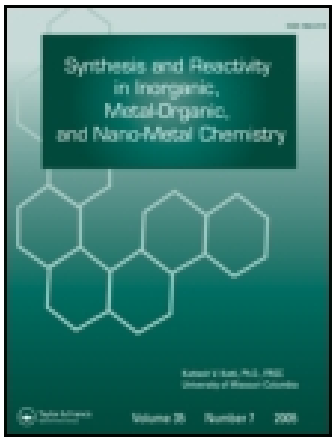

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SYNTHESIS AND CHARACTERIZATION OF SOME ALKYL(DIFERROCENYL)PHOSPHINES AND ALKYL(DIFERROCENYL)PHOSPHINE OXIDES

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SYNTHESIS AND CHARACTERIZATION OF SOME ALKYL(DIFERROCENYL)-PHOSPHINES AND ALKYL(DIFERRO-CENYL)PHOSPHINE OXIDES

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ABSTRACT

Reaction of ferrocene with alkyldichlorophosphines ($RPCl_2$, R = Me, Et, *t*-Bu) in the presence of aluminum chloride produces diferrocenyl(alkyl)phosphines (Fc_2PR, (**1a**)–(**3a**), R = Me, Et, *t*-Bu) and diferrocenyl(alkyl) phosphine oxides $Fc_2P(O)R$, (**1b**)–(**3b**) in low yields. Diferrocenyl(ethyl)phosphine oxide (**2b**) crystallizes in the P1 space group with one equivalent of water in the crystal. Compounds (**1a**)–(**3a**) are oxidized at lower potentials than the corresponding phenyl derivative, Fc_2PPh. Cyclic voltammetry of (**1a**)–(**3a**) indicates

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that the first oxidation is irreversible. The corresponding diferrocenyl(alkyl)phosphine oxides (**1b**)–(**3b**) are more difficult to oxidize than (**1a**)–(**3a**) but show two reversible oxidations separated by 140–160 mV.

INTRODUCTION

Ferrocenyl substituted phosphines are of interest in asymmetric synthesis[1] and in the preparation of high molecular phosphorus-bridged polyferrocenes[2]. Much of the work in these areas has focused on the readily available ferrocenyl(aryl)phosphines (*e.g.* 1,1′-bis(diphenylphosphino)ferrocene). As part of our investigation of electron transfer between iron centers in heteroatom-bridged, mixed valent biferrocenes[3], we were interested in the synthesis and characterization of alkyl(diferrocenyl)phosphines Fc_2PR (**1a**) R = Me, (**2a**) R = Et, (**3a**) R = *t*-Bu. Dialkyl(ferrocenyl)phosphines, $FcPR_2$ (where $Fc = \eta^5\text{-}C_5H_5FeC_5H_4$, for R = Me, *i*-Pr, and *t*-Bu) are prepared by Friedel Crafts reactions between ferrocene and the corresponding alkyl(chloro)phosphines[4–6]. Surprisingly, the Friedel Crafts route has not been extensively applied to the synthesis of alkyl(diferrocenyl)phosphines. Synthesis of Fc_2PEt and $FcP(Pr\text{-}i)_2$ by this route is described in a footnote in a paper on their use as ligands in osmium carbonyl clusters but details of their synthesis are missing[6]. The synthesis of alkyl(diferrocenyl)phosphines, Fc_2PR, by reduction of the corresponding phosphine oxides with lithium aluminum hydride and aluminum chloride has been reported[7]. Unfortunately, this method is hampered by low yield syntheses of the starting diferrocenyl(alkyl)phosphine oxides[7], $Fc_2P(O)R$. The present paper describes the synthesis of three alkyl(diferrocenyl)phosphines, (**1a**)–(**3a**) and the corresponding alkyl(diferrocenyl)phosphine oxides, $Fc_2P(O)R$ (**1b**) R = Me, (**2b**) R = Et, (**3c**) R = *t*-Bu. Compounds (**1**)–(**3**) were characterized by elemental analyses, cyclic voltammetry, IR, ^1H and ^{31}P NMR. The single crystal X-ray structure of $Fc_2P(O)Et{\cdot}H_2O$(**2b**·H_2O) is also reported.

EXPERIMENTAL

Materials and Methods

All compounds described in this work were handled using Schlenk techniques, an M. I. Braun glovebox under a purified argon atmosphere, or

on a vacuum line equipped with oil diffusion and mechanical pumps (10^{-2} Torr)[8]. Ferrocene, alkyldichlorophosphines and $AlCl_3$ were purchased from Strem Chemical Co. and used as received. Hexane, benzene, and toluene were purified by refluxing over Na/benzophenone and distilled prior to use. Dichloromethane and acetonitrile were distilled from P_2O_5 and CaH_2, respectively. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried as described above. Melting points were determined on an Electrothermal 9100 apparatus in capillaries sealed with epoxy under argon and are uncorrected. Elemental analyses (C, H) were performed by Desert Analytics, Inc., Tucson, AZ.

^1H and $^{31}P\{^1H\}$ spectra were recorded on a Varian 300XL spectrometer in 5 mm tubes equipped with a Teflon valve (J. Youngs). Proton chemical shifts are listed relative to residual protons in the solvent (C_6D_5H at δ 7.15 ppm). Phosphorus chemical shifts (Table II) are referenced to external 85% H_3PO_4 at δ 0.00 ppm. Infrared spectra were obtained as KBr pellets on a Mattson Satellite FTIR interfaced with a Digital PC3000 computer.

Oxidation potentials of (**1**)–(**3**) were determined on a BAS 100B Electrochemical Analyzer in CH_2Cl_2 solution (2 mM) containing 0.1 M [*n*-Bu_4N][ClO_4] (Fluka Chemical Co.) as the supporting electrolyte. A 1.2 mm gold disk working electrode (BAS), platinum counter electrode and Ag/Ag^+ reference electrodes (Ag wire in 10 mM $AgNO_3$ and 0.1 M [NEt_4][BF_4] in CH_3CN)[9] were used. All experiments were performed under a nitrogen or argon atmosphere at a scan rate of 100 mV/s.

Synthesis of Diferrocenyl(methyl)phosphine (1a) and Diferrocenyl(methyl)phosphine Oxide (1b)

A slurry of ferrocene, (3.72 g, 20 mmols) and $AlCl_3$ (1.33 g, 10 mmols) in hexane (35 mL) was stirred under nitrogen, warmed slightly, and allowed to cool to room temperature. Methyldichlorophosphine, (1.17 g, 10 mmols) in hexane (20 mL) was added dropwise to the stirring reaction mixture. A dark brown precipitate formed rapidly. After addition was completed, the mixture was refluxed for 24 hours. Upon cooling, the supernatant containing unreacted ferrocene was decanted leaving a dark brown solid. The solid was extracted with hot hexane and the ferrocene-containing washings discarded. The remaining solid was washed with 10 mL portions of boiling, de-ionized, de-gassed water until the solid turned yellow. The blue-green aqueous washings were decanted and discarded. The resultant yellow solid was extracted with hot benzene until the extracts were colorless. The combined benzene extracts were dried over Na_2SO_4 and filtered under nitrogen.

Solvent was removed *in vacuo* yielding a yellow orange solid. Residual ferrocene was removed *via* sublimation (100 °C, 10^{-2} mmHg). The non-volatile solid was taken up in a minimum amount of benzene and chromatographed on a 2×15 cm alumina column under nitrogen. Diferrocenyl(methyl)phosphine (**1a**) was eluted with benzene. Diferrocenyl(methyl)-phosphine oxide (**1b**) was subsequently eluted with $CHCl_3$. Evaporation of the solvent under vacuum yielded 0.62 g (15% yield) of (**1a**) and 0.11 g (2.6% yield) of (**1b**). The phosphine (**1a**) can be re-crystallized from ethanol or toluene.

Synthesis of Diferrocenyl(ethyl)phosphine (2a) and Diferrocenyl(ethyl)phosphine Oxide (2b)

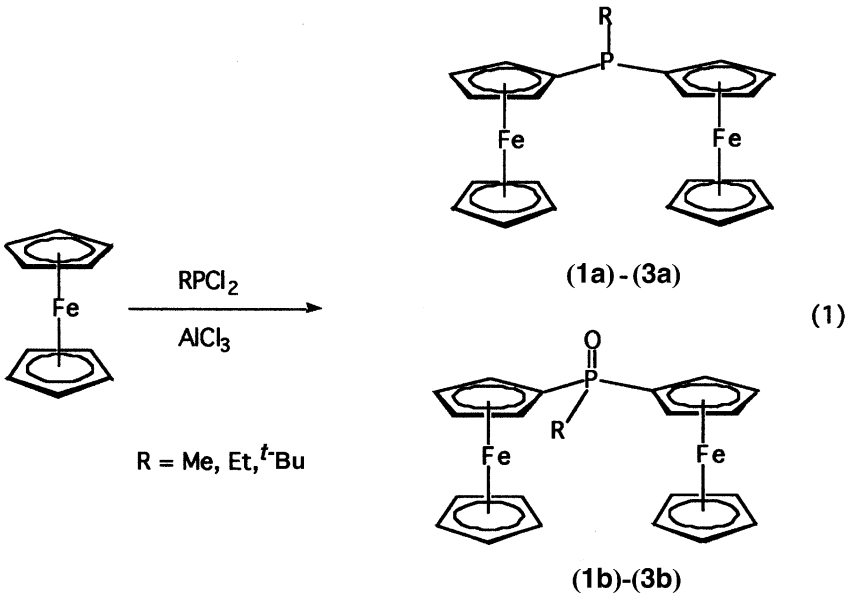
Ferrocene (3.72 g, 20 mmols), $AlCl_3$, (1.33 g, 10 mmols) and $EtPCl_2$, (1.33 g, 10 mmols) were reacted as described for (**1**). After work-up and chromatography, 1.08 g (25%) of diferrocenyl(ethyl)phosphine (**2a**) and 0.278 g (6%) of diferrocenyl(ethyl)phosphine oxide (**2b**) were isolated.

Synthesis of Diferrocenyl(*t*-butyl)phosphine (3a) and Diferrocenyl(*t*-butyl)phosphine Oxide (3b)

Ferrocene (8.07 g, 43.4 mmols), $AlCl_3$, (2.89 g, 21.7 mmols) and *t*-$BuPCl_2$, (3.45 g, 21.7 mmols) were reacted for 48 h as described for (**1**). After work-up and chromatography, 0.89 g (9%) of diferrocenyl(*t*-butyl)-phosphine (**3a**) and 1.1 g (11%) of diferrocenyl(*t*-butyl)phosphine oxide (**3b**) were isolated. Both (**3a**) and (**3b**) were re-crystallized from benzene or toluene.

Solid State Structure Determination of ($2b \cdot H_2O$)

Single crystals suitable for X-ray diffraction were grown by slow cooling of toluene solutions of (**2b**) to 0 °C. The mother liquor was removed by cannula and the crystals washed with cold toluene before drying in vacuum. An orange plate ($0.84 \times 0.43 \times 0.11$ mm) was mounted in a sealed capillary. Data were collected on a Siemens R3m/V diffractometer. Solution and refinement were performed using Siemens SHELXTL PLUS Release 4.11 (VMS) software. The structure was solved using a Patterson map and refined by full-matrix least squares for which the function minimized was $\Sigma w(\mathrm{Fo}-\mathrm{Fc})^2$ where $w^{-1} = \sigma^2(\mathrm{F}) + 0.006\,\mathrm{F}^2$. Hydrogen atoms were located



(1)

by optimization from the difference Fourier map with some refinement of selected hydrogens. Positional parameters for the non-hydrogen atoms can be found in the supplemental material.

Crystals of (**3a**) were obtained from toluene but crumbled upon drying and were unsuitable for X-ray diffraction.

RESULTS AND DISCUSSION

Synthesis of Diferrocenyl(alkyl)phosphines and Diferrocenyl(alkyl)phosphine Oxides

Diferrocenyl(alkyl)phosphines (**1a**)–(**3a**) can prepared in 5–25% yield microanalyses (Table I) by Friedel-Crafts reaction of ferrocene with alkyldichlorophosphines using the published procedure for diferrocenyl(phenyl)phosphine [Eq. (1)][10]. Significant amounts of ferrocene are recovered during the purification procedure. As mentioned, the synthesis of Fc_2PEt (**2a**) was reported in a footnote[6–7] but yields and additional characterization data are not reported[6]. Compared to Fc_2PPh, the yields of (**1a**)–(**3a**) (Table I) are quite low but reflect those reported for other ferrocenyl(alkyl)-

Table I. Elemental Analysis and Yields for (**1**)–(**3**)

	Compound	Formula	% Yield	M.p. (°C)	Calculated % C	Calculated % H	Found % C	Found % H
(**1a**)	$Fc_2PMe{\cdot}H_2O$	$C_{21}HFe_2P{\cdot}H_2O$	15	149–149.5	59.34	5.22	59.56	5.18
(**1b**)	Fc_2PEt	$C_{21}H_{21}Fe_2OP$	3	156–158	58.38	4.58	58.69	4.99
(**2a**)	FC_2Pt-Bu	$C_{22}H_{23}Fe_2P$	25	118–120	61.44	5.39	61.51	5.66
(**2b**)	$Fc_2P(O)Me{\cdot}H_2O$	$C_{22}H_{23}Fe_2OP{\cdot}H_2O$	6	140–142	58.06	5.32	58.28	5.27
(**3a**)	$Fc_2P(O)Et$	$C_{24}H_{27}Fe_2P$	9	151–153	62.87	5.94	63.18	6.05
(**3b**)	$FC_2P(O)t$-$Bu{\cdot}1/3C_6H_6$	$C_{24}H_{27}Fe_2OP{\cdot}1/3C_6H_6$	11	108–110	62.43	5.84	62.51	6.19

phosphines[4,6]. For example, ferrocenyldimethylphosphine was prepared in 23% yield from dichloroferrocenylphosphine. The starting material, however, was synthesized from ferrocene and (dimethylamino)dichlorophosphine with low and irreproducible yields ranging from 0 to 25%[4b]. The overall yield for $FcPMe_2$ ($\approx$6%) is within the range of our yields for (**1a**)–(**3a**). Better yields of (**1a**) and (**2a**) are realized by reduction of the corresponding phosphine oxides (**1b**) and (**1b**) with lithium aluminum hydride and aluminum chloride, but yields of the oxides themselves are quite low[7].

Compounds (**1a**)–(**3a**) are thermally stable, orange solids which are slightly soluble in hexane and soluble in benzene, toluene and methylene chloride. Exposure to air leads to rapid oxidation of (**1a**)–(**3a**) to the corresponding phosphine oxides. We have experienced considerable difficulty in obtaining accurate microanalyses (Table I) for compounds (**1a**)–(**3a**). Chromatography and repeated recrystallizations were required to obtain pure compounds. A similar problem was encountered in the synthesis of $FcPMe_2$ where the phosphine proved to be an extremely strong σ-donor capable of extracting and complexing aluminum compounds during purification by chromatography on alumina[4b]. Separation of (**1a**)–(**3a**) from the corresponding phosphine oxides (**1b**)–(**3b**) by fractional crystallization was unsuccessful. Analyses of (**1a**) were consistent with the presence of an equivalent of water. Melting points for (**1a**) and (**2a**) are within ± 1 °C of the literature values[7]. Good microanalyses for solvent-free (**2a**) and (**3a**) were achieved, possibly as the greater steric bulk of the larger alkyl group renders coordination to the phosphine more difficult.

Low yields of diferrocenyl(alkyl)phosphine oxides (**1b**)–(**3b**) are obtained as by-products of the synthesis of (**1a**)–(**3a**) and can be separated by chromatography on alumina with benzene and chloroform eluents . No attempt was made to optimize the yields of (**1b**)–(**3b**). The source of the oxygen in (**1b**)–(**3b**) is unknown but formation of the phosphine oxides is still detected even when working under rigorously air-free conditions. The role of water used during the hydrolysis of the aluminate intermediates in the Friedel-Crafts reaction on the formation of (**1b**)–(**3b**) is not known. Addition of de-oxygenated water to solutions of (**2a**) does not produce (**2b**). Surface reactions with alumina can not be ruled out based on the literature pertaining to the purification of $FcPMe_2$[4b]. Elemental analyses of diferrocenyl(ethyl)phosphine oxide (**2b**) are consistent with retention of water even after recrystallization from rigorously dried aromatic hydrocarbon solvents. The presence of water in (**2b**) is confirmed by a single crystal X-ray structure (vide infra). Based on microanalyses, diferrocenyl (*t*-butyl)phosphine oxide (**3b**) retains benzene from either the chromatography or crystallization steps.

Table II. NMR Spectral Data for (**1**)–(**3**)

Compound	^{1}H	$^{31}P\{^{1}H\}$
(**1a**)	4.19 m (2H), 4.15 m (2H), 4.08 m (2H), 4.05 s (10H), 4.00 m (2H), 1.45 d (3H, $J_{PH} = 9$ Hz)	0.25 s
(**2a**)	4.21 br m (2H), 4.15 br m (2H), 4.11 br m (2H), 4.05 s (12H), 1.83 q (2H, $J_{PH} = 8$ *Hz*), 1.17 d of t (3H, $J_{PH} = 8$ Hz)	−34.7 s
(**3a**)	4.23 br m (4H), 4.12 s (10H), 4.05 br m (4H), 1.18 d (9H, $J_{PH} = 9$ Hz)	−0.5 s
(**1b**)	4.39 br m (2H), 4.20 s (12H), 4.16 br m (2H), 4.06 br m (2H), 1.58 d (3H, $J_{PH} = 13$ Hz)	26.9 s
(**2b**)	4.30 br m (2H), 4.27 br m (2H), 4.21 s (10H), 4.06 br m (2H), 4.02 br m (2H), 1.81 d of q (2H, $J_{PH} = 11$ Hz), 1.19 d of t (3H, $J_{PH} = 11$ Hz)	31.4 s
(**3b**)	4.36 br s (2H), 4.28 br s (2H), 4.25 br s (2H), 4.06 s (10H), 4.02 br s (2H), 1.13 d (9H, $J_{PH} = 15$ Hz)	43.2 s

NMR Spectroscopy of (1)–(3)

The ^{1}H NMR spectra (Table II) of (**1a**)–(**3a**) are similar to those reported for diferrocenyl(phenyl)phosphine[10]. The unsubstituted ring appears as a singlet in all three compounds. Four multiplets are observed for the substituted ring protons in (**1a**)[20]. By analogy to dimethyl- and diphenyl(ferrocenyl)phosphine, the upfield resonance are assigned to the protons attached to the ring carbons adjacent to the phosphorus[4b,10]. Three multiplets are observed for the substituted ring protons in (**2a**). Integration of the spectra of (**2a**) indicates that the resonance for the fourth proton on the substituted ring lies under the resonance assigned to the unsubstituted Cp ring. A similar spectrum is reported for $Os_3(CO)_{11}(PEtFc_2)$. The observation of three or four resonances of equal intensity (2H each) for the substituted ring protons of (**1a**) and (**2a**) is the result of chemical inequivalence of the protons of the unsubstituted ring from slow inversion about the phosphorus. The ^{1}H NMR spectrum of (**3a**), however, consists of only two signals for the substituted ring protons and a singlet for the unsubstituted ring protons. ^{31}P NMR spectra of all three diferrocenyl(alkyl)phosphines were singlets.

The ^{1}H NMR spectra of (**1b**)–(**3b**) (Table II) reveal four resonances for the substituted ring protons in each case and a single resonance for the unsubstituted cyclopentadienyl ring. Small differences in chemical shift are observed between the spectra for (**1a**)–(**3a**) and the spectra of the phosphine oxides (**1b**)–(**3b**). In general, there is a downfield shift of the protons in (**1b**)–(**3b**) relative to (**1a**)–(**3a**). The magnitude of the chemical shift difference is sufficient to distinguish the phosphine oxide from the phosphine by NMR. The furthest upfield resonances in (**1b**)–(**3b**) are again tentatively assigned to protons attached to the ring carbons adjacent to the phosphorous by analogy to literature studies of ferrocenyl(phenyl)phosphines[10]. A single resonance is observed in the ^{31}P{H} NMR spectrum of all three diferrocenyl(alkyl)phosphine oxides at chemical shifts downfield from the corresponding phosphines (**1a**)–(**3a**). Large differences in ^{31}P NMR chemical shifts are common between aryl or alkyl phosphines and their phosphine oxides[11].

IR Spectra of (1)–(3)

Infrared spectra of (**1**)–(**3**) are summarized in Table III. The spectra of all six compounds are similar with bands assigned to ferrocenes C-C stretching, CH stretching, C-H in plane and out-of-plane bending modes are observed at similar energies as in diferrocenyl(phenyl)phosphine oxide[12]. Low

Table III. IR Spectral Data (cm^{-1}) for (**1**)–(**3**) in KBr

Compound	ν(P=O)	ν(C-H)	ν(CC)	δ(CH in-plane)	δ(CH out-of-plane)	ν(P-C)	ν(FcP)
(**1a**)	—	3050 w	1384 m	1157 s	819 s	442–506 s	1024 m
(**2a**)	—	3050 w	1383 m	1154 s	817 s	442–490 s	1028 m
(**3a**)	—	3088 w	1339 m	1154 s	814 s	462 s	1024 m
(**1b**)	1181 s	3103 w	1368 m	1195 s	819 s	421–542 s	1025 m
(**2b**)	1188 s	3180 w	1412 m	1150 s	817 s	424–550 s	1028 m
(**3b**)	1198 s	3066 w	1387 m	1167 s	814 s	411–522 s	1033 m

Table IV. Crystal Structure Data and Refinement for (**2b**·H_2O)

Crystal Data	
Molecular Formula	$C_{22}H_{23}Fe_2OP \cdot H_2O$
Color, Habit	Orange plates
Crystal size (mm)	$0.84 \times 0.43 \times 0.11$
Crystal System	Triclinic
Space Group	P1 (No. 2)
Unit Cell Dimensions	$a = 9.115\ (5)$ Å $b = 9.195\ (4)$ Å $c = 12.024\ (6)$ Å $\alpha = 95.51\ (4)^\circ$ $\beta = 97.04\ (4)^\circ$ $\gamma = 90.69\ (4)$ Å
Volume	995.2(9) $Å^3$
Z	2
Formula Weight	464.1
Density (calc.)	1.549 Mg/m^3
Absorption Coefficient	1.551 mm^{-1}
F(000)	480
Data Collection	
Diffractometer Used	Siemens R3m/V
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	296
Monochromator	Highly oriented graphite crystal
2θ Range	5.0 to 50.0°
Scan Type	2θ-θ
Scan Speed	Constant; 2.00°/min in ω
Scan Range (ω)	0.70° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 197 reflections
Index Ranges	$-10 \leq h \leq 10,\ -10 \leq k \leq 10,\ -14 \leq l \leq 14$
Reflections Collected	6996
Independent Reflections	3515 ($R_{int} = 0.98\%$)
Observed Reflections	2817 ($F > 6.0\ \sigma(F)$)
Absorption Correction	Semi-empirical
Min./Max. Transmission	0.5729/0.8992
Solution and Refinement	
System Used	Siemens SHELXTL PLUS Release 4.11 (VMS)

(continued)

Table IV. Continued

Solution	Patterson map
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Extinction Correction	not necessary
Hydrogen Atoms	optimized from diff. Fourier; some refined
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.008\ F^2$
Number of Parameters refined	249
Final R Indices (obs. data)	R = 2.85% wR = 4.05%
R Indices (all data)	R = 3.86 % wR = 4.45%
Goodness-of-Fit	1.19
Largest and Mean Δ/σ	0.002, 0.000
Data-to-Parameter Ratio	11.3:1
Largest Difference Peak	0.41 eÅ^{-3}
Largest Difference Hole	−0.33 eÅ^{-3}

energy absorptions between 400 and 525 $cm^{-1}$are assigned to P-C vibrational modes while the absorptions in the region 1015–1045 are typical of ferrocene-phosphorous moieties[12]. The phosphine oxides (**1b**)–(**3b**) show ν(P=O) at 1177 cm^{-1}, within the range observed for alkyl- and arylphosphine oxides (Ph_3P=O, ν(P=O) 1195 cm^{-1}, Me_3P=O, ν(P=O) 1170 cm^{-1})[11].

Crystal Structure of Diferrocenyl(ethyl)phosphine Oxide (2b·H_2O)

A single crystal of diferrocenyl(ethyl)phosphine oxide monohydrate (**2b**·H_2O) suitable for single crystal X-ray diffraction was grown by slow cooling of a toluene solution. Crystal data and specifics of the data collection and refinement of (**2b**·H_2O) are summarized in Table IV. Selected bond distances and bond angles are listed in Table V. The geometry about the phosphorus atom (Fig. 1) is tetrahedral with C-P-O angles (112–114°) slightly larger than the C-P-C angles (106°). These angles are nearly identical to those reported for both Ph_3P=O and Me_3P=O[11]. The phosphorus- oxygen bond distance (1.485 Å) and the three phosphorus-carbon distances (1.78–1.80 Å) are also the same as those in both alkyl and aryl phosphine oxide structures. There is nothing unusual about the ferrocenyl ligands as bond distances (average $d_{Fe\text{-}C} = 2.038$ Å) and geometry are similar to those observed in ferrocene itself (average $d_{Fe\text{-}C} = 2.045$ Å)[13].

The most interesting feature of the solid state structure of (**2b**·H_2O) is the inclusion of one equivalent of water in the structure (Fig. 2). The

Table V. Selected Bond Lengths and Angles For (**2b**·H_2O)

Bond Lengths (Å)			
Fe(1)-C(11)	2.033 (3)	Fe(1)-C(12)	2.045 (3)
Fe(1)-C(13)	2.053 (3)	Fe(1)-C(14)	2.053 (3)
Fe(1)-C(15)	2.034 (3)	Fe(1)-C(21)	2.047 (3)
Fe(1)-C(22)	2.046 (4)	Fe(1)-C(23)	2.023 (4)
Fe(1)-C(24)	2.026 (3)	Fe(1)-C(25)	2.041 (3)
Fe(2)-C(31)	2.024 (3)	Fe(2)-C(32)	2.036 (3)
Fe(2)-C(33)	2.039 (3)	Fe(2)-C(34)	2.044 (4)
Fe(2)-C(35)	2.036 (3)	Fe(2)-C(41)	2.044 (4)
Fe(2)-C(42)	2.036 (3)	Fe(2)-C(43)	2.025 (4)
Fe(2)-C(44)	2.022 (4)	Fe(2)-C(45)	2.044 (4)
P(1)-O(1)	1.485 (2)	P(1)-C(1)	1.803 (3)
P(1)-C(11)	1.782 (3)	P(1)-C(31)	1.780 (3)
C(1)-C(2)	1.520 (5)	C(11)-C(15)	1.428 (4)
C(11)-C(12)	1.429 (4)	C(12)-C(13)	1.416 (4)
C(13)-C(14)	1.407 (5)	C(14)-C(15)	1.422 (4)
C(21)-C(22)	1.408 (5)	C(21)-C(25)	1.373 (5)
C(22)-C(23)	1.409 (5)	C(23)-C(24)	1.421 (6)
C(24)-C(25)	1.388 (5)	C(31)-C(35)	1.430 (4)
C(31)-C(32)	1.434 (4)	C(32)-C(33)	1.417 (5)
C(33)-C(34)	1.404 (6)	C(34)-C(35)	1.414 (5)
C(41)-C(42)	1.384 (5)	C(41)-C(45)	1.386 (5)
C(42)-C(43)	1.419 (6)	C(43)-C(44)	1.415 (6)
C(44)-C(45)	1.383 (7)	O(3W)-H(3A)	0.863 (55)
O(3W)-H(3B)	0.838 (48)	O(1)···H(3A)	1.977
O(1)···O(3W)	2.814	O(1)···H(3B)	2.060
Bond Angles (°)			
C(1)-P(1)-C(11)	105.8 (1)	C(1)-P(1)-C(31)	105.9 (1)
O(1)-P(1)-C(1)	112.0 (1)	C(11)-P(1)-C(31)	105.8 (1)
O(1)-P(1)-C(31)	114.8 (1)	O(1)-P(1)-C(11)	111.8 (1)
Fe(1)-C(11)-P(1)	127.2 (1)	Fe(2)-C(31)-P(1)	125.5 (1)
P(1)-C(1)-C(2)	112.7 (2)	H(3A)-O(3W)-H(3B)	121.8 (1)
O(3W)-H(3A)···O(1)	163 (5)	O(3W)-H(3B)···O(1)	147 (5)

compound is exposed to water only during the hydrolysis of the diferrocenyl(ethyl)phosphine aluminate salts in the synthesis of (**2a**) and (**2b**). Water is retained by (**2b**) during chromatography, recrystallization from non-polar solvents, drying under vacuum and storage in an inert atmosphere. The orientation of the water molecules points the hydrogens toward the phosphorus-oxygen bonds of two molecules of (**2b**). The average P=O···H

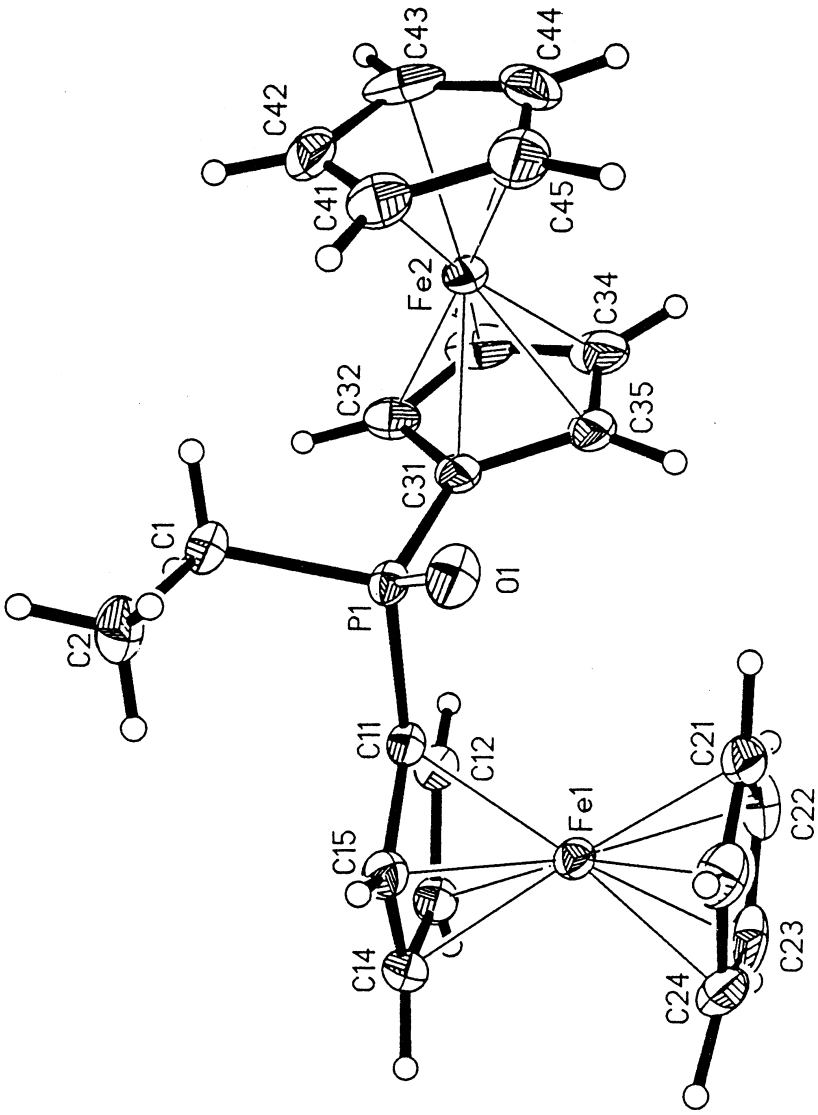


Figure 1. Molecular structure of diferrocenyl(ethyl)phosphine oxide monohydrate (**2b**·H_2O).

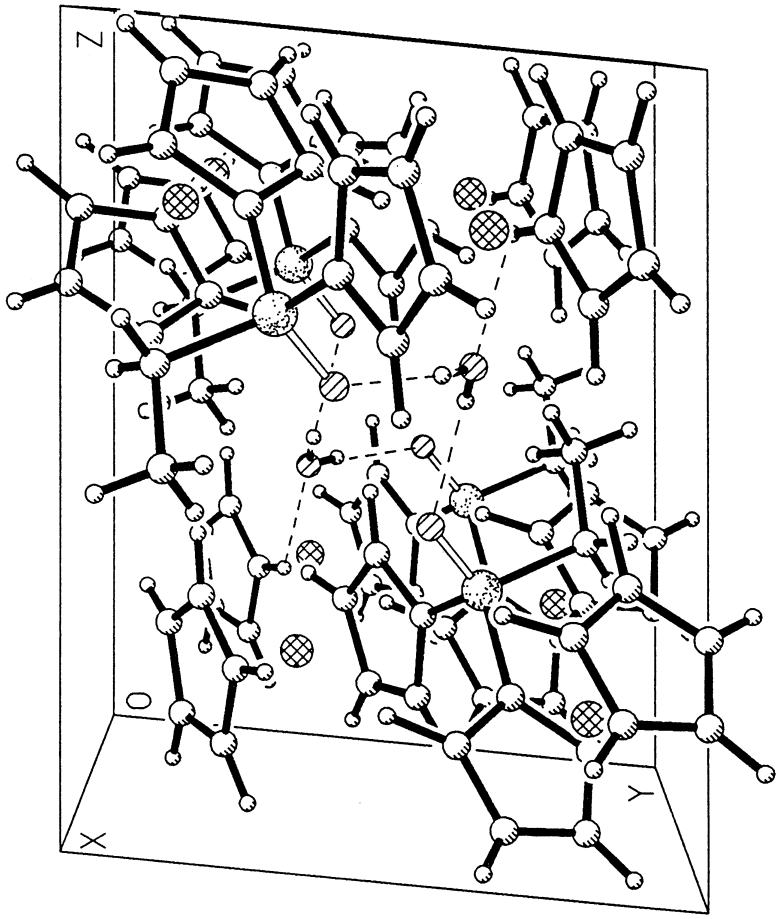


Figure 2. Packing diagram for (**2b**·H_2O) showing the interactions between P=O systems and the H_2O molecules of solvation. Iron atoms are cross-hatched, oxygen atoms are striped diagonally and phosphorus atoms are stipled.

Table VI. Electrochemical Data for **1–3**[a]

Compound	$E_{pa}(E_{pc})$	$(mV)^{0/+}$ ΔE^b	i_{pe}/i_{po}	$E_{pa}(E_{pc})^{+/2+}$	ΔE^b	i_{pa}/i_{pc}	$E_{pa}(E_{pc})^{2+/3+}$	ΔE^b	$E^{+/2+} - E^{0/+}$
Fc_2PMe (**1a**)	70[c]	[c]		390 (300)	90				320
Fc_2PEt (**2a**)	75(32)	43		397 (310)	86				322
Fc_2Pt-Bu (**3a**)	80[c]	[c]		387 (334)	53		633 (560)	73	307
$Fc_2P(O)Me$ (**1b**)	254	54	1.83	394	54	0.73			140
$Fc_2P(O)Et$ (**2b**)	254	60	1.65	406	56	0.70			152
$Fc_2P(O)t$-Bu (**3b**)	244	60	1.47	407	55	0.90			163

[a]Experimental conditions: 1–2 mM solution in CH_3CN containing 0.1–0.2 M [n-Bu_4N][ClO_4] as the supporting electrolyte. Potentials in mV relative to Ag/Ag^+ at 0.00 at a scan rate 100 mV/s.

[b]$\Delta E = E_{pa} - E_{pc}$.

[c]no cathodic wave observed.

distance of 2.019 Å is consistent with the presence of hydrogen bonds between the phosphoryl oxygen and the included water[14]. Hydrogen bonding in hydrates of triphenylphosphine has been reported but not crystallographically demonstrated[11]. To our knowledge, the structure in Fig. 1 represents the first structurally characterized ferrocenyl(alkyl)phosphine oxide. The structures of 1,1′-diphenylphosphinoferrocene oxide and sulfide were reported but details are missing[11].

Electrochemistry of Diferrocenyl(alkyl)phosphines and Phosphine Oxides

Electrochemical oxidation of (**1a**)–(**3a**) in CH_2Cl_2 reveals two oxidations separated by $\approx$300 to 330 mV (Table VI). As expected, the electron-rich, diferrocenyl(alkyl)phosphines are easier to oxidize than diferrocenyl(phenyl)phosphine but are still oxidized at potentials more positive than ferrocene itself[3,15]. The diferrocenyl(alkyl)phosphine oxides (**1b**)–(**3b**) are more difficult to oxidize than the corresponding phosphines (**1a**)–(**3a**) with much smaller separations between the first and second oxidations ($\approx$ 140–160 mV, Table VI). The oxidations of (**1b**)–(**3b**), however, appear to be more reversible (I_{pc}/I_{pa} = 0.70 to 1.83) than for the ferrocenylphosphines (**1a**)–(**3a**).

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