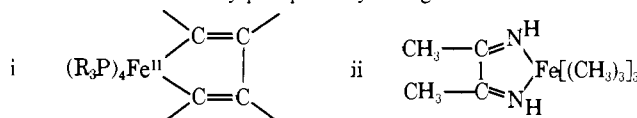# Chemistry of Zero- and Low-Valent Metal Phosphine and Phosphite Complexes. 4.[1] The Iron System

T. V. Harris, J. W. Rathke, and E. L. Muetterties*

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853. Received May 1, 1978

Abstract: Sodium amalgam reduction of tertiary phosphine and phosphite adducts of iron(II) chloride, $FeCl_2[PR_3]_x$ ($x = 2$, 3), in the presence of excess phosphine or phosphite ligand yielded binary phosphine- and phosphite-iron complexes. The reaction products from amalgam reductions of the phosphine and of the phosphite iron complexes were quite different. With trimethyl phosphite, $Fe[P(OCH_3)_3]_5$, structurally analogous to $Fe(CO)_5$, was obtained, but with trimethylphosphine, the product of stoichiometry $Fe[P(CH_3)_3]_4$ was shown to be an iron(II) hydride complex, $FeH[CH_2P(CH_3)_2][P(CH_3)_3]_4$. Modification of the trimethyl phosphite reduction system by addition of disubstituted acetylenes led to the formation of novel acetylene complexes $Fe[P(OCH_3)_3]_3[RC_2R']$ with R and R' an alkyl or aryl group. In contrast the analogous reduction of the trimethylphosphine adduct in the presence of dimethylacetylene gave an iron(II) ferrole, i. Addition of potential two- and four-electron donor molecules during the reduction in the trimethylphosphine system gave a series of substituted iron(0)–phosphine com-

plexes including $Fe[P(CH_3)_3]_3(CO)_2$, $C_4H_6Fe[P(CH_3)_3]_3$, and the heterocycle ii. The reaction chemistry of the phosphine- and phosphite-iron complexes is described. Steric and electronic variances in the phosphine and phosphite ligands markedly affected the chemistry of these two series of iron(0) and iron(II) complexes. Other structurally and chemically described derivatives include $Fe[P(OCH_3)_3]_3(CO)_2$, $Fe[P(CH_3)_3]_3(PF_3)_2$, $Fe[P(OCH_3)_3]_3(PF_3)_2$, $Fe[P(OCH_3)_3]_2[(CH_3)_3CNC]_3$-$(C_6H_5C_2C_6H_5)$, $Fe[P(OCH_3)_3]_2(CO)_2(C_6H_5C_2C_6H_5)$, $HFe[P(OCH_3)_3]_5^+PF_6^-$, $CH_3Fe[P(OCH_3)_3]_5^+PF_6^-$, $C_2H_5Fe[P-(OCH_3)_3]_5^+PF_6^-$, $XFe[P(OCH_3)_3]_5^+PF_6^-$ (X = Cl, I), $C_4H_6Fe[P(CH_3)_3]_3$, $C_4H_7Fe[P(CH_3)_3]_3^+PF_6^-$, $H_4Fe[P(OCH_3)_3]_3$, and η^6-arene $Fe[P(OCH_3)_3]_2$.

Introduction

We are attempting the synthesis of low-valent metal complexes of phosphines and phosphites in groups to the left of cobalt, and we describe here the synthesis and chemistry of trimethylphosphine and trimethyl phosphite iron complexes.[1,2] To date, the low-valent binary metal phosphine and phosphite groups primarily include those of cobalt[3-16] and nickel,[17-29] although a wide range of zerovalent metal phosphine complexes based on bidentate phosphines has been prepared largely by Chatt and co-workers.[30]

Results and Discussion

Synthesis of Zerovalent Iron Complexes. We have found the reduction of iron(II) halide-phosphine or phosphite complexes in the presence of excess phosphine or phosphite to be straightforward, general syntheses of not only the binary zerovalent complexes but also of a variety of complexes that additionally incorporate other ligands, such as acetylenes, and of various iron metallocyclic compounds. Sodium amalgam appeared to be the most generally effective reductant.

Iron(II) halides reacted with trialkyl phosphites to form either yellow, paramagnetic, five-coordinate complexes, $FeX_2[P(OR)_3]_3$, or pale green, paramagnetic, four-coordinate complexes, $FeX_2[P(OR)_3]_2$. Steric features of the phosphite seemed to largely determine the reaction course; thus trimethyl and triethyl phosphite formed five-coordinate adducts and triisopropyl phosphite formed four-coordinate adducts. Similarly, trimethylphosphine, which has a comparable cone angle to triisopropyl phosphite,[31] formed a pale green four-coordinate complex. The phosphite ligands in $FeCl_2[P(OCH_3)_3]_3$ were labile but not readily displaced by other types of ligands; however, the chloride ion ligands were easily displaced and these were abstracted in the presence of $P(OCH_3)_3$ and noncomplexing anions to yield $Fe[P(OCH_3)_3]_5Cl^+$ and $Fe[P-(OCH_3)_3]_6^{2+}$.

* Address correspondence to author at Department of Chemistry, University of California, Berkeley, Calif. 94720.

Synthesis and Properties of $Fe[P(OCH_3)_3]_5$. Sodium amalgam reduction of $FeCl_2[P(OCH_3)_3]_3$ in the presence of excess trimethyl phosphite yielded $Fe[P(OCH_3)_3]_5$. This complex was yellow, soluble in all hydrocarbons, and decomposed under vacuum at 120 °C to give trimethyl phosphite and a brown-black, intractable residue of approximate composition $FeP-(OCH_3)_3$. In air, the pentacoordinate complex rapidly decomposed; it was both water and oxygen sensitive. Solution studies of the oxygen reaction gave no indication of a well-defined intermediate in the oxidation reaction; trimethyl phosphate was the major terminal oxidation product. The hydrolysis reaction is discussed below.

Pentakis(trimethyl phosphite)iron(0), like all other known ML_5 complexes, was stereochemically nonrigid. The $^{31}P\{^1H\}$ NMR spectrum was a singlet at 20 °C and an A_2B_3 multiplet at −80 °C. The latter establishes a trigonal bipyramidal geometry for this molecule. An intramolecular ligand exchange process was responsible for the exchange collapse of the A_2B_3 pattern at higher temperatures since no fast (NMR time scale) ligand exchange was observed between the iron complex and free trimethyl phosphite to temperatures of 70 °C.[32]

The dominant chemical characteristic of the zerovalent iron complex was facile attack on the iron atom by electrophilic reagents, a feature consistent with the expected high electron density on the iron atom. This chemistry, based largely on protonation and alkylation reactions, is described below.

$XFe[P(OCH_3)_3]_5^+$ Octahedral Derivatives. Protonation of $Fe[P(OCH_3)_3]_5$ by weak acids occurred within the time of mixing to form quantitatively $HFe[P(OCH_3)_3]_5^+$, which was most conveniently obtained as a pure, microcrystalline salt by reaction of the iron(0) complex with ammonium hexafluorophosphate:

$$Fe[P(OCH_3)_3]_5 + NH_4PF_6$$
$$\rightarrow HFe[P(OCH_3)_3]_5^+PF_6^- + NH_3 \quad (1)$$
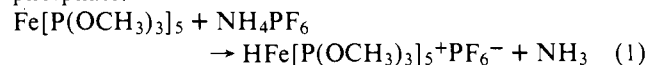
An analogous reaction with methyl iodide was also rapid; here the product was $CH_3Fe[P(OCH_3)_3]_5^+$, a stable and isolable species. ^1H NMR evidence for the unstable $C_2H_5Fe[P-$

$(OCH_3)_3]_5^+$ analogue was obtained from a spectral study of the reaction of equimolar amounts of C_2H_5I and $Fe[P(OCH_3)_3]_5$ in CD_3CN. Another set of octahedral $XFe[P(OR)_3]_5^+$ complexes with X = Cl and I and R = CH_3 and C_2H_5 was prepared by reaction of the $FeX_2[P(OR)_3]_3$ complexes with $Na^+B(C_6H_5)_4^-$ and $P(OR)_3$ in methanol. All these complexes (hydride, methyl, halide) displayed temperature-invariant AB_4 $^{31}P\{^1H\}$ spectra.[34]

The chemical properties of the octahedral hydride and alkyl complexes varied. All data for the hydride derivative pointed toward a relatively robust complex. This hydrido complex did not decompose in the solid state at 200 °C and did not decompose in solution at 120 °C. There was no evidence for phosphite ligand dissociation:

$$HFe[P(OCH_3)_3]_5^+ \rightleftharpoons HFe[P(OCH_3)_3]_4^+ + P(OCH_3)_3 \quad (2)$$
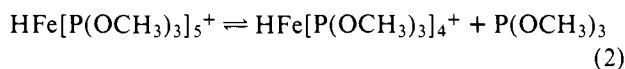
No ligand exchange between $HFe[P(OCH_3)_3]_5^+$ and $P(OC_2H_5)_3$ was detected within a 2-week period at 25 °C. Additionally, a solution of $HFe[P(OCH_3)_3]_5^+$ in CD_3OD showed no deuterium (CD_3O-) incorporation over a 1-week period. This is an indication that phosphite dissociation was not significant since it has been demonstrated that transesterification of phosphite ligands of transition metal complexes in alcohols occurs rapidly when there is phosphite dissociation.[36] Consistently, there was no detectable interaction of the hydride with ethylene or allene even at elevated temperatures and pressures and the hydride did not isomerize 1-hexene. By way of contrast, $Ni[P(OC_2H_5)_3]_4$ was reversibly protonated to the hydride $HNi[P(OC_2H_5)_3]_4^+$,[37] which through phosphite dissociation was in equilibrium with $HNi[P(OC_2H_5)_3]_3^+$. The latter complex was an active catalyst or catalyst precursor for olefin isomerization and reacted with dienes for form η^3-allylnickel complexes.[38]

The methyl cation had a lower thermal stability (decomposed at ~95 °C) than the hydrido cation but was isolable in pure form and was indefinitely stable at room temperature under an inert atmosphere. In contrast, the ethyl complex, $C_2H_5Fe[P(OCH_3)_3]_5^+$, slowly decomposed in solution at 20 °C to irreversibly yield ethylene and $HFe[P(OCH_3)_3]_5^+$. This decomposition, which most likely followed the well-established β-hydrogen abstraction mechanism, would require a ligand predissociation

$$C_2H_5Fe[P(OCH_3)_3]_5^+ \rightleftharpoons C_2H_5Fe[P(OCH_3)_3]_4^+ + P(OCH_3)_3 \quad (3)$$
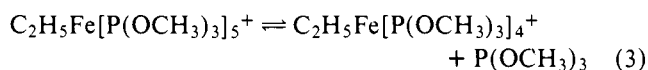
for the subsequent hydride abstraction (eq 4) to proceed. Since

$$C_2H_5Fe[P(OCH_3)_3]_4^+ \rightleftharpoons H(C_2H_4)Fe[P(OCH_3)_3]_4^+$$
$$\xrightarrow{P(OCH_3)_3} HFe[P(OCH_3)_3]_5^+ + C_2H_4 \quad (4)$$
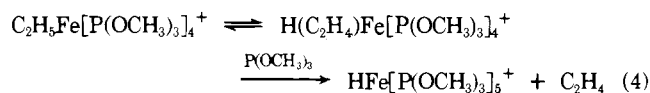
the decomposition of the ethyl cation occurred slowly over a 2-week period,[39] the equilibrium constant for ligand dissociation (eq 3) may be quite small, although certainly larger than that for the analogous cationic hydride.

Attempts to prepare other alkyl iron complexes by reaction of alkyl halides with $Fe[P(OCH_3)_3]_5$ were largely unsuccessful. Benzyl iodide reacted to form quantitatively bibenzyl and $Fe[P(OCH_3)_3]_3I_2$. Allyl halides similarly gave 1,5-hexadiene, although allyl iodide gave small amounts of η^3-$C_3H_5Fe[P(OCH_3)_3]_4^+$.[1a]

Hydrolysis of Fe[P(OCH_3)_3]_5. Hydrolysis of $Fe[P(OCH_3)_3]_5$ with limited amounts of water in acetonitrile solution did not lead to the formation of $HFe[P(OCH_3)_3]_5^+$. The hydride complex itself is resistant to hydrolysis; there was no reaction of this hydride with 1 or 3 equiv of water during a 2-week period. Thus the hydride complex, if it had been formed through protonation of $Fe[P(OCH_3)_3]_5$ by water, should have survived

the "hydrolysis" conditions. Water is simply too weak an acid to substantially protonate $Fe[P(OCH_3)_3]_5$. Hydrolysis of $Fe[P(OCH_3)_3]_5$ may be initiated by a predissociation step, loss of phosphite

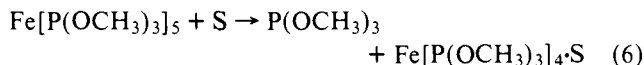$$Fe[P(OCH_3)_3]_5 \rightleftharpoons Fe[P(OCH_3)_3]_4 + P(OCH_3)_3 \quad (5)$$

followed by an attack of water on the $Fe[P(OCH_3)_3]_4$ intermediate. NMR studies (^{31}P) demonstrated that a large number (ca. seven) of hydrolysis products were formed. Although $HFe[P(OCH_3)_3]_5^+$ was not an intermediate in the hydrolysis reaction, ^1H NMR showed that small amounts of three different hydrides were formed in the hydrolysis reaction of $Fe[P(OCH_3)_3]_5$; the concentrations of these hydrides were a function of the water to iron reaction ratio. Only one of these hydrides displayed sufficient fine structure to allow a limited structural interpretation. This hydride gave an ^1H NMR spectrum consisting of a quintet of doublets ($J_{H-P_4} = 53.0$, $J_{H-P} = 23.3$ Hz) and a $^1H\{^{31}P\}$ singlet. Thus this hydride may be formulated as a neutral or cationic $HFe[P(OCH_3)_3]_4L^{+ \text{ or } 0}$ where H and L are trans and L is a partially hydrolyzed phosphorus ligand.[41]

Hydrogen Addition to Fe[P(OCH_3)_3]_5. Pentakis(trimethyl phosphite)iron(0), dissolved in tetrahydrofuran, quantitatively reacted with hydrogen during a several-week period to form $H_2Fe[P(OCH_3)_3]_4$ and trimethyl phosphite. The reverse reaction of $H_2Fe[P(OCH_3)_3]_4$ and trimethyl phosphite did not detectably proceed at 110–120 °C to give hydrogen and $Fe[P(OCH_3)_3]_5$. This behavior is in sharp contrast to the isoelectronic complex $Co[P(OCH_3)_3]_5^+$,[42] which showed no evidence of reaction with hydrogen. In fact, $H_2Co[P(OCH_3)_3]_4^+$ reacted quantitatively with trimethyl phosphite to give $Co[P(OCH_3)_3]_5^+$ and hydrogen.[42] This sharp variance in chemical equilibrium for the iron and cobalt systems may be largely ascribed to the positive charge on the cobalt complexes which dramatically lowers the probability of hydrogen oxidative addition relative to ligand (phosphite) addition.

Reaction of hydrogen with $Fe[P(OCH_3)_3]_5$ was more rapid in methanol than in tetrahydrofuran or benzene but $H_2Fe[P(OCH_3)_3]_4$ was a relatively minor product. A number of other uncharacterized iron hydrides were formed but a clean separation of these complexes was not achieved.

Ligand Exchange in Fe[P(OCH_3)_3]_5. Ligand dissociation in $Fe[P(OCH_3)_3]_5$ was a more facile process than in $HFe[P(OCH_3)_3]_5^+$. Nevertheless, rates of ligand interchange and substitution were low. Thus a 2:1 mixture of $P(OC_2H_5)_3$ and $Fe[P(OCH_3)_3]_5$ in CD_3CN showed a very slight amount of ligand exchange by NMR 1 h after mixing and total equilibration to a mixture of $Fe[P(OCH_3)_3]_x[P(OC_2H_5)_3]_{5-x}$ complexes only after a 1-week period. The rate of ligand exchange was solvent dependent. Reaction of $Fe[P(OCH_3)_3]_5$ with carbon monoxide in polar solvents yielded a mixture of $Fe[P(OCH_3)_3]_4(CO)$ and $Fe[P(OCH_3)_3]_3(CO)_2$. The carbon monoxide substitution rate was vanishingly low in benzene, moderate (complete within 1 day) in diethyl ether, and fast (complete within 2 h) in methanol. An enhanced substitution rate in methanol cannot be due to protonation of the zerovalent iron complex and subsequent reaction of $HFe[P(OCH_3)_3]_5^+$,[43] a complex of demonstrated low reactivity.

Substitution reactions of the coordinatively saturated complex $Fe[P(OCH_3)_3]_5$ should follow either dissociative or interchange mechanisms. Consistent with a dissociative mechanism was the demonstration of CD_3O incorporation into the iron(0) complex which indicates that ligand dissociation to $Fe[P(OCH_3)_3]_4$ and trimethyl phosphite does occur. The solvent-dependent rates of carbon monoxide substitution and hydrogen oxidative addition suggest participation by polar, potentially coordinating solvent molecules in an interchange step

$$Fe[P(OCH_3)_3]_5 + S \rightarrow P(OCH_3)_3$$
$$+ Fe[P(OCH_3)_3]_4 \cdot S \quad (6)$$

followed by a step in which the incoming ligand displaces the weakly bound solvent molecule:

$$Fe[P(OCH_3)_3]_4 \cdot S + ligand$$
$$\rightarrow Fe[P(OCH_3)_3]_4 \cdot ligand + S \quad (7)$$
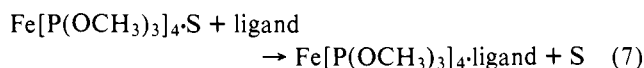
Beer's law behavior of solutions of $Fe[P(OCH_3)_3]_5$ was consistent with the promotion of phosphite dissociation by polar solvents. Thus a plot of absorbance vs. concentration (Figure 1) for a solution of $Fe[P(OCH_3)_3]_5$ in pentane over the concentration range 1×10^{-3} to 1×10^{-5} M was linear, whereas the same plot for a solution in methanol over the same concentration range showed an increasing deviation from linearity with decreasing concentration. Formation of the coordinately unsaturated complex $Fe[P(OCH_3)_3]_4$ or the labile coordinately saturated species, $Fe[P(OCH_3)_3]_4(CH_3OH)$, are two possible explanations for deviation from linear Beer's law behavior in methanol.

Reduction of $FeX_2[P(OR)_3]_3$ in the Presence of Acetylenes. Sodium amalgam reduction of $FeCl_2[P(OCH_3)_3]_3$ consistently produced $Fe[P(OCH_3)_3]_5$ in the presence of 1,3-butadiene or acetonitrile (see below) even in the absence of additional trimethyl phosphite. However, reduction of the complex in the presence of disubstituted acetylenes produced $Fe[P(OCH_3)_3]_3(RC_2R')$ even in the presence of additional trimethyl phosphite. Thus, the reactivity of possible intermediates like $Fe[P(OCH_3)_3]_3$ toward donor molecules decreases in the order $RC{\equiv}CR' > P(OCH_3)_3 \gg$ 1,3-butadiene $\sim CH_3CN$.

The $Fe[P(OR)_3]_3(R'C_2R')$ complexes with $R = CH_3$ and C_2H_5 and with $R' =$ alkyl or aryl were diamagnetic, purple crystals or oils. ^1H NMR spectra of the trimethyl phosphite complexes showed a phosphite methyl multiplet, aryl resonances for aryl acetylenes, and a methyl quartet for methyl-substituted acetylenes. The last NMR feature established equivalent spin–spin coupling of all three phosphorus atoms to the methyl protons and suggested that the complexes were monomeric.[44] Spectroscopic equivalence of all phosphite ligands was indicated by the singlet $^{31}P\{^1H\}$ NMR resonance from 25 to $-70\,°C$.

A preliminary single-crystal X-ray study[46] established the monomeric character of the diphenylacetylene complex in the solid state. The solid-state geometry is close to pseudotetrahedral using the center of the acetylenic bond as the fourth "coordination" side; however, the FeP_3 substructure does not have C_{3v} symmetry. Alternatively, the geometry may be described as square pyramidal (five coordinate) with the acetylenic carbon atoms defining two basal sites of the pyramid. We prefer the latter description of a formal d^6-Fe^{II} complex with a $C_2R_2{}^{2-}$ ligand; oxidative-addition reactions seem to prevail with these zerovalent iron phosphite and phosphine complexes. The actual geometry, **1**, is approximately intermediate between

1
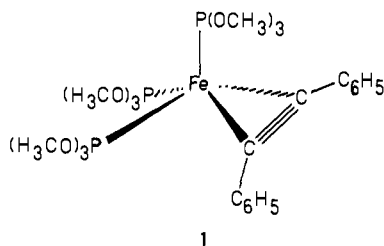
the two idealized representations; the acetylenic $C{\equiv}C$ separation was 1.332 (10) Å. Two related "four"-coordinate molecules are the diamagnetic d^6 $W(C_2H_5C_2C_2H_5)_3CO$ complex,[47] which may have near C_3 or C_{3v} symmetry, **2**, since it shows ^1H NMR inequivalence between the ethyl group protons distal and proximal to the carbonyl ligand, and the d^8
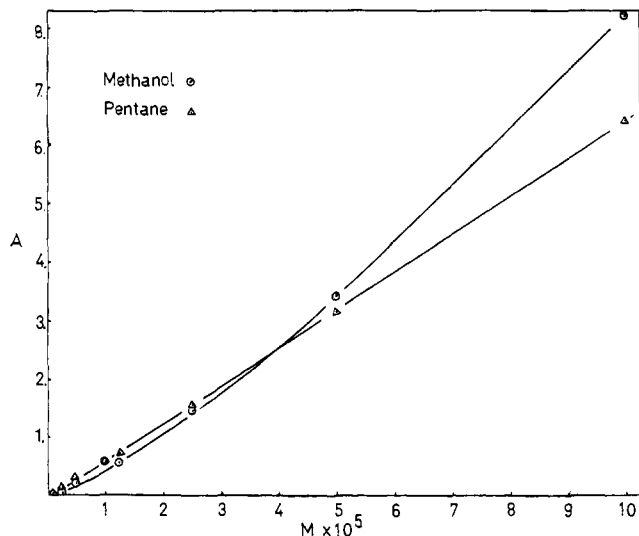
Figure 1. Beer's law plots for solutions of $Fe[P(OCH_3)_3]_5$ in methanol and pentane at 26.75 nm.
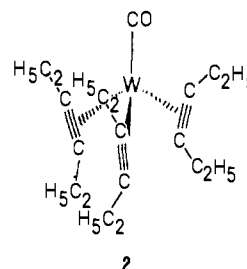
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$IrCl[P(C_6H_5)_3]_2(acetylene)$ complexes,[48] which were considered as trigonal bipyramidal with the acetylenic carbon atoms at equatorial sites.[49]

The character of ligand displacement reactions with $Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5)$ was relatively complex. In the presence of excess trimethyl phosphite, the acetylene complex exhibited no tendency to undergo fast (*NMR time scale*) phosphite ligand exchange at 20 °C. Exchange did occur as demonstrated by NMR experiments with mixtures of $Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5)$ and triisopropyl phosphite, where the latter rapidly (*time of mixing*) displaced a small amount of the trimethyl phosphite ligand. Furthermore, NMR studies showed no evidence for the formation of $Fe[P(OCH_3)_3]_4$-$(C_6H_5C_2C_6H_5)$. Thus the equilibrium constant for

$$Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5) + P(OCH_3)_3 \rightleftharpoons$$
$$Fe[P(OCH_3)_3]_4(C_6H_5C_2C_6H_5) \quad (8)$$
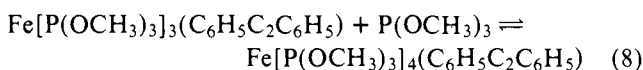
must be relatively small. The reaction product from the acetylene complex with 1 or more equiv of carbon monoxide was fast and invariant. Addition and displacement was the net sequence whereby the conventional five-coordinate $Fe[P(OCH_3)_3]_2(CO)_2(C_6H_5C_2C_6H_5)$ complex was produced. NMR (^1H and ^{31}P) equivalence of the phosphite ligands and of the phenyl ligands did not allow a definitive characterization of solution structure, but structure **3** is the most probable iso-
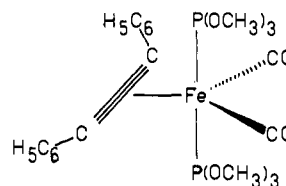
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meric representation because of the character of the ν_{CO} region in the infrared and the large P–P coupling observed in the

Table I. Results of 1-Hexene and 3-Hexyne Hydrogenation and Isomerization with $Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5)$ and H_2 in Pentane at 22 °C

| complex (wt, mg)	hydrocarbon (subst/cat. ratio)	time, days	products	(yield, %)
R = CH₃ (12)	1-hexene (600:1)	4	*n*-hexane	24
			1-hexene	70
			cis,trans-3-hexene	0.2
			trans-2-hexene	3
			cis-2-hexene	3
(25)	1-hexene (50:1)	4	*n*-hexane	49
			1-hexene	2
			cis,trans-3-hexene	5
			trans-2-hexene	25
			cis-2-hexene	18
(25)[a]	1-hexene (400:1)	5	1-hexene[f]	100
(25)	none	6	*b, c*	
(25)	1-hexene (50:1)	2 h[d]	*n*-hexane	10
			1-hexene	72
			cis,trans-3-hexene	3
			trans-2-hexene	4
			cis-2-hexene	11
(25)	1-hexene (300:1)[e]	3	*n*-hexane	18
			1-hexene	76
			cis,trans-3-hexene	trace
			trans-2-hexene	1
			cis-2-hexene	4
(25)[a]	1-hexene[e]	4	1-hexene	98
			3-hexenes +	
			trans-2-hexene	0.7
			cis-2-hexene	0.5
(25)	3-hexyne (50:1)	9[g]	*n*-hexane[f]	14
			1-hexene	2
			cis,trans-3-hexene	trace
			3-hexyne	84

a No H_2 present. *b* $C_6H_5C_2C_6H_5$ in residue identified by ¹H NMR spectrum. *c* $C_6H_5C_2C_6H_5$, $C_6H_5CH=CHC_6H_5$, and $C_6H_5CH_2CH_2C_6H_5$ identified by mass spectrum. *d* Stopped when color changed from purple to violet. *e* Hydrocarbon added after generation of orange species. *f* Residue contained $Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5)$. *g* Color became violet in 4 days; no further color change during 5 days.

proton resonance of the phosphite protons. Less conventional was the *tert*-butyl isocyanide reaction in which the only product was $Fe[P(OCH_3)_3]_2[CNC(CH_3)_3]_3(C_6H_5C_2C_6H_5)$ irrespective of the iron complex to isocyanide reactant ratio. The proposed structure of this product, based on NMR and IR data, is **4**. In the $^{31}P\{^1H\}$ NMR spectrum of the complex, there were two singlets that were invariant[50] over the temperature

4
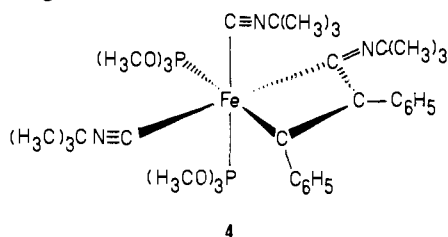
range of 20 to −85 °C, and in the ¹H NMR spectrum there were three $C(CH_3)_3$ proton resonances and two phosphite doublets; all these data are consistent with structure **4**. A single-crystal X-ray diffraction study of the complex has been initiated. One of the two phosphites can be displaced by an isocyanide at 40 °C to give a derivative of **4**.

Reduction and Catalytic Properties of $Fe[P(OCH_3)_3]_3$-$(C_6H_5C_2C_6H_5)$. Hydrogen reacted with solutions of the purple $Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5)$ complex in pentane or benzene to give an orange solution. Phosphorus and proton NMR data defined the principal reaction product as the fluxional tetrahydride $H_4Fe[P(OCH_3)_3]_3$. This is the first reported case of a tetrahydride complex of the iron group with phosphite ligands, although similar iron tetrahydrides with phosphine ligands have been reported[51] and analogous ruthenium[52] and osmium[53] tetrahydrides with aryl phosphine ligands are es-

tablished. Other minor iron reaction products included $H_2Fe[P(OCH_3)_3]_4$ (from thermal decomposition of the tetrahydride), a complex of unknown molecularity, {HFe[P-$(OCH_3)_3]_2$},[54] and an unidentified species which had a singlet hydride resonance at δ +19.45. The organic products consisted of unreduced acetylene as well as stilbene and bibenzyl. Hydrogenation in benzene produced small amounts of two iron–arene complexes, one of which was identified by NMR as $(\eta^6\text{-}C_6H_6)Fe[P(OCH_3)_3]_2$. There was no evidence for hydrogenation of the benzene solvent in these reactions.

The hydrogenation of $Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5)$ was inhibited by the presence of excess diphenylacetylene. With 3-hexyne, a small amount of 3-hexyne was hydrogenated and both the 3-hexyne and diphenylacetylene iron complexes, $Fe[P(OCH_3)_3]_3RC_2R$, were recovered. When the hydrogenation reaction was effected in a 2-butyne solution, the principal organometallic product was the 2-butyne iron complex, with no evidence of hydride formation. Hydrogenated diphenylacetylene products (stilbene and bibenzyl) were also detected.

The hydrogenation and isomerization of 1-hexene was catalyzed by $Fe[P(OCH_3)_3]_3(C_6H_5C_2C_6H_5)$ (as a catalyst precursor). Results of catalytic reactions are shown in Table I. At a ratio of 50 hexene per iron complex, hexane, 2-hexenes, and 3-hexenes were produced in 25, 6, and 0.2% conversions, respectively, in a 4-day period. At a lower reactant to catalyst ratio, the predominant products were hexane (49%) and 2-hexenes (43%). The tetrahydride, $H_4Fe[P(OCH_3)_3]_3$, demonstrated to be a major product in the hydrogen–Fe[P-$(OR)_3]_3(C_6H_5C_2C_6H_5)$ reaction, showed comparable catalytic activity to the acetylene complex and must be an important catalytic precursor. The key catalytic intermediate is probably

the coordinately unsaturated dihydride $H_2Fe[P(OCH_3)_3]_3$, which would be in equilibrium with the tetrahydride:

$$H_4Fe[P(OCH_3)_3]_3 \rightleftharpoons H_2 + H_2Fe[P(OCH_3)_3]_3 \quad (9)$$

The catalytic cycle probably involves a sequence of reactions, eqs 10–13, which is analogous to the mechanism proposed for

$$H_2Fe[P(OCH_3)_3]_3 + C_2H_4 \rightleftharpoons H_2Fe[P(OCH_3)_3]_3(C_2H_4) \quad (10)$$

$$H_2Fe[P(OCH_3)_3]_3(C_2H_4)$$
$$\rightarrow HFe[P(OCH_3)_3]_3(C_2H_5) \quad (11)$$

$$HFe[P(OCH_3)_3]_3(C_2H_5) + C_2H_4 \rightarrow C_2H_6$$
$$+ Fe[P(OCH_3)_3]_3(C_2H_4) \quad (12)$$

$$H_2 + Fe[P(OCH_3)_3]_3(C_2H_4)$$
$$\rightarrow H_2Fe[P(OCH_3)_3]_3(C_2H_4) \quad (13)$$

the hydrogenation of terminal olefins catalyzed by $H_4Ru[P(C_6H_5)_3]_3$ and $H_2(N_2)Ru[P(C_6H_5)_3]_3$.

Synthesis and Properties of "Fe[P(CH₃)₃]₄". Sodium amalgam reduction of the iron(II) chloride–trimethylphosphine complex in the presence of excess trimethylphosphine yielded a yellow solid that had low thermal stability at 20 °C while impure.[57] Purification was achieved by vacuum sublimation at 60 °C. The solid in the gas phase had the composition $Fe[P(CH_3)_3]_4$ as established by mass spectral analysis and a solution molecular weight (cryoscopic in benzene) of a monomer.[1b] The pure complex in a solution of trimethylphosphine was stable for 1 year in an evacuated sealed tube.

The ^1H NMR spectrum of $Fe[P(CH_3)_3]_4$ consisted of a high-field hydride multiplet that was a doublet of triplets of partially resolved doublets, a broad CH_2 resonance, and four doublet (PH coupling) CH_3 resonances of intensity 3, 3, 3, and 2, respectively; the $^{31}P\{^1H\}$ NMR spectrum consisted of four multiplet resonances of equal intensity. These spectral features and the molecular weight data are consistent with structure **5** but the difficulty in molecular weight determinations of

5

air-sensitive complexes raises justifiable questions regarding a formulation of the complex as a monomer. Significantly, an analogous ruthenium complex $\{HRuCH_2P(CH_3)CH_2\text{-}CH_2P(CH_3)_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]\}$ has a similar stereochemistry but it is a dimer in the solid state.[58] The structural issue will not be resolved until a single-crystal X-ray determination is completed.

The ^1H NMR spectrum of $\{HFeCH_2P(CH_3)_2[P(CH_3)_3]_3\}$ was invariant from low temperatures to 20 °C, above which irreversible decomposition occurred. An NMR study of the complex in the presence of trimethylphosphine suggested that an equilibrium

$$\{HFeCH_2P(CH_3)_2[P(CH_3)_3]_3\}$$
$$+ P(CH_3)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe[P(CH_3)_3]_5 \quad (14)$$

between the iron(II) complex and a five-coordinate iron(0) complex might be extant.[59] The ^{31}P spectrum of the iron(II) complex was invariant in this mixture from -20 to 20 °C and identical with that for the complex alone, but the trimethylphosphine resonance above -50 °C was broadened and slightly shifted from that for a solution of the phosphine. A slowly attained equilibrium

$$\{HFeCH_2P(CH_3)_2[P(CH_3)_3]_3\} \rightleftharpoons [(CH_3)_3P]_4Fe \quad (15)$$

between the iron(II) complex and a zerovalent, four-coordinate $Fe[P(CH_3)_3]_4$ complex would be one of the step sequences in eq 14. The four-coordinate complex should be paramagnetic (if tetrahedral) and could generate a line-broadening effect on the free $(CH_3)_3P$ resonance through the reaction

$$Fe[P(CH_3)_3]_4 + P(CH_3)_3 \rightleftharpoons Fe[P(CH_3)_3]_5 \quad (16)$$

An equilibrium like eq 15 could account for the facile hydrogen addition observed for solutions of the iron(II) complex to give the stable $H_2Fe[P(CH_3)_3]_4$ complex.[60]

Further evidence for the reversibility of the internal oxidative addition reaction was obtained from the facile reaction of $\{HFeCH_2P(CH_3)_2[P(CH_3)_3]_3\}$ with donor molecules like PF_3 whereby conventional zerovalent five-coordinate complexes, $Fe[P(CH_3)_3]_xL_{5-x}$, were formed. With PF_3, the stereochemically nonrigid $Fe[P(CH_3)_3]_3(PF_3)_2$ molecule was formed. At 20 °C, the $P(CH_3)_3$ and PF_3 ligands were equivalent on the NMR time scale, but at -93 °C the ^{31}P spectrum showed two phosphine resonances, a nonbinomial quintet and a triplet of doublets of respective relative intensities 1 and 2, and a quartet ($J_{PF} = 1234$ Hz) of multiplets for the PF_3 ligands. These data are consistent with either trigonal bipyramidal, **6**, or square pyramidal, **7**, geometric forms, and thus

6   **7**

are consistent with theoretical predictions that the stronger π-acceptor ligand in a d^8 complex will tend to go to equatorial (in **6**) or basal (in **7**) positions in the idealized polytopal forms. In the fully analogous $Fe[P(OCH_3)_3]_3(PF_3)_2$ molecule a similar stereochemistry should prevail; this phosphite complex was stereochemically nonrigid to -100 °C. The previously discussed $Fe[P(OCH_3)_3]_3(CO)_2$ complex should also have the CO ligands in the same position as PF_3 in **6** and **7** and the same applies to $Fe[P(CH_3)_3]_3(CO)_2$, which was stereochemically nonrigid to -85 °C and was obtained from the reaction of CO with $\{HFeCH_2P(CH_3)_2[P(CH_3)_3]_3\}$.

Reduction of $FeCl_2[P(CH_3)_3]_2$ in the Presence of Other Ligands. The reduction behavior of $FeCl_2[P(CH_3)_3]_2$ in the presence of trimethylphosphine and a second donor molecule differed from the phosphite reaction systems. Thus, sodium amalgam reduction of $FeCl_2[P(CH_3)_3]_2$ in the presence of butadiene and trimethylphosphine gave in high yield a complex with the composition $C_4H_6Fe[P(CH_3)_3]_3$. The ^1H NMR spectrum for C_4H_6 consisted of three separate resonances of relative intensities 2:2:2. This molecule was stereochemically nonrigid; the $^{31}P\{^1H\}$ resonance was a singlet at 85 °C and an AB_2 pattern at -40 °C. These spectral data are consistent with structure **8**, which is the established[61] geometry and stereo-

8   **9**

chemistry for $\eta^4\text{-}C_4H_6Fe(CO)_3$,[62] but are not consistent with the alternative iron(II) complex **9** unless there are accidental degeneracies in the NMR spectrum. Other analogous complexes are $C_4H_6Fe(PF_3)_3$,[62] which was stereochemically

nonrigid and yielded a slow exchange limiting AB_2 ^{31}P spectrum only at -100 °C, and $C_4H_6Ru(4$-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane)$_3$,[63] which gave an AB_2 ^{31}P pattern at -80 °C. By contrast to this phosphine reaction system, reduction of $FeCl_2[P(OCH_3)_3]_3$ in the presence of butadiene produced no butadiene complex; the major product was $Fe[P(OCH_3)_3]_5$ (see above).

The butadiene reaction product $C_4H_6Fe[P(CH_3)_3]_3$ was readily protonated by NH_4PF_6 to give a dark red, microcrystalline complex, $H(C_4H_6)Fe[P(CH_3)_3]_3^+PF_6^-$. The infrared spectrum had a band at 1570 cm^{-1} which was essentially absent in the deuterated complex and was thus ascribed to ν_{Fe-H}, although this absorption position was low compared to other Fe–H stretching frequencies.[64] Structurally definitive were the ^{1}H DNMR spectra. At ambient temperature, the phosphine methyl resonance was a quartet and an ostensible hydride resonance was a singlet at $\delta +6.53$ ppm. As the temperature was lowered, the methyl resonance broadened to a singlet and finally resolved into three singlets at -80 °C, while the hydride broadened and disappeared. At -120 °C, new resonances appeared at $\delta +2$ (intensity 2) and $+17.05$ (intensity 1). On the basis of these NMR data and on a report of similar spectral behavior first reported for an analogous complex, H(cyclooctadiene)Fe[P(OCH$_3$)$_3$]$_3^+$,[66,67] we propose that $H(C_4H_6)Fe[P(CH_3)_3]_3^+$ has structure **10** in which three carbon atoms of the butadiene comprise an η^3-allyl ligand and

10   11
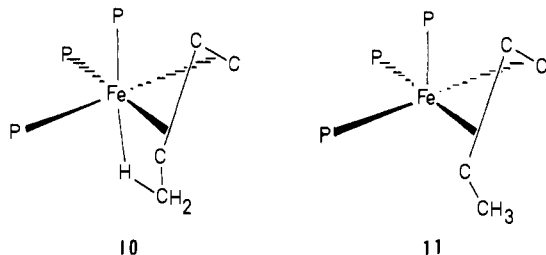
the fourth carbon does not substantially interact directly with the iron atom but is bound through an Fe–H–C bridging interaction. This structure is fully consistent with the low-temperature, ^{1}H NMR spectra. A plausible physical process that would account for the dynamic features of the NMR spectra is rotation of the unsymmetrically bound (at iron) methyl group—an η^3-methylallyl species **11** could be an intermediate in the exchange process whereby the bridging hydride and the terminal methylene protons are equilibrated. Deuteration of $C_4H_6Fe[P(CH_3)_3]_3$ with ND_4^+ followed by ceric ion oxidation gave C_4H_6 and C_4H_5D. This chemistry is fully consistent with this structural conclusion for $H(C_4H_6)Fe[P(CH_3)_3]_3^+$.

The observation of allylic butadiene bonding in H(cyclooctadiene)Fe[P(OCH$_3$)$_3$]$_3^+$ raises a justifiable question about the bonding of the butadiene group in electron-rich complexes like $(C_4H_6)Fe[P(CH_3)_3]_3$, although the η^4-diene formulation yields an 18-electron structure. A crystal structure of such a complex should be completed to resolve the bonding issue.

Sodium amalgam reduction of $FeCl_2[P(CH_3)_3]_2$ in the presence of trimethylphosphine and 2-butyne produced a volatile, thermally unstable, blue $Fe[P(CH_3)_3]_4(C_4H_6)_2$ compound whose ^{1}H NMR spectrum consisted of a complex $P(CH_3)_3$ multiplet and two CH_3 resonances (nonphosphine protons). The structure is given in **12**. Hexamethylbenzene was
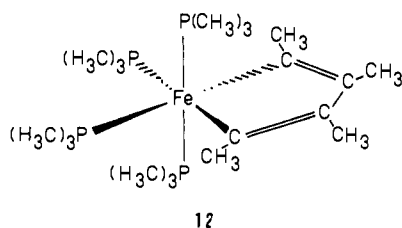
12

also produced in the synthesis reaction. The catalyst for the benzene formation was probably $HFeCH_2P(CH_3)_2$-$[P(CH_3)_3]_3$ since the pure complex catalyzed the polymerization of 2-butyne to trimer, tetramer, and pentamers.

$FeCl_2[P(CH_3)_3]_2$ reacted with acetonitrile to form an orange compound formulated as $Fe[P(CH_3)_3]_3(CH_3$-$CN)_3^{2+}FeCl_4^{2-}$. This orange compound on reduction with sodium amalgam in the presence of acetonitrile and trimethylphosphine yielded a volatile, dark green complex formulated as a square pyramidal, **13**, or trigonal bipyramidal, **14**, form

13   14
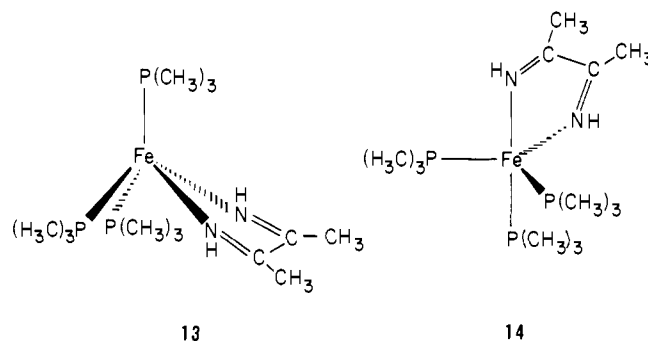
based on NMR and infrared data. This zerovalent iron complex had three ^{1}H NMR resonances with intensity ratios of 2:6:27 and an infrared stretching frequency at 1560 cm^{-1}. In similar compounds, the infrared band in this region has been assigned to $\nu_{C=N}$.[68] In the perdeuterio compound prepared from CD_3CN, this band was shifted to 1535 cm^{-1}; the isotopic shift was most likely due to the combination of an N–D stretching vibration with the $\nu(C=N)$ normal mode. Stereochemical nonrigidity in this molecule was maintained to -115 °C where the [31]P{[1]H} remained a singlet, a feature consistent with either **13** or **14**.

The very intense green color of this iron(0) heterocycle can be attributed to extensive π-electron delocalization in the heterocyclic ring. Several series of α-diamine complexes including $(RC=NR')_2Mo[P(C_6H_5)_3]_2(CO)_2$ have been prepared[69] and their intense blue to black colors have been attributed to π-electron delocalization.[70]

Comparisons. The chemistry of these zerovalent or low-valent iron complexes with phosphorus ligands has been shown to be demonstrably different from that of iron pentacarbonyl; furthermore, the chemistry of the phosphine and phosphite systems differs in significant, qualitative details.

The difference between the phosphite and phosphine iron systems might be attributed to steric factors since there are substantial differences in cone angles for trimethylphosphine and trimethyl phosphite. Thus the failure to isolate $Fe[P(CH_3)_3]_5$ could be laid to steric factors; this thesis is in a sense supported by the experimental success in the isolation of $Fe[P(OR)_3]_5$ with R the n-propyl group and the experimental failure with R the isopropyl group.[34] However, we attribute the major role to electronic factors. Prevailing internal C–H oxidative addition in "Fe[P(CH$_3$)$_3$]$_4$" over a fifth ligand addition in contrast to ligand addition in the phosphite system is consistent with the stronger σ and weaker π acceptor properties of the phosphine ligand. In fact, the tendency to generate iron(II) derivatives in the various syntheses is more pronounced in the phosphine system. Acetylenes yielded complexes **12** in the phosphine system whereas acetylenes gave the rather unusual and formally coordinately unsaturated $[(RO)_3P]_3$-Fe^0(acetylene) complexes in the phosphite system. Also the structure of diene–FeL$_3$ complexes may be a function of metal atom electron density (or donor–acceptor properties of L). In the carbonyl case, the diene is the conventional η^4-diene ligand whereas internal oxidative addition might occur for phosphines and phosphites so as to give a polydentate η^3-allyl and σ-CH$_2$ ligand–iron interaction (see compound ii in Abstract).

Experimental Section

Procedure, Reagents and Solvents. All operations, unless otherwise specified, were carried out in a drybox (Vacuum Atmospheres Dri Lab with a Model HE-493 Dri Train) or in a conventional vacuum system.

Solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Pentane, benzene, toluene, diethyl ether, and tetrahydrofuran were dried over sodium benzophenone ketyl; trialkyl phosphites over metallic sodium; acetonitrile by reflux over calcium hydride; methanol by reflux over sodium methoxide; dichloromethane by reflux over phosphorus pentoxide. Olefinic and acetylenic compounds (except diphenylacetylene) for synthetic and catalytic reactions were dried over calcium hydride, vacuum transferred, and purified by chromatography on a column of activated neutral alumina. Alumina for column chromatography (Woelm neutral, activity III) was used as received or was further deactivated by slurrying in a 1:4 (v/v) mixture of trimethyl phosphite and the appropriate solvent immediately prior to column preparation. Excess phosphite was then removed by solvent washing in the latter modification. Anhydrous $FeCl_2$ was obtained from Alfa Inorganics and stored in a drybox. *tert*-Butyl isocyanide was prepared by a literature method. Prepurified hydrogen (99.95%) was purchased from Matheson and Co. Other reagents were purchased from commercial sources in the highest available purity and used as received.

Physical Measurements. Solution ^1H NMR spectra were obtained at 60 MHz with a Varian Associates A-60A spectrometer and at 90 MHz with Varian Associates EM-390 or Bruker HX-90 (equipped with a Digilab Fourier accessory) spectrometers. Spectra were recorded at ambient spectrometer temperature unless otherwise noted and are referenced to internal tetramethylsilane. Samples were prepared with dried, deoxygenated solvents. Samples for studies of long duration or for low-temperature studies were sealed under vacuum.

Solution ^{31}P NMR spectra were measured at 36.43 MHz with a Bruker HX-90 spectrometer in the Fourier transform mode. Unless otherwise reported, phosphite spectra are referenced to external trimethyl phosphite and phosphine spectra to external trimethylphosphine.

Chemical shifts are reported in δ with the upfield direction being positive.

Infrared spectra (of Nujol mulls, unless otherwise indicated) were recorded with a Perkin-Elmer Model 137 or 337 spectrometer. Mass spectra were obtained with an AEI MS902/CIS-2 (source) mass spectrometer by electron impact ionization at 70 eV or by chemical ionization with methane at 500 eV. Gas chromatograph mass spectra were obtained with a Finnigan Model 3300 GC/MS with System Industries System 150 data system. Melting points of samples sealed under argon were measured with a Mel-Temp apparatus and are uncorrected. The C_4 and C_6 hydrocarbons from catalytic reactions were analyzed by gas chromatography as previously described.[4] Propene, allyl bromide, and hexadiene isomers were analyzed by gas chromatography on both OV-101 (3%, 12 ft × 1/8 in.) and dimethylsulfolane (15%, 12 ft × 1/8 in.) columns.

Elemental analyses were performed by Pascher Microanalytical Laboratory, Bonn, Germany, or Schwartzkopf Microanalytical Laboratory, Woodside, N.Y.

Fe[P(OCH₃)₃]₃Cl₂. Iron(II) chloride (3.23 g, 0.0254 mol) was refluxed for 1 h in a mixture of 100 mL of tetrahydrofuran and 50 mL of trimethyl phosphite. During this period the initially insoluble $FeCl_2$ reacted to form a large quantity of yellow solid, yield 98%. The product was purified by recrystallization from hot tetrahydrofuran containing trimethyl phosphite: mp gradual dec; ^1H NMR paramagnetic. Anal. Calcd for $C_9H_{27}Cl_2O_9P_3Fe$: C, 21.66; H, 5.45; Cl, 14.21; P, 18.62; Fe, 11.19. Found: C, 21.63; H, 5.43; Cl, 14.12; P, 18.32; Fe, 11.52. Similar products were obtained with FeI_2 and $P(OCH_3)_3$ and with $FeCl_2$ and $P(OCH_2CH_3)_3$.

Fe[P[OCH(CH₃)₂]₃]₂Cl₂. This compound was prepared from $FeCl_2$ and triisopropyl phosphite in a manner similar to the preparation of $Fe[P(OCH_3)_3]_3Cl_2$. The tetrahydrofuran solution containing the crude product was filtered and the solvent removed under vacuum by rotary evaporation. The product was a pale green compound which formed crystals from a cooled solution containing triisopropyl phosphite and a powder when evaporated to dryness, ^1H NMR (acetonitrile-d_3) paramagnetic. Anal. Calcd for $C_{18}H_{42}Cl_2O_6P_2Fe$: C, 39.80; H, 7.79; Cl, 13.05; P, 11.40; Fe, 10.28. Found: C, 39.26; H, 7.71; Cl, 13.10; P, 11.45; Fe, 10.40. A CD_3CN solution of the compound was

yellow, but turned distinctly orange when exposed to air.

Fe[P(CH₃)₃]₂Cl₂. Iron(II) chloride (5.0 g, 0.039 mol) was dissolved in a mixture of $P(CH_3)_3$ (6.0 g, 0.079 mol) and 100 mL of tetrahydrofuran by refluxing for 1 h. The solution was filtered to remove a small amount of red solid. Removal of the solvent under vacuum by rotary evaporation caused precipitation of pale green needles in three fractions. The middle fraction was collected on a frit, washed with pentane, and dried: mp 118–112 °C dec; ^1H NMR paramagnetic. Anal. Calcd for $C_6H_{18}Cl_2P_2Fe$: C, 25.84; H, 6.50; Cl, 25.42; P, 22.21; Fe, 20.02. Found: C, 24.48; H, 6.49; Cl, 25.79; P, 22.65; Fe, 20.95.

In a finely divided state the complex appeared colorless. Tetrahydrofuran and dichloromethane solutions of the compound reacted with air and dry O_2 to give bright red solutions. The complex did not cause isomerization or hydrogenation of 1-hexene in dichloromethane at 25 °C and 1 atm H_2 during a 2-week period.

Fe[P(OCH₃)₃]₅. A mixture of 25 mL (0.210 mol) of trimethyl phosphite, 20 g (0.040 mol) of $Fe[P(OCH_3)_3]_3Cl_2$, and 300 mL of diethyl ether was stirred with sodium amalgam (1.84 g, 0.08 mol of Na; 25 mL of amalgam). The initially insoluble $Fe[P(OCH_3)_3]_3Cl_2$ dissolved slowly to give a blue-green solution. After 7 days, the reaction mixture was filtered to remove insoluble material and amalgam. The solvent was removed under vacuum by rotary evaporation and the residue extracted with pentane. The pentane extract was concentrated and eluted with pentane through a chromatographic column (5 × 35 cm) of activity 1 alumina deactivated with pure trimethyl phosphite. The yellow band was collected and the solvent evaporated to give a yellow solid soluble in most organic solvents. The compound was air sensitive and sublimed at 80 °C to a −196 °C probe with some loss due to decomposition: mp >160 °C dec; ^1H NMR (acetonitrile-d_3) δ −3.52 (complex multiplet); $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C) δ −39.4 (A_2B_3 multiplet) (J_{P-P} = 145 Hz); mass spectrum found 676, 552 [Fe{P(OCH₃)₃}₄], 428 [Fe{P(OCH₃)₃}₃], 304 Fe[P(OCH₃)₃]₂ (calcd for $C_{15}H_{45}O_{15}P_5$ ^{56}Fe, 676). Anal. Calcd for $C_{15}H_{45}O_{15}P_5Fe$: C, 26.64; H, 6.70; P, 22.90; Fe, 8.26. Found: C, 26.85; H, 6.75; P, 22.88; Fe, 8.85.

HFe[P(OCH₃)₃]₅⁺PF₆⁻. Pentakis(trimethyl phosphite)iron(0) (1.00 g, 0.001 48 mol) was added to a solution of NH_4PF_6 (0.5 g, 0.003 07 mol) in 20 mL of tetrahydrofuran. The yellow color of $Fe[P(OCH_3)_3]_5$ disappeared, leaving a light yellow-brown solution. The solvent was removed under vacuum by rotary evaporation and the residue was extracted with dichloromethane in which NH_4PF_6 was insoluble. The solvent was evaporated and the residue recrystallized from hot tetrahydrofuran, giving colorless crystals: yield 1.02 g (84%); mp ~250 °C dec; ^1H NMR (chloroform-d) δ +12.4 (m, 1), −3.66 (m, 36), −3.75 (m, 9); $^{31}P\{^1H\}$ NMR (chloroform-d) δ −28.0 (AB_4 multiplet) ($J_{PP} \simeq$ 82 Hz). Anal. Calcd for $C_{15}H_{45}F_6O_{15}Fe$: C, 21.91; H, 5.64; P, 22.60; Fe, 6.79. Found: C, 21.78; H, 5.43; P, 23.25; Fe, 6.91.

The compound did not isomerize 1-hexene or react with ethylene at 5.3 atm after 24 h in $CDCl_3$ solution.

Fe[P(OCH₃)₃]₆²⁺B₁₂H₁₂²⁻. Anhydrous FeI_2 (3.1 g, 0.01 mol) was dissolved in 50 mL of methanol (anhydrous) containing 50 mL of $P(OCH_3)_3$. The dark blue-green solution was filtered to remove a small amount of red solid. To this solution was added $Li_2B_{12}H_{12} \cdot xH_2O$ (2.0 g, 0.013 mol). Within a few seconds, yellow crystals began to form. The solution was allowed to stand for 12 h during which time the blue-green color faded and a large amount of yellow crystals formed. These were collected on a frit and washed with methanol: yield 7.2 g (74%); ^1H NMR (acetonitrile-d_3) δ −3.82 (m); ^{31}P NMR (acetonitrile-d_3) δ −9.78 (s). Anal. Calcd for $C_{18}H_{54}B_{12}O_{18}P_6Fe$: C, 22.96; H, 7.07; P, 19.76; Fe, 5.92. Found: C, 22.79; H, 7.12; P, 19.54; Fe, 6.30.

The complex was air stable. Exchange between coordinated and uncoordinated $P(OCH_3)_3$ was not observed in the NMR spectrum at 40 °C. A similar compound was analogously obtained with $P(OCH_2CH_3)_3$ in ethanol.

Fe[P(OCH₃)₃]₅Cl⁺B(C₆H₅)₄⁻. Iron(II) chloride (2.52 g, 0.002 00 mol) was dissolved in 30 mL of methanol (commercial grade) and 35 mL of trimethyl phosphite contained in a three-necked round-bottom flask (N_2 atmosphere). The mixture was stirred for 10 min and then filtered through a Schlenk filter funnel. To the filtrate was added dropwise a solution of 0.684 g (0.020 mol) of $NaB(C_6H_5)_4$. A yellow precipitate slowly formed over the period of 1 h. The mixture was filtered and the yellow solid dried for 12 h under vacuum. The compound was a yellow, microcrystalline solid: mp 115 °C discolored, 169 °C dec; ^1H NMR (acetone-d_6) δ −3.49 (s), −3.60 (s), −3.71 (s), −3.88 (m), −6.92 (m), −7.37 (m); $^{31}P\{^1H\}$ NMR (acetone-d_6, −80

°C) δ −15.2 (AB$_4$ multiplet) (J_{P-P} = 120 Hz). Anal. Calcd for $C_{39}H_{65}BClO_{15}P_5Fe$: C, 45.44; H, 6.36; Cl, 3.44; P, 15.02; Fe, 5.42. Found: C, 45.25; H, 6.36; Cl, 4.08; P, 14.57; Fe, 5.54.

$Fe[P(OCH_2CH_3)_3]_5{}^+B(C_6H_5)_4{}^-$. Anhydrous FeI_2 (3.11 g, 0.0100 mol) was dissolved in 50 mL of ethanol and 50 mL of triethyl phosphite. After the solution was filtered to remove a red solid, $NaB(C_6H_5)_4$ (6.8 g, 0.020 mol) was added. Over the period of 1 h, a precipitate formed. This was collected and washed with ethanol to yield 10.8 g (81.0%) of a golden, microcrystalline solid: ^{1}H NMR (chloroform-*d*) δ 1.28 (t, 44), −4.03 (m, 30), −7.9 (m, 26); ^{31}P{^{1}H} NMR (acetone-*d$_6$*, −80 °C) δ −16.8 (AB$_4$ multiplet) (J = 120 Hz). Anal. Calcd for $C_{54}H_{95}BIO_{15}P_5Fe$: C, 48.66; H, 7.18; P, 11.62; Fe, 4.19. Found: C, 48.81; H, 7.24; P, 11.55; Fe, 4.38.

$CH_3Fe[P(OCH_3)_3]_5{}^+PF_6{}^-$. Pentakis(trimethyl phosphite)iron(0) (1.00 g, 0.001 48 mol) and methyl iodide (0.5 mL, 0.0080 mol) were dissolved in 25 mL of dichloromethane. The solution was allowed to stand at 25 °C for 10 h. Removal of the solvent under vacuum by rotary evaporation gave a residue which was washed with diethyl ether. To this solid was added NH_4PF_6 (1.00 g, 0.001 63 mol) slurried in 50 mL of tetrahydrofuran. Evaporation of the solvent gave a solid which was extracted with dichloromethane. Insoluble NH_4PF_6 and NH_4I were removed by filtration. Evaporation of the dichloromethane solution gave a solid which was recrystallized from hot tetrahydrofuran as colorless crystals: yield 0.97 g (78%); ^{1}H NMR (chloroform-*d*) δ 0.15 (m, 3) and −3.72 (m, 45); ^{31}P{^{1}H} NMR (chloroform-*d*, −40 °C) δ −22.3 (AB$_4$ multiplet) ($J_{P-P} \simeq$ 64 Hz). Anal. Calcd for $C_{16}H_{48}F_6O_{15}P_6Fe$: C, 22.98; H, 5.79; P, 22.22; Fe, 6.67. Found: C, 23.56; H, 5.91; P, 22.40; Fe, 6.87.

^{31}P NMR Spectra Simulations. First- and second-order ^{31}P NMR spectra of $XFe[P(OCH_3)_3]_5{}^+$, X = H, CH_3, Cl, and $IFe[P(OC_2H_5)_3]_5{}^+$ were simulated on the Cornell University IBM 370 computer with the program PZNMRX provided by Dr. P. Meakin. The calculated spectra were compared by direct overlap to experimental spectra.

Reaction of $Fe[P(OCH_3)_3]_5$ with CH_3CH_2I. Ethyl iodide (2 mL, 0.025 mol) was condensed into a solution of $Fe[P(OCH_3)_3]_5$ (2.00 g, 0.002 95 mol) in 10 mL of dichloromethane. The mixture was allowed to stand in a sealed tube for 2 days. Volatile materials were separated by trap to trap distillation. Dichloromethane and unreacted ethyl iodide were condensed in a −112 °C trap. Ethylene (56% based on $Fe[P(OCH_3)_3]_5$) passed through the −112 °C trap and was identified by comparison of its IR spectrum to that of an authentic sample. The solid residue was recrystallized from hot tetrahydrofuran and identified as $HFe[P(OCH_3)_3]_5{}^+I^-$ by its ^{1}H NMR spectrum.

Reaction of a 1:1 mixture of ethyl iodide and $Fe[P(OCH_3)_3]_5$ in CD_3CN in a sealed NMR tube was monitored by ^{1}H NMR at 20 °C. Initially, the spectrum consisted of a mixture of resonances of ethyl iodide and the iron(0) complex. After several hours, a broad triplet at δ −1.14 and a multiplet at δ +0.26 appeared and began to increase in intensity. These two resonances were assigned to an ethyl group coordinated to the iron atom in $C_2H_5Fe[P(OCH_3)_3]_5{}^+$. Both resonances were shifted upfield from the corresponding resonances in ethyl iodide. The position of methylene resonance at δ 0.26 was consistent with the methyl resonance at δ 0.15 in the corresponding methyl cation. The methoxy resonance was a mixture of several species. The highest concentration of the ethyl complex was reached after 5 h. At long reaction time, ethylene and $HFe[P(OCH_3)_3]_5{}^+$ were observed in the NMR spectrum. After 13 days, over 80% of the ethyl iodide had reacted and the main species present were the ethyl and hydride cations.

Reaction of $Fe[P(OCH_3)_3]_5$ with Allyl Iodide and Allyl Bromide. Solutions of $Fe[P(OCH_3)_3]_5$ with allyl iodide in tetrahydrofuran consistently turned emerald green after a few minutes. After standing overnight, they were worked up by metathesis with NH_4PF_6. The major product, identified by NMR, was $Fe[P(OCH_3)_3]_6{}^{2+}(PF_6{}^-)_2$. The same emerald green color could be obtained by reacting $Fe[P(OCH_3)_3]_5$ with I_2. In a few cases, a small amount of (η^3-C_3H_5)-$Fe[P(OCH_3)_3]_4{}^+PF_6{}^-$ was isolated.

An equimolar mixture of $Fe[P(OCH_3)_3]_5$ and allyl bromide in tetrahydrofuran was allowed to react overnight. After 24 h, the initially yellow solution was greenish. The volatile materials were removed on the vacuum line and analyzed by gas chromatography. Allyl bromide and 1,5-hexadiene, but no propene, were found.

Reaction of $Fe[P(OCH_3)_3]_5$ with Benzyl Iodide. A solution of $Fe[P(OCH_3)_3]_5$ (1.00 g, 0.001 48 mol) and benzyl iodide (0.19 mL, 0.0015 mol) in 10 mL of dichloromethane was allowed to stand at 25

°C for 1 h. The initial yellow color characteristic of $Fe[P(OCH_3)_3]_5$ changed to green. The solvent was removed under vacuum by rotary evaporation. Pentane-soluble material was identified as $C_6H_5CH_2CH_2C_6H_5$ by the mass spectrum and by comparison of its ^{1}H NMR spectrum to that of an authentic sample. The yellow-green, pentane-insoluble material was identified as $Fe[P(OCH_3)_3]_3I_2$ by its ^{1}H NMR spectrum in acetonitrile-*d$_3$*.

$Fe[P(OCH_3)_3]_3(CO)_2$. A solution of $Fe[P(OCH_3)_3]_5$ (1.00 g, 0.001 48 mol) in 5 mL of methanol was placed in an 80-mL vacuum line reaction tube. Carbon monoxide was condensed into the tube (~700 Torr at −196 °C). The flask and contents were warmed to room temperature and the solution was stirred for 24 h. The solvent and excess CO were removed under vacuum. The residue was dissolved in 50 mL of pentane. After filtration, the solution was concentrated under vacuum by rotary evaporation. Colorless crystals deposited from the cold solution: yield 0.41 g (57%); ^{1}H NMR (benzene-*d$_6$*) δ −3.77 (d) (J_{P-H} = 11 Hz); ^{31}P NMR (acetonitrile-*d$_3$*, −35 °C) δ −48.6 (s); IR ν(CO) 1940, 1875 cm^{-1}.[71] Anal. Calcd for $C_{11}H_{27}O_{11}P_3Fe$: C, 27.29; H, 5.62; Fe, 11.54. Found: C, 27.48; H, 5.46; Fe, 11.75.

A similar reaction in diethyl ether gave an oil showing three carbonyl stretching bands in the infrared spectrum at 1990, 1940, and 1875 cm^{-1}. Partial removal of $Fe[P(OCH_3)_3]_3(CO)_2$ by fractional crystallization caused an increase in the relative intensity of the band at 1990 cm^{-1}. The compound responsible for the band at 1990 cm^{-1} was probably $Fe[P(OCH_3)_3]_4(CO)$ since the intensity of this band relative to those due to the dicarbonyl decreased with increasing reaction time.

A benzene solution of $Fe[P(OCH_3)_3]_5$ did not react with CO during a 12-h period.

$Fe[P(OCH_3)_3]_3(PF_3)_2$. Pentakis(trimethyl phosphite)iron(0) (1.00 g, 0.001 48 mol) was dissolved in 10 mL of dichloromethane in a vacuum line reaction tube. Phosphorus trifluoride (0.0061 mol) (passed through a −131 °C trap) was condensed into the tube. The solution was stirred for 2 days at 25 °C and then the volatile materials were removed on the vacuum line. The residue was extracted with pentane and the volume of the pentane solution reduced to 20 mL. Cooling to −45 °C caused the formation of colorless crystals which were collected on a precooled frit: yield 0.67 g (75%); ^{1}H NMR spectrum δ −3.59 (m); ^{31}P{^{1}H} NMR (toluene-*d$_8$*, 27 °C) PF$_3$ (quartet of quartets) (J_{PF} = 1213, J_{PP} = 62 Hz), $P(OCH_3)_3$ (t) (J_{PP} = 62 Hz). Anal. Calcd for $C_9H_{27}F_6O_9P_5Fe$: C, 17.90; H, 4.51; P, 25.64; Fe, 9.25. Found: C, 18.30; H, 4.52; P, 26.04; Fe, 9.43.

Attempted Reaction of $Fe[P(OCH_3)_3]_5$ and Diphenylacetylene. Pentakis(trimethyl phosphite)iron(0) (0.50 g, 0.000 74 mol) and diphenylacetylene (0.13 g, 0.000 74 mol) were dissolved in 20 mL of toluene and heated to 75 °C for 4 h. No obvious color change occurred. The residue from the reaction mixture was eluted through a column of SX-2 Bio-Beads with toluene, which separated diphenylacetylene from $Fe[P(OCH_3)_3]_5$. Pentakis(trimethyl phosphite)iron(0) was recovered and identified by its ^{1}H NMR spectrum.

Reduction of $Fe[P(OCH_3)_3]_3Cl_2$ in the Presence of 1,3-Butadiene. Dichlorotris(trimethyl phosphite)iron(II) was reduced with sodium amalgam in the presence of a twofold excess of 1,3-butadiene in acetonitrile. No $P(OCH_3)_3$ was added. After 18 h, the reaction mixture was yellow. Workup as described for $Fe[P(OCH_3)_3]_5$ gave a yellow solid which was eluted with pentane through a trimethyl phosphite deactivated alumina column. The yellow product was identified as $Fe[P(OCH_3)_3]_5$ by mass spectroscopy. Similar results were obtained when $P(OCH_3)_3$ was added to the reaction mixture.

Hydrogenation of $Fe[P(OCH_3)_3]_5$ and Attempted Dehydrogenation of $H_2Fe[P(OCH_3)_3]_4$. Solutions of $Fe[P(OCH_3)_3]_5$ in benzene, tetrahydrofuran, and methanol were placed in tubes, charged with ~2 atm of hydrogen, and sealed. After 3–4 weeks, the product of hydrogenation in methanol consisted of ~30% $H_2Fe[P(OCH_3)_3]_4$ and a complex, unidentified hydride species. Reaction in tetrahydrofuran gave $H_2Fe[P(OCH_3)_3]_4$ as the only hydride product. Qualitative observations of color change (the hydride was colorless) indicated that reaction in methanol was faster than reaction in either of the two nonprotic solvents. Conversely, heating $H_2Fe[P(OCH_3)_3]_4$ at reflux in toluene with excess trimethyl phosphite in a closed system on a vacuum line gave no evidence for reductive elimination of H_2 and formation of $Fe[P(OCH_3)_3]_5$.

Ligand Exchange Experiments. To determine whether ligand exchange occurred in $Fe[P(OCH_3)_3]_5$ and $HFe[P(OCH_3)_3]_5{}^+$, mixtures of these complexes with trimethyl and triethyl phosphite in sealed NMR tubes were monitored by ^{1}H NMR over a course of several

weeks.

Hydrolysis of Fe[P(OCH₃)₃]₅ and HFe[P(OCH₃)₃]₅⁺. The reactions of Fe[P(OCH₃)₃]₅ with 1 and 3 equiv of H₂O in CD₃CN in sealed NMR tubes were studied by ¹H and ³¹P NMR. ³¹P NMR showed that a large number of species were formed. In contrast, HFe[P(OCH₃)₃]₅⁺ in CD₃CN did not react with 1, 3, and 20 equiv of H₂O over several days.

Beer's Law Plots. Solutions of Fe[P(OCH₃)₃]₅ in pentane and methanol over a concentration range of 1×10^{-3} to 1×10^{-5} M were prepared by serial dilution in a drybox. Sample and solvent blanks were placed in Teflon-capped quartz cells with path lengths varying from 0.1 to 5 cm. Solutions of the iron(0) complex in these cells did not decompose noticeably over at least 1 h. Spectra were recorded from 350 to 200 nm with a Cary 14 recording spectrophotometer. The instrument was zeroed at 350 nm before beginning each scan to eliminate cell and instrument error. Absorbance was monitored at 267.5 nm (ϵ 7 × 10³ L mol⁻¹ cm⁻¹). Plots of absorbance (corrected to a path length of 1 cm) against concentration for the solutions in pentane and methanol are given in Figure 1.

Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅). Dichlorotris(trimethyl phosphite)-iron(II) (40.5 g, 0.0810 mol) was slurried in a mixture of 200 mL of diethyl ether and diphenylacetylene (14.4 g, 0.0810 mol). Sodium amalgam (7.373 g, 0.162 mol, 75 mL) was added and the reaction mixture was stirred for 2 days at 25 °C. The insoluble Fe[P(OCH₃)₃]₃Cl₂ slowly reacted to give a greenish color within 1 h which was replaced by a brownish purple color at the end of 1 day. The reaction mixture was filtered (slowly, as frits easily clogged) to remove insoluble material and then the solvent was removed under vacuum by rotary evaporation. The residue was extracted with pentane, and the pentane solution filtered and evaporated to a purple oil. The purple compound was separated from unreacted diphenylacetylene and a yellow compound by eluting four times through a column of alumina (trimethyl phosphite deactivated alumina may also be used) with toluene. Colorless diphenylacetylene eluted off the column at the same time as a faint yellow band. A second, more intense yellow band separated from the purple band. When the yellow and purple bands were well separated, the column was eluted with a 4:1 (v/v) mixture of toluene and tetrahydrofuran or diethyl ether. A concentrated pentane solution of the purple compound was cooled to −40 °C overnight, yielding 1.80 g (3.66%) of single and twinned monoclinic deep purple crystals: mp 56–57 °C; ¹H NMR (acetone-d_6) δ −3.38 (m, 27), −7.22 (m, 6), −7.63 (m, 4); ³¹P{¹H} NMR (acetone-d_6, 40 °C) δ −55 (s). Anal. Calcd for C₂₃H₃₇O₉P₃Fe: C, 45.56; H, 6.15; P, 15.33; Fe, 9.21. Found: C, 45.90; H, 6.27; P, 15.45; Fe, 9.10.

Fe[P(OCH₃)₃]₃(C₆H₅C₂CH₃). Dichlorotris(trimethyl phosphite)-iron(II) (5.0 g, 0.010 mol) was slurried in 100 mL of diethyl ether containing 2.5 mL (0.020 mol) of phenylmethylacetylene. Sodium amalgam (0.62 g, 0.027 mmol, 20 mL) was added and the reaction mixture stirred at 25 °C for 2 days. The reaction mixture was filtered and the filtrate evaporated to dryness. The residue was extracted with pentane and the solution filtered. The pentane solvent was then evaporated. The crude product was purified by eluting through a column of trimethyl phosphite deactivated alumina with toluene five times. This gave a purple oil which could not be crystallized: ¹H NMR (acetone-d_6) δ −2.91 (q, 3.1) (J = 1.0 Hz), −3.53 (m, 27.1), −7.24 (m, 3.8), −7.71 (m, 2.0); mass spectrum 544 (calcd for C₁₇H₃₅O₉P₃⁵⁶Fe, 544), 428 (Fe[P(OCH₃)₃]₃), 420 (Fe[P(OCH₃)₃]₂(CH₃C₂C₆H₅)), 302 (Fe[P(OCH₃)₃]₂), 296 (Fe[P(OCH₃)₃](CH₃C₂C₆H₅)), 180 (Fe[P(OCH₃)₃]), 172 Fe(CH₃C₂C₆H₅); higher mass fragments at 569, 568, and 564 of low intensity were also observed.

Fe[P(OCH₃)₃]₃(CH₃CH₂C₂CH₂CH₃). Dichlorotris(trimethyl phosphite)iron(II) (5.0 g, 0.010 mol) was slurried in a mixture of diethyl ether (100 mL, 0.010 mol). Sodium amalgam (0.75 g, 0.033 mol, 40 mL) was added and the reaction mixture stirred for 2 days. The reaction mixture was filtered and evaporated to dryness. The residue was eluted twice through trimethyl phosphite deactivated alumina with toluene to remove a yellow impurity, giving a purple, waxy solid which could not be crystallized: ¹H NMR (benzene-d_6) δ −1.35 (t) (J_{H-H} = 7.4 Hz), −3.31 (q, partially obscured by resonance at −3.45 (J_{H-H} = 7.6 Hz), −3.45 (m); ³¹P{¹H} NMR (acetone-d_6, −80 °C) δ −59.4 (s); mass spectrum 510 (calcd for C₁₅H₃₇O₉P₃⁵⁶Fe, 510), 428 (Fe[P(OCH₃)₃]₃), 386 (Fe[P(OCH₃)₃]₂(C₂H₅C₂C₂H₅)), 304 (Fe[P(OCH₃)₃]₂), 262 (Fe[P(OCH₃)₃](C₂H₅C₂C₂H₅)), 180 (Fe[P(OCH₃)₃]); fragments at 552 and 566 were also observed (552 can be assigned to Fe[P(OCH₃)₃]₄). Anal. Calcd for C₁₅H₃₇O₉P₃Fe:

C, 35.37; H, 7.31; P, 18.21; Fe, 10.95. Found: C, 35.90; H, 7.47; P, 17.95; Fe, 10.72.

Fe[P(OCH₃)₃]₃(CH₃C₂CH₃). This compound was prepared by reduction of Fe[P(OCH₃)₃]₃Cl₂ in the presence of 2-butyne in the same manner as the other acetylene complexes. Chromatography of the product of this preparation through trimethyl phosphite deactivated activity III alumina gave a purple oil which was still contaminated by other species containing phosphite. Further chromatography could not remove this impurity. ¹H NMR showed, however, the characteristic methoxy multiplet and a resonance due to the methyl group of the coordinated acetylene group. Mass spectrum: 482 (calcd for C₁₃H₃₃O₉P₃⁵⁶Fe, 482), 428 (Fe[P(OCH₃)₃]₃), 358 (Fe[P(OCH₃)₃]₂(CH₃C₂CH₃)), 304 (Fe[P(OCH₃)₃]₂), 234 (Fe[P(OCH₃)₃](CH₃C₂CH₃)), 180 (Fe[P(OCH₃)₃]).

The compound was prepared in essentially pure form by hydrogenation of Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) in 2-butyne. No color change occurred during 2 weeks. The volatile liquids were removed on a vacuum line and analyzed by gas chromatography. Purple and white solids were sublimed at 50 °C from the solid purple residue to a cold finger cooled to −196 °C. An NMR spectrum showed resonances due to diphenylacetylene, stilbene, bibenzyl, and Fe[P(OCH₃)₃]₃(CH₃C₂CH₃): ¹H NMR (acetone-d_6) δ −3.37 (m, 27), −2.57 (quartet, 6) (J = 0.9 Hz). Traces of butane and butene (<1%) were formed by hydrogenation of 2-butyne. The sublimation residue contained primarily the 2-butyne complex. Diphenylacetylene, bibenzyl, and a trace of hexamethylbenzene were also observed.

Fe[P(OCH₂CH₃)₃]₃(C₆H₅C₂C₆H₅). Dichlorotris(triethyl phosphite)iron(II) was prepared from 4.66 g (0.037 mol) of anhydrous FeCl₂ and the appropriate amount of triethyl phosphite as described for Fe[P(OCH₃)₃]₃Cl₂. The crude product was taken into a drybox and slurried in a mixture of 300 mL of diethyl ether, 6 mL (0.034 mol) of triethyl phosphite, and 6.9 g (0.037 mol) of diphenylacetylene. Sodium amalgam (1.8 g, 0.078 mol, 50 mL) was added and the reaction mixture was stirred for 10 days. The reaction mixture was decanted from the amalgam and filtered. Removal of solvent from the filtrate under vacuum gave a residue which was eluted twice through a column of trimethyl phosphite deactivated alumina with toluene. The purple compound was then eluted with toluene through a column of Bio-Beads (SX-2). The toluene was removed under vacuum and the resulting residue dissolved in acetonitrile. The acetonitrile solution was cooled at −45 °C for 12 h, giving a purple solid: yield 0.244 g (0.90%); mp 27–31 °C; ¹H NMR (acetone-d_6) δ −1.10 (t, 27), −3.77 (m, 18), −7.21 (m, 6.9), −7.63 (m, 3.9). Anal. Calcd for C₃₂H₅₅O₉P₃Fe: C, 52.47; H, 7.57; P, 12.68; Fe, 7.62. Found: C, 52.36; H, 7.56; P, 12.65; Fe, 7.59.

Fe[P{OCH(CH₃)₂}₃]₃(C₆H₅C₂C₆H₅). A mixture of 7.45 g (0.0137 mol) of Fe[P{OCH(CH₃)₂}₃]₂Cl₂ and 4.89 g (0.0275 mol) of diphenylacetylene was dissolved in a mixture of 200 mL of diethyl ether and 50 mL of tetrahydrofuran. Following addition of triisopropyl phosphite (2.96 mL, 0.0138 mol) and sodium amalgam (0.632 g, 0.0274 mol, 50 mL), the mixture was stirred in a closed system. After 5 min, the initially light green solution became dark green, and after 1 h it appeared purplish. The reaction mixture was filtered after stirring for 1 day and the filtrate was evaporated to dryness. The residue was eluted with pentane through a column of activity I alumina. A purple band separated from dark material on the column was collected. The fraction contained a considerable amount of diphenylacetylene. After removal of solvent under vacuum, a considerable portion of the acetylene was removed by sublimation at 50 °C to a liquid nitrogen cooled cold finger. The blue residue was dissolved in pentane and cooled to −40 °C overnight. A small amount of orange residue precipitated and was discarded. The pentane was removed under vacuum leaving a blue residue still contaminated with diphenylacetylene: ¹H NMR (acetone-d_6) δ −7.5 (complex multiplet), −4.78 (complex 14-line multiplet, 1), −1.18 (d, 6). The identity of the compound was inferred from the color and from the downfield shift (0.45 ppm) of the isopropyl proton resonance. The isopropyl proton resonance in the compound was more complex than that in the free ligand.

Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅)₂. The second yellow band from chromatography of crude Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) was collected from several preparations to give a small amount of a yellow powder. This yellow material was chromatographed several times to remove the last traces of diphenylacetylene. Further purification was achieved by crystallization twice from toluene–pentane mixtures at −40 °C: ¹H NMR (benzene-d_6) δ −3.32 (m), −7.05 (m), −7.77 (m). Anal. Calcd for C₃₇H₄₇O₉P₃Fe: C, 56.65; H, 6.04; P, 11.84; Fe, 7.12.

Found: C, 56.60; H, 6.11; P, 11.17; Fe, 6.90.

The methoxy multiplet was identical with that found in Fe[P-(OCH₃)₃]₃(C₆H₅C₂C₆H₅). An integration of aromatic and methoxy protons could not be obtained owing to overlapping resonances from the solvent. The complex was not very soluble in nonaromatic solvents.

Fe[P(OCH₃)₃]₂(CO)₂(C₆H₅C₂C₆H₅). A 40-mL vacuum line reaction tube containing Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) (0.25 g, 0.000 412 mol) in 10 mL of tetrahydrofuran was charged with an excess of CO at −196 °C. The tube was warmed to room temperature and an instantaneous color change to bright yellow occurred with shaking. The solvent was evaporated to a mixture of yellow and orange solids in an oil. The addition of pentane to the residue resulted in the formation of a yellow, microcrystalline precipitate: yield 0.13 g (58%); mp darkened 95 °C, softened 109.5, 118.5–121 °C dec; ¹H NMR (acetone-d_6, chemical shifts based on solvent resonance) δ −3.36 (t, 19.1) (J = 5 Hz), −7.30 (m, 7.4), −7.88 (m, 4.0); ³¹P{¹H} NMR (acetone-d_6, −85 °C) δ −0.7 ppm (s); IR (tetrahydrofuran solution) ν (C≡O) 1955 s, 1890 s, 1830 m cm⁻¹. Anal. Calcd for C₂₂H₂₈O₈P₂Fe: C, 49.09; H, 5.24; P, 11.51; Fe, 10.38. Found: C, 49.65; H, 5.33; P, 11.80; Fe, 10.45.

Fe[P(OCH₃)₃]₂[(CH₃)₃CNC]₃(C₆H₅C₂C₆H₅). To a solution of 0.50 g of Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) (0.000 82 mol) in 10 mL of tetrahydrofuran was added an excess of 3 equiv of *tert*-butyl isocyanide. With agitation there was a very rapid color change from dark purple to bright yellow. The solvent was removed under vacuum to yield a mixture of orange and yellow oils. The oils were dissolved in toluene and concentrated to a very small volume. Pentane was added to the concentrated solution until cloudiness occurred. Upon standing overnight, a yellow, crystalline solid separated from the mixture. The solvent was decanted and the crystals were dried under vacuum. More crystalline, yellow solid was obtained from successive crystallizations: yield 0.26 g (43%); mp 129 °C, slight darkening, 134 °C, crystals became powder, 217–221 °C dec; ¹H NMR (acetone-d_6) δ −0.76 (s, 9), −1.23 (s, 9), −1.66 (s, 9), −3.13 (d, 9) (J = 11 Hz), −3.79 (d, 9) (J = 11 Hz), −7.16 (m, 10); ³¹P{¹H} NMR (acetone-d_6, −85 °C) δ −32.0 (s), −44.9 (s); IR (tetrahydrofuran solution) ν(C≡N) 2110, 2070, 1700, 1670 sh cm⁻¹. Anal. Calcd for C₃₅H₅₅N₃O₆P₂Fe: C, 57.46; H, 7.58; N, 5.74; P, 8.47; Fe, 7.63. Found: C, 57.82; H, 7.68; N, 5.83; P, 8.63; Fe, 7.58.

Fe[P(OCH₃)₃][(CH₃)₃CNC]₄[C₆H₅C₆H₅]. A titration of Fe[P-(OCH₃)₃]₃C₆H₅C₂C₆H₅ in acetone-d_6 with a 1-equiv portion of (CH₃)₃CNC in an NMR tube was monitored by NMR. When 4 equiv was added, yellow crystals precipitated from the solution while the sample was in the NMR probe at 35–40 °C. The solid was collected, washed with pentane, and dried. The yellow solid was purified by recrystallizing twice from cold pentane–toluene: ¹H NMR (benzene-d_6) δ −0.80 (s, 9), −1.13 (s, 9), −1.35 (s, 9), −1.71 (s, 9), −3.53 (d, 9) (J = 10.5 Hz), −7.08 (m, overlapped with solvent resonance); IR (tetrahydrofuran solution) ν(C≡N) 2130, 2070, 1700 cm⁻¹. Anal. Calcd for C₃₇H₅₅N₄O₃PFe: C, 64.34; H, 8.03; N, 8.11; P, 4.48; Fe, 8.09. Found: C, 63.60; H, 7.95; N, 8.19; P, 5.01; Fe, 8.18.

Reaction of Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) with Allyl Bromide. Allyl bromide (5 mL, 0.06 mol, purified by chromatography on activated alumina) was vacuum transferred into a tube containing 0.55 g (0.000 91 mol) of Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅). The resulting purple solution was heated in a 90 °C oil bath. After 6 min, the color changed from purple to dark orange. The unreacted allyl bromide was removed under vacuum. Elemental analysis and the infrared spectrum indicated that the orange residue contained Fe[P(OCH₃)₃]₃Br₂. This residue was dissolved in 10 mL of tetrahydrofuran and converted to Fe[P(OCH₃)₃]₅Br⁺PF₆⁻ by the addition of sodium hexafluorophosphate (0.155 g, 0.000 93 mol) and trimethyl phosphite (1 mL, 0.008 mol). The mixture was heated to ~60 °C for 20 min. After cooling, the reaction mixture was evaporated to dryness by rotary evaporation. The residue was extracted with dichloromethane and filtered. The addition of 2 mL of tetrahydrofuran precipitated a yellow solid. The solid was purified by recrystallization twice from a mixture of dichloromethane and tetrahydrofuran, giving a microcrystalline solid: yield 0.49 g (60%); ¹H NMR (acetone-d_6) δ −3.60 (m, 9), −3.86 (m, 35); IR ν(P–F) 845, 555 cm⁻¹. Anal. Calcd for C₁₅H₄₅BrF₆O₁₅P₆Fe: C, 19.91; H, 5.03; P, 20.62; Fe, 6.20. Found: C, 20.31; H, 5.03; P, 20.79; Fe, 6.21. When the reaction of Fe[P-(OCH₃)₃]₃(C₆H₅C₂C₆H₅) with allyl bromide was mediated by solvent, no reaction occurred, even at elevated temperature.

Ligand Exchange in Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅). Equimolar solutions of triisopropyl or trimethyl phosphite and the acetylene complex in acetone-d_6 were sealed in NMR tubes and monitored at room temperature by ¹H NMR.

Catalytic Hydrogenation and Isomerization of 1-Hexene with Fe[P(OR)₃]₃(RC₂R). In a typical experiment, 4.2 × 10⁻⁵ mol (25–30 mg) of Fe[P(OR₃)₃]₃(C₆H₅C₂C₆H₅) was dissolved in a mixture of the unsaturated hydrocarbon and 1 mL of pentane. The frozen solution was degassed and then hydrogen was admitted (~1 atm at −196 °C). After appropriate reaction time, hydrogen and volatile compounds were separated on a vacuum line and the C₆ hydrocarbons analyzed. In most reactions, the initial purple color of the acetylene complex was replaced by an orange color in ca. 3 h. Results are given in Table 1.

Reactions of Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) with Hydrogen. A solution of ca. 0.2 g of Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) in benzene was stirred in a reaction tube under ca. 2 atm of H₂ for 6 h when the purple color of the original complex turned dark orange. A solid, dark orange residue was recovered. From this residue white and yellow materials were sublimed at 50 °C to a −196 °C cold finger. The yellow solid was rapidly washed from the cold finger with pentane and the pentane removed under vacuum. A solution of the yellow material in acetone-d_6 was sealed in an NMR tube under vacuum for ¹H and ³¹P NMR studies. The sample was kept at liquid nitrogen temperature until a spectrum was recorded. The greenish orange residue left after sublimation was similarly sealed in an NMR tube and saved for NMR analysis. Analysis of the recovered solvent showed that no hydrogenation of benzene occurred.

A solution of the acetylene complex in pentane was hydrogenated. In this case, nothing but white acetylene hydrogenation products sublimed. The orange residue was dissolved in acetone-d_6, sealed in an NMR tube, and stored at liquid nitrogen temperatures.

The following species were identified by ¹H and ³¹P NMR. H₄Fe[P(OCH₃)₃]₃: ¹H NMR (benzene-d_6, hydride) δ +12.22 (quartet) ($J_{P–H}$ = 25.8 Hz); ³¹P{¹H} NMR (acetone-d_6, −70 °C) δ −57.6 (s); ³¹P {alkyl H} NMR (acetone-d_6, −70 °C) δ −57.6 (quintet) ($J_{P–H}$ = 25.2 Hz). H₂Fe[P(OCH₃)₃]₄: ¹H NMR (benzene-d_6, hydride) δ +14.33 (nonbinomial quintet); ³¹P{¹H} NMR (acetone-d_6, −70 °C) δ −51.7 (A₂B₂ multiplet). {HFe[P(OCH₃)₃]₂}$_x$: ¹H NMR (benzene-d_6) δ +22.6 (t) ($J_{P–H}$ = 89.1 Hz); ³¹P{¹H} NMR (acetone-d_6, −70 °C) δ −64.6 (s); ³¹P{alkyl H} NMR (acetone-d_6, −70 °C) δ −64.6 (d) ($J_{P–H}$ = 94.5 Hz). (η⁶-C₆H₆)Fe[P(OCH₃)₃]₂: ¹H NMR (benzene-d_6, arene) δ −4.73 (t) (J = 2.7 Hz); ³¹P{¹H} NMR (acetone-d_6, −70 °C) δ −45.6 (s); ³¹P{alkyl H} NMR (acetone-d_6, −70 °C) δ −45.6 (s). (η⁴-C₆H₆)Fe[P(OCH₃)₃]₃ (speculative assignment): ¹H NMR (benzene-d_6, arene) δ −4.72 (m, 4) and −4.40 (m, 2).

Attempted Hydrogenation of Benzene with H₄FeP(OCH₃)₃. The tetrahydride was prepared in situ at room temperature and at 70–75 °C by stirring solutions of Fe[P(OCH₃)₃]₃(C₆H₅C₂C₆H₅) in benzene with hydrogen at ca. 2 atm. The solutions were stirred for 11 days. At the end of this period, analysis by gas chromatography showed that no hydrogenation of benzene had occurred in either reaction. At room temperature H₄Fe[P(OCH₃)₃] decomposed to ca. 56% H₂Fe[P-(OCH₃)₃]₄ in an 11-day period. The arene complex (η⁶-C₆H₆)-Fe[P(OCH₃)₃]₂ and a trace of the complex tentatively identified as (η⁴-C₆H₆)Fe[P(OCH₃)₃]₃ were also formed. At 70–75 °C, H₄Fe[P(OCH₃)₃]₃ decomposed partly to a paramagnetic species. Despite line broadening in the NMR spectrum, it appears that a substantial amount of η⁶-arene complex may have been formed.

HFe[CH₂P(CH₃)₂][P(CH₃)₃]₃. Dichlorobis(trimethylphosphine)-iron(II) (1.00 g, 0.003 58 mol) was dissolved in 25 mL of tetrahydrofuran containing P(CH₃)₃ (1.6 g, 0.02 mol). To the light blue-green solution was added sodium amalgam (0.50 g, 0.022 mol, 25 mL). The mixture was stirred at 0 °C for 1 h and the solvent removed on the vacuum line. The flask was then taken into the drybox as rapidly as possible. The residue was extracted with pentane and the yellow solution filtered. Removal of solvent under vacuum by rotary evaporation gave a partially crystalline solid which solidified to a yellow-brown solid when stirred with a spatula. Pure yellow solid was obtained by sublimation at 25 °C (with some loss due to decomposition) to a −196 °C cold finger: ¹H NMR (toluene-d_8, −40 °C) δ +13.6 (dtd) (J = 70.2, 56.4, 26.5 Hz), 1.00 (broad), −1.07 (d) (J = 5.2 Hz), −1.23 (dd) (J = 5.8, 0.8 Hz), −1.30 (dd) (J = 6.5, 1.1 Hz), −1.47 (d) (10.2 Hz); ³¹P{¹H} NMR (toluene-d_8, −70 °C) δ −45.1 (quartet) (J_{av} = 38.2 Hz), −86.6 (quartet) (J_{av} = 33.9 Hz), −93.2 (t) (J_{av} = 35.2 Hz), −100.6 (t) (J_{av} = 33.9 Hz); IR ν(Fe–H) 1820 cm⁻¹; mass spectrum (chemical ionization), 361 (calcd for C₁₂H₃₆P₄⁵⁶Fe + 1, 361).

Fe[P(CH₃)₃]₃(CO)₂. Iron(II) chloride (0.630 g, 0.005 00 mol) was refluxed with a mixture of P(CH₃)₃ (2 mL, 0.02 mol) and 50 mL of tetrahydrofuran for 0.5 h, producing a green solution. The solution was decanted into a reaction tube without filtration and sodium amalgam (0.45 g, 0.019 mol, 25 mL) was then added. The reaction mixture was stirred for 1 h at 0 °C to produce a yellow solution of HFe[CH₂P(CH₃)₂][P(CH₃)₃]₃. An excess of CO was added to the tube and the mixture stirred at 25 °C for 18 h. The solvent was then removed under vacuum and the residue extracted with pentane. The pentane extract was filtered and evaporated to give a yellow residue containing a black impurity. The residue was eluted through a column of deactivated alumina (column was packed in tetrahydrofuran, washed with acetonitrile for further deactivation, and then washed with pentane) with a 50:50 mixture of pentane and toluene. Three yellow bands eluted and were collected. A green band then began to elute, but spread out and disappeared. A fourth yellow band was then eluted with tetrahydrofuran. The combined yellow fractions were eluted again under the same conditions on a fresh column. The first yellow band was collected separately, but the second and third bands could not be separated. The fourth band, containing the bulk of the material, was collected and evaporated to dryness. The residue was recrystallized from cold pentane to give a yellow, crystalline material: yield 0.240 g (14.1%); mp 76.2–76.8 °C; ¹H NMR (benzene-d_6) δ −1.26 (d) (J = 7 Hz); ³¹P{¹H} NMR (acetone-d_6, −85 °C) δ −88.8 (s); IR (pentane solution) ν(CO) 1895 s, 1835 s, 1805 w sh cm⁻¹; mass spectrum, 340 (calcd for C₁₁H₂₇O₂P₃⁵⁶Fe, 340), 312 (Fe[P(CH₃)₃]₃(CO)), 284 (Fe[P(CH₃)₃]₃), 264 (Fe[P(CH₃)₃]₂(CO)₂), 208 (Fe[P(CH₃)₃]₂), 132 (Fe[P(CH₃)₃]). Anal. Calcd for C₁₁H₂₇O₂P₃Fe: C, 38.85; H, 8.00; P, 27.32; Fe, 16.42. Found: C, 39.08; H, 7.99; P, 28.00; Fe, 16.46.

Fe[P(CH₃)₃]₃(PF₃)₂. Dichlorobis(trimethylphosphine)iron(II) (1.00 g, 0.003 58 mol) was dissolved in 20 mL of tetrahydrofuran containing P(CH₃)₃ (16 g, 0.021 mol). The solution was stirred with sodium amalgam (0.5 g, 0.022 mol, 20 mL) at 0 °C for 24 h. The yellow solution was decanted from the amalgam into a reaction tube and phosphorus trifluoride (0.016 mol) (passed through a −131 °C trap) was condensed into the reaction tube. The solution was stirred for 2 h at 25 °C after which volatile materials were removed on the vacuum line and the residue was extracted with pentane. The extract was filtered and the solvent removed under vacuum to give yellow crystals contaminated with a brown impurity: yield 0.8 g; ¹H NMR (toluene-d_8) δ −1.24 (m); ³¹P{¹H} NMR (toluene-d_8, −93 °C) δ −26.5 (quintet) (J = 67 Hz), −38.9 (td) (J_t = 133, J_d = 67 Hz), −80.8 (quartet of multiplets) (J_{PF} = 1234 Hz); mass spectrum, 472 (calcd for C₉H₂₇F₆P₅⁵⁶Fe, 460), (Fe[P(CH₃)₃]₂(PF₃)₃), 384 (Fe[P(CH₃)₃]₂(PF₃)₂), 296 (Fe[P(CH₃)₃]₂(PF₃)), 220 (Fe[P(CH₃)₃](PF₃)), 208 (Fe[P(CH₃)₃]₂), 132 (Fe[P(CH₃)₃]).

H₂Fe[P(CH₃)₃]₄. A reaction tube containing HFe[CH₂P(CH₃)₂][P(CH₃)₃]₃ (0.500 g, 0.001 39 mol) in 10 mL of tetrahydrofuran was charged with hydrogen (0.0041 mol) at 760 Torr. The solution was stirred for 9 days at 25 °C during which some metallic iron formed. The tetrahydrofuran solution was evaporated and the residue extracted with 100 mL of pentane. The pentane solution was filtered and the solvent removed under vacuum to give a yellow oil. Stirring the oil with a spatula caused crystallization to a bright yellow solid: yield 0.35 g (70%); ¹H NMR (toluene-d_8, −70 °C) δ 14.1 (dt) ($J_{HP\ trans}$ = 27 ± 5, $J_{HP\ cis}$ = 71 ± 5 Hz), and −1.23 (d) (J = 12 ± 2.5 Hz).

[(CH₃)₂C₂]₂Fe[P(CH₃)₃]₄. Dichlorobis(trimethylphosphine)iron(II) (1.0 g, 0.003 58 mol) was dissolved in 50 mL of tetrahydrofuran containing P(CH₃)₃ (16 g, 0.021 mol) and 2 mL of 2-butyne (0.025 mol). The light green solution was stirred with sodium amalgam (0.5 g, 0.022 mol, 25 mL) for 2.5 h at 25 °C, resulting in a dark blue solution. The solution was decanted from the amalgam and the solvent removed under vacuum by rotary evaporation. The residue was extracted with pentane and the pentane extract filtered and evaporated to a blue oil which sublimed at 50–60 °C (with some decomposition) as a mixture of blue and colorless crystals: ¹H NMR (toluene-d_8, 0 °C) δ −1.23 (m, 36), −2.12 (−CCH₃, C₆(CH₃)₆), −2.63 (s, 6); mass spectrum, 468 (calcd for C₂₀H₄₈P₄⁵⁶Fe, 468), 392 ([(CH₃)₂C₂]₂Fe[P(CH₃)₃]₃), 208 (Fe[P(CH₃)₃]₂), 162 (C₆(CH₃)₆), 147 (C₆(CH₃)₅). The colorless crystals were hexamethylbenzene.

(CH₃CNH)₂[FeP(CH₃)₃]. To a solution of P(CH₃)₃ (2.0 g, 0.026 mol) in 25 mL of acetonitrile, Fe[P(CH₃)₃]₂Cl₂ (0.77 g, 0.0028 mol) was added. A slightly soluble orange solid, analyzing as Fe[P(CH₃)₃]₃(CH₃CN)₃²⁺FeCl₄²⁻, formed. The mixture was stirred with

sodium amalgam (0.50 g, 0.022 mol, 20 mL) for 12 h. The resulting dark blue-green solution was decanted from the amalgam and evaporated to an oil. Extraction of the oil with pentane followed by evaporation of the solvent under vacuum gave a dark green oil. Stirring this material with a spatula caused crystallization, converting the oil to a nearly black solid: yield 0.28 g (27%); ¹H NMR (acetonitrile-d_3) δ −1.23 (m, 27), −1.95 (s, 6), −6.73 (broad, 2); ³¹P NMR (toluene-d_8, 25 °C) δ −94.7 (s), (−114 °C) δ −98.2 (s); IR ν(C≡N) 1560 cm⁻¹; mass spectrum, 368 (calcd for C₁₃H₃₅N₂P₃⁵⁶Fe, 368), 292 [(NHCCH₃)₂Fe[P(CH₃)₃]₂], 216 [(CNHCH₃)₂FeP(CH₃)₃].

The compound was also prepared using acetonitrile-d_3 instead of acetonitrile. The infrared spectrum showed a band at 1535 cm⁻¹.

(C₄H₆)Fe[P(CH₃)₃]₃. Dichlorobis(trimethylphosphine)iron(11) (1.00 g, 0.003 58 mol) was dissolved in a mixture of P(CH₃)₃ (1.6 g, 0.021 mol) and 50 mL of tetrahydrofuran. To this mixture was added sodium amalgam (0.5 g, 0.02 mol, 25 mL) and then 1,3-butadiene (0.0061 mol) was condensed into the reaction tube. The reaction mixture was stirred for 24 h at 25 °C. The tetrahydrofuran solution was decanted from the amalgam and filtered. The solvent was removed from the filtrate under vacuum. The resulting residue was extracted with pentane. The extract was filtered and evaporated to give a yellow-orange, crystalline solid: yield 1.1 g (91%); ¹H NMR (toluene-d_8, −40 °C) δ +1.46 (broad, 2), −0.55 (broad, 2), −0.88 (t, 18), −1.32 (d, 9), −4.33 (broad, 2); ³¹P{¹H} NMR (acetone-d_6, −60 °C) δ −90.4 (m, 1) and −88.8 (d, 2); mass spectrum, 338 (calcd for C₁₃H₃₃P₃⁵⁶Fe, 338), 284 [Fe{P(CH₃)₃}₃], 262 (C₄H₆Fe[P(CH₃)₃]₂), 208 [Fe{P(CH₃)₃}₂]. Anal. Calcd for C₁₃H₃₃P₃Fe: C, 46.17; H, 9.84; P, 27.48; Fe, 16.51. Found: C, 46.44; H, 9.86; P, 27.71; Fe, 16.43.

H(C₄H₆)Fe[P(CH₃)₃]₃⁺PF₆⁻. To a solution of (C₄H₆)Fe[P(CH₃)₃]₃ (0.310 g, 0.000 917 mol) in 3 mL of tetrahydrofuran was added solid NH₄PF₆ (0.149 g, 0.000 914 mol). With swirling the initially yellow solution turned dark orange red and a dark red, microcrystalline solid formed within 5 min. The supernatant was decanted off and the solid washed with small portions of pentane, tetrahydrofuran, and pentane again, yield 0.292 g (65.8%). The product was recrystallized from acetone solution by slow addition of pentane: ¹H NMR (acetone-d_6) δ −5.40 (broad, 2) −2.00 (broad, obscured by solvent resonance), −1.40 (quartet, 25) (J = 2.7 Hz), +0.54 (broad, 2), and +6.51 (singlet, 3); ³¹P{¹H} NMR (acetone-d_6, −72.5 °C) δ −108.5 (dd, 1) (J = 69.53 Hz), −81.4 (dd, 1) (J = 53.11 Hz), and −75.4 (dd, 1) (J = 68.11 Hz); IR ν(Fe–H) 1570, ν(P–F) 835 cm⁻¹. Anal. Calcd for C₁₃H₃₄F₆P₄Fe: C, 32.12; H, 7.08; P. 25.59; Fe, 11.54. Found: C, 32.12; H, 7.07; P, 26.25; Fe, 11.59.

ND₄PF₆. Deuterated ammonium hexafluorophosphate was prepared by repeated recrystallization of NH₄PF₆ from D₂O. The IR spectrum showed only a trace of the N–H stretching band.

D(C₄H₆)Fe[P(CH₃)₃]₃⁺PF₆⁻. This compound was prepared from (C₄H₆)Fe[P(CH₃)₃]₃ and ND₄PF₆ as described for the protonated compound: ¹H NMR (acetone-d_6, hydride) δ +6.53 (s, 1) and +7.00 (s, 1); IR no band near 1570 cm⁻¹ was observed. In contrast, the protonated complex from NH₄PF₆ recrystallized from H₂O showed only the hydride resonance at 6.51 ppm.

H–D Exchange in D(C₄H₆)Fe[P(CH₃)₃]₃⁺PF₆⁻. Solutions of H(C₄H₆)Fe[P(CH₃)₃]₃⁺PF₆⁻ and D(C₄H₆)Fe[P(CH₃)₃]₃⁺PF₆⁻ in acetone were stirred for 4 days. The solid compounds were recovered, slurried in pentane, and decomposed with aqueous ceric ammonium nitrate for 4 h. Butadiene in the pentane layers was identified by GC/MS. Comparison of mass spectra of butadiene from the deuterated and undeuterated iron complexes showed that significant incorporation of one deuterium atom into the butadiene of the deuterated iron complex had occurred.

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