

Iron Complexes Containing the Tripodal Tetraphosphine Ligand $P(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$

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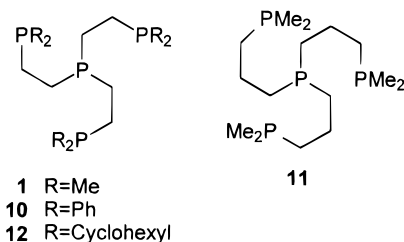
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The preparation and characterization of iron(II) complexes containing the tripodal tetraphosphine ligand tris[2-(dimethylphosphino)ethyl]phosphine, $P(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (PP_3 , **1**), are reported. The complex $\text{FeCl}_2(\text{PP}_3)$ (**2**) was formed by the reaction of PP_3 with anhydrous iron(II) chloride. The complexes $\text{FeHCl}(\text{PP}_3)$ (**3**) and $\text{FeH}_2(\text{PP}_3)$ (**4**) were formed by the reaction of **2** with lithium aluminum hydride. Likewise, the complexes $\text{FeMeCl}(\text{PP}_3)$ (**5**) and $\text{FeMe}_2(\text{PP}_3)$ (**6**) were formed by the reaction of **2** with methyllithium or dimethylmagnesium. Reaction of **2** with CO afforded a mixture of isomeric carbonyl chloride complexes $[\text{Fe}(\text{CO})\text{Cl}(\text{PP}_3)]^+$ (**7** and **8**). Reaction of **2** with PPh_3 afforded $[\text{Fe}(\text{PPh}_3)\text{Cl}(\text{PP}_3)]^+$ (**9**). The air-sensitive complexes **2–9** were characterized by multinuclear NMR spectroscopy, and **9** was characterized by X-ray crystallography. Crystals of **9** (BPh_4 salt), $\text{C}_{54}\text{H}_{65}\text{BClFeP}_5$, M 971.09, are monoclinic, space group $P2_1/c$, $a = 13.246(3)$ Å, $b = 30.314(2)$ Å, $c = 14.338(2)$ Å, $\beta = 100.92(2)^\circ$, $Z = 4$; $R = 0.058$.

Introduction

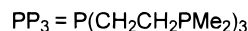
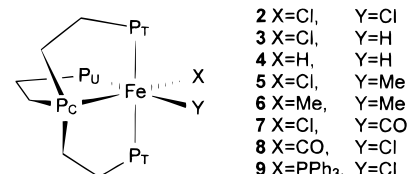
Metal complexes containing polydentate phosphine ligands are an important class of organometallic compounds, and many metal phosphine complexes facilitate C–H activation and act as catalysts for organic transformations.¹ Phosphines are strong donor ligands, and the polydentate architecture provides stability and restricts the arrangement of donors in the ligand sphere. In octahedral complexes, tripodal tetradentate phosphine ligands enforce a *cis* geometry of the two remaining ligands. One of the most thoroughly studied tripodal tetradentate phosphine ligands is $P(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (**10**), and metal complexes of **10** act as catalysts for a variety of organic transformations.²

Ruthenium and iron complexes of the related ligand $P(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (**11**) undergo C–H insertion reactions with alkene and arene substrates.³ In the molecular hydrogen complexes $[\text{M}(\text{P}_4)\text{H}(\text{H}_2)]^+$ ($\text{M} = \text{Fe}, \text{Ru}$; $\text{P}_4 = P(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (**10**),⁴ $P(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (**11**),⁵ $P(\text{CH}_2\text{CH}_2\text{PCy}_2)_3$ (**12**)⁶), the interaction between the hydride and dihydrogen ligands constrained in *cis* coordination sites has led to speculation of the existence of complexes of the ligand “ H_3 ”.



Although the related “hybrid” of ligands **10** and **11**, $P(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (PP_3 , **1**), has been known since 1975,⁷ its reported coordination chemistry has been limited to that of a single complex, $[\text{NiCl}(\text{PP}_3)]^+$,⁸ presumably due to the difficult and low-yielding synthesis of **1**. We have recently reported⁹ a new, efficient and high-yielding synthesis of **1**, which has facilitated the current investigation of iron complexes of **1**.

In this paper we report the synthesis of the iron(II) complexes $\text{FeXY}(\text{PP}_3)$ ($\text{X} = \text{Cl}, \text{Y} = \text{Cl}$ (**2**); $\text{X} = \text{Cl}, \text{Y} = \text{H}$ (**3**); $\text{X} = \text{H}, \text{Y} = \text{H}$ (**4**); $\text{X} = \text{Cl}, \text{Y} = \text{Me}$ (**5**); $\text{X} = \text{Me}, \text{Y} = \text{Me}$ (**6**); $\text{X} = \text{Cl}, \text{Y} = \text{CO}$ (**7**); $\text{X} = \text{CO}, \text{Y} = \text{Cl}$ (**8**); and $\text{X} = \text{PPh}_3, \text{Y} = \text{Cl}$ (**9**)). Complexes **2–9** have been completely characterized by multinuclear NMR spectroscopy, and **9** was structurally characterized by X-ray crystallography.



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. Lithium aluminum hydride was obtained from Aldrich and used as a THF solution (approximately 1 M). Methyllithium was used as a solution in hexane (approximately 2.4 M) as supplied by Aldrich. Dimethylmagnesium was prepared as a THF solution (approximately 1 M) using the procedure of Ludher *et al.*¹⁰ THF, benzene, toluene, pentane, and hexane were dried over sodium before distillation from sodium and benzophenone under nitrogen. Ethanol and methanol were distilled from magnesium under nitrogen.

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Table 1. Crystallographic Data for [Fe(PPh₃)Cl(PP₃)]⁺ **9** (BPh₄⁻ Salt)

A. Crystal Data	
empirical formula	C ₅₄ H ₆₅ BClFeP ₅
formula wt	971.09
cryst color, habit	red, prism
cryst dimens	0.50 × 0.38 × 0.38 mm
cryst syst	monoclinic
lattice type	primitive
no. of rflns used for unit cell determination (2θ range)	24 (19.12–24.24°)
lattice params	$a = 13.246(3) \text{ \AA}$ $b = 30.314(2) \text{ \AA}$ $c = 14.338(2) \text{ \AA}$ $\beta = 100.92(2)^\circ$ $V = 5653(1) \text{ \AA}^3$
space group	$P2_1/c$ (No. 14)
Z value	4
D _{calc}	1.141 g/cm ³
F ₀₀₀	2048.00
μ(Mo Kα)	4.87 cm ⁻¹
B. Intensity Measurements	
temperature	21.0 °C
2θ _{max}	44.9°
hkl range	–14 to 14, –1 to 32, –1 to 15
no. of rflns measd	
total	8884
unique	7557 (R _{int} = 0.080)
C. Structure Solution and Refinement	
function minimized	$\sum w(F_o - F_c)^2$
least squares wts	1/σ ² (F _o)
no. of observations (I > 2.00σ(I))	5097
no. of variables	560
rfln:param ratio	9.10
residuals: R; R _w	0.058; 0.057
goodness-of-fit indicator	3.01
max peak in final diff map	0.77 e/Å ³
min peak in final diff map	–0.37 e/Å ³

¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker AMX400 or AMX600 spectrometers at the temperatures quoted. ¹H and ¹³C chemical shifts were internally referenced to residual solvent resonances. ³¹P spectra were referenced to external neat trimethyl phosphite at 140.85 ppm. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR; all frequencies are quoted in cm⁻¹. EI (electron ionization) mass spectra (both low and high resolution) were recorded on a Kratos MS9/MS50 double-focusing mass spectrometer with an accelerating voltage of 8000 V, a source temperature of 150–350 °C, and an electron energy of 70 eV. Perfluorokerosene was used as a calibrant for high-resolution spectra. Chemical ionization (CI) mass spectra were recorded on a Finnigan MAT TSQ-46 mass spectrometer (San Jose, CA) fitted with a desorption probe, with a source temperature of 140 °C and an electron energy of 100 eV. The ionization gas, methane (>99.999%) or ammonia (>99.999%), is as quoted. Elemental analyses were carried out at the Joint Elemental Analysis Facility, The University of Sydney. Melting points were recorded on a Gallenkamp heating stage and are uncorrected.

Crystal Structure Determination. The crystallographic data for **9** (BPh₄⁻ salt) are summarized in Table 1. The complex decayed rapidly on exposure to the atmosphere. Accordingly, a red prism of C₅₄H₆₅BClFeP₅ having approximate dimensions of 0.50 × 0.38 × 0.38 mm was coated with a heavy hydrocarbon oil and inserted in a thin glass capillary. The capillary was then mounted on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation. Cell constants obtained from a least-squares refinement using the setting angles of 24 reflections in the range 19.12° < 2θ < 24.24° corresponded to a primitive monoclinic cell, and systematic absences of *h*0*l*, *l* ≠ 2*n*, and 0*k*0, *k* ≠ 2*n*, uniquely determined the space group to be $P2_1/c$ (No. 14). Diffraction data were collected at a temperature of 21 ± 1 °C using ω/θ scans to a maximum 2θ value of 44.9°. The intensities of three representative reflections measured every 2 h decreased by 10.1% during the course of the data collection, and a linear correction factor was accordingly applied to the data. The linear absorption

coefficient for the complex with Mo Kα radiation is 4.9 cm⁻¹, and an absorption correction was not applied to the data. The data were corrected for Lorentz and polarization effects.

All calculations were performed using the teXsan¹¹ crystallographic software package. The structure was solved by direct methods¹² and expanded using Fourier techniques.¹³ Neutral atom scattering factors were taken from Cromer and Waber.¹⁴ Anomalous dispersion effects were included in the structure factor calculation,¹⁵ and the values for Δ*f*' and Δ*f*" were those of Creagh and McAuley.¹⁶ The values for the mass attenuation coefficients are those of Creagh and Hubbell.¹⁷ Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in the full matrix least squares refinement at calculated positions with group temperature factors. An ORTEP¹⁸ representation of the structure is provided in Figure 8.

FeCl₂(PP₃) (2). Solutions of anhydrous iron(II) chloride (50 mg, 0.39 mmol) in THF (10 mL) and **1** (110 mg, 0.37 mmol) in THF (10 mL) were simultaneously added to THF (50 mL), with rapid stirring. The resulting deep red solution deposited a small quantity of an orange-brown precipitate during the reaction, and this was removed by filtration. Removal of the THF *in vacuo* left a red solid, which was extracted into benzene (10 mL). The addition of hexane (50 mL) resulted in the precipitation of the product, which was collected by filtration. **2** was obtained as a red-purple crystalline solid (116 mg, 74%; mp 145–151 °C dec).

³¹P{¹H} NMR spectrum (162 MHz, THF-*d*₈, 233 K): δ 179.3 (dt, 1P, P_C, ²J_{P(C)–P(T)}} = 24.8 Hz, ²J_{P(C)–P(U)}} = 32.4 Hz); 53.2 (dd, 2P, P_T, ²J_{P(T)–P(U)}} = 47.7 Hz); 83.1 (dt, 1P, P_{U}}).

¹H{³¹P} NMR spectrum (400 MHz, THF-*d*₈, 233 K): δ 1.81, 1.97, 2.20, 2.54 (4 × m, 4 × 2H, –P_CCHHCHHP_T–); 1.51, 1.74 (2 × m, 2 × 2H, –P_CCH₂CH₂P_U–); 1.50, 1.72 (2 × s, 2 × 6H, 2 × P_T(CH₃)); 1.31 (s, 6H, P_U(CH₃)₂).

¹³C{¹H} NMR spectrum (101 MHz, THF, 233 K): δ 14.1 (t, P_TCH₃, ¹J_{P(T)–C}} = 6.7 Hz); 19.0 (t, P_TCH₃, ¹J_{P(T)–C}} = 11.0 Hz); 18.6 (d, P_U(CH₃)₂, ¹J_{P(U)–C}} = 18.6 Hz); 24.5 (m, –P_CCH₂CH₂P_T–); 31.2 (m, –P_CCH₂CH₂P_T–); 27.7 (dd, –P_CCH₂CH₂P_U–, ¹J_{P(C)–C}} = 26.2 Hz, ²J_{P(U)–C}} = 11.4 Hz); 31.5 (m, –P_CCH₂CH₂P_U–).

MS (+Cl, CH₄) *m/z* >200: 424 (Fe³⁵Cl₂(PP₃) + 1, 3), 392 (Fe³⁷Cl(PP₃) + 1, 5), 391 (Fe³⁷Cl(PP₃), 21), 390 (Fe³⁵Cl(PP₃) + 1, 15), 389 (Fe³⁵Cl(PP₃), 65), 354 (Fe(PP₃), 14), 331 ((PP₃)O₂, 27), 327 (32), 315 ((PP₃)O, 25), 300 ((PP₃) + 2, 15), 299 ((PP₃) + 1, 100), 283 ((PP₃) – CH₃, 24), 209 (P(CH₂CH₂PMe₂)₂, 11).

FeHCl(PP₃) (3). A THF solution of lithium aluminum hydride was added dropwise to a solution of **2** (116 mg, 0.27 mmol) in THF (30 mL), resulting in a color change from deep red to bright yellow. The reaction was rapid at room temperature, and the color change allowed the end point to be determined accurately. The reaction mixture was filtered, the solvent removed *in vacuo*, and the residue extracted into benzene (20 mL). The volume of the solution was reduced *in vacuo* to approximately 3 mL, and the addition of hexane (10 mL) resulted in the precipitation of the product, which was collected by filtration. **3** was obtained as bright yellow needles (83 mg, 78%; mp 176.5–177.5 °C).

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$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, toluene- d_8 , 300 K): δ 184.8 (dt, 1P, P_C , $^2J_{P(C)-P(T)} = 30.5$ Hz, $^2J_{P(C)-P(U)} = 22.9$ Hz); 61.3 (dd, 2P, P_T , $^2J_{P(T)-P(U)} = 22.9$ Hz); 60.0 (dt, 1P, P_U).

$^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (600 MHz, toluene- d_8 , 303 K): δ -11.63 (s, ^1H , FeH); 1.30, 1.70 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CH}_2\text{CHHP}_T^-$); 1.21, 1.34 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CHHCH}_2\text{P}_T^-$); 1.07 (m, 2H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$); 1.22 (m, 2H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$); 1.40, 1.88 (2 \times s, 2 \times 6H, 2 \times $\text{Pr}(\text{CH}_3)_2$); 1.45 (s, 6H, $\text{P}_U(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, benzene- d_6) δ 25.1 (dt, $\text{P}_T(\text{CH}_3)$, $^1J_{P(T)-C} = 16.3$ Hz, $^3J_{P(U)-C} = 6.8$ Hz); 18.7 (m, $\text{P}_T(\text{CH}_3)$); 19.1 (dt, $\text{P}_U(\text{CH}_3)_2$, $^1J_{P(U)-C} = 10.5$ Hz, $^3J_{P(T)-C} = 3.4$ Hz); 27.1 (ddt, $-\text{P}_T\text{CH}_2\text{CH}_2\text{P}_C^-$, $^1J_{P(C)-C} = 22.6$ Hz, $^2J_{P(T)-C} = 8.9$ Hz, $^3J_{P(U)-C} = 1.6$ Hz); 34.4 (dt, $-\text{P}_T\text{CH}_2\text{CH}_2\text{P}_C^-$, $^1J_{P(T)-C} = 15.3$ Hz, $^2J_{P(C)-C} = 15.3$ Hz); 27.7 (dd, $-\text{P}_U\text{CH}_2\text{CH}_2\text{P}_C^-$, $^1J_{P(C)-C} = 18.4$ Hz, $^2J_{P(U)-C} = 18.4$ Hz); 33.4 (dd, $-\text{P}_U\text{CH}_2\text{CH}_2\text{P}_C^-$, $^1J_{P(U)-C} = 25.8$ Hz, $^2J_{P(C)-C} = 15.3$ Hz).

MS (EI) m/z : 392 (FeH $^{37}\text{Cl}(\text{PP}_3)$, 16), 391 (Fe $^{37}\text{Cl}(\text{PP}_3)$, 21), 390 (FeH $^{35}\text{Cl}(\text{PP}_3)$, 45), 389 (Fe $^{35}\text{Cl}(\text{PP}_3)$, 44), 388 (15), 354 (Fe(PP $_3$), 49), 338 (Fe(PP $_3$) - CH $_4$, 59), 300 (PP $_3$ + 2, 59), 283 (PP $_3$ - CH $_3$, 30), 272 (26), 238 (42), 211 (34), 209 (P(CH $_2\text{CH}_2\text{PMe}_2$) $_2$, 66), 61 (100).

HRMS: Calcd for C $_{12}\text{H}_{31}\text{ClFeP}_4$ 390.0414; found 390.0428.

Anal. Calcd for C $_{12}\text{H}_{31}\text{ClFeP}_4$: C, 36.90; H, 8.00. Found: C, 36.5; H, 8.0.

FeH $_2$ (PP $_3$) (4). A THF solution of **3** was prepared as above. A THF solution of lithium aluminum hydride was added dropwise, resulting in a distinct color change from bright to very pale yellow. The reaction mixture was filtered and the solvent removed *in vacuo*, leaving a pale yellow gum, which was extracted into benzene (15 mL). The benzene extract was filtered and the solvent removed *in vacuo*. The residue was extracted into hexane (10 mL) and the resultant mixture filtered. Removal of the hexane *in vacuo* afforded **4** (68 mg, 90% from **3**) as a highly air-sensitive, waxy, pale yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, toluene- d_8 , 300 K): δ 187.2 (q, 1P, P_C , $^2J_{P(C)-P(E)} = 20.9$ Hz); 68.7 (d, 3P, P_E).

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, toluene- d_8 , 198 K): δ 185.6 (br, 1P, P_C); 67.7 (br, 2P, P_T); 70.5 (br, 1P, P_U).

$^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (400 MHz, benzene- d_6 , 300 K): δ -11.03 (s, 2H, FeH); 1.62 (m, 6H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_E^-$), 1.55 (m, 6H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_E^-$); 1.54 (s, 18H, $\text{P}_E(\text{CH}_3)_2$).

$^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (high-field region only, 400 MHz, toluene- d_8 , 198 K): δ -14.20, -7.70 (2 \times br, 2 \times ^1H , 2 \times FeH).

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, benzene- d_6 , 300 K) δ 26.6 (m, P_ECH_3); 38.8 (m, $-\text{P}_E\text{CH}_2\text{CH}_2\text{P}_C^-$); 27.9 (m, $-\text{P}_E\text{CH}_2\text{CH}_2\text{P}_C^-$).

MS (EI) m/z : 356 (M, 1), 355 (FeH(PP $_3$), 5), 354 (Fe(PP $_3$), 29), 283 (PP $_3$ - CH $_3$, 14), 266 (11), 210 (HP(CH $_2\text{CH}_2\text{PMe}_2$) $_2$, 12), 209 (P(CH $_2\text{CH}_2\text{PMe}_2$) $_2$, 33), 31 (100).

FeMeCl(PP $_3$) (5). A hexane solution of methylolithium was added dropwise to a solution of **2** (100 mg, 0.24 mmol) in THF (30 mL), resulting in a color change from deep red to orange. The reaction was rapid at room temperature and the color change allowed the end point to be determined accurately. The reaction mixture was filtered, the solvent removed *in vacuo*, and the residue extracted into benzene (20 mL). The solvent was removed *in vacuo*, affording **5** (67 mg, 70%) as an orange-yellow powder.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, benzene- d_6 , 300 K): δ 188.4 (dt, 1P, P_C , $^2J_{P(C)-P(T)} = 30.0$ Hz, $^2J_{P(C)-P(U)} = 11.4$ Hz); 64.1 (dd, 2P, P_T , $^2J_{P(T)-P(U)} = 25.4$ Hz); 59.8 (dt, 1P, P_U).

$^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (600 MHz, benzene- d_6 , 303 K): δ -0.10 (s, 3H, FeCH $_3$); 1.24, 2.08 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CH}_2\text{CHHP}_T^-$); 1.37, 1.37 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CHHCH}_2\text{P}_T^-$); 0.99 (m, 2H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$); 1.17 (m, 2H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$); 1.38, 1.80 (2 \times s, 2 \times 6H, 2 \times $\text{Pr}(\text{CH}_3)_2$); 1.56 (s, 6H, $\text{P}_U(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$ NMR spectrum (101 MHz, benzene- d_6 , 300 K) δ 2.0 (s, FeCH $_3$); 13.1, 20.4 (2 \times s, 2 \times $\text{Pr}(\text{CH}_3)_2$); 22.0 (s, $\text{P}_U(\text{CH}_3)_2$); 32.1 (s, $-\text{P}_T\text{CH}_2\text{CH}_2\text{P}_C^-$); 25.5 (s, $-\text{P}_T\text{CH}_2\text{CH}_2\text{P}_C^-$); 33.2 (s, $-\text{P}_U\text{CH}_2\text{CH}_2\text{P}_C^-$); 28.7 (s, $-\text{P}_U\text{CH}_2\text{CH}_2\text{P}_C^-$).

MS (+Cl, CH $_4$) m/z > 300: 407 (Fe $^{37}\text{ClMe}(\text{PP}_3)$ + 1, 4), 405 (Fe $^{35}\text{ClMe}(\text{PP}_3)$ + 1, 11), 391 (Fe $^{37}\text{Cl}(\text{PP}_3)$, 11), 390 (12), 389 (Fe $^{35}\text{Cl}(\text{PP}_3)$, 44), 363 ((PP $_3$) $_2$ + 1, 15), 359 (17), 355 (Fe(PP $_3$) + 1, 16), 347 ((PP $_3$) $_2$ + 1, 30), 343 (17), 332(13), 331 ((PP $_3$) $_2$ + 1, 100), 329 (16), 327 (41), 316 (15), 315 ((PP $_3$) $_2$ + 1, 100), 313 (12), 311 (10).

FeMe $_2$ (PP $_3$) (6). A solution of **5** in THF was prepared as above. A hexane solution of methylolithium was added, resulting in a color change from deep orange to pale yellow. The reaction was rapid at room temperature, and the color change allowed the end point to be determined accurately. The reaction mixture was filtered, the solvent removed *in vacuo*, and the residue extracted into benzene (20 mL). The solvent was removed *in vacuo*, affording **6** (52 mg, 82% from **5**), as a waxy, air-sensitive, yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, toluene- d_8 , 220 K): δ 179.8 (t, 1P, P_C , $^2J_{P(C)-P(T)} = 14.4$ Hz, $^2J_{P(C)-P(U)} = 0$ Hz); 69.5 (dd, 2P, P_T , $^2J_{P(T)-P(U)} = 27.4$ Hz); 67.5 (t, 1P, P_U).

$^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (600 MHz, toluene- d_8 , 303 K): δ -0.88, 0.12 (2 \times s, 2 \times 3H, 2 \times FeCH $_3$); 1.38, 2.13 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CH}_2\text{CHHP}_T^-$); 1.59, 1.61 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CHHCH}_2\text{P}_T^-$); 1.26, 1.26 (m, 2 \times 2H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$); 1.14, 1.41 (2 \times s, 2 \times 6H, 2 \times $\text{Pr}(\text{CH}_3)_2$); 1.23 (s, 6H, $\text{P}_U(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$ NMR spectrum (101 MHz, benzene- d_6 , 300 K): δ 1.8, 2.5 (2 \times s, 2 \times FeCH $_3$); 12.5, 21.7 (2 \times s, 2 \times $\text{Pr}(\text{CH}_3)_2$); 22.9 (s, $\text{P}_U(\text{CH}_3)_2$); 24.8 (s, $-\text{P}_T\text{CH}_2\text{CH}_2\text{P}_C^-$); 35.7 (s, $-\text{P}_T\text{CH}_2\text{CH}_2\text{P}_C^-$); 29.2 (s, $-\text{P}_U\text{CH}_2\text{CH}_2\text{P}_C^-$); 36.0 (s, $-\text{P}_U\text{CH}_2\text{CH}_2\text{P}_C^-$).

MS (+Cl, CH $_4$) m/z > 135: 385 (M + 1, 13), 384 (M, 95), 369 (FeMe(PP $_3$), 98), 354 (Fe(PP $_3$), 11), 353 (Fe(PP $_3$) - 1, 19), 299 ((PP $_3$) + 1, 21), 181 (15), 153 (13), 135 (100).

[Fe(CO)Cl(PP $_3$)] $^+$ (7 and 8). An atmosphere of carbon monoxide was introduced over a solution of **2** (30 mg, 71 μmol) in ethanol (5 mL), resulting in a rapid color change from deep red to bright yellow. A solution of sodium tetraphenylborate (40 mg, 120 μmol) in ethanol (2 mL) was added immediately, resulting in the formation of a yellow precipitate, which was isolated by filtration. The crude product was washed with ethanol (10 mL) and dried *in vacuo* to give **7** (BPh $_4$ salt) as a pale yellow powder (35 mg, 67%; mp 285–290 $^\circ\text{C}$ dec).

Heating of an ethanol solution of **7** (chloride salt) resulted in the formation of a second product, assigned as the isomeric carbonyl chloride complex **8**. The reaction could not be forced to completion, apparently reaching equilibrium (ratio **7**:**8** = 1:5) on heating at 60 $^\circ\text{C}$ for 10 days. A solution of sodium tetraphenylborate (10 mg, 29 μmol) in ethanol (2 mL) was added, resulting in the formation of a yellow precipitate, which was isolated by filtration, washed with ethanol (10 mL), and dried *in vacuo* to afford a mixture of the carbonyl chloride complexes **7** and **8** (BPh $_4$ salts).

A. [Fe(CO)Cl(PP $_3$)] $^+$ (7) (Kinetic Product, CO *Trans* to P_U). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (BPh $_4$ salt, 162 MHz, acetone- d_6 , 300 K): δ 163.9 (dt, 1P, P_C , $^2J_{P(C)-P(T)} = 19.8$ Hz, $^2J_{P(C)-P(U)} = 44.3$ Hz); 44.4 (dd, 2P, P_T , $^2J_{P(T)-P(U)} = 54.9$ Hz); 58.6 (dt, 1P, P_U).

$^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (BPh $_4$ salt, 600 MHz, acetone- d_6 , 288 K): δ 2.25, 2.74 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CH}_2\text{CHHP}_T^-$); 2.14, 2.71 (2 \times m, 2 \times 2H, $-\text{P}_C\text{CHHCH}_2\text{P}_T^-$); 2.40 (m, 2H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$); 2.28 (m, 2H, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$); 1.85, 2.01 (2 \times s, 2 \times 6H, 2 \times $\text{Pr}(\text{CH}_3)_2$); 1.83 (s, 6H, $\text{P}_U(\text{CH}_3)_2$); 7.46 (br, 8H, BPh_{ortho}); 7.08 (t, 8H, $^3J_{\text{H-H}} = 7.1$ Hz, BPh_{meta}); 6.93 (t, 4H, BPh_{para}).

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (BPh $_4$ salt, carbonyl region of ^{13}C -labeled complex, 101 MHz, acetone- d_6 , 300 K): δ 212.9 (ddt, FeCO, $^2J_{P(C)-C} = 15.9$ Hz, $^2J_{P(T)-C} = 45.1$ Hz, $^2J_{P(U)-C} = 31.8$ Hz).

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (chloride salt, 101 MHz, MeOH, 300 K): δ 14.5 (t, P_TCH_3 , $^1J_{P(T)-C} = 10.0$ Hz); 17.3 (dt, P_TCH_3 , $^1J_{P(T)-C} = 15.3$ Hz, $^3J_{P(U)-C} = 3.8$ Hz); 15.3 (dt, $\text{P}_U(\text{CH}_3)_2$, $^1J_{P(U)-C} = 24.3$ Hz, $^3J_{P(T)-C} = 3.8$ Hz); 26.0 (dt, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_T^-$, $^1J_{P(C)-C} = 30.0$ Hz, $^2J_{P(T)-C} = 6.7$ Hz); 30.5 (dt, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_T^-$, $^1J_{P(T)-C} = 15.7$ Hz, $^2J_{P(C)-C} = 8.1$ Hz); 24.8 (dd, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$, $^1J_{P(C)-C} = 25.7$ Hz, $^2J_{P(U)-C} = 13.8$ Hz); 31.5 (dd, $-\text{P}_C\text{CH}_2\text{CH}_2\text{P}_U^-$, $^1J_{P(U)-C} = 31.0$ Hz, $^2J_{P(C)-C} = 9.5$ Hz).

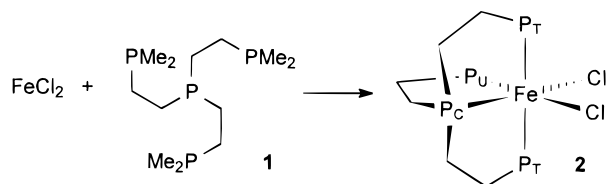
MS (+Cl, NH $_3$) m/z > 200: 437 (FeCO $^{37}\text{Cl}(\text{PP}_3)$ + NH $_4$, 4), 435 (FeCO $^{35}\text{Cl}(\text{PP}_3)$ + NH $_4$, 11), 391 (Fe $^{37}\text{Cl}(\text{PP}_3)$, 18), 390 (Fe $^{35}\text{Cl}(\text{PP}_3)$ + 1, 33), 389 (Fe $^{35}\text{Cl}(\text{PP}_3)$, 78), 384 (FeCO(PP $_3$) + 2, 12), 383 (FeCO(PP $_3$) + 1, 100), 377 (11), 376 (53), 370 (12), 354 (Fe(PP $_3$), 12), 299 ((PP $_3$) + 1, 38), 279 (25), 260 (28), 259 (13).

IR ν_{max} (BPh $_4$ salt, Nujol): 1952 cm^{-1} .

Anal. Calcd for C $_{37}\text{H}_{50}\text{BClFeOP}_4$: C, 60.31; H, 6.84. Found: C, 60.2; H, 7.4.

B. [Fe(CO)Cl(PP $_3$)] $^+$ (8) (Thermodynamic Product, CO *Trans* to P_C). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (BPh $_4$ salt, 162 MHz, acetone- d_6 , 300

Scheme 1



K): δ 168.9 (dt, 1P, P_C , ${}^2J_{P(C)-P(T)} = 30.5$ Hz, ${}^2J_{P(C)-P(U)} = 38.1$ Hz); 60.5 (dd, 2P, P_T , ${}^2J_{P(T)-P(U)} = 40.1$ Hz); 77.9 (dt, 1P, P_U).

${}^1H\{^{31}P\}$ NMR spectrum (BPh₄ salt, 600 MHz, acetone-*d*₆, 283 K): δ 2.35, 2.81 (2 \times m, 2 \times 2H, $-P_CCH_2CHHP_T^-$); 2.74, 2.74 (2 \times m, 2 \times 2H, $-P_CCHHCH_2P_T^-$); 2.55 (m, 2H, $-P_CCH_2CH_2P_U^-$); 2.16 (m, 2H, $-P_CCH_2CH_2P_U^-$); 1.85, 1.93 (2 \times s, 2 \times 6H, 2 \times $P_T(CH_3)$); 1.58 (s, 6H, $P_U(CH_3)_2$); 7.46 (br, 8H, BPh_{ortho}); 7.08 (t, 8H, ${}^3J_{H-H} = 7.1$ Hz, BPh_{meta}); 6.93 (t, 4H, BPh_{para}).

${}^{13}C\{^1H\}$ NMR spectrum (BPh₄ salt, carbonyl region of ${}^{13}CO$ -labeled complex, 101 MHz, acetone-*d*₆, 300 K): δ 214.5 (ddt, $FeCO$, ${}^2J_{P(C)-C} = 43.9$ Hz, ${}^2J_{P(T)-C} = 17.2$ Hz, ${}^2J_{P(U)-C} = 21.0$ Hz).

${}^{13}C\{^1H\}$ NMR spectrum (chloride salt, 101 MHz, MeOH, 300 K): δ 15.8 (dt, P_TCH_3 , ${}^1J_{P(T)-C} = 17.6$ Hz, ${}^3J_{P(U)-C} = 1.9$ Hz); 19.0 (t, P_TCH_3 , ${}^1J_{P(T)-C} = 11.4$ Hz); 19.1 (dt, $P_U(CH_3)_2$, ${}^1J_{P(U)-C} = 28.1$ Hz, ${}^3J_{P(T)-C} = 2.4$ Hz); 24.0 (dt, $-P_CCH_2CH_2P_T^-$, ${}^1J_{P(C)-C} = 26.7$ Hz, ${}^2J_{P(T)-C} = 8.1$ Hz); 32.3 (dt, $-P_CCH_2CH_2P_T^-$, ${}^1J_{P(T)-C} = 15.7$ Hz, ${}^2J_{P(C)-C} = 11.4$ Hz); 24.9 (dd, $-P_CCH_2CH_2P_U^-$, ${}^1J_{P(C)-C} = 27.2$ Hz, ${}^2J_{P(U)-C} = 12.9$ Hz); 32.9 (dd, $-P_CCH_2CH_2P_U^-$, ${}^1J_{P(U)-C} = 30.5$ Hz, ${}^2J_{P(C)-C} = 12.4$ Hz).

IR ν_{max} (BPh₄ salt, Nujol): 1913 cm^{-1} .

[FeCl(PPh₃)(PP₃)]⁺ (9). Triphenylphosphine (50 mg, 191 μ mol) was added to a solution of **2** (50 mg, 118 μ mol) in methanol (10 mL). The resultant red solution was indistinguishable in color from the starting complex. A solution of sodium tetraphenylborate (50 mg, 146 μ mol) in methanol (2 mL) was added, resulting in the formation of a red precipitate, which was isolated by filtration. The crude product was washed with methanol (10 mL) and dried *in vacuo* to afford **9** (BPh₄ salt) as a red crystalline solid (87 mg, 76%; mp 181–182 $^\circ C$ dec).

${}^{31}P\{^1H\}$ NMR spectrum (BPh₄ salt, 162 MHz, acetone-*d*₆, 300 K): δ 167.6 (ddt, 1P, P_C , ${}^2J_{P(C)-P(T)} = 28.6$ Hz, ${}^2J_{P(C)-P(U)} = 32.4$ Hz, ${}^2J_{P(C)-PPh_3} = 104.9$ Hz); 39.6 (ddd, 2P, P_T , ${}^2J_{P(T)-P(U)} = 36.2$ Hz, ${}^2J_{P(T)-PPh_3} = 36.2$ Hz); 56.9 (ddt, 1P, P_U , ${}^2J_{P(U)-PPh_3} = 34.3$ Hz); 41.8 (ddt, 1P, PPh_3).

${}^1H\{^{31}P\}$ NMR spectrum (BPh₄ salt, 600 MHz, acetone-*d*₆, 283 K): δ 2.09, 2.35 (2 \times m, 2 \times 2H, $-P_CCH_2CHHP_T^-$); 2.41, 2.43 (2 \times m, 2 \times 2H, $-P_CCHHCH_2P_T^-$); 2.14 (m, 2H, $-P_CCH_2CH_2P_U^-$); 2.73 (m, 2H, $-P_CCH_2CH_2P_U^-$); 0.61, 1.57 (2 \times s, 2 \times 6H, 2 \times $P_T(CH_3)$); 1.14 (s, 6H, $P_U(CH_3)_2$); 7.72 (m, 2H, PPh_{ortho}); 7.68 (m, 3H, PPh_{meta} , PPh_{para}); 7.46 (br, 8H, BPh_{ortho}); 7.08 (t, 8H, ${}^3J_{H-H} = 7.1$ Hz, BPh_{meta}); 6.93 (t, 4H, BPh_{para}).

${}^{13}C\{^1H\}$ NMR spectrum (chloride salt, 101 MHz, EtOH, 300 K): δ 14.9 (t, P_TCH_3 , ${}^1J_{P(T)-C} = 13.7$ Hz); 19.5 (t, P_TCH_3 , ${}^1J_{P(T)-C} = 8.2$ Hz); 20.0 (d, $P_U(CH_3)_2$, ${}^1J_{P(U)-C} = 19.2$ Hz); 24.1 (dt, $-P_CCH_2CH_2P_T^-$, ${}^1J_{P(C)-C} = 28.4$ Hz, ${}^2J_{P(T)-C} = 6.2$ Hz); 35.2 (m, $-P_CCH_2CH_2P_T^-$); 24.5 (dd, $-P_CCH_2CH_2P_U^-$, ${}^1J_{P(C)-C} = 24.3$ Hz, ${}^2J_{P(U)-C} = 10.2$ Hz); 37.6 (dm, $-P_CCH_2CH_2P_U^-$, ${}^1J_{P(U)-C} = 33.6$ Hz); 137.5 (d, PPh_{ipso} , ${}^1J_{P-C} = 28.4$ Hz); 129.3 (d, PPh , $J_{P-C} = 8.2$ Hz); 135.5 (d, PPh , $J_{P-C} = 9.7$ Hz); 131.4 (d, PPh_{para} , ${}^4J_{P-C} = 1.7$ Hz).

Crystal data for **9** (BPh₄ salt) are summarized in Table 1. The atom numbering is given in Figure 8.

Results and Discussion

Preparation of 2. The iron(II) dichloride complex **2** was synthesized by the simultaneous, dropwise addition of a THF solution of **1** and a THF solution of anhydrous iron(II) chloride to rapidly stirring THF (Scheme 1). This procedure resulted in the instantaneous formation of a deep red solution with some orange-brown precipitate, which was removed by filtration.

At 300 K, only broad resonances were detected in the ${}^{31}P$ NMR spectrum of **2**. Sharper resonances were detected at lower

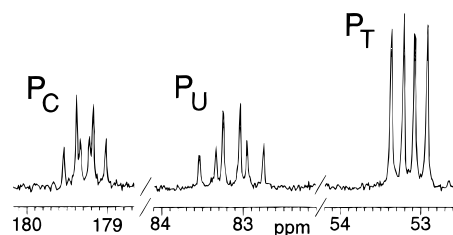
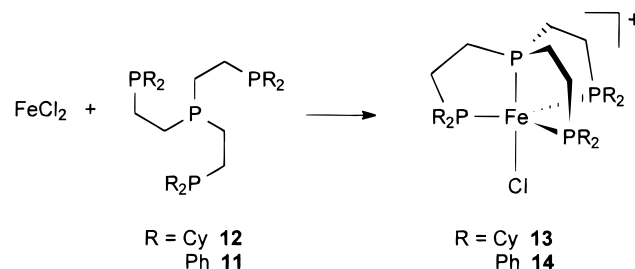


Figure 1. ${}^{31}P\{^1H\}$ NMR spectrum (162 MHz, 233 K, THF-*d*₈) of **2**.

Scheme 2



temperatures (Figure 1). Similar behavior has been noted for the octahedral iron dichloride complexes containing the hindered bis(phosphine) ligands DEPE and DPrPE, and the spectral broadness was attributed to temperature dependent paramagnetism.¹⁹ At 233 K, the ${}^{31}P\{^1H\}$ NMR spectrum of **2** contains three sharp multiplet resonances at δ 179.3 (dt), 83.1 (dt), and 53.2 (dd) ppm in the ratio 1:1:2, respectively (Figure 1). The central phosphorus of the tripodal ligand (P_C) is easily identified as the resonance at δ 179.3 ppm due to its extreme low-field shift, which is due to P_C being at the bridgehead of three fused five-membered chelate rings.²⁰ An apparent plane of symmetry through the iron and two chloro ligands renders two of the three terminal phosphorus atoms equivalent (P_T), and these are assigned to the resonance at δ 53.2 ppm. The remaining resonance at δ 83.1 ppm was assigned to the remaining unique terminal phosphorus (P_U). The 1H NMR spectrum of **2** contains three methyl and six methylene resonances and was assigned by analysis of the 2D COSY spectrum.

Crystals of **2** were obtained by slow cooling of a saturated benzene/hexane solution to approximately 0 $^\circ C$. The solid was extremely air- and moisture-sensitive, and X-ray diffraction data were collected at low temperature (-55 $^\circ C$). The data could not be fully refined, and although only a poor quality structure was obtained, it nonetheless supports the proposed structure of **2**.²¹

Other tripodal tetraphosphine ligands with ethylene ($-CH_2-CH_2-$) linkages between the central and terminal phosphorus atoms react with iron(II) chloride to give trigonal bipyramidal monochloride complexes (Scheme 2) rather than octahedral complexes analogous to **2**. Reaction of the cyclohexyl-substituted tripodal ligand $P(CH_2CH_2PCy_2)_3$ (**12**) or the phenyl-substituted tripodal ligand $P(CH_2CH_2PPh_2)_3$ (**10**) with iron(II) chloride in dichloromethane affords the cationic complexes $[FeP(CH_2CH_2PR_2)_3Cl]^+$, **13**⁶ or **14**,²² respectively (Scheme 2).

(19) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872.

(20) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(21) Details of crystal structure determination for **2**: $C_{12}H_{30}Cl_2FeP_4$, $M = 425.02$, red, space group $P2_1/a$, $a = 15.312(6)$ \AA , $b = 16.398(8)$ \AA , $c = 15.469(5)$ \AA , $\beta = 93.12(4)^\circ$, $V = 3878(2)$ \AA^3 , $D_{calc} = 1.456$ $g\ cm^{-3}$, $Z = 8$, $F(000) = 1776.00$, $R = 11.5\%$.

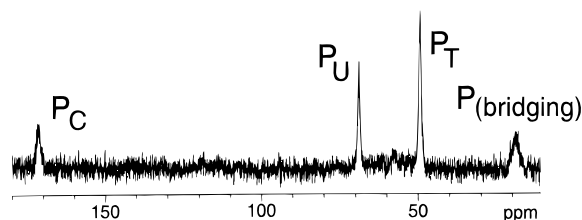


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, 300 K, MeOH) of **17**.

Both **13** and **14** are paramagnetic, and **13** was reported to give no ^{31}P NMR spectrum.⁶ In contrast, at low temperatures (233 K), the iron dichloride complex $[\text{FeP}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3\text{Cl}_2]$ (**2**) gives rise to sharp ^{31}P NMR spectra in all solvents, including methanol. However, the addition of a methanol solution of sodium tetraphenylborate to a methanol solution of **2** resulted in the immediate precipitation of a red solid, which has not been further characterized.²³

Byproducts in the Preparation of 2. Simultaneous addition of iron(II) chloride and the ligand $\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$, where neither species was in excess of the other, gave the highest yields of **2**. When either species is in excess, a larger quantity of the orange-brown precipitate is formed, and this has been attributed to the multi-iron complexes **17** containing bridging PP_3 ligands.

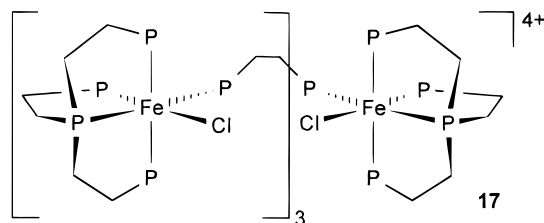
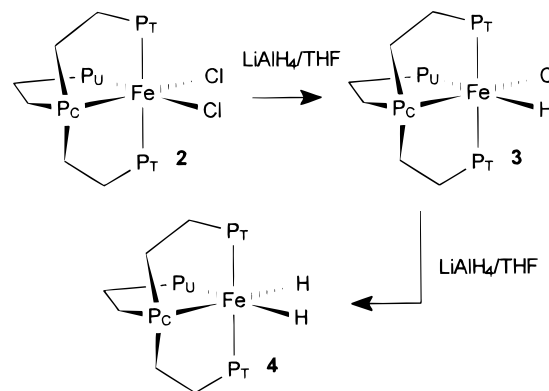


Figure 3. Schematic representation showing significant NOESY interactions between the hydride ligand and the PP_3 ligand in **3**. The thickness of the arrows indicates the relative intensity of the NOESY cross peak.

Scheme 3



Decomposition is more rapid at higher temperatures, occurring within seconds at 150 °C in the solid state. The phosphorus atoms of the bridging PP_3 ligand in **17** are bound strongly to the metal and cannot easily be displaced in subsequent reactions.

Preparation of 3 and 4. The iron chloro hydride complex **3** was synthesized by the careful reduction of the dichloride complex **2** with lithium aluminum hydride in THF, and more forcing reduction conditions afforded the dihydride **4** (Scheme 3). A THF solution of LiAlH_4 was added dropwise to a THF solution of **2**, resulting in a color change from red to bright yellow. The reaction was rapid at room temperature, and the color change allowed the end point to be determined accurately. Complex **3** is soluble in most organic solvents, although it reacts with methanol and haloalkanes.²⁴ The complex is least soluble in alkanes and can be recrystallized from alkane solvent (pentane or hexane) to afford bright yellow, needle-like crystals.

$^{31}\text{P}\{^1\text{H}\}$ NMR of **3** indicated the presence of a single product giving rise to three multiplets at δ 184.8 (dt, P_C), 61.3 (dd, P_T), and 60.0 (dt, P_U) ppm in the ratio 1:2:1, respectively. Complete assignment of the ^1H NMR resonances of **3** was achieved by analysis of the ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra as well as the 2D COSY and NOESY spectra. The resonance due to the hydride ligand of **3** appears at δ -11.63 ppm and in the phosphorus-coupled spectrum is split into a doublet of doublets of triplets (ddt) by the ^{31}P nuclei. Assignment of heteronuclear P-H couplings was achieved by selective ^{31}P decoupling ($^2J_{\text{H-P}(C)} = 44.4$ Hz, $^2J_{\text{H-P}(T)} = 69.1$ Hz, $^2J_{\text{H-P}(U)} = 44.1$ Hz).

There are two possible stereoisomers of **3** which can be formed, with the hydride either *cis* or *trans* to the central phosphorus atom, P_C . The position of the hydride was determined from the NOESY spectrum. Strong correlations were observed between the hydride resonance and 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

(22) King, R. B.; Kapoor, R. N.; Saran, M. S.; Kapoor, P. N. *Inorg. Chem.* **1971**, *10*, 1851.

(23) The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the red solid, at low temperature (203 K), in acetone- d_6 , shows the presence of at least three complexes. Major product (ca. 65%) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, acetone- d_6 , 203 K): δ 167.3 (br, 1P, P_C), 86.8 (br, 1P, P_U), 51.4 (br, 2P, P_T). Minor product (ca. 30%) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, acetone- d_6 , 203 K): δ 172.6 (dt, 1P, P_C , $^2J_{\text{P}(C)-\text{P}(U)} = 24.4$ Hz, $^2J_{\text{P}(C)-\text{P}(T)} = 21.4$ Hz), 78.8 (dt, 1P, P_U , $^2J_{\text{P}(T)-\text{P}(U)} = 42.7$ Hz), 48.7 (dd, 2P, P_T); minor product (ca. 5%) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, acetone- d_6 , 203 K): δ 171.1 (dt, 1P, P_C , $^2J_{\text{P}(C)-\text{P}(U)} = 30.5$ Hz, $^2J_{\text{P}(C)-\text{P}(T)} = 22.9$ Hz), 77.4 (dt, 1P, P_U , $^2J_{\text{P}(T)-\text{P}(U)} = 42.7$ Hz), 49.5 (dd, 2P, P_T).

(24) Details of the chemistry of alkoxy complexes will be published elsewhere.

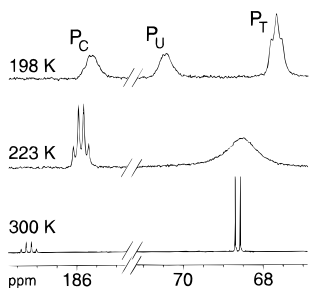


Figure 4. Variable temperature ³¹P{¹H} NMR spectra (162 MHz, toluene-*d*₈) of FeH₂(PP₃) **4**.

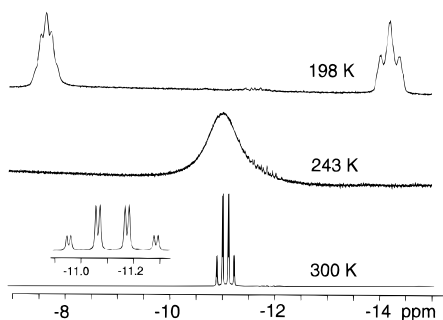


Figure 5. Variable temperature ¹H NMR spectra (400 MHz, toluene-*d*₈) of **4** (hydride region only). The inset is an expansion of the hydride resonance showing fine structure at 300 K.

between the hydride and Me_C. This clearly locates 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).^{3c}

Reaction of a THF solution of the chloro hydride complex **3** with lithium aluminum hydride afforded the dihydride complex **4** (Scheme 3). Extraction into an aromatic solvent (benzene or toluene) followed by extraction into an alkane solvent (pentane or hexane) afforded **4** as a very pale yellow, highly air-sensitive solid which was soluble in most organic solvents.

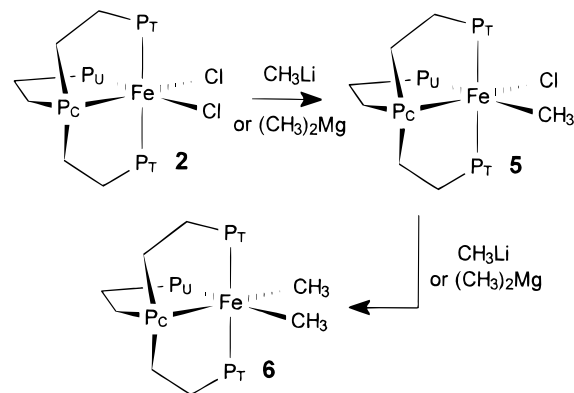
The ³¹P{¹H} NMR spectrum of **4**, at 300 K, contains only two sharp resonances, at δ 187.2 (q, P_C) and 68.7 ppm (d, P_T and P_U) in the ratio 1:3, with a ³¹P–³¹P coupling constant of 20.9 Hz (Figure 4). This spectrum is consistent with fast exchange occurring between the terminal phosphorus environments, P_T and P_U. At 223 K the exchange was slowed, causing significant broadening of the resonances due to P_T and P_U. At 198 K, two broad resonances were observed for the terminal phosphorus nuclei, at δ 70.5 (P_U) and 67.7 (P_T) ppm in the ratio 1:2, respectively.

The ¹H NMR spectrum of **4** shows similar exchange (Figure 5), with the two hydride resonances in fast exchange at 300 K and giving rise to a single sharp multiplet resonance at δ –11.03 ppm (dq, ²J_{H–P(C)} = 44.9 Hz, ²J_{H–P(terminal)} = 7.2 Hz). At 243 K, the hydride resonance is very broad. At 198 K, two broad resonances are apparent at δ –7.70 and –14.21 ppm.

The broadness of the resonances precluded the measurement of ³¹P–³¹P and ³¹P–¹H coupling constants and also precluded the use of 2D COSY and/or NOESY experiments to make unambiguous assignment of the two hydride resonances. The ³¹P and ¹H spectra of **4** are very similar to those reported for FeH₂[(PCH₂CH₂PPh₂)₃].^{25,26}

There are a number of possible mechanisms for the observed exchange between hydride and terminal phosphine resonances. Studies of tetraphosphite dihydride complexes of iron have

Scheme 4



modeled the exchange in terms of the concerted “tetrahedral jump” mechanism.²⁷ However, the bulky, monodentate phosphite ligands are quite different from PP₃. Alternative mechanisms include the reversible loss of a hydride ligand or the temporary detachment of one of the bound phosphines to give a five-coordinate complex which could undergo facile pseudorotation before recoordination of the pendant phosphine. Facile substitution of a phosphine *trans* to hydride is not unexpected since hydride ligands have a strong *trans* effect.

The observed exchange of hydride ligands and phosphine ligands occurs at approximately the same rate. This may be because they are part of the same process; however, separate mechanisms for each exchange process occurring at similar rates cannot be ruled out.

When dissolved in methanol or ethanol, the dihydride **4** affords an equilibrium mixture of [FeH(H₂)(PP₃)]⁺ and the alkoxy hydride complexes FeH(OMe)(PP₃) or FeH(OEt)(PP₃), respectively. The alkoxy complexes are unstable and on standing or heating undergo further reactions.²⁴

Preparation of 5 and 6. The iron methyl chloride complex **5** was prepared by the reaction of the iron dichloride complex **2** with either dimethylmagnesium or methylolithium, in THF solution (Scheme 4). A THF solution of either dimethylmagnesium or methylolithium was added dropwise to a THF solution of **2**, resulting in a color change from red to orange. The reaction was rapid at room temperature, and the color change allowed the end point to be determined accurately. The chloro methyl complex **5** is soluble in most organic solvents, although it reacts rapidly with alcohols or other protic solvents.

In the monomethylation of **2**, there are two possible isomers which could be formed, *i.e.*, with the methyl ligand either *cis* or *trans* to the central phosphorus atom, P_C. ³¹P{¹H} NMR indicated the presence of a single isomer giving rise to three multiplets at δ 188.4 (dt, P_C), 64.1 (dd, P_T), and 59.8 (dt, P_U) ppm in the ratio 1:2:1, respectively.

Complete assignment of the ¹H NMR spectrum of **5** was achieved by analysis of the ¹H and ¹H{³¹P} NMR spectra as well as the 2D COSY and NOESY spectra. The resonance due to the methyl ligand of **5** appears at δ –0.26 ppm and in the phosphorus-coupled spectrum is split (ddt) by the ³¹P nuclei. Selective ³¹P decoupling allowed the assignment of ³¹P–CH₃ couplings (3.2, 9.7, and 1.6 Hz to P_C, P_T, and P_U, respectively).

The position of the iron-bound methyl relative to the central phosphorus atom was established from the NOESY spectrum. Strong NOEs were observed between the iron-bound methyl

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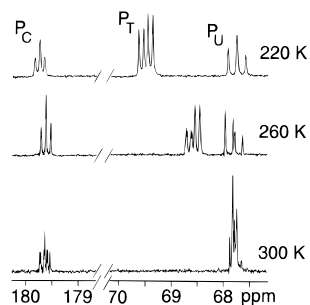


Figure 6. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz, toluene- d_8) of **6**.

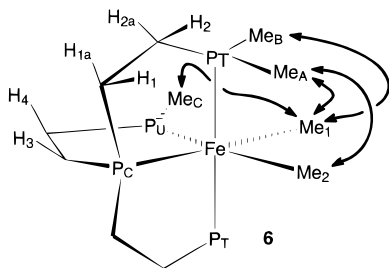


Figure 7. Schematic representation showing significant NOESY interactions between the methyl ligands and the PP_3 ligand in **6**.

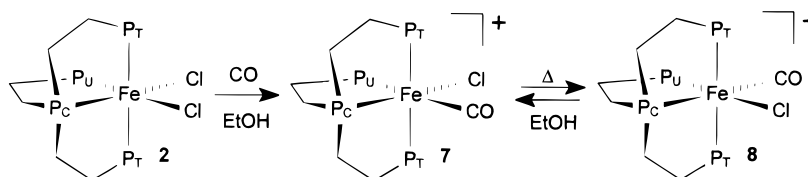
and Me_A , H_1 , and H_2 . No correlations were observed to Me_B or Me_C . This set of results unambiguously places the iron-bound methyl *cis* to the central phosphorus atom, the same site as the hydride ligand occupies in the chloro hydride complex **3**.

Reaction of dimethylmagnesium or methyl lithium with the methyl chloride complex **5** or reaction of excess methylating reagent with the dichloride complex **2** afforded the dimethyl complex **6** (Scheme 4). The ^{31}P NMR spectrum of **6** at 300 K contains two complex multiplet resonances, centered at δ 179.7 ppm, due to the central phosphorus, P_C , and at δ 67.8 ppm, due to the terminal phosphorus atoms, P_T and P_U , in the ratio 1:3. The appearance of only one terminal phosphorus resonance in this complex is due to the near coincidence of the chemical shifts of P_T and P_U . The chemical shift of P_U is notably temperature dependent, and first-order ^{31}P spectra are clearly resolved at lower temperatures (Figure 6).

Two iron-bound methyl resonances appear in the ^1H NMR spectrum, at 0.12 ppm (Me_1) and -0.88 ppm (Me_2), each appearing as a ddt. ^{31}P couplings to Me_1 were 1.4, 8.7, and 8.7 Hz to P_C , P_T , and P_U , respectively. ^{31}P couplings to Me_2 were 5.9, 9.7, and 8.3 Hz to P_C , P_T , and P_U , respectively.

The resonances of the PP_3 ligand in the ^1H NMR spectrum of **6** were assigned using the 2D COSY and NOESY spectra in a fashion analogous to that used for the chloro hydride complex **3**. The positions of the methyl ligands relative to P_C were determined from the NOESY spectrum. Strong correlations were observed between Me_1 and all three methyl groups Me_A , Me_B , and Me_C , showing Me_1 to be *trans* to the central phosphorus, P_C . Strong correlations between Me_2 and Me_A , H_1 , and H_2 showed Me_2 to be *cis* to the central phosphorus, P_C (Figure 7).

Scheme 5



Preparation of 7 and 8. Substitution of a chloro ligand of the iron(II) dichloride complex **2** by carbon monoxide yielded two isomeric iron(II) carbonyl chloride complexes **7** and **8** (Scheme 5). The introduction of an atmosphere of carbon monoxide over a degassed ethanol solution of the dichloride complex **2** resulted in a rapid color change from red to yellow. The addition of an ethanol solution of sodium tetraphenylborate precipitated **7** as the tetraphenylborate salt. The ^{31}P NMR spectrum contained three signals at δ 163.9 (dt, P_C), 58.6 (dt, P_U), and 44.9 (dd, P_T) ppm in the ratio 1:1:2, respectively.

By using ^{13}C -labeled carbon monoxide, ^{31}P - ^{13}C coupling constants to the carbonyl ligand were determined from the ^{31}P and ^{13}C NMR spectra. The ^{31}P NMR spectrum of the ^{13}C -labeled complex contained an extra doublet coupling in each resonance; $^2J_{\text{C-P(C)}} = 15.9$ Hz, $^2J_{\text{C-P(U)}} = 31.8$ Hz, $^2J_{\text{C-P(T)}} = 45.1$ Hz. The ^{13}C ligand gave rise to a ddt resonance at δ 212.9 ppm in the ^{13}C NMR spectrum.

Heating an ethanol solution of the carbonyl chloride complex **7** (chloride salt) at 60 °C resulted in the formation of another product, assigned as the isomeric carbonyl chloride complex **8**. This reaction was followed by ^{31}P NMR, which showed the depletion of the signals due to **7** in favor of the three new signals of **8** at δ 168.9 (dt, P_C), 77.9 (dt, P_U), and 60.5 (dd, P_T) ppm. The reaction could not be forced to completion, the two complexes, **7** and **8**, apparently reaching equilibrium after heating at 60 °C for 10 days with a ratio **8:7** of 5:1.

The use of ^{13}C confirmed that this second product also has one carbonyl ligand. The ^{13}C - ^{31}P coupling constants ($^2J_{\text{C-P(C)}} = 43.9$ Hz, $^2J_{\text{C-P(U)}} = 21.0$ Hz, $^2J_{\text{C-P(T)}} = 17.2$ Hz) are very different from those of **7**. The ^{13}C NMR spectrum contained a ddt resonance at δ 213.3 ppm assigned to the carbonyl ligand of **8**. The relative stereochemistry of **7** and **8** was tentatively assigned from the relative magnitudes of their ^{13}C - ^{31}P coupling constants.²⁸

Preparation of 9. The preparation of **9** was achieved by the addition of triphenylphosphine to a methanol solution of **2** (Scheme 6). No notable color change occurred, the resultant solution being essentially indistinguishable from the red color of **2**. The addition of a methanol solution of sodium tetraphenylborate resulted in the precipitation of the tetraphenylborate salt of **9**, which was soluble in acetone.

The ^{31}P NMR spectrum of **9** contained four resonances at δ 167.6, 56.9, 41.8, and 39.6 ppm in the ratio 1:1:1:2, respectively. The central phosphorus, P_C , was assigned to the resonance at δ 167.6 ppm due to its extreme low-field shift. P_T was also easily assigned to the resonance at δ 39.6 ppm by reference to the relative integrated intensities. The resonance at δ 41.8 ppm was assigned to the bound triphenylphosphine due to the large, 104.9 Hz coupling to P_C , which is characteristic of the *trans* ^{31}P - ^{31}P coupling constant. The resonance at δ 56.9 ppm was assigned to P_U .

The full assignment of the ^1H NMR spectrum of **9** was achieved using 2D COSY and NOESY experiments. The NOESY spectrum contained roughly equal enhancements from the ortho phenyl protons of the bound triphenylphosphine to all three PP_3 methyl resonances, confirming that the triphenylphosphine is *trans* to P_C .

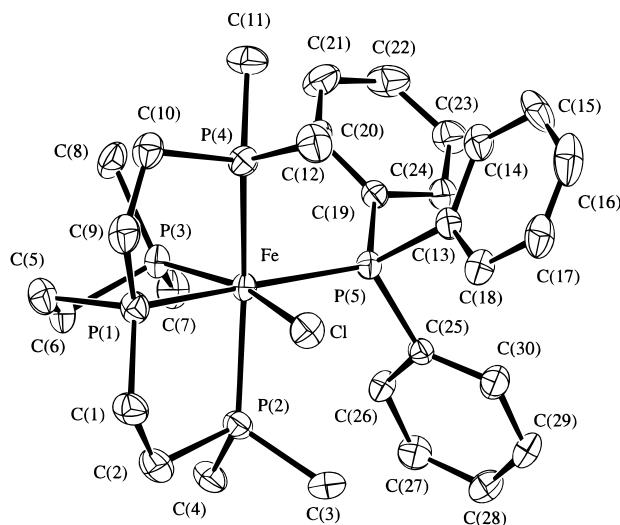


Figure 8. ORTEP plot (25% thermal ellipsoids, non-hydrogen atoms) of the complex cation of **9** (BPh₄ salt).

Scheme 6

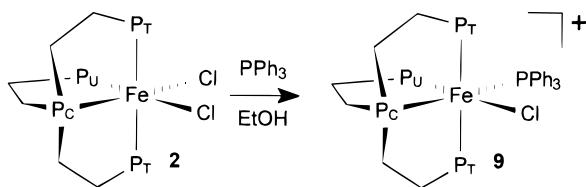


Table 2. Selected Bond Lengths (Å) for Iron(II) Complexes **9** (This Work), **15**,³¹ and **16**³²

	9	15	16
Fe-P _C	2.202(2)	2.202(5)	2.151(3)
Fe-P _U	2.234(2)	2.231(5)	2.224(3)
Fe-P _T ^a	2.312(2)	2.338(5)	2.259(4)
Fe-P _T ^a	2.312(2)	2.306(5)	2.297(3)
Fe-Cl[1]	2.356(2)	2.388(4)	
Fe-Cl[2]/PPH ₃	2.361(2)	2.410(4)	

^a Two *trans* terminal phosphines, P_T.

X-ray Crystal Structure of 9 (BPh₄ Salt). Crystals of **9**, suitable for X-ray diffraction, were obtained by cooling a saturated acetone solution of **9** to 5 °C. The structure determination confirmed the *trans* arrangement of P_C and triphenylphosphine (Figure 8). The crystal data parameters are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

The four phosphorus atoms of the PP₃ ligand and the two chloro ligands of **9** are arranged in a distorted octahedron. The distortion from an octahedral arrangement is due to the natural bite angle²⁹ of PP₃ being less than the required 90°. Chelation angles of less than 90° are also observed in complexes of other

(28) The related iron(II) carbonyl complexes [FeH(CO)(PP₃)]⁺ and [FeMe(CO)(PP₃)]⁺ have also been prepared.³³ The carbonyl ligand in both these complexes was shown (unambiguously) to be *trans* to P_C using ¹H-¹H NOESY experiments. The magnitudes of the ¹³C-³¹P coupling constants for the ¹³C-labeled complexes are as follows: [FeH(CO)(PP₃)]⁺, ²J_{C-P(C)} = 31.5 Hz, ²J_{C-P(T)} = 20.0 Hz, ²J_{C-P(U)} = 17.2 Hz; [FeMe(CO)(PP₃)]⁺, ²J_{C-P(C)} = 40.7 Hz, ²J_{C-P(T)} = 19.6 Hz, ²J_{C-P(U)} = 16.0 Hz. The similarity of these coupling constants to those of the second (thermodynamically favored) carbonyl chloride complex **8** (²J_{C-P(C)} = 43.9 Hz, ²J_{C-P(T)} = 17.2 Hz, ²J_{C-P(U)} = 21.0 Hz) and their marked difference from those of the first (kinetically favored) carbonyl chloride complex **7** (²J_{C-P(C)} = 15.9 Hz, ²J_{C-P(T)} = 45.1 Hz, ²J_{C-P(U)} = 31.8 Hz) indicate that the carbonyl is *trans* to P_C in **8** and *trans* to P_U in **7**. The synthesis and full characterization of [FeH(CO)(PP₃)]⁺ and [FeMe(CO)(PP₃)]⁺ will be reported elsewhere.

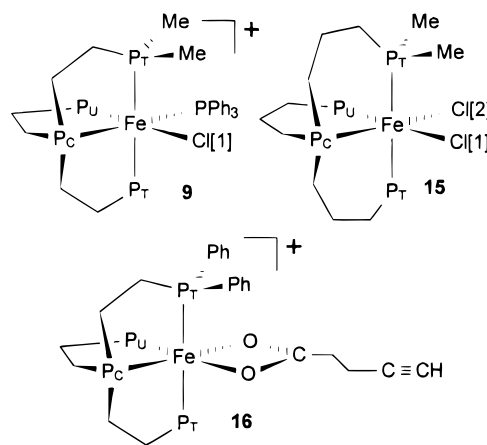
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Table 3. Selected Bond Angles (deg) for Iron(II) Complexes **9** (This Work), **15**,³¹ and **16**³²

	9	15	16
P _C -Fe-P _U	83.85(9)	97.1(2)	85.3(1)
P _C -Fe-P _T ^a	83.24(9)	95.4(2)	86.3(1)
P _C -Fe-P _T ^a	83.66(9)	88.9(2)	82.7(1)
P _C -Fe-Cl[1]	82.14(9)	85.6(2)	
P _C -Fe-Cl[2]/PPH ₃	174.5(1)	179.0(2)	
P _U -Fe-P _T ^a	93.40(9)	99.7(2)	97.1(1)
P _U -Fe-P _T ^a	98.71(9)	95.3(2)	98.9(1)
P _U -Fe-Cl[1]	165.22(9)	176.9(2)	
P _U -Fe-Cl[2]/PPH ₃	101.59(8)	83.7(2)	
P _T -Fe-P _T	161.07(9)	168.8(2)	159.7(2)
P _T -Fe-Cl[1] ^a	80.32(8)	81.5(2)	
P _T -Fe-Cl[1] ^a	84.41(8)	83.2(2)	
P _T -Fe-Cl[2]/PPH ₃ ^a	97.40(8)	83.7(2)	
P _T -Fe-Cl[2]/PPH ₃ ^a	94.37(8)	91.5(2)	
Cl[1]-Fe-Cl[2]/PPH ₃	92.52(8)	93.6(2)	

^a Two *trans* terminal phosphines, P_T.

ligands containing phosphine groups separated by an ethylene bridge. For example, the chelation angle in the iron dichloride complexes of the diphosphines DMPE,³⁰ DEPE,¹⁸ and DPrPE¹⁸ are 85.8°, 85.3°, and 84.6°, respectively. The chelation angles in **9** (Table 3) are 83.9° and 83.5° for P_C-Fe-P_U and P_C-Fe-P_T (average), respectively. The distortion is most noticeable in the angle between the *trans* phosphines (161.07°), nearly 20° from the ideal octahedral angle. Many octahedral iron(II) complexes of **10** have been synthesized, and an X-ray diffraction structure of the η²-pentynato complex **16** has been reported.³² The Fe-P bond lengths and angles for **16** are included in Tables 2 and 3.



The Fe-P bond lengths of **16** on average are slightly shorter than those of **9** and **15**, due to the presence of the harder carboxylate ligand. The P-Fe-P bond angles for **16** are very similar to those for **9**; in both cases the chelation angles are significantly less than 90°.

Comparison of **9** with the iron dichloride complex **15**³¹ of the related tripodal tetraphosphine ligand, **11**, with three carbon links between the phosphorus atoms, highlights the differences imparted to complexes by the two ligands (Table 3). Whereas **1** has a natural bite angle of less than 90°, **11** has a natural bite angle of greater than 90°. In **15**, the *trans* phosphines are bent toward the front chloro ligand (Cl[1]) by 11.2°, whereas in **9** they are bent by 18.9°, essentially away from the chloro and triphenylphosphine ligands.

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Conclusions

Iron(II) complexes containing the tripodal tetraphosphine ligand $P(CH_2CH_2PMe_2)_3$ (**1**) were synthesized. Reaction of the dichloride complex $FeCl_2(PP_3)$ (**2**) with $LiAlH_4$ afforded $FeHCl(PP_3)$ (**3**) and $FeH_2(PP_3)$ (**4**); reaction of **2** with Me_2Mg or $MeLi$ afforded $FeMeCl(PP_3)$ (**5**) and $FeMe_2(PP_3)$ (**6**). Reaction of **2** with CO afforded the isomeric carbonyl hydride complexes $[FeCOCl(PP_3)]^+$ (**7** and **8**); and reaction of **2** with PPh_3 afforded $[Fe(PPh_3)Cl(PP_3)]^+$ (**9**). The structure of **9** was determined by X-ray crystallography, and the core structure was significantly distorted from octahedral coordination due to the small natural bite angle of the PP_3 ligand. The dihydride complex $FeH_2(PP_3)$ (**4**) shows dynamic NMR behavior in both the 1H and ^{31}P spectra.

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Supporting Information Available: Listings of atom coordinates, anisotropic thermal parameters, bond lengths and angles, torsion angles, nonbonded contacts, and details of least squares planes for $[Fe(PPh_3)Cl(PP_3)]^+$ (**9**) (BPh_4 salt) (15 pages). Ordering information is given on any current masthead page.

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