mathbf{P_T}$, $^2J_{\mathrm{P(T)-P(U)}} = 18.6$ Hz, $^2J_{\mathrm{P(T)-PPh_3}} = 45.1$ Hz); 49.6 (ddt, 1P, $\mathbf{P_U}$, $^2J_{\mathrm{P(U)-PPh_3}} = 30.5$ Hz); 74.2 (ddt, 1P, **P**Ph$_3$). ^{1}H{^{31}P} NMR spectrum (BPh$_4$ salt, 600 MHz, acetone-d_6, 288 K), δ: −15.17 (s, 1H, Fe−**H**); 2.00, 2.25 (2 × m, 2 × 2H, $-\mathrm{P_CCH_2C\mathbf{HH}P_T}-$); 2.17, 2.52 (2 × m, 2 × 2H, $-\mathrm{P_CC\mathbf{HH}CH_2P_T}-$); 2.17 (m, 2H, $-\mathrm{P_CC\mathbf{H_2}CH_2P_T}-$); 1.98 (m, 2H, $-\mathrm{P_CCH_2C\mathbf{H_2}P_U}-$); 1.00, 1.27 (2 × s, 2 × 6H, 2 × $-\mathrm{P_T(C\mathbf{H_3})}$); 1.55 (s, 6H, $-\mathrm{P_U(C\mathbf{H_3})_2}$); 7.70 (m, 5H, P**Ph**); 7.46 (br, 8H, B$\mathbf{Ph_{ortho}}$); 7.08 (t, 8H, $^3J_{\mathrm{H-H}} = 7.1$ Hz, B$\mathbf{Ph_{meta}}$); 6.93 (t, 4H, B$\mathbf{Ph_{para}}$). ^{13}C{^{1}H} NMR spectrum (chloride salt, 101 MHz, methanol, 300 K), δ: 24.7 (dt, $-\mathrm{P_T(\mathbf{C}H_3)}$, $^1J_{\mathrm{P(T)-C}} = 16.4$ Hz, $^3J_{\mathrm{P(U)-C}} = 5.9$ Hz); 17.8 (t, $-\mathrm{P_T(\mathbf{C}H_3)}$, $^1J_{\mathrm{P(T)-C}} = 5.9$ Hz); 20.3 (dt, $-\mathrm{P_U(\mathbf{C}H_3)_2}$, $^1J_{\mathrm{P(U)-C}} = 17.6$ Hz, $^3J_{\mathrm{P(T)-C}} = 2.3$ Hz); 25.5 (ddt, $-\mathrm{P_TCH_2\mathbf{C}H_2P_C}-$, $^1J_{\mathrm{P(C)-C}} = 28.8$ Hz, $^2J_{\mathrm{P(T)-C}} = 8.8$ Hz, $^3J_{\mathrm{P(U)-C}} = 2.3$ Hz); 36.9 (m, $-\mathrm{P_T\mathbf{C}H_2CH_2P_C}-$); 25.2 (dt, $-\mathrm{P_UCH_2\mathbf{C}H_2P_C}-$, $^1J_{\mathrm{P(C)-C}} = 20.0$ Hz, $^2J_{\mathrm{P(U)-C}} = 16.4$ Hz); 37.1 (m, $-\mathrm{P_U\mathbf{C}H_2CH_2P_C}-$); 140.8 (br, $\mathbf{Ph_{ipso}}$); 135.8, 128.5 (br, $\mathbf{Ph_{ortho}}$, $\mathbf{Ph_{meta}}$); 130.2 (br, $\mathbf{Ph_{para}}$). Anal. Calcd for C$_{54}$H$_{66}$BFeP$_4$: C, 69.17; H, 7.20. Found: C, 68.8; H, 7.2.

Fe(CO)(PP$_3$), 12. [FeH(CO)(PP$_3$)]$^+$, **7** (BPh$_4$ salt) (30 mg, 43 μmol), was partially dissolved in THF (5 mL), and potassium *tert*-butoxide (15 mg, 130 μmol) was added. The suspension of **7** dissolved, affording a yellow solution. The THF solvent was removed *in vacuo* and the residue extracted into benzene. The resulting mixture was filtered, the solvent removed from the filtrate *in vacuo*, and the residue extracted into hexane. Filtration of the resulting mixture and removal of hexane from the filtrate *in vacuo* afforded Fe(CO)(PP$_3$), **12** (12 mg, 73%).

^{31}P{^{1}H} NMR spectrum (162 MHz, benzene-d_6, 300 K), δ: 188.1 (q, 1P, $\mathbf{P_C}$, $^2J_{\mathrm{P(C)-P(E)}} = 53.0$ Hz); 73.4 (d, 3P, $\mathbf{P_E}$). ^{1}H{^{31}P} NMR spectrum (400 MHz, benzene-d_6, 300 K), δ: 1.55, 1.60 (2 × m, 2 × 6H, $-\mathrm{P_CC\mathbf{H_2}C\mathbf{H_2}P_E}-$); 1.58 (s, 18H, $-\mathrm{P_E(C\mathbf{H_3})}$). ^{13}C{^{1}H} NMR spectrum (101 MHz, benzene-d_6, 300 K, carbonyl region only), δ: 237.7 (dq, **C**O, $^2J_{\mathrm{P(C)-C}} = 27.7$ Hz, $^2J_{\mathrm{P(E)-C}} = 23.3$ Hz). MS (+CI, CH$_4$), *m/z* > 200: 383 (M + 1, 27), 382 (M, 79), 359 (13), 347 (PP$_3$O$_3$ + 1, 15), 343 (21), 331 (PP$_3$O$_2$ + 1, 58), 315 (PP$_3$O + 1, 100), 299 (PP$_3$ + 1, 18), 225 (11). IR $\nu_{\max}$ (Nujol): 1855 cm^{-1} ($-$CO).

Fe(N$_2$)(PP$_3$), 13. [FeH(N$_2$)(PP$_3$)]$^+$, **8** (BPh$_4$ salt) (30 mg, 43 μmol), was partially dissolved in THF (5 mL), and potassium *tert*-butoxide (15 mg, 130 μmol) was added. The suspension of **8** dissolved, affording a yellow solution. The THF solvent was removed *in vacuo*, and the residue was extracted into benzene. The resulting mixture was filtered, the solvent removed from the filtrate *in vacuo*, and the residue was

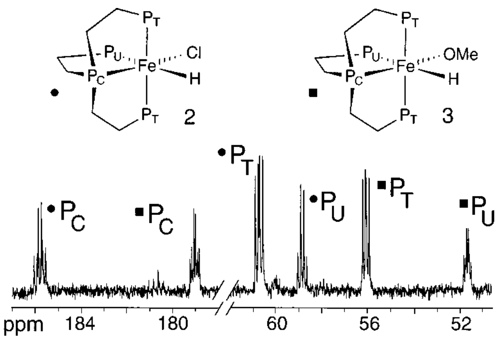
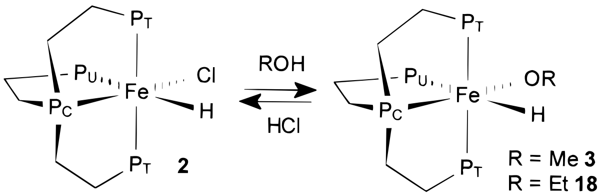


Figure 1. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, methanol) of $FeHCl(PP_3)$, **2** and $FeH(OMe)(PP_3)$, **3**.

Scheme 1



extracted into hexane. Filtration of the resulting mixture and removal of hexane from the filtrate *in vacuo* afforded $Fe(N_2)(PP_3)$, **13** (11 mg, 67%).

$^{31}P\{^1H\}$ NMR spectrum (162 MHz, benzene-d_6, 300 K), δ: 181.7 (q, 1P, $\mathbf{P_C}$, $^2J_{P(C)-P(E)} = 45.8$ Hz); 66.0 (d, 3P, $\mathbf{P_E}$). $^1H\{^{31}P\}$ NMR spectrum (400 MHz, benzene-d_6, 300 K), δ: 1.40−1.50 (2 × m, 2 × 6H, $-P_CC\mathbf{H_2}C\mathbf{H_2}P_E-$); 1.60 (s, 18H, $-P_E(C\mathbf{H_3})$). $^{13}C\{^1H\}$ NMR spectrum (101 MHz, benzene-d_6, 300 K), δ: 23.9 (m, $-P(\mathbf{C}H_3)_2$), 29.4, 35.2 (2 × m, 2 × $-\mathbf{C}H_2-$). IR ν_{max} (Nujol): 2013 cm^{-1} ($-N_2$).

Results and Discussion

Reaction of $FeHCl(PP_3)$, 2, with Methanol. Dissolution of $FeHCl(PP_3)$, **2**,[9] in methanol affords an equilibrium mixture of **2** and the methoxy hydrido complex **3** (Scheme 1).

The $^{31}P\{^1H\}$ NMR spectrum of a solution of **2** in methanol contains resonances of **2** and **3** (Figure 1). The resonances at δ 185.8 (dt, P_C), 60.7 (dd, P_T) and 58.8 (dt, P_U) ppm were assigned to **2**. The chemical shifts of **2** (in methanol) are slightly different to those observed in other solvents;[9] however, the $^{31}P-^{31}P$ coupling constants vary little between solvents (in toluene solution the chemical shifts of **2** are δ 183.8 (P_C), 60.2 (P_T), and 58.8 (P_U)). The remaining resonances at δ 179.0 (dt, P_C), 56.1 (dd, P_T), and 50.2 (dt, P_U) in the $^{31}P\{^1H\}$ NMR spectrum were assigned to **3**.

While $FeH(OMe)(PP_3)$, **3**, has not been characterized as an isolated pure compound, the complex has been prepared independently by the reaction of $FeH(Ph)(PP_3)$ with methanol in benzene solution.[10,11] This reaction proceeds via the facile (thermal) elimination of benzene from $FeH(Ph)(PP_3)$ followed by the oxidative addition to the O−H bond of methanol to the coordinatively unsaturated complex $[Fe(PP_3)]$. In toluene-d_8 as solvent, the ^1H NMR spectrum of **3** has been fully assigned using COSY and NOESY experiments.[10]

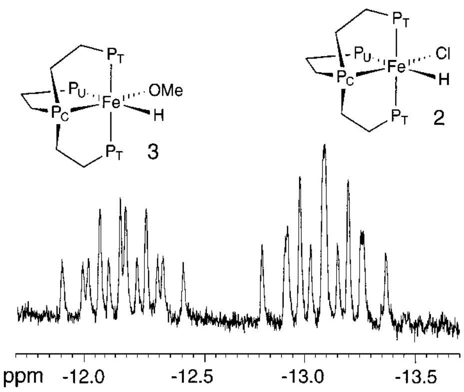


Figure 2. High-field region of the ^1H NMR spectrum (400 MHz, 300 K, methanol-d_4) of $FeHCl(PP_3)$, **2**, and $FeH(OMe)(PP_3)$, **3**.

The hydride region of the ^1H NMR spectrum of the mixture of **2** and **3** in methanol-d_4 contains two multiplet resonances at δ −13.09 (due to **2**) and δ −12.18 (due to **3**) (Figure 2). Again, the ^1H chemical shift of the hydride resonance of **2** was significantly different in methanol solution from that in nonprotic solvents (in toluene-d_8, the shift of the hydride resonance of **2** is −11.63 ppm).[9]

Integration of the resonances in the $^{31}P\{^1H\}$ NMR spectrum of a mixture containing 10 mg of **2** in 0.5 mL of methanol showed the ratio **2**:**3** to be approximately 1.4:1. Removal of the methanol solvent and reconstitution into a nonprotic solvent, *e.g.* toluene, result in complete reversion to **2**. The addition of sodium chloride to a methanol solution containing **2** and **3** increased the proportion of **2**. Conversely, the addition of a base, *e.g.* sodium hydroxide, increased the proportion of **3**.

Dissolution of **2** in ethanol (approximately 10 mg of **2** in 0.5 mL of ethanol) also resulted in an equilibrium between **2** and the ethoxy hydrido complex **18** (Scheme 1). In this case, the equilibrium lies significantly further toward **2** with a **2**:**18** ratio of approximately 18:1.

When the samples were allowed to stand in methanol-d_4, the intensity of the hydride resonances of both **2** and **3** decreased due to the incorporation of deuterium. This was also evident in the $^{31}P\{^1H\}$ NMR spectrum from the presence of new resonances containing 1:1:1 triplet couplings (due to $^{31}P-^2D$ coupling), slightly isotopically shifted from those due **2** and **3**. The ^{31}P chemical shifts of $FeDCl(PP_3)$, **2-*d*$_1$**, were isotopically shifted with respect to $FeHCl(PP_3)$, **2**, by 130 ppb downfield for P_C, 230 ppb downfield for P_T, and 270 ppb upfield for P_U. The ^{31}P chemical shifts of $FeD(OMe)(PP_3)$, **3-*d*$_1$**, were isotopically shifted with respect to $FeH(OMe)(PP_3)$, **3**, by 160 ppb downfield for P_C, 220 ppb downfield for P_T, and 250 ppb upfield for P_U.

On prolonged standing in alcohol solvent (>16 h at room temperature or 2 h at 60 °C), **2** reacts further to form the dihydrogen hydrido complex $[FeH(H_2)(PP_3)]^+$, **19**, and the carbonyl hydrido complex $[FeH(CO)(PP_3)]^+$, **7**. The molecular hydrogen complex **19** has been synthesized independently by protonation of the dihydride $[FeH_2(PP_3)]$ and fully characterized.[10,12] The molecular hydrogen complex is similar to that formed by related iron phosphine complexes.[3−5] The formation of **7** is discussed in detail elsewhere but could proceed via β-hydride elimination from the alkoxide complexes.[10]

Substitution Reactions of $FeHCl(PP_3)$, 2. Both the chloro and hydride ligands of the chloro hydrido complex **2** are potentially labile and susceptible to displacement and substitution. Each of the substitution reactions of **2** proceed with initial substitution of the chloro ligand. Substitution of hydrido

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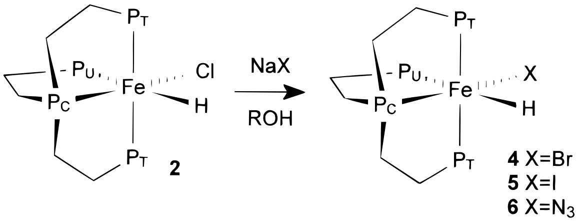
(10) Field, L. D.; Messerle, B. A.; Smernik, R. J.; *J. Organomet. Chem.*, **1997**, submitted for publication.

(11) $^{31}P\{^1H\}$ NMR spectrum (162 MHz, toluene-d_8, 300 K), δ: 174.9 (dt, 1P, $\mathbf{P_C}$, $^2J_{P(C)-P(T)} = 25.4$ Hz, $^2J_{P(C)-P(U)} = 11.9$ Hz); 53.6 (dd, 2P, $\mathbf{P_T}$, $^2J_{P(T)-P(U)} = 20.3$ Hz); 50.0 (dt, 1P, $\mathbf{P_U}$). $^1H\{^{31}P\}$ NMR spectrum (600 MHz, toluene-d_8, 283 K), δ: −11.42 (s, 1H, Fe−$\mathbf{H}$); 1.32, 1.68 (2 × m, 2 × 2H, $-P_CCH_2C\mathbf{HH}P_T-$); 1.19, 1.20 (2 × m, 2 × 2H, $-P_CC\mathbf{HH}CH_2P_T-$); 0.93 (m, 2H, $-P_CC\mathbf{H_2}CH_2P_U-$); 1.22 (m, 2H, $-P_CCH_2C\mathbf{H_2}P_U-$); 1.40, 1.96 (2 × s, 2 × 6H, 2 × $-P_T(C\mathbf{H_3})$); 1.64 (s, 6H, $-P_U(C\mathbf{H_3})_2$); 3.73 (s, 3H, $-OC\mathbf{H_3}$).

(12) Smernik, R. J. Ph.D. Thesis, The University of Sydney, 1996.

Scheme 2



Scheme 3

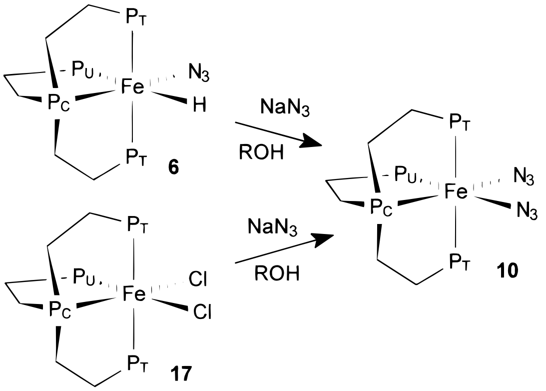


Table 1. ^{31}P NMR (162 MHz, 300 K) Data for Complexes **2**[9] and **4**−**11**

	δ			J (Hz)[a]		
	P_C	P_T	P_U	J_{C-T}	J_{C-U}	J_{T-U}
$FeHCl(PP_3)$, **2**[b]	184.8	61.3	60.0	30.5	22.9	22.9
$FeHBr(PP_3)$, **4**[c]	189.7	59.9	58.1	30.5	24.0	21.8
$FeHI(PP_3)$, **5**[c]	195.4	58.6	56.1	32.7	26.2	22.9
$FeH(N_3)(PP_3)$, **6**[b]	179.8	61.4	59.4	26.9	18.2	21.1
$Fe(N_3)_2(PP_3)$ **10**[e]	169.0	53.7	79.9	27.5	30.5	44.3
$[FeH(CO)(PP_3)]^+$, **7**[d]	174.3	67.2	67.9	33.1	36.6	17.8
$[FeH(N_2)(PP_3)],^+$, **8**[d]	172.3	63.2	61.4	30.5	27.1	17.0
$[((FeH(PP_3))_2(N_2)]^{2+}$, **11**[d]	172.7	62.2	59.6	30.5	25.4	17.0
$[FeH(PPh_3)(PP_3)]^+$, **9**[d]	173.4	52.3	49.6	35.8	21.2	18.6

[a] Signs of coupling constants not implied. [b] In toluene-d_8. [c] In benzene-d_6. [d] BPh_4 salt in acetone-d_6. [e] In methanol-d_4 (233 K).

ligands, in protic solvent, usually proceeds via protonation of the hydride complex to form a molecular hydrogen complex from which dihydrogen is displaced by an incoming ligand. Molecular hydrogen complexes of the form $[Fe(H_2)X(PP_3)]^+$ were not observed directly in the course of this investigation.

Reaction of FeHCl(PP$_3$), 2, with Halides and Azide. The addition of sodium bromide or iodide to a methanol (or ethanol) solution of **2** (containing the alkoxy hydrido complex **3** or **18**) results in the formation of $FeHBr(PP_3)$, **4**, or $FeHI(PP_3)$, **5**, respectively (Scheme 2). Both **4** and **5** are stable to the removal of the alcohol solvent and reconstitution into a nonprotic solvent.

Similarly, the addition of sodium azide to a methanol (or ethanol) solution of **2** results in the formation of $FeH(N_3)(PP_3)$, **6**, at short reaction times (Scheme 2). On prolonged standing or heating in the presence of excess sodium azide, **6** is converted to the dark orange bis(azide) complex **10** (Scheme 3), which can also be prepared by the reaction of $FeCl_2(PP_3)$, **17**, with excess sodium azide.

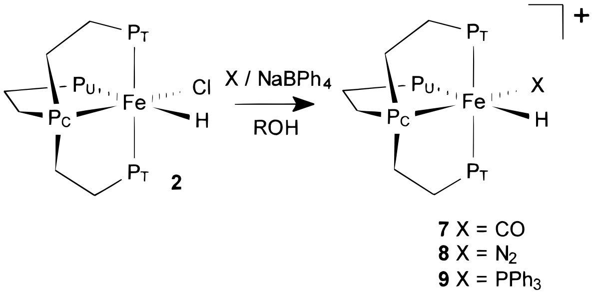
The ^{31}P NMR spectra of the halo hydrido complexes **2**, **4**, and **5** are very similar (Table 1). The largest variation is in the chemical shift of P_C, which increases down the group (Cl < Br < I). The ^{31}P NMR spectrum of the azido hydrido complex **6** is also similar to those of the halo hydrido complexes. The ^{31}P NMR spectrum of the bisazido complex **16** is quite different and more closely resembles that of the dichloride complex $FeCl_2(PP_3)$.[9]

Table 2. ^{1}H NMR (400 MHz, 300 K) Data for Hydride Resonances of Complexes **2**,[9] **4**−**9**, and **11**

	δ	J (Hz)[a]		
	hydride (H)	$J_{H-P(C)}$	$J_{H-P(T)}$	$J_{H-P(U)}$
$FeHCl(PP_3)$, **2**[b]	−11.63	44.4	69.1	44.1
$FeHBr(PP_3)$, **4**[c]	−11.89	44.6	69.5	42.4
$FeHI(PP_3)$, **5**[c]	−12.69	45.8	69.5	40.1
$FeH(N_3)(PP_3)$, **6**[b]	−12.04	42.1	67.7	40.9
$[FeH(CO)(PP_3)]^+$, **7**[d]	−13.56	39.4	61.0	16.5
$[FeH(N_2)(PP_3)]^+$, **8**[d]	−12.66	43.9	61.6	26.9
$[((FeH(PP_3))_2(N_2)]^{2+}$, **11**[d]	−12.50	43.3	62.3	28.1
$[FeH(PPh_3)(PP_3)]^+$, **9**[d]	−15.17	44.7	64.0	18.6

[a] Signs of coupling constants not implied. [b] In toluene-d_8. [c] In benzene-d_6. [d] BPh_4 salt in acetone-d_6.

Scheme 4



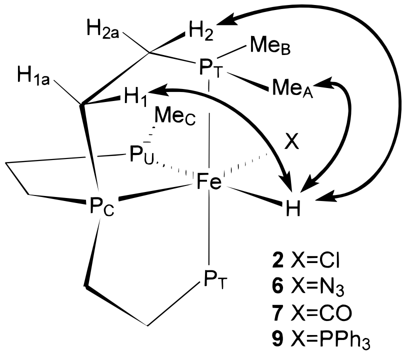
The hydride ^{1}H NMR resonances of the halo hydrido complexes **2**, **4**, and **5** and the azido hydrido complex **6** are also very similar, especially with respect to ^{31}P−^{1}H coupling constants (Table 2).

Reaction of FeHCl(PP$_3$), 2, with Carbon Monoxide, Dinitrogen, and Triphenylphosphine. Displacement of the chloro ligand of **2** can be achieved not only by anionic ligands such as halides and azide but also by neutral ligands such as CO, N_2, and PPh_3 to give the corresponding charged hydrido complexes (Scheme 4).

The carbonyl hydride complex $[FeH(CO)(PP_3)]^+$, **7**, is readily formed by placing an ethanol or methanol solution of **2** (containing the alkoxy hydrido complex **3** or **18**) under an atmosphere of CO. Similarly, the triphenylphosphine hydride complex $[FeH(PPh_3)(PP_3)]^+$, **9**, is formed by the addition of triphenylphosphine to an ethanol or methanol solution of **2**. The addition of an alcohol solution of sodium tetraphenylborate to a solution of the chloride salts of **7** and **9** results in their precipitation as tetraphenylborate salts which are soluble in acetone.

Placing an ethanol or methanol solution of **2** under an atmosphere of nitrogen affords two products: $[FeH(N_2)(PP_3)]^+$, **8**, and $[FeH(PP_3)N{\equiv}NFeH(PP_3)]^{2+}$, **11**. The ratio **11**:**8** increases on standing in solution, even under an atmosphere of nitrogen, with **11** accounting for over 80% of the ^{31}P NMR signal after 2 days at room temperature. Some byproducts, including $[FeH(H_2)(PP_3)]^+$, **19**, are also formed in the reaction mixture after an extended reaction period. The addition of sodium tetraphenylborate results in the formation of a pale yellow precipitate. The tetraphenylborate salt of **11** is only sparingly soluble in acetone. This allowed its isolation from the more soluble byproducts (including **8** and **19**) by discarding an initial acetone extract.

The addition of sodium tetraphenylborate to an ethanol solution of **2** under an argon atmosphere and then changing the atmosphere to nitrogen allowed isolation of $[FeH(N_2)(PP_3)]^+$,



2 X=Cl
6 X=N_3
7 X=CO
9 X=PPh_3

Figure 3. Schematic representation showing significant NOESY interactions between the hydride ligand and the PP_3 ligand in $FeHX(PP_3)$ complexes: **2** (X = Cl),[9] **6** (X = N_3), **7** (X = CO), and **9** (X = PPh_3).

8, as the tetraphenylborate salt, free from the bis(iron) complex **11**. The tetraphenylborate salt of **8** is soluble in acetone; however, solutions of **8** in acetone are unstable at room temperature, degrading over a period of a few hours to give a number of unidentified products. No such degradation of **8** is observed for ethanol solutions of the chloride and ethoxide salts.

Complex **8** shows a strong N_2 stretch at 2117 cm^{-1} in the IR spectrum, whereas **11** contains no N_2 stretches in its IR spectra but exhibits two strong bands at 2055 and 2065 cm^{-1} in the Raman spectrum. The presence of two bands may be due to site splitting in the crystal lattice of **11**. The stretching frequencies of **8** and **11** are consistent with N_2 stretches of similar mono- and binuclear iron complexes containing terminal and bridging nitrogen ligands.[13,14]

The ^{31}P and ^{1}H NMR spectra of **8** and **11** are very similar, as would be expected for complexes with closely aligned donor sets. $^{2}J_{H-P(U)}$ is consistently smaller for the cationic complexes **7**−**9** and **11** than for the neutral complexes **2** and **4**−**6** (Table 2). The presence of a single carbonyl ligand in **7** was confirmed by using ^{13}CO. A ddt resonance at δ 218.9 was observed in the $^{13}C\{^{1}H\}$ NMR spectrum, the splitting due to coupling to the phosphorus nuclei ($^{2}J_{P(C)-C} = 31.5$ Hz, $^{2}J_{P(T)-C} = 20.0$ Hz, $^{2}J_{P(U)-C} = 17.2$ Hz). The ^{31}P resonance of the triphenylphosphine ligand of **9** (at δ 74.2) appears as a ddt with splitting due to coupling to the other ^{31}P nuclei ($^{2}J_{P(C)-PPh_3} = 70.3$ Hz, $^{2}J_{P(T)-PPh_3} = 45.1$ Hz, $^{2}J_{P(U)-PPh_3} = 30.5$ Hz). The relatively large, 70.3 Hz, coupling between P_C and the P in the triphenylphosphine ligand indicated their *trans* arrangement, and this stereochemistry was confirmed by $^{1}H-^{1}H$ NOESY spectroscopy.

Stereochemistry of the Hydride Complexes 4−**8.** There are two possible stereoisomers of the hydride complexes $FeHX(PP_3)$, with the hydride either *cis* or *trans* to the central phosphorus atom, P_C. The position of the hydride in $FeHCl(PP_3)$, **2**, was determined from its NOESY spectrum.[9] Strong correlations were observed between the hydride resonance and those for Me_A, H_1, and H_2 (Figure 3). A very weak correlation was observed between the hydride and Me_B, and no correlation was observed between the hydride and Me_C. This places the hydride *cis* to the central phosphorus atom, since if it were *trans*, a NOESY correlation would be expected between the hydride and the methyl groups on the unique phosphorus (Me_C).

The similarity of the ^{31}P and ^{1}H NMR spectra of **4**−**6** to those of **2** indicates that they are all of the same relative stereochemistry. This was confirmed for the azido hydrido complex **6**, whose ^{1}H NOESY spectrum showed the characteristically strong correlations between the hydride resonance and those of Me_A, H_1, and H_2 and no correlation between the hydride and Me_C. The same characteristic correlations were also observed in the ^{1}H NOESY spectra of **7** and **9**, again indicating that the hydride is *cis* to P_C. The similarity of the ^{31}P and ^{1}H NMR spectra of **8** and **11** to those of the isoelectronic complex **7** suggests that **8** and **11** have the same relative stereochemistry as **7**. In the ^{1}H NOESY spectrum of the triphenylphosphine hydride complex **9**, correlations observed between the *ortho* protons of the triphenylphosphine and Me_A, Me_B, and Me_C were all strong and were of approximately equal intensity, as would be expected for a ligand *trans* to P_C (Figure 4).[9]

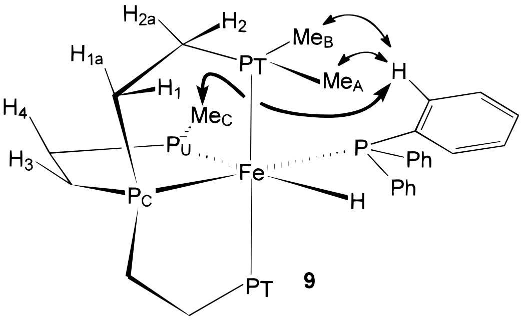


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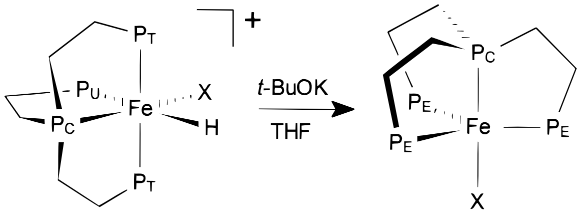
Figure 4. Schematic representation showing significant NOESY interactions between the ortho protons of the triphenylphosphine ligand and the PP_3 ligand in $[FeH(PPh_3)(PP_3)]^+$, **9**.

Scheme 5



7 X = CO
8 X = N_2

12 X = CO
13 X = N_2

Deprotonation of $[FeH(CO)(PP_3)]^+$, 7, and $[FeH(N_2)(PP_3)]^+$, 8. Addition of a strong base (potassium *tert*-butoxide) to suspensions of **7** and **8** in THF deprotonates the hydrido complexes to give the iron(0) complexes $Fe(CO)(PP_3)$, **12**, and $Fe(N_2)(PP_3)$, **13**, respectively (Scheme 5). Similar deprotonation reactions have been observed for related iron complexes of the bidentate phosphine ligand DMPE.[14] The $^{31}P\{^{1}H\}$ NMR spectrum of **12** consists of two resonances at δ 188.1 (q, P_C) and 73.4 (d, P_E) in the ratio 1:3, respectively, with a $^{31}P-^{31}P$ coupling constant of 53.0 Hz. The $^{31}P\{^{1}H\}$ NMR spectrum of **13** is similar, with two resonances at δ 181.7 (q, P_C) and 66.0 (d, P_E) in the ratio 1:3, respectively, with a $^{31}P-^{31}P$ coupling constant of 45.8 Hz. The spectra are consistent with trigonal bipyramidal structures, in which the central phosphorus (P_C) and the carbonyl or dinitrogen ligands occupy axial sites and the three terminal phosphorus atoms of PP_3 (P_E) occupy equivalent equatorial sites.

The IR stretches of the CO and N_2 ligands of the iron(0) complexes **12** (1855 cm^{-1}) and **13** (2013 cm^{-1}) show a shift to lower frequency compared to those of the corresponding iron(II) complexes **7** (1936 cm^{-1}) and **8** (2117 cm^{-1}), reflecting the increased back-donation from the more electron rich iron(0) complexes.

The five-coordinate complexes **12** and **13** are protonated on dissolution in ethanol to give the cations **7** and **8**, respectively

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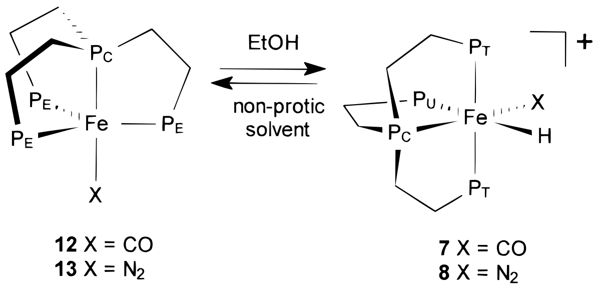
(13) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589 and references therein.

(14) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3041.

Scheme 6



12 X = CO
13 X = N_2

7 X = CO
8 X = N_2

(Scheme 6). Removal of ethanol solvent and reconstitution into neutral solvent re-form **12** and **13**.

Conclusions

Iron(II) hydride complexes containing the tripodal tetraphosphine ligand tris[2-(dimethylphosphino)ethyl]phosphine, $P(CH_2CH_2PMe_2)_3$ (PP_3), **1**, were prepared. Dissolution of the chloro hydrido complex $FeHCl(PP_3)$, **2**, in methanol or ethanol afforded an equilibrium mixture of **2** and the alkoxy hydrido complex $FeH(OMe)(PP_3)$, **3**, or $FeH(OEt)(PP_3)$, **18**. Reaction of a methanol solution containing **2** and **3** with anionic or neutral ligands afforded the corresponding hydride complexes: reaction with NaBr afforded $FeHBr(PP_3)$, **4**; reaction with NaI afforded $FeHI(PP_3)$, **5**; reaction with NaN_3 afforded $FeHN_3(PP_3)$, **6**; reaction with CO afforded $[FeH(CO)(PP_3)]^+$, **7**; reaction with N_2 afforded $[FeH(N_2)(PP_3)]^+$, **8**; and reaction with PPh_3 afforded $[FeHPPh_3(PP_3)]^+$, **9**. In some cases, further reaction of the product iron hydride complexes was observed. Reaction of $FeHN_3(PP_3)$, **6**, with NaN_3 for an extended period afforded $Fe(N_3)_2(PP_3)$, **10**. On standing, in solution, $[FeH(N_2)(PP_3)]^+$, **8**, was converted to the dinitrogen-bridged complex $[FeH(PP_3)N{\equiv}NFeH(PP_3)]^{2+}$, **11**. The carbonyl hydride complex **7** and the dinitrogen hydride complex **8** were deprotonated to give the neutral iron(0) complexes $Fe(CO)(PP_3)$, **12**, and $Fe(N_2)(PP_3)$, **13**, respectively.

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