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Synthesis of Iron(II) Phosphite Complexes

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The cationic iron(II) complexes, $[Fe(P(OR)_3)_5X]^+$, have been prepared by reactions involving oxidation of $Fe(P(OR)_3)_5$ (for X = H, Me, CF_3) or addition of phosphites to iron bis(tetrahydrofuran) dihalide complexes (for X = Cl, Br, I). This latter reaction proceeds, under different conditions, through two distinctly different isolable species, both of which have the formulation $Fe(P(OR)_3)_3X_2$. The complexes have been characterized by spectroscopic techniques including simulation of the $^{31}P\{^1H\}$ NMR spectra.

Introduction

Divalent iron complexes of alkyl and aryl phosphine ligands have been studied in some detail [1]. Relatively less attention has been devoted to the trialkyl and triaryl phosphite complexes [2]. This has been due in part to the susceptibility of the ligands to hydrolysis and Arbuzov rearrangement. On the other hand their appreciably stronger π-acceptor properties and decreased steric requirements [3] make their study of considerable interst. In an investigation of the chemistry of the zerovalent species, $Fe(P(OMe)_3)_5$ [4–6], a number of complexes of the type $[Fe(P(OMe)_3)_5X][Y]$ were encountered. A systematic study of these divalent species was undertaken, including a detailed investigation of their ^{31}P nmr properties. The results of the study are reported here.

Results and Discussion

Reaction of Phosphites with Iron(II) Halides

The preparations of $Fe(THF)_2Cl_2$ [7], **1**, (THF = tetrahydrofuran) and $Fe(THF)_{1.5}Cl_2$ [8] have been reported previously. We have prepared $Fe(THF)_2X_2$ where X = Br, **2** and I, **3**, by Soxhlet extraction of the anhydrous ferrous halides with THF. Attempted preparation of the dichloro species by the same technique gave variable results which were dependent on the source (presumably the purity) of the $FeCl_2$ and the reaction conditions. Analyses varied between 1.5 and 2 molecules of THF per metal but the composition of the solvated dichloride seemed to have no effect upon subsequent reactions. All three solvated dihalides were similar in appearance to the diaquo complex $Fe(H_2O)_2Cl_2$.

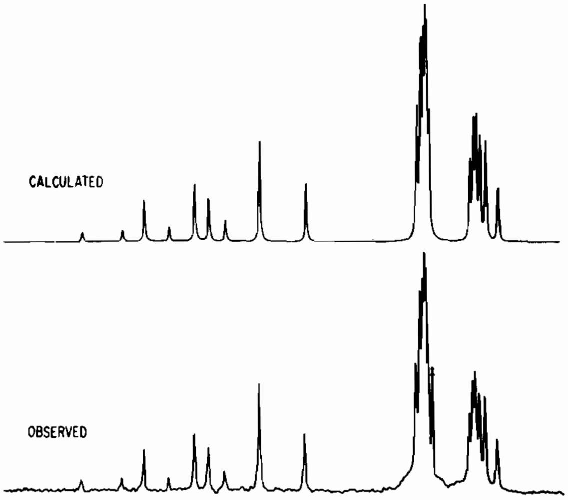

Figure 1. Calculated and observed $^{31}P\{^1H\}$ NMR spectra for $[Fe(P(OMe)_3)_5Cl][BPh_4]$.

The reaction of $Fe(THF)_2X_2$ species with alkyl phosphites, P, proceeds through a complicated series of equilibria, 1a–1e. The four- and five-coordinate species are paramagnetic while the six-coordinate species are diamagnetic. Useful information about these equilibria can be

$$Fe(THF)_2X_2 \xrightleftharpoons{P} FeP_3X_2 \quad (1a)$$

$$FeP_3X_2 \rightleftharpoons [FeP_3X]^+X^- \quad (1b)$$

$$FeP_3X_2 \xrightleftharpoons{P} FeP_4X_2 \quad (1c)$$

$$FeP_4X_2 \xrightleftharpoons{P} [FeP_5X]X \quad (1d)$$

$$[FeP_5X]X \xrightleftharpoons{P} [FeP_6]X_2 \quad (1e)$$

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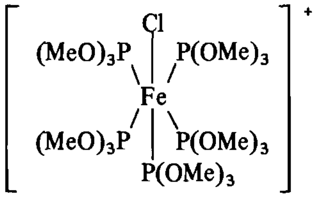
**Contribution No. 2590.

TABLE I. $^{31}P\{^1H\}$ NMR Data for Selected Iron Phosphite Complexes.[c]

	δA (ppm)	δB_4 (ppm)	J_{AB} Hz
$[Fe(P(OMe)_3)_5H]^+$	166.4	169.7	82.5
$[Fe(P(OMe)_3)_5Me]^+$	167.9	168.9	79.5
$[Fe(P(OMe)_3)_5CH_3CN]^{2+}$	156.4	149.4	130
$[Fe(P(OMe)_3)_5Cl]^+$	163.4	149.3	126
$[Fe(P(OMe)_3)_5Br]^+$	165.2	151.2	124
$[Fe(P(OMe)_3)_5I]^+$	174.0	154.5	124
$[Fe(P(OMe)_3)_6]^{2+}$	150.8	–	–
$[Fe(P(OEt)_3)_5H]^+$	161.8	164.4	93
$[Fe(P(OEt)_3)_5Cl]^+$	159.6	145.0	125
$[Fe(P(OEt)_3)_5Br]^+$	161.0	146.0	124
$[Fe(P(OEt)_3)_5I]^+$	170.0	151.0	123
Trans-$Fe(P(OMe)_3)_4Cl_2$	157.3	–	–
Trans-$Fe(P(OMe)_3)_4Br_2$	157.8	–	–
Cis-$FeP(OEt)_3)_4H_2$	183.1[a]	185.3	56
$Fe(P(OMe)_3)_5$	187.8[b]	176.4	145
$Fe(P)(OEt)_3)_5$	180.9[b]	171.1	144.5

[a] A_2B_2 spin system, recorded in toluene-d_8. [b] A_2B_3 spin systems, recorded in pentane. [c] Recorded in CH_2Cl_2.

obtained by ^{31}P NMR. For example, the reaction of 1 with $P(OMe)_3$ in methylene chloride yields the characteristic spectrum (AB_4 spin system) (see Table I and Figure 1) of $[Fe(P(OMe)_3)_5Cl]^+$, 4, even at low concentrations of phosphite (Fe:P = 1:1–3). No other diamagnetic species are observed at room temperature, but if the temperature is lowered to −80 °C, an additional single line appears at 157.3 ppm. This species, thought to be *trans*-$Fe(P(OMe)_3)_4Cl_2$, 5, is presumably in fast exchange with a paramagnetic species at room temperature according to equation (1c) and is therefore unobserved. At higher concentrations of phosphite (Fe:P = 1:5–10) the spectrum is unchanged at room temperature, but at low temperature the singlet at 157.3 ppm is reduced in relative intensity and free phosphite begins to appear at 140 ppm. In the presence of a large excess of phosphite, at room temperature a very broad resonance appears below 140 ppm, shifting towards 140 ppm and sharpening as the excess is increased. This is again consistent with the rapid exchange process given by equation 1c. Similar results are obtained with other phosphite ligands and halides. The spectroscopic parameters are listed in Table I.



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Attempted isolation of products from the $FeCl_2/P(OMe)_3$/THF system points out some of the other equilibria listed in equations (1a–1e). At low concentrations of phosphite [Fe:$P(OMe)_3$ = 1:3] it is possible to isolate $Fe(THF)_2Cl_2$ from solution according to the reverse of equation 1a. When phosphite is used in large excess, the only products isolated are of the formula $Fe(P(OMe)_3)_3Cl_2$. Two distinct forms of the yellow crystalline solid could be obtained (equation (1b)), but the variables which determined which form would be prepared in any given reaction were not ascertained. At times the FeP_3X_2 would remain in solution in THF, and addition of ether precipitated a highly crystalline material having a relatively low melting point. On other occasions, the FeP_3X_2 would precipitate spontaneously as a powder which would not melt up to 300 °C. These two species were indistinguishable in solution, displaying the behavior described above for Fe:P = 1:3. No definitive information on their structures was obtained. The low-melting form is presumably the five-coordinate molecular species. The less soluble non-melting form could be an ionic species, $[Fe(P(OMe)_3)_3Cl][Cl]$, or a chlorine-bridged oligomer. The latter possibility is deemed to be unlikely because there was no evidence for bridging in solution; bridging would yield six coordination and the complexes should be diamagnetic.

Attempts to isolate $[Fe(P(OMe)_3)_5Cl][Cl]$ from the $FeCl_2/P(OMe)_3$/THF system were unsuccessful even though it was apparent from $^{31}P\{^1H\}$ NMR

TABLE II. Melting Points and Analyses for Selected Iron Complexes.

Complex	M.P. (°C)	Analyses					
		Carbon		Hydrogen		Phosphorus	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$Fe(THF)_2Cl_2$	>300	35.5	35–25	5.9	6–5	26.2	26–30 (Cl)
$Fe(THF)_2Br_2$	>300	26.7	26.5	4.5	4.5	44.4	44.8 (Br)
$Fe(THF)_2I_2$	>300	21.2	21.3	3.5	3.8	55.9	54.9 (I)
$Fe(P(OMe)_3)_3Cl_2$	>300	21.7	21.4	5.5	5.4	18.6	18.9
$Fe(P(OMe)_3)_3Cl_2$	150	21.7	21.2	5.5	5.4	18.6	19.9
$Fe(P(OMe)_3)_3Br_2$	>300	19.3	18.9	4.9	4.8	16.6	16.7
$Fe(P(OMe)_3)_3Br_2$	175	19.3	19.3	4.9	4.9	16.6	16.4
$Fe(P(OEt)_3)_3Cl_2$	>300	34.6	34.2	7.3	7.3	14.9	14.1
$Fe(P(OEt)_3)_3Cl_2$	79	34.6	34.2	7.3	7.0	14.9	13.8
$Fe(P(OEt)_3)_3Br_2$	>300	30.3	30.3	6.4	6.3	13.0	13.5
$Fe(P(OEt)_3)_3Br_2$	92	30.3	30.6	6.4	6.7	13.0	12.8
$Fe(P(OMe)_2Ph)_3Cl_2$	91	45.2	44.8	5.2	4.8	14.6	14.8
$Fe(P(OCH_2)_3CEt)_3Cl_2$	104	35.3	35.6	5.4	5.7	15.5	15.6
$Fe(P(OCH_2)_3CEt)_3Br_2$	135	30.8	30.5	4.7	4.8	13.2	13.4
$[Fe(P(OMe)_3)_5Cl][BPh_4]$	130	45.4	45.3	6.4	6.1	15.0	14.6
$[Fe(P(OMe)_3)_5Br][BPh_4]$	182	43.6	43.9	6.1	5.8	14.4	14.6
$[Fe(P(OMe)_3)_5I][BPh_4]$	174	41.7	41.4	5.8	5.8	13.7	13.2
$[Fe(P(OMe)_3)_5H][PF_6]$	255	21.9	21.4	5.6	5.5	22.6	22.4
$[Fe(P(OMe)_3)_5Me][BPh_4]$	143	47.6	47.3	6.8	6.7	15.3	16.2
$[Fe(P(OMe)_3)_5CH_3CN][SbF_6]_2$	Dec.	17.2	17.3	4.0	4.0	13.0	13.7
$[Fe(P(OEt)_3)_5Cl][BPh_4]$	101	52.2	51.9	7.7	7.5	12.5	12.4
$[Fe(P(OEt)_3)_5Br][BPh_4]$	102	50.5	50.2	7.5	7.3	12.1	12.0
$[Fe(P(OEt)_3)_5I][BPh_4]$	124	48.7	48.7	7.2	7.0	11.6	11.7
$[Fe(P(OEt)_3)_5H][BF_4]$	244	37.0	36.5	7.8	7.3	15.9	15.9
$[Fe(P(OMe)_3)_6][BPh_4]_2$	280	55.1	54.2	6.6	6.5	12.9	13.8

experiments that it exists in very appreciable concentrations in solution. This difficulty was overcome by running the reaction in methanol instead of THF. Addition of tetraphenylborate, BPh_4^-, to the methanolic solution of $FeCl_2$ and $P(OMe)_3$ precipitated the highly crystalline yellow product $[Fe(P(OMe)_3)_5Cl]$ $[BPh_4]$. Once the cationic product has been isolated it is stable to redissolution in THF or other solvents; there is no dissociation of phosphite ligand in the absence of a second halide to fill the vacant coordination site.

Under somewhat more extreme conditions, it is possible to replace the second chloride ion by phosphite yielding the species, $[Fe(P(OMe)_3)_6]^{++}$. This is best accomplished by forcing equation (1e) to the right by precipitation of the dication with a similar sized dianion.

Similar reactions can be carried out using other phosphites or halides. The spectral parameters are listed in Table I, and the physical properties are listed in Table II.

Preparation and Reactions of $Fe(P(OR)_3)_5$ Complexes

The FeP_3X_2 complexes can be reduced with sodium amalgam in the presence of excess phosphite (presumably in the form of $[FeP_5X][X]$) to give the zerovalent five coordinate species FeP_5 ($P = P(OMe)_3$ [4–6, 9, 10] and $P(OEt)_3$) [4–6]). The reaction is best accomplished with X = Br [10], but satisfactory results are also obtained with X = Cl and I. The fluxional nature of this five coordinate species has been detailed elsewhere [4, 5]. We have found these zerovalent species to be exceptionally electron rich, an aspect displayed throughout their chemistry.

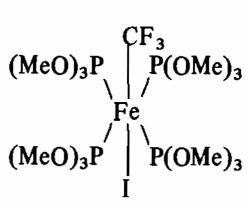
When $Fe(P(OMe)_3)_5$ is dissolved in methanol, it exists to a slight degree in the protonated form $[Fe(P(OMe)_3)_5H]^+$, according to equation (2).

$$Fe(P(OMe)_3)_5 + MeOH \rightleftharpoons [Fe(P(OMe)_3)_5H]^+ + [OMe]^- \qquad (2)$$

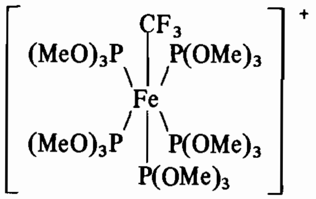
This reaction implies a pK_A of ~19 for the protonated form. This should be compared with $Ni(P(OMe)_3)_4$ which requires the relatively strong acid system, H_2SO_4 in methanol, to carry out the protonation. The hydride can be isolated by use of a stronger acid such as NH_4^+ and a suitable counterion such as BF_4^- or BPh_4^-. The protonation has even been carried out using a β-diketone [12].

Reaction of $Fe(P(OMe)_3)_5$ with methyl iodide or $[Me_3O][BF_4]$ gives the cation $[Fe(P(OMe)_3)_5Me]^+$. The methyl resonance is observed as a quintet above TMS due to coupling with the four equatorial phosphites. The coupling to the *trans* axial phosphite is small.

Mixing of $FeP(OMe)_3)_5$ with CF_3I led to an unexpectedly rapid reaction, precipitating yellow-green solids from ether. A methanol solution of the precipitated material displayed two weak ^{19}F resonances having phosphorus coupling attributable to



(−11.6 ppm, quintet, J_{PF} = 52.5 Hz) and



(−80.8 ppm, doublet of quintets, J_{PF} = 79.5 and 52.5 Hz). The ^{31}P NMR spectrum showed that the major product was $[Fe(P(OMe)_3)_5I]^+$ with a few minor impurities. The yield of the iodo complex increased as the quantity of CF_3I was increased from one to two equivalents. Thus reaction with CF_3I is not a suitable route to the CF_3 complex.

A similar rapid reaction was observed with excess $CFCl_3$, giving $[Fe(P(OMe)_3)_5Cl]^+$ in good yield. The volatile components of this reaction were analyzed by G.C./M.S. and found to be CH_3Cl, FClC=CFCl, $CFCl_2CH_3$, $CHFCl_2$ and $P(OMe)_2F$ in addition to the solvent, $CFCl_3$, and free phosphite. These products are consistent with rapid electron transfer from the zerovalent iron complex to $CFCl_3$ to yield ultimately $CFCl_2^-$ and Cl^-. Subsequent dissociation of Cl^- from the carbanion yields another Cl^- and :CFCl which can attack phosphite or dimerize to give olefin. It is not clear whether the initial reaction involves one- or two-electron transfer, but the remarkable difference between the CF_3I and CH_3I reactions is presumably a result of the high electron capture cross section of fluorohalocarbons.

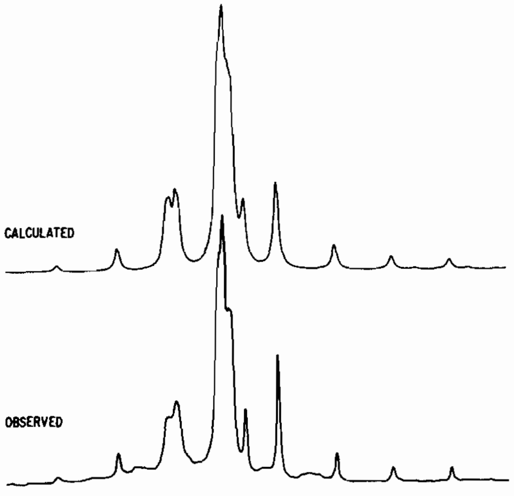


Figure 2. Calculated and observed $^{31}P\{^1H\}$ NMR spectra for $[Fe(P(OMe)_3)_5H][PF_6]$.

Another indication of the high electron density on the metal center in $Fe(P(OMe)_3)_5$ is a variety of facile one electron oxidations. Silver(I) or tropylium salts react with $Fe(P(OMe)_3)_5$ in acetonitrile to give $[Fe(P(OMe)_3)_5(CH_3CN)]^{2+}$ through two consecutive one electron transfers. Attempts to prepare a non-solvated five-coordinate Fe(II) species were unsuccessful because of disproportionation to $[Fe(P(OMe)_3)_6]^{2+}$ and other unknown species. Reaction of $Fe(P(OMe)_3)_5$ with tetracyanoethylene (TCNE) yields [13] oxidized iron species and the radical anion $TCNE^{\overline{\cdot}}$ in reactions similar to those observed in the bis(diphenylphosphino)ethane iron system [14].

NMR Characterization of $[FeP_5X]^+$ *Species*

The $^{31}P\{^1H\}$ NMR spectra for all of the $[FeP_5X]^+$ species were complex non-first order patterns. Simulation of the spectra was essential to their identification as arising from AB_4 spin systems, and to qualitative assessment of compound purity. The pattern for any given spectrum is determined by a single ratio, J/δ. Preliminary assignments of spectral parameters were made by comparison with a computer generated library of calculated spectra over a wide range of J/δ. Final parameters were then obtained by direct trial and error overlay of observed and calculated spectra. Representative spectra are presented in Figures 1–4 to aid in the identification of these products.

The spectral parameters of the AB_4 spin systems do not clearly correlate with any conventional measure of steric or electronic effects. The coupling constants might seem to vary inversely with the steric size of the sixth substituent, but acetonitrile has a smaller cone angle than any of the halides [3].

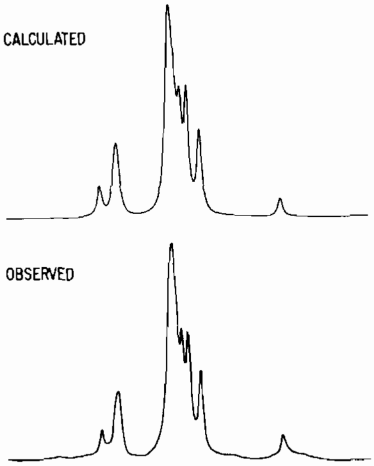


Figure 3. Calculated and observed $^{31}P\{^1H\}$ NMR spectra for $[Fe(P(OMe)_3)_5Me][BPh_4]$.

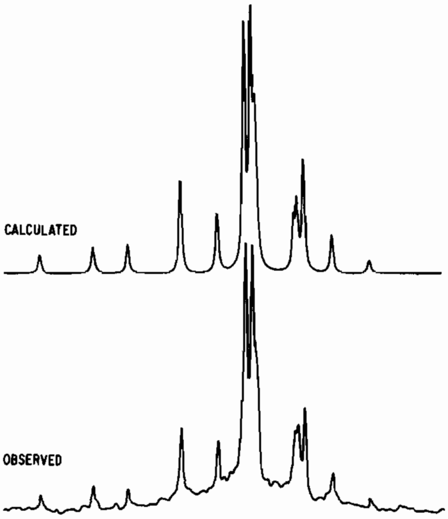


Figure 4. Calculated and observed $^{31}P\{^1H\}$ NMR spectra for $[Fe(P(OMe)_3)_5(CH_3CN)][SbF_6]_2$.

J_{A-B} is largest for the complexes having a readily dissociable sixth ligand so it may well be related to the strength of the bond to the sixth ligand.

Experimental

All reactions were carried out in the nitrogen atmosphere of a Vacuum Atmospheres dry box using standard procedures. Tetrahydrofuran was distilled under argon from sodium/benzophenone just prior to use. All other solvents were dried over molecular sieves and purged with nitrogen. Anhydrous ferrous chloride was prepared by the literature technique and found to be superior to commercially available material. All other reagents were commercially available and used without further purification. The preparation of $Fe(P(OMe)_3)_5$ is described elsewhere [10].

$^{31}P\{^1H\}$ Fourier mode NMR spectra (36.43 MHz) were recorded using 10-mm tubes on a Bruker HFX-90 spectrometer. Proton and ^{19}F NMR spectra were recorded in the CW mode on Varian HRS6-IX-VFT 220/300 and XL-100 spectrometers respectively. Field desorption mass spectra were recorded on a CEC-21-110B spectrometer using a technique described elsewhere [15]. GC mass spectra were run on a Du Pont 21-490 GCMS using a UCON-LLB-550x column held at 85 °C for 12 minutes and programmed 6°/minute to 150 °C. Analyses were carried out in our microanalytical facilities. Melting points are uncorrected.

Dibromobis(tetrahydrofuran)iron(II)

A Soxhlet extractor was set up under N_2 and charged with $FeBr_2$ (100 g, 0.46 mol). The $FeBr_2$ was extracted with THF to yield an orange solution. As the extraction continued, large crystals formed. After 12 hours, all the $FeBr_2$ had been extracted. The extract was cooled and filtered yielding large white flaky crystals which were washed with ether and dried under vacuum. Yield = 150 g, 90%. Under prolonged storage, the white material begins to turn orange because of loss of THF. The color can be removed by recrystallization from THF.

Dichlorobis(tetrahydrofuran)iron(II)

An analogous procedure gave the dichloro complex in 50 to 80% yield dependent on the source and history of the starting material.

Preparation of Two Forms of FeL_3X_2 Complexes

In preparing the FeL_3X_2 complexes it was observed that two distinct forms with the same composition could be isolated. The only difference established between the two is their melting points. One class melts around 100 °C and the other does not melt up to 300 °C. The first is assumed to be the five-coordinate molecular complex, FeL_3X_2. The second is presumably the four-coordinate cationic species $[FeL_3X]^+X^-$. These complexes have not been further characterized. Typical preparations of the two species are given.

Preparation of low melting $Fe(P(OEt)_3)_3Br_2$

$Fe(THF)_2Br_2$ was suspended in toluene and $P(OEt)_3$ was added until all material went into solution. Then a small amount of ether was introduced followed by addition of pentane. The pentane was added very slowly and a flocculent precipitate appeared. Addition was continued until the fine fibrous crystals were very dense. Evaporation of a small quantity of the pentane dropped the temperature of the solution and more product crystallized. The product was collected by vacuum filtration and was washed with pentane before drying under vacuum. This material is benzene soluble.

Preparation of high melting $Fe(P(OMe)_3)_3Cl_2$

A suspension of $FeCl_2$ (2.54 g, 20 mmol) in THF (100 ml) was refluxed for 3 hours with $P(OMe)_3$ (9.4 ml, 80 mmol). The mixture was filtered hot to remove unreacted $FeCl_2$ and cooled to room temperature. The bright yellow crystals which precipitated were filtered and dried under vacuum.

$[Fe(P(OMe)_3)_5Cl]$ $[BPh_4]$

A solution of $Fe(P(OMe)_3)_3Cl_2$ (low-melting form) (3.0 g, 6.0 mmol) in methanol (40 ml) was reacted with excess $P(OMe)_3$ (2 ml, 16 mmol). A methanol solution of $NaBPh_4$ (2.06 g, 6 mmol) was then added. Large, yellow, platelike crystals usually began to precipitate before the addition was complete. Stirring was continued for 10 minutes and the product was then collected by vacuum filtration, washed with methanol and ether, and dried under vacuum. A final recrystallization from acetone/methanol was used to obtain analytically pure material.

Preparation of $[Fe(P(OMe)_3)_5H]$ $[PF_6]$

A solution of $Fe[P(OMe)_3]_5$ (2.03 g, 3.0 mmol) in methanol was reacted with a methanol solution of NH_4PF_6. The yellow iron solution lightened and was almost decolorized during this process. The solution was reduced in volume, and slow addition of ether precipitated a white crystalline product. The crystals were collected by vacuum filtration and dried under vacuum. M.P. >265 °C.

The ^1H spectrum consists of a single broad phosphite resonance at $\tau = 6.36$ and a hydride resonance consisting of the X part of an AB_4X spectrum at $\tau = 22.7$. $J_{HP_A} = 25$ Hz, $J_{HP_B} = 55$ Hz. F.D.M.S.: Calcd. for $FeP_5O_{15}C_{15}H_{46}^+$: 677; obs: 677.

Preparation of $[Fe(P(OMe)_3)_5Me]$ $[BPh_4]$

A solution of $Fe(P(OMe)_3)_5$ (2.03 g, 3.0 mmol) in THF was stirred with a threefold excess of MeI for several days. The solution turned from yellow to yellow green. Addition of a stoichiometric quantity of $NaBPh_4$ followed by very slow addition of ether precipitated a white crystalline compound which was collected by vacuum filtration. M.P.: >265 °C.

The methyl proton resonance was observed at −0.17 ppm (above TMS) as the X_3 part of an AB_4X_3 spectrum (Quintet, $J_{H-P_{cis}} = 6.6$ Hz; $J_{H-P_{trans}}$ was not observed). F.D.M.S.: Calcd. for $FeP_5O_{15}C_{16}H_{48}^+$: 691; obs: 692.

Reaction of $Fe(P(OMe)_3)_5$ *with* CF_3I

A solution of $Fe(P(OMe)_3)_5$ (2.03 g, 3.0 mmol) in ether was treated with CF_3I (70 ml 3.0 mmol) at room temperature with stirring. A rapid reaction gave a greenish-yellow precipitate which was collected by vacuum filtration. ^{19}F NMR of the crude product in methanol gave two weak signals assigned to *trans*-$Fe(P(OMe)_3)_4(CF_3)(I)$ (quintet at −11.62 ppm, $J_{PF} = 52.5$ Hz) and $[Fe(P(OMe)_3)_5CF_3]^+$ $[I]^-$ doublet of quintets at −80.85 ppm, $J_{PF} = 79.5$ and 52.5 Hz). ^{31}P NMR indicated that the major product was $[Fe(P(OMe)_3)_5I]^+$ $[I]^-$ and, after one recrystallization from CH_2Cl_2/MeOH, there were no fluorine-containing species left.

Reaction of $Fe(P(OMe)_3)_5$ *with* $CFCl_3$

A solution of $Fe(P(OMe)_3)_5$ (0.02 g, 0.03 mmol) in THF (0.5 ml) was mixed with $CFCl_3$ (1.5 ml vapor; 0.06 mmol) giving a rapid reaction. The vapor phase was sampled by GCMS giving the following peaks: CH_3Cl (6.58 min); FClC=CFCl (10.03 min); $CFCl_3$ (13.08 min); CH_3CFCl_2 (16.05 min); $CHCFCl_2$ (18.32 min); $P(OMe)_2F$ (22.14 min); $P(OMe)_3$ (37.00 min).

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