Precursors to Water-Soluble Dinitrogen Carriers. Synthesis of Water-Soluble Complexes of Iron(II) Containing Water-Soluble Chelating Phosphine Ligands of the Type 1,2-Bis(bis(hydroxyalkyl)phosphino)ethane

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The reactions of the water-soluble chelating phosphines 1,2-bis(bis(hydroxyalkyl)phosphino)ethane (alkyl = *n*-propyl, DHPrPE; *n*-butyl, DHBuPE; *n*-pentyl, DHPePE) with $FeCl_2 \cdot 4H_2O$ and $FeSO_4 \cdot 7H_2O$ were studied as routes to water-soluble complexes that will bind small molecules, dinitrogen in particular. The products that form and their stereochemistry depend on the solvent, the counteranion, and the alkyl chain length on the phosphine. In alcoholic solvents, the reaction of $FeCl_2 \cdot 4H_2O$ with 2 equiv of DHBuPE or DHPePE gave *trans*-Fe(L₂)₂Cl₂. The analogous reactions in water with DHBuPE and DHPePE gave only cis products, and the reaction of $FeSO_4 \cdot 7H_2O$ with any of the phosphines gave only *cis*-Fe(L₂)₂SO₄. These results are interpreted as follows. The trans stereochemistry of the products from the reactions of $FeCl_2 \cdot 4H_2O$ in alcohols is suggested to be the consequence of the trans geometry of the $Fe(H_2O)_4Cl_2$ complex, i.e., substitution of the water molecules by the phosphines retains the geometry of the starting material. The formation of *cis*-Fe(DHPrPE)₂Cl₂ is an exception to this result because the coordination of two −OH groups forms two six-membered rings, as shown in the X-ray structure of the molecule. DHBuPE and DHPePE reacted with $FeSO_4 \cdot 7H_2O$ in water to initially yield *cis*-Fe(P₂)₂SO₄ compounds, but subsequent substitution reactions occurred over several hours to give sequentially *trans*-Fe(DHBuPE)₂(H₂O)(SO₄) and then *trans*-[Fe-(DHBuPE)₂(H₂O)₂]SO₄. The rate constants and activation reactions for these aquation reactions were determined and are consistent with dissociatively activated mechanisms. The *cis*- and *trans*-Fe(L₂)₂X (X = (Cl)₂ or SO₄) complexes react with N₂, CO, and CH₃CN to yield trans complexes with bound N₂, CO, or CH₃CN. The crystal structures of the *cis*-Fe(DHPrPE)₂SO₄, *trans*-Fe(DHPrPE)₂(CO)SO₄, *trans*-Fe(DHBuPE)₂Cl₂, *trans*-[Fe(DHBuPE)₂(CO)(Cl)][B(C₆H₅)₄], *trans*-Fe(DMeOPrPE)₂Cl₂, *trans*-Fe(DMeOPrPE)₂Br₂, and *trans*-[Fe(DHBuPE)₂Cl₂]Cl complexes are reported. As expected from using water-soluble phosphines, the complexes reported herein are water soluble (generally greater than 0.5 M at 23 °C).

Introduction

The ability of iron−diphosphine complexes to coordinate N₂[1] suggests they may be useful compounds for separating N₂ from nitrogen-containing natural gas streams.[2] For a transition metal complex to be successfully deployed in a nitrogen-removal process, it must exhibit reversible N₂ absorption and desorption at process-related pressures and

it must have a high selectivity for N₂ over CH₄. In a homogeneous process, high selectivity for N₂ over CH₄ requires that the transition metal complex bind N₂ strongly and have high solubility in a solvent in which CH₄ is poorly

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(1) For overviews of this research area, see: (a) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1987**, *23*, 197. (b) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (c) Leigh, G. J. *Sci. Prog. (Oxford)* **1989**, *291*, 389−412. (d) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200−202*, 379−409. (e) Bazhenova, T. A.; Shilov, A. E. *Coord. Chem. Rev.* **1995**, *144*, 69−145. (f) Poveda, A.; Perilla, I. C.; Perez, C. R. *J. Coord. Chem.* **200**, *54*, 427−440. (g) Hidai, M.; Mizobe, Y. *Top. Organomet. Chem.* **1999**, *3*, 227−241. (h) Shilov, A. E. *New J. Chem.* **1992**, *16*, 213−18.

soluble. Water is an ideal solvent for such a process. However, the known iron−diphosphine complexes are water insoluble, and it is necessary to modify them accordingly. The method we chose to impart water solubility was to use phosphines that are water soluble. Sulfonated phosphines are often used in this capacity,[3,4] but we found that sulfonate groups are often non-innocent and can affect the ability of the iron compounds to react with N_2 or other small molecules. For example, when sulfonated phosphines were used for the chemistry reported herein, N_2 binding was greatly decreased due to competitive binding of the sulfonate group to the iron center.[4d] To avoid this problem, we decided to focus on phosphine ligands that have hydroxyl groups as the water-solubilizing entity. Examples of the phosphines that have been developed are the 1,2-bis(bis(hydroxyalkyl)-phosphino)ethane ligands and the related methoxy derivative, shown below.[4]

n = 1, DHMPE; n = 3, DHPrPE;
n = 4, DHBuPE; n = 5, DHPePE;

DMeOPrPE
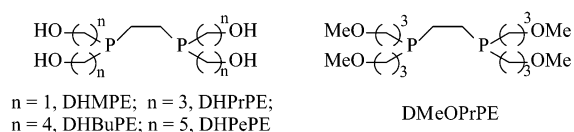
In this paper, we report the synthesis and characterization of the complexes formed in the reactions of these ligands with $FeCl_2 \cdot 4H_2O$, and we compare these compounds to the analogous complexes that have water-insoluble chelating phosphine ligands such as depe (1,2-bis(diethylphos-phino)ethane). In addition, we report the reactions of $FeSO_4 \cdot 7H_2O$ with the 1,2-bis(bis(hydroxyalkyl)phosphino)ethane ligands. The reactions of these complexes with N_2, CO, and CH_3CN are also discussed, and the crystal structures of the cis-$Fe(DHPrPE)_2SO_4$, trans-$Fe(DHPrPE)_2(CO)SO_4$, trans-Fe-$(DHBuPE)_2Cl_2$, trans-$[Fe(DHBuPE)_2(CO)(Cl)][B(C_6H_5)_4]$, trans-$Fe(DMeOPrPE)_2Cl_2$, trans-$Fe(DMeOPrPE)_2Br_2$, and trans-$[Fe(DHBuPE)_2Cl_2]Cl$ complexes are reported. As part of this investigation, we also studied the effect of solvent and counterion on the products obtained in the preparatory reactions. These investigations led to the unexpected and previously unreported results that the transition metal compound stereochemistry is dependent on solvent, coun-teranion, and alkyl chain length on the phosphine.

Experimental Section

Materials and Reagents. Unless otherwise noted, all manipula-tions were carried out in an argon-filled Vacuum Atmospheres Co. glovebox or on a Schlenk line with nitrogen. The 1,2-bis(bis-(hydroxyalkyl)phosphino)ethane ligands were prepared as reported previously.[4b] 1,2-Bis(diethylphosphino)ethane (depe) was obtained from Strem Chemical Co. and used without further purification.

Iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were obtained from Aldrich. Reagent grade methanol, ethanol, and acetonitrile were deoxygenated with an argon purge before being brought into the glovebox. The anhydrous Na_2SO_4 (Aldrich) was used as received. CO was obtained from Linde.

Instrumentation and Procedures. $^{31}P\{^1H\}$ NMR were run on either a VARIAN GEMINI 2000 NMR spectrometer (at BRI) at 121.47 MHz and referenced externally to 1% H_3PO_4 or on a Varian Unity/Inova 300 spectrometer (at UO) at an operating frequency of 299.95 and 121.42 MHz for ^1H and ^{31}P nuclei, respectively. The ^1H and $^{31}P\{^1H\}$ NMR obtained on the latter instrument were referenced to the solvent peak and to an external standard of 1% H_3PO_4 in D_2O, respectively. The samples were sealed under argon in 5 mm tubes fitted with Teflon valves. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT infrared spectropho-tometer (at BRI) or on a Nicolet Magna 550 FT-IR spectrometer (at UO) with OMNIC software. Samples were prepared as either Nujol mulls with NaCl or AgCl windows or in solution with CaF_2 or ZnSe cells. UV−vis spectra were recorded with a Perkin-Elmer Lambda 6 spectrophotometer. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Kinetics Studies. All of the kinetics experiments were performed in H_2O in a thermostated cell. The water was purified to a resistivity of 17−18 MΩ·cm with a Barnstead Nanopure II system. The water was bubbled with oxygen-free N_2 for 1 h prior to use. The reactions were monitored by recording the disappearance of cis-$Fe(DHBuPE)_2$-(SO_4) at $\lambda_{max} = 500$ nm. The kinetics experiments in the presence of Na_2SO_4 were carried out at 293 K. Values of the rate constants reported are an average of at least three individual measurements.

X-ray Structural Analyses. Crystals of **1**, **5**, **8**, **9**, and **10** for X-ray work were manipulated under hydrocarbon grease and sealed in special glass capillaries in the glovebox. The data crystals of **2** and **4**, which remained stable during data collection, were coated with epoxy resin and mounted on glass fibers. Cell dimensions and orientation matrices were determined from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the following θ ranges: **1**, 15−16°; **8**, 14−15°; **2**, 13−14°; **9**, 12−14°; **4**, 14−15°; **5**, 14−15°; and **10**, 14−15°. Table 1 contains a summary of crystal data and the final residuals; fuller tables with particulars of data collection and structure refinement are in the Supporting Information. Data were collected to θ 25° for **1**, **2**, **4**, **5**, and **10** and to θ 22.5° for **8**. Because of crystal decay, data for the weakly diffracting **9** were collected from two crystals, ranges 1.5−20° and 20−23° θ, and the data sets were corrected for decay before they were combined. Structure solutions were obtained from *SIR92 E*-maps.[6] Small absorption corrections were applied to the

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(5) The ^1H NMR spectra of the molecules reported herein were relatively broad and generally similar to the spectra of the uncoordinated phosphine ligand. Therefore, they were nondiagnostic in terms of checking for either purity of the sample or the identity of the molecule. In contrast, the $^{31}P\{^1H\}$ NMR spectra of the molecules were simple, had no overlapping peaks, and were spread over a wide range of chemical shifts. Thus, they provided an excellent means for character-izing and identifying the products and for checking their purity. For the sake of completeness, the ^1H NMR spectra of the complexes are reported in the Experimental Section. For comparison, the ^1H NMR spectra of the ligands are as follows: DHPrPE (MeOH), 1.52 (m, br, 8 H, 4 × P−CH_2), 1.57 (m, br, 4 H, P−CH_2CH_2−P), 1.64 (m, br, 8 H, 4 × CH_2), 3.61 (t, 8 H, 4 × CH_2−OH), 4.8 (s, OH); DHBuPE (D_2O), 1.47 (m, br, 20 H), 1.59 (m, br, 8 H), 3.54 (t, 8 H, 4 × CH_2-OH), 4.80 (s, OH); DHPePE (MeOH), 1.38 (m, br, 28 H), 1.47 (m, br, 8 H), 3.46 (t, 8 H, 4 × CH_2OH), 4.8 (OH).
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Table 1. Crystallographic Data for *trans*-Fe(DHBuPE)$_2$Cl$_2$ (**1**), *cis*-Fe(DHPrPE)$_2$SO$_4$ (**2**), *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (**4**), *trans*-Fe(DMeOPrPE)$_2$Br$_2$ (**5**), *trans*-[Fe(DHBuPE)$_2$(CO)(Cl)][B(C$_6$H$_5$)$_4$] (**8**), *trans*-Fe(DHPrPE)$_2$(CO)SO$_4$ (**9**), and *trans*-[Fe(DHBuPE)$_2$Cl$_2$]Cl (**10**)

	1	2	4	5	8	9	10
compd	C$_{36}$H$_{80}$Cl$_2$-FeO$_8$P$_4$	C$_{28}$H$_{64}$FeO$_{12}$P$_4$S·0.5H$_2$O	C$_{36}$H$_{80}$Cl$_2$-FeO$_8$P$_4$	C$_{36}$H$_{80}$Br$_2$-FeO$_8$P$_4$	C$_{61}$H$_{100}$BCl-FeO$_9$P$_4$	C$_{29}$H$_{64}$-FeO$_{13}$P$_4$S	C$_{36}$H$_{80}$Cl$_3$-FeO$_8$P$_4$
fw	891.67	813.62	891.67	980.57	1203.5	832.62	927.12
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/n$	$C2/c$
a, Å	10.487(3)	10.023(2)	19.747(2)	19.750(2)	10.495(2)	11.6314(8)	14.830(2)
b, Å	10.553(6)	22.427(3)	12.739(1)	12.780(3)	13.037(5)	15.943(2)	21.455(3)
c, Å	12.432(3)	17.195(3)	19.783(2)	20.078(5)	24.822(7)	21.422(3)	15.306(4)
α, deg	64.98(4)	90	90	90	91.61(3)	90	90
β, deg	81.00(2)	100.07(2)	111.39(1)	111.76(2)	99.18(2)	100.152(8)	100.13(2)
γ, deg	67.12(4)	90	90	90	100.96(2)	90	90
V, Å^3	1149(2)	3806(1)	4634(2)	4707(2)	3284(3)	3910(2)	4649(2)
Z	1	4	4	4	2	4	4
d_{calc}, g cm^{-3}	1.289	1.420	1.278	1.384	1.217	1.414	1.325
T, °C	21	22	22	22	21	21	23
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ, cm^{-1}	6.24	6.68	6.19	22.0	4.14	6.52	6.78
rel trans coeff	0.93–1.00	0.92–1.00	0.94–1.00	0.87–1.00	0.96–1.00	0.95–1.00	0.94–1.00
no. of obsd reflns[a]	3550	4361	2607	3299	6254	3368	2472
total indep reflns	4031	6698	3079	4130	8558	5416	4091
$R(F)$[a,b]	0.033	0.084	0.041	0.042	0.063	0.093	0.077
$wR(F^2)$[c]	0.076	0.151	0.096	0.080	0.114	0.155	0.155

[a] $I \geq \sigma(I)$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$.; [c] $wR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$; all independent data.

data for **2** (based on the isotropically refined structure[7]) and for **5** (based on azimuthal scans). The precision of the analyses of **8**, **2**, **9**, and **10** has been restricted by considerable disorder in the side chains; some carbon atoms showed large vibrational anisotropy and unusual apparent bond lengths, and alternative positions were evident in difference maps for some oxygen atoms of the terminal OH groups. The fractional oxygens were generally refined with isotropic thermal parameters. In addition, each of the two independent cations on crystal inversion centers in **8** clearly contained two composite (CO)$_{0.5}$Cl$_{0.5}$ ligands in trans coordination sites. Hydrogen atoms of CH$_2$ groups were included at calculated, updated, positions with $B(H) = 1.2B_{eq}(C)$. Hydrogen atoms of OH groups, where discernible, were included at the observed positions without refinement. There was no evidence for solvent of crystallization in any compound. The TEXSAN[8] program suite, incorporating complex scattering factors,[9] was used in all calculations.

Synthesis of *cis*-Fe(DHPrPE)$_2$SO$_4$ (2). FeSO$_4$·7H$_2$O (1.70 g, 6.11 mmol) and DHPrPE (4.00 g, 12.3 mmol) were stirred overnight in 20 mL of methanol to give a deep purple solution. 1-Propanol (100 mL) was added with stirring and within a few moments a microcrystalline purple solid formed. After 2 h, the solid was collected by filtration, rinsed with 1-propanol, and dried in vacuo. Yield: 4.1 g, 83%. Anal. Calcd for FeC$_{28}$H$_{64}$O$_{12}$P$_4$S: C, 41.80; H, 8.02; P, 15.40; Fe, 6.94. Found: C, 41.90; H, 8.20; P, 14.65, 14.40; Fe, 6.49, 6.57. Dark purple X-ray quality crystals were isolated by cooling a hot saturated 1-propanol solution containing a few drops of methanol as a cosolvent. ^{1}H NMR (CD$_3$OD) at 23 °C: δ 1.3 (m, br), 1.7 (m, br), 2.0 (m, br), 2.3 (m, br), 3.2 (m, br), 3.5 (m, br), 3.7 (m, br), 4.0 (m, br), 4.9 (s, OH).

Reaction of FeCl$_2$·4H$_2$O with DHPrPE. DHPrPE (4.00 g, 12.3 mmol) and FeCl$_2$·4H$_2$O (1.21 g, 6.09 mmol) were dissolved in 30 mL of methanol, giving a deep purple solution. The purple solid was isolated by removing the methanol under vacuum. The ^{31}P-$\{^1$H$\}$ NMR (CD$_3$OD) of the purple solid showed it was a complex

mixture of products. Separation of the mixture was not pursued (see the Discussion section).

Synthesis of *cis*-Fe(DHBuPE)$_2$(SO$_4$) (3). A solution of DHBuPE (1.374 g, 3.596 mmol) in 5 mL of ethanol was slowly added to a stirred solution of FeSO$_4$·7H$_2$O (0.500 g, 1.798 mmol) in ethanol at room temperature. The solution was stirred for 24 h in a glovebox and then filtered through a pipet containing glass wool. The solvent was removed and a purple, oily residue was obtained. The residue was washed with diethyl ether (3 × 25 mL) and then dried under vacuum. The product was a purple solid (yield 87%). IR (Nujol): ν(SO$_4$) 1170, 1122, 947, 637, 607, and 532 cm^{-1}. ^{1}H NMR (CD$_3$-OD) at 23 °C: δ 1.7 (m, br), 2.2 (m, br), 3.6 (m, br), 4.9 (s, OH). Anal. Calcd for C$_{36}$H$_{80}$FeO$_{12}$P$_4$S: C, 47.16; H, 8.80. Found: C, 47.41; H, 8.85.

Synthesis of *trans*-Fe(DHBuPE)$_2$Cl$_2$ (1). DHBuPE (5.00 g, 13.1 mmol) was dissolved in 40 mL of absolute ethanol. FeCl$_2$·4H$_2$O (1.30 g, 6.54 mmol) was added with stirring, giving a green-brown homogeneous solution. The mixture was stirred for 48 h. Diethyl ether (200 mL) was then added over 1–2 min to induce rapid crystallization of a green microcrystalline solid. Yield: 4.95 g, 85%. ^{1}H NMR (CD$_3$OD) at 23 °C: δ 1.5 (m, br), 1.6 (m, br), 1.8 (m, br), 1.9 (m, br), 2.0 (m, br), 2.3 (m, br), 3.6 (m, br), 3.7 (m, br), 4.9 (s, OH). Anal. Calcd for FeC$_{36}$H$_{80}$Cl$_2$O$_8$P$_4$: C, 48.49; H, 9.04; P, 13.89; Fe, 6.26; Cl, 7.95. Found: C, 48.82; H, 9.46; P, 12.97; Fe, 6.30; Cl, 8.04. Green X-ray quality crystals were grown from a saturated ethanol solution by addition of a small amount of toluene.

Synthesis of *trans*-[Fe(DHBuPE)$_2$Cl$_2$]Cl (10). DHBuPE (0.095 g, 0.25 mmol) was added to a stirred solution of FeCl$_3$·6H$_2$O (0.032 g, 0.12 mmol) in 20 mL of absolute ethanol. The solution instantaneously changed from a bright yellowish-green to a deep purple. The mixture was stirred at room temperature for 24 h. Diethyl ether (∼20 mL) was then added, causing a purple solid to precipitate from the reaction solution. The solid was filtered and washed with diethyl ether (∼20 mL). Crystals for X-ray analysis (Figure S4) were grown by evaporation from ethanol and sealed in a 0.7-mm glass capillary.

Generation of *trans*-Fe(DHPePE)$_2$Cl$_2$. This complex was generated in situ by dissolving DHPePE (0.345 g, 0.79 mmol) and FeCl$_2$·4H$_2$O (0.078 g, 0.39 mmol) in 5.0 mL of methanol. The

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Table 2. NMR Data

complex	^{31}P NMR	temp (K)	solvent
trans-Fe(DEPE)$_2$Cl$_2$[a]	62.5	223	toluene
trans-Fe(DHBuPE)$_2$Cl$_2$ (**1**)	55.0 (s, br)	193	CD$_3$OD
trans-Fe(DHPePE)$_2$Cl$_2$	53.2 (s, br)	296	CD$_3$OD
cis-Fe(DHBuPE)$_2$Cl$_2$	cannot be observed	296	H$_2$O
cis-Fe(DHPePE)$_2$Cl$_2$	cannot be observed	296	H$_2$O
cis-Fe(DEPE)$_2$SO$_4$	82.9 (t, $J = 34$ Hz)	193	CD$_3$OD
	64.2 (t, $J = 34$ Hz)		
cis-Fe(DHPrPE)$_2$SO$_4$ (**2**)	71.5 (t, $J = 33$ Hz)	193	CD$_3$OD
	57.9 (t, $J = 33$ Hz)		
cis-Fe(DHBuPE)$_2$SO$_4$ (**3**)	79.0 (t, $J = 34$ Hz)	193	CD$_3$OD
	60.0 (t, $J = 34$ Hz)		
cis-Fe(DHPePE)$_2$SO$_4$	79.0 (t, $J = 34$ Hz)	193	CD$_3$OD
	59.7 (t, $J = 34$ Hz)		
cis-[Fe(DHPrPE)$_2$]SO$_4$ (**2**)	70.0 (t, $J = 34$ Hz)	296	H$_2$O
	56.8 (t, $J = 34$ Hz)		
cis-[Fe(DHBuPE)$_2$SO$_4$] (**3**)	cannot be observed	296	H$_2$O
cis-Fe(DHPePE)$_2$SO$_4$	cannot be observed	296	H$_2$O
trans-[Fe(DEPE)$_2$(CO)Cl$^+$]Cl[b]	ν(C≡O) 1906	296	Nujol
trans-[Fe(DHBuPE)$_2$(CO)Cl$^+$][BPh$_4$] (**8**)	63.4 (s)	296	CD$_3$OD
	ν(C≡O) 1928		1-propanol
trans-[Fe(DHPePE)$_2$(CO)Cl$^+$]Cl$^-$	62.9	296	CD$_3$OD
trans-Fe(DEPE)$_2$(CO)(SO$_4$)	69.1 *(s)*	296	CD$_3$OD
	ν(C≡O) 1928		
trans-Fe(DHPrPE)$_2$(CO)SO$_4$ (**9**)	66.8 (s)	296	CD$_3$OD
	ν(C≡O) 1927		
trans-Fe(DHBuPE)$_2$(CO)SO$_4$	64.3 (s)	296	CD$_3$OD
	ν(C≡O) 1926		
trans-Fe(DHPePE)$_2$(CO)SO$_4$	64.4	296	CD$_3$OD
trans-Fe(DHPrPE)$_2$(CH$_3$CN)SO$_4$	62.2 (s)	296	CH$_3$CN
trans-Fe(DHBuPE)$_2$(CH$_3$CN)SO$_4$	62.0 (s)	296	CH$_3$CN
trans-Fe(DHPePE)$_2$(CH$_3$CN)SO$_4$	61.5 (s)	296	CH$_3$CN
trans-Fe(DMeOPrPE)$_2$Cl$_2$ (**4**)	61.5	193	CD$_3$OD
trans-Fe(DMeOPrPE)$_2$Br$_2$ (**5**)	58.7	247	toluene
trans-Fe(DHBuPE)$_2$(H$_2$O)(SO$_4$) (**6**)	54.6 (s)	233	CD$_3$OD
trans-[Fe(DHBuPE)$_2$(H$_2$O)$_2$](SO$_4$)(**7**)	55.8 (s)	233	CD$_3$OD

[a] Reference 11b. [b] Reference 11a.

resulting solution was yellow-brown. The complex was characterized by NMR (Table 2) but was not isolated.

Synthesis of 1,2-Bis(dimethoxypropylphosphino)ethane (DMeOPrPE). Methylallyl ether (34.0 g, 472 mmol) and 1,2-diphosphinoethane (10.0 g, 106 mmol) were combined in a 500-mL round-bottom flask containing 100 mL of methanol. VAZO 67 (DuPont, 2.5 g) was added as the free-radical initiator and the flask was sealed with a rubber septum held in place with a steel worm clamp. The flask was placed in an oil bath at 60 °C and stirred for 2 days behind a blast shield. (**Safety note**: Because round-bottom flasks are not designed to handle high pressures, it is recommended that the temperature in the flask not exceed 60 °C. Use a blast shield for this procedure.) The mixture was cooled to room temperature followed by workup under inert atmosphere in an argon-filled glovebox. Solvent was removed under vacuum with heating. The resulting yellowish syrup was then dissolved in 300 mL of water by stirring with dropwise addition of 50% aqueous sulfuric acid until the pH was 4. The mixture was filtered to remove the white flocculant impurity. The solution was then neutralized with sodium carbonate and extracted three times with diethyl ether. The ether extracts were combined and then dried over anhydrous sodium sulfate. The ether solution was isolated by filtration and the solvent removed with vacuum to give the pure ligand. Yield: 33.1 g, 82%. ^{31}P{^{1}H} NMR, −26.7 (s).

Synthesis of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (4) and *trans*-Fe-(DMeOPrPE)$_2$Br$_2$ (5). DMeOPrPE (12.79 g, 33.4 mmol) and FeCl$_2$·4H$_2$O (3.32 g, 16.7 mmol) were dissolved in 30 mL of anhydrous toluene with stirring under argon atmosphere at ambient temperature. The resulting green solution was carefully decanted into a clean flask, leaving a small amount of oily, red impurity in

the original vessel. Approximately 20 mL of the toluene was removed under vacuum followed by addition of anhydrous *n*-hexane (50 mL). Vacuum was applied to remove some of the hexane and chill the mixture. A green crystalline product was obtained by filtration followed by hexane rinse and drying in vacuo. Yield 8.0 g, 54%. ^{1}H NMR (CD$_3$OD) at 23 °C: δ 1.7 (m, br), 3.4 (s), 3.9 (m, br), 4.9 (s, OH). The bromide analogue **5** was prepared similarly.

Synthesis of *trans*-Fe(DHBuPE)$_2$(H$_2$O)(SO$_4$) (6). *cis*-Fe-(DHBuPE)$_2$(SO$_4$) (0.50 g., 0.54 mmol) was dissolved in deionized H$_2$O under N$_2$ and stirred for 30 min at 23 °C. The solution changed color from purple to red and some yellow solid was observed. The solution was filtered through glass wool in a pipet, the water was removed under vacuum, and a red oily residue was obtained. The red residue was washed 3 times with 10 mL of diethyl ether and dried under high vacuum for 3 days. The compound was stored in the glovebox. IR (Nujol): ν(H$_2$O), 1653; ν(SO$_4$), see Table 4. ^{31}P-{^{1}H} NMR (CD$_3$OD): δ 54.6 (s). Anal. Calcd for C$_{36}$H$_{82}$-FeO$_{13}$P$_4$S: C, 46.25; H, 8.84. Found: C, 46.35; H, 8.84.

Synthesis of *trans*-[Fe(DHBuPE)$_2$(H$_2$O)$_2$](SO$_4$) (7). The synthesis of *trans*-[Fe(DHBuPE)$_2$(H$_2$O)$_2$](SO$_4$) was carried out as above except the solution was stirred for at least 2 h at 23 °C. A yellow-orange solution resulted, which yielded a yellow oil on removal of the water. A small amount of orange material precipitated when the reaction was over and this was removed by filtration prior to removing the solvent. However, if the starting material is compound **6**, no precipitate is observed and the filtration step is not necessary. ^{31}P{^{1}H} NMR (CD$_3$OD): δ 55.8 (s). ^{1}H NMR (CD$_3$OD) at 23 °C: δ 0.5 (m, br), 1.0 (m, br), 1.3 (m, br), 1.9 (m, br), 2.5 (m, br), 2.7

Table 3. Summary of the Reactions and Products

Fe complex	phosphine (L$_2$)	solvent^a	product	product from reaction with CO or CH$_3$CN (L′)
FeCl$_2$·4H$_2$O	DPPE, DPPP, and many other water-insoluble chelating phosphines	THF or hexane	*trans*-Fe(L$_2$)$_2$Cl$_2$	*trans*-Fe(L$_2$)$_2$(L′)Cl$^+$
FeCl$_2$·4H$_2$O	DEPE	hexane	*trans*-Fe(L$_2$)$_2$Cl$_2$	
FeCl$_2$·4H$_2$O	DEPE	MeOH	*cis*-Fe(L$_2$)$_2$Cl$_2$	
FeCl$_2$·4H$_2$O	DHPrPE	alcohol	mixture of *cis*- and *trans*-Fe(L$_2$)Cl$_2$	*trans*-Fe(L$_2$)$_2$(L′)Cl$^+$
FeCl$_2$·4H$_2$O	DHBuPE	alcohol	*trans*-Fe(L$_2$)$_2$Cl$_2$	*trans*-Fe(L$_2$)$_2$(L′)Cl$^+$
FeCl$_2$·4H$_2$O	DHPePE	alcohol	*trans*-Fe(L$_2$)$_2$Cl$_2$	*trans*-Fe(L$_2$)$_2$(L′)Cl$^+$
FeCl$_2$·4H$_2$O	DMeOPrPE	toluene	*trans*-Fe(L$_2$)$_2$Cl$_2$	*trans*-Fe(L$_2$)$_2$(L′)Cl$^+$
FeCl$_2$·4H$_2$O	DHPrPE	H$_2$O	mixture of *cis*- and *trans*-Fe(L$_2$)Cl$_2$	*trans*-Fe(L$_2$)$_2$(L′)Cl$^+$
FeCl$_2$·4H$_2$O	DHBuPE	H$_2$O	*cis*-Fe(L$_2$)$_2$Cl$_2$	
FeCl$_2$·4H$_2$O	DHPePE	H$_2$O	*cis*-Fe(L$_2$)$_2$Cl$_2$	
FeSO$_4$·7H$_2$O	DHPrPE	alcohol	*cis*-Fe(L$_2$)$_2$SO$_4$	*trans*-Fe(L$_2$)$_2$(L′)SO$_4^+$
FeSO$_4$·7H$_2$O	DHBuPE	alcohol	*cis*-Fe(L$_2$)$_2$SO$_4$	*trans*-Fe(L$_2$)$_2$(L′)SO$_4^+$
FeSO$_4$·7H$_2$O	DHPePE	alcohol	*cis*-Fe(L$_2$)$_2$SO$_4$	*trans*-Fe(L$_2$)$_2$(L′)SO$_4^+$
FeSO$_4$·7H$_2$O	DHPrPE	H$_2$O	*cis*-Fe(L$_2$)$_2$SO$_4$	*trans*-Fe(L$_2$)$_2$(L′)SO$_4^+$
FeSO$_4$·7H$_2$O	DHBuPE	H$_2$O	*cis*-Fe(L$_2$)$_2$SO$_4$	
FeSO$_4$·7H$_2$O	DHPePE	H$_2$O	*cis*-Fe(L$_2$)$_2$SO$_4$	

^{a} Alcohol refers to methanol or ethanol.

Table 4. Selected Infrared Data

compd	proposed coordination of the SO$_4^{2-}$	SO$_4$ (cm^{-1})			ref
		ν_1	ν_3	ν_4	
uncoordinated SO$_4^{2-}$	uncoordinated	983^a (w)	1104 (s)	613 (s)	25a
Cu(en)$_3$SO$_4$	uncoordinated		1088	609	25b
FeSO$_4$·7H$_2$O	uncoordinated	980 (w)	1090 (s)	630 (s)	
trans-[Fe(DHBuPE)$_2$(H$_2$O)$_2$]SO$_4$ **(7)**	uncoordinated^e	c	1150	640, 605	b
cis-[Fe(DHPrPE)$_2$]SO$_4$ **(2)**	uncoordinated	c	1088 (s)	630 (s)	b
cis-Fe(DHBuPE)$_2$SO$_4$ **(3)**	bidentate	947	1170, 1122^c	637, 607, 584	b
Pd(phen)SO$_4$	bidentate	955	1240, 1125, 1040−1015		26a
Pd(py)SO$_4$·H$_2$O	bidentate	930	1235, 1125, 1020		26a
Co(en)$_2$SO$_4$Br	bidentate	993	1211, 1176, 1075	647, 632, 515	26c
Ir(PPh$_3$)$_2$(CO)I(SO$_4$)	bidentate	856	1296, 1172, 880	662, 610	26b
Ru(PPh$_3$)$_2$(NO)Cl(SO$_4$)	bidentate	860	1300, 1170, 885		26b
Cu(bipy)SO$_4$·2H$_2$O	bridging	971	1166, 1096, 1053−1035		26a
[(μ-NH$_2$)(μ-SO$_4$)Co$_2$(NH$_3$)$_4$]$^{-3}$	bridging	995	1170, 1105, 1055		26a
Pd(NH$_3$)$_2$SO$_4$	bridging	960	1195, 1110, 1035		26a
trans-Fe(DHBuPE)$_2$(H$_2$O)(SO$_4$) **(6)**	monodentate	c	1130^d	638, 604	
Pd(NH$_3$)$_2$SO$_4$·H$_2$O	monodentate	970	1140−1110, 1050−1030	617, 593	26a
Co(en)$_2$SO$_4$Br·2H$_2$O	monodentate	978	1130, 1070	645, 652	26c
Cu(en)$_2$SO$_4$	monodentate	965	1114, 1070	613, 602	25b
Fe(DHBuPE)$_2$(CO)SO$_4$	monodentate	939	1154	617, 593	b

^{a} Raman Frequency. ^{b} This work. ^{c} The weak band in the 970-cm^{-1} region is obscured by the Nujol band at 973 cm^{-1}. ^{d} The sulfate band in the 1050-cm^{-1} region is obscured by strong DHBuPE bands. ^{e} Symmetry likely lowered by ion-pairing or other type of outersphere bonding to complex.

(m, br), 3.0 (m, br), 4.9 (s, OH). Anal. Calcd for C$_{36}$H$_{84}$FeO$_{14}$P$_4$S: C, 45.38; H, 8.89. Found: C, 45.56; H, 9.08.

Synthesis of *trans*-[Fe(DHBuPE)$_2$(CO)Cl][B(C$_6$H$_5$)$_4$] (8). *trans*-Fe(DHBuPE)$_2$Cl$_2$ (1.50 g, 1.68 mmol) was dissolved in 30 mL of 1-propanol. NaBPh$_4$ (0.59 g, 1.72 mmol) was added with stirring, giving a green-brown homogeneous solution. The mixture was stirred overnight at ambient temperature under 45 psig of carbon monoxide in a sealed 120-mL Fisher-Porter bottle. The resulting yellow mixture was filtered to remove NaCl, leaving a yellow solution. Crystals were obtained by adding toluene to the solution and letting it stand for several days. ^{1}H NMR (CD$_3$OD) at 23 °C: δ 1.6 (m, br), 2.0 (m, br), 2.1 (m, br), 2.3 (m, br), 3.6 (m, br), 4.9 (s, OH), 6.8 (m, br), 6.9 (m, br), 7.3 (m, br). Anal. Calcd for FeC$_{61}$H$_{100}$BClO$_9$P$_4$: C, 60.88; H, 8.38; P, 10.29; Fe, 4.64; Cl, 2.94. Found: C, 62.84; H, 8.12; P, 11.97; Fe, 4.34; Cl, 3.46. In light of the rather poor elemental analysis for this compound, the purity of this compound was demonstrated by ^{31}P{^{1}H} NMR. See Figure S1 in the Supporting Information.

Synthesis of *trans*-Fe(DHBuPE)$_2$(CO)(SO$_4$). *cis*-Fe(DHBuPE)$_2$-(SO$_4$) (0.50 g, 0.54 mmol) was dissolved in 5 mL of methanol under

N$_2$. The solution was subjected to 3 freeze−pump−thaw cycles and the flask was then filled with CO at 1 atm and stirred for 1 h at room temperature. The solution changed from purple to yellow. The CO was released and the solution was filtered through a pipet containing glass wool. The solvent was removed under vacuum and a yellow oily residue was obtained. The residue was washed three times (10 mL) with diethyl ether and dried under vacuum overnight. A yellow solid was obtained in 80% yield. IR(CH$_3$-OH): ν(CO) 1928 cm^{-1}. IR (Nujol): ν(CO) 1917 cm^{-1}; ν(SO$_4$) 1154, 939, 617, and 593 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_3$OD): δ 66.4 (s). ^{1}H NMR (CD$_3$OD) at 23 °C: δ 1.7 (m, br), 1.8 (m, br), 2.0 (m, br), 2.1 (m, br), 2.5 (m, br), 2.8 (m, br), 3.6 (m, br), 4.9 (s, OH). Anal. Calcd for C$_{37}$H$_{80}$FeO$_{13}$P$_4$S: C, 47.04; H, 8.53. Found: C, 46.50; H, 9.37.

Synthesis of *trans*-Fe(DHPrPE)$_2$CO(SO$_4$) (9). *cis*-Fe(DHPrPE)$_2$-SO$_4$ (2.10 g, 2.61 mmol) was slurried in 30 mL of absolute ethanol and placed in a Fischer-Porter tube. The tube was sealed and removed from the glovebox, and the argon atmosphere was exchanged for 40 psig of carbon monoxide. The sample was then stirred for 12 h at 60 °C, after which time the sample was cooled

to room temperature, the CO atmosphere replaced with argon, and the Fischer-Porter tube returned to the glovebox for workup. The yellow solid was collected on a glass frit and dried under vacuum. Yield: 1.66 g (1.99 mmol, 76%). ^{1}H NMR (CD$_3$OD) at 23 °C: δ 1.7 (m, br), 1.9 (m, br), 2.1 (m, br), 2.5 (m, br), 2.7 (m, br), 3.6 (m, br), 4.9 (s, OH). This synthesis was also carried out in methanol with the same result except that the solvent must be removed in vacuo to recover the product. X-ray quality crystals were obtained by cooling a hot saturated 1-propanol solution of the product.

Synthesis of *trans*-Fe(DHBuPE)$_2$(MeCN)$_2$(SO$_4$). *cis*-Fe(DHBu-PE)$_2$(SO$_4$) (0.400 g; 0.436 mmol) was dissolved in 5 mL of methanol in the glovebox and 2 drops of CH$_3$CN was added to the solution. The solution changed from purple to yellow immediately. The reaction mixture was stirred for 30 min and the solution was filtered through a short pipet containing glass wool. The solvent was removed under vacuum and an oily residue was obtained. The residue was washed with diethyl ether (3 × 10 mL) and the solid thus obtained was dried in a vacuum. The product was a yellow-orange solid (yield 87%). IR(MeOH): (ν_{CN}) 2257 cm^{-1}. IR (Nujol): (ν_{CN}) 2266 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_3$OD): δ 61.7 (s). Anal. Calcd for C$_{40}$H$_{86}$FeN$_2$O$_{12}$P$_4$S·2H$_2$O: C, 46.42; H, 8.77; N, 2.71. Found: C, 46.43; H, 8.52; N, 2.67.

Reactions of *cis*-Fe(DHPePE)$_2$SO$_4$ with CO and CH$_3$CN. A solution of FeSO$_4$ (0.05 M) with 2 equiv of DHPePE in either water or methanol was stirred under 45 psig of CO for several hours. Although the solution changed color to yellow within a few minutes, the extra reaction time was allowed to ensure completion of the reaction. The reaction with acetonitrile was carried out in an NMR tube by adding 1.1 equiv of acetonitrile to the *cis*-Fe(DHPePE)$_2$SO$_4$ solution, generated in situ as described above. The NMR spectra of the products (presumably *trans*-[Fe(DHPePE)$_2$(CO)SO$_4$] and *trans*-[Fe(DHBuPE)$_2$(CH$_3$CN)$_2$]SO$_4$), respectively, were recorded (Table 2), but the products were not characterized further.

Preparation of Dinitrogen Complexes. The Fe sulfate complexes were stirred under dinitrogen in methanol but no dinitrogen binding was observed, as indicated by NMR and IR spectroscopy. The Fe chloride complexes were found to bind dinitrogen when stirred in methanol in the presence of NaBPh$_4$. The dinitrogen complexes were prepared following the method previously reported by Leigh.[10] A typical preparation is the following for [Fe(Cl)(N$_2$)-(DMeOPrPe)$_2$$^+$]BPh$_4$$^-$. Fe(Cl)$_2$(DMeOPrPe)$_2$ (5.00 g, 5.60 mmol) and NaBPh$_4$ (1.92 g, 5.61 mmol) were dissolved in 40 mL of anhydrous THF in a Fisher−Porter tube and stirred under 50 psig of dinitrogen. The green solution immediately turned brown and the pressure of the dinitrogen slowly decreased as the product complex was formed. After 24 h, the solution was filtered to remove the white precipitate of NaCl. The presence of metal-bound dinitrogen was confirmed by FTIR spectroscopy of the solution, which showed a stretch at 2094 cm^{-1}. The ^{31}P{^{1}H} NMR of the complex in acetone-d_6 under 40 psig of dinitrogen (in a 5 mm NMR tube with Teflon valve) showed a single peak at 60 ppm. Because the dinitrogen binding is readily reversible, the product was not isolated in pure form.

Results and Discussion

There are numerous reports on the reactions of iron(II) chloride with water-insoluble 1,2-bis(bis(alkyl)phosphino)-ethanes in nonaqueous solvents.[11] These reactions yield green

(10) Hughes; D. L.; Leigh; G. J.; Jiminez-Tenorio, M.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 75.
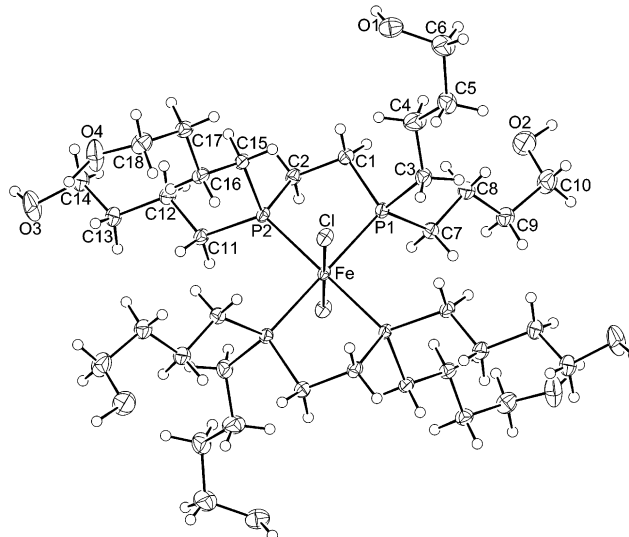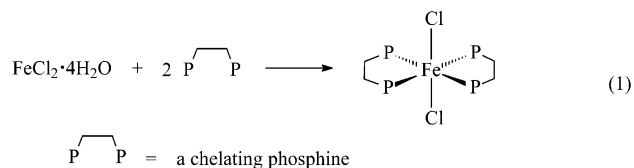
Figure 1. Molecular structure of the *trans*-Fe(DHBuPE)$_2$Cl$_2$ (**1**) complex.

octahedral complexes with two equatorial bidentate phosphines and two trans chloride ligands (eq 1). In contrast,

$$FeCl_2 \cdot 4H_2O \ + \ 2 \ P \frown P \longrightarrow \tag{1}$$

P⌒P = a chelating phosphine

this study found that the reactions of Fe(II) salts with the water-soluble DHPrPE, DHBuPE, and DHPePE ligands gave cis and/or trans products, depending on the solvent, the anion, and the alkyl chain length of the phosphine. The effect of each of these parameters is discussed in the sections below.

Effect of Chain Length. The reaction of 2 equiv of DHBuPE with FeCl$_2$·4H$_2$O in ethanol formed a green solution from which a green product was isolated by addition of ether to the reaction solution. Elemental analysis suggested the molecular formula Fe(DHBuPE)$_2$Cl$_2$, a result confirmed by the X-ray crystal structure of the product (Figure 1). The product has a trans geometry, analogous to the products that are formed by reaction of FeCl$_2$·4H$_2$O with the water-insoluble DEPE, DPrPE, and DBPE chelating diphosphines.[11] These latter complexes have broad ^{31}P NMR resonances at room temperature,[11b] and similarly, *trans*-Fe(DHBuPE)$_2$Cl$_2$ (**1**) also showed a very broad signal at room temperature. This broad band sharpened considerably at −80 °C to give a resonance centered at about 55 ppm.

In contrast to the reaction above, the reaction of 2 equiv of DHPrPE with FeCl$_2$·4H$_2$O in ethanol gave a deep purple solution. Removal of the solvent gave a solid whose ^{31}P-{^{1}H} NMR spectrum in methanol-d_4 showed the presence of more than one product. (Peaks at ≈ 79, 71, and 53 ppm suggested the presence of at least cis and trans isomers of

(11) (a) Bellerby, J. M.; Mays, M. J.; Sears, P. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1232−1236. (b) Baker, M. V.; Field, L. D.; Hambly, T. W. *Inorg. Chem.* **1988**, 27, 2872−2876. (c) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Raithby, P. R.; Fuhrmann, K.; Friend, R. H. *J. Organomet. Chem.* **1992**, 433, 135−139.

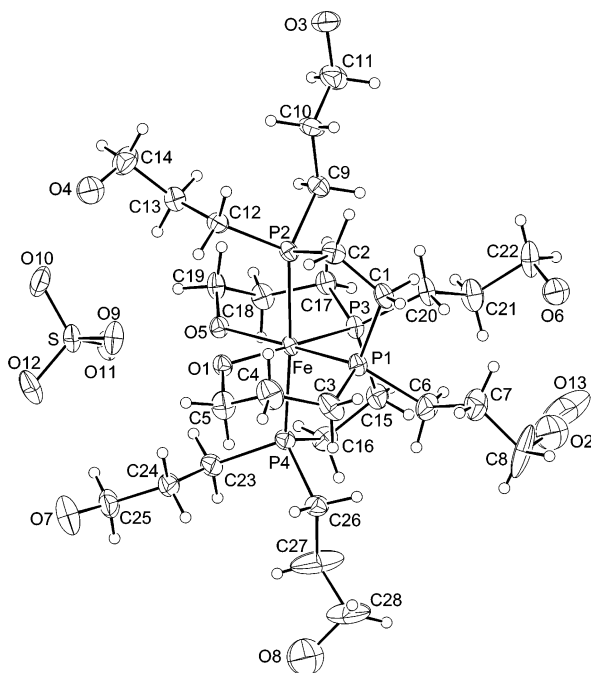**Figure 2.** Molecular structure of the *cis*-Fe(DHPrPE)$_2$SO$_4$ (**2**) complex.

Figure 3. Variable-temperature ^{31}P{^{1}H} NMR spectra of *cis*-Fe-(DHBuPE)$_2$SO$_4$ in methanol-d_4. The peaks labeled "#" and "*" are assigned to the substitution products *trans*-Fe(DHBuPE)$_2$(CD$_3$OD)(SO$_4$) and *trans*-[Fe(DHBuPE)$_2$(CD$_3$OD)$_2$]SO$_4$ (see text).

Fe(DHPrPE)$_2$Cl$_2$.) Attempts to separate and isolate the products of the reaction were unsuccessful, and therefore the synthesis was repeated by using FeSO$_4$·7H$_2$O in place of FeCl$_2$·4H$_2$O. (The strategy here was to replace the two chloride ligands with a chelating ligand, which might stabilize the cis isomer so it could be isolated. Note that in the solid state FeSO$_4$·7H$_2$O contains Fe^{2+} as the Fe(H$_2$O)$_6^{2+}$ complex,[12] whereas FeCl$_2$·4H$_2$O contains *trans*-Fe(H$_2$O)$_4$-Cl$_2$.[13]) As with FeCl$_2$·4H$_2$O, a deep purple solution resulted from the reaction, giving a product with the molecular formula Fe(DHPrPE)$_2$SO$_4$. The NMR of the solution at −80 °C consisted of two triplet resonances at 57.9 and 71.5 ppm (J_{P-P} = 34 Hz), suggestive of a cis geometry. Purple crystals of X-ray diffraction quality were isolated and the crystal structure is shown in Figure 2. As predicted from the NMR spectrum, the complex indeed has a cis geometry. Note that the hydroxyl groups on the propyl chains are non-innocent; two of them coordinate to the Fe to form six-membered rings. Similar coordination of the −OH groups in the DHBuPE ligand in complex **1** (Figure 1) apparently does not occur, probably because the resulting structure would have unfavored seven-membered rings. (*cis*-[Fe(DHPrPE)$_2$]SO$_4$ is designated as **2**.)

In the final experiment of this series, FeCl$_2$·4H$_2$O was reacted with 2 equiv of DHPePE in methanol. As was the case with DHBuPE, a green solution formed containing the trans isomer, as indicated by the single resonance at 53.2 ppm in the ^{31}P NMR spectrum of the solution (Table 2).

The results above are summarized in Table 3 and as follows: FeCl$_2$·4H$_2$O reacts with DHBuPE and DHPePE in methanol or ethanol to form *trans*-Fe(L$_2$)$_2$Cl$_2$. With DHPrPE,
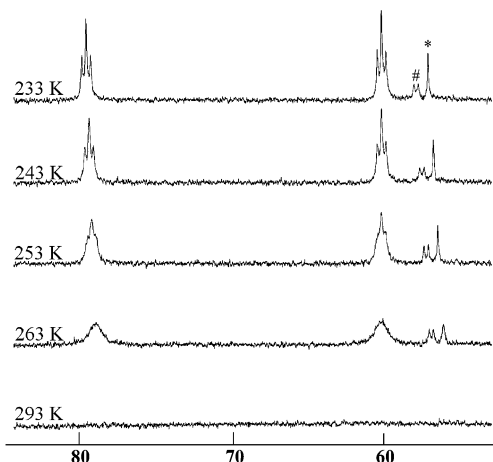
a mixture of cis and trans isomers is formed. As discussed further below, it is suggested that, with the DHPrPE ligand, coordination of two hydroxyl groups stabilizes the cis isomer by forming two six-membered rings; the extra stability this chelation imparts to the molecule drives the conversion of the trans to the cis isomer. Finally, it is noted that FeCl$_2$·4H$_2$O also reacts with water-insoluble chelating phosphine ligands in THF to form trans products.[11] Thus, with the exception of the DHPrPE ligand, the hydroxy alkyl and "regular" alkyl ligands react similarly with FeCl$_2$·4H$_2$O.

Effect of Anion. In contrast to the results above with FeCl$_2$·4H$_2$O, the reaction of FeSO$_4$·7H$_2$O with any of the chelating water-soluble phosphines (DHPrPE, DHBuPE, DHPePE) *in methanol* gave *cis*-Fe(L$_2$)$_2$SO$_4$ (eq 2), as
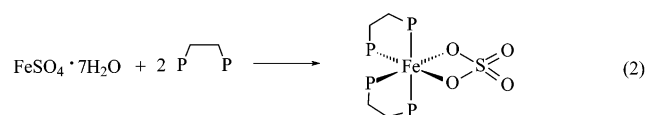
indicated by the characteristic two resonances in the ^{31}P-{^{1}H} NMR spectra at 193 K (Table 2). A sample spectrum, that of *cis*-Fe(DHBuPE)$_2$SO$_4$ (**3**), is shown in Figure 3; note that at room temperature the characteristic triplets are broad, featureless resonances, a result usually attributed either to a diamagnetic/paramagnetic crossover or to a rapid decoordination/re-coordination of one bonding atom in the bidentate ligand.[11b] Likewise, reaction of FeSO$_4$·7H$_2$O with DEPE in methanol gave the cis product, again indicated by two triplet resonances at −80 °C in the ^{31}P NMR spectrum. Evidence for a coordinated bidentate sulfate ligand in these complexes is discussed next. (The two resonances at "*" and "#" ppm in the spectra in Figure 3 are attributed to the methanolysis products *trans*-[Fe(DHBuPE)$_2$(CH$_3$OH)(SO$_4$)] and *trans*-[Fe-(DHBuPE)$_2$(CH$_3$OH)$_2$]SO$_4$. These species are also formed in other reactions and are discussed in a later section.)

Recall that the sulfate ligand is not coordinated to the Fe in *cis*-[Fe(DHPrPE)$_2$]SO$_4$. To determine if *cis*-Fe-(DHBuPE)$_2$SO$_4$ has a similar coordination sphere, repeated attempts were made to grow crystals for X-ray analysis.

(12) Nicholls, D. In *Comprehensive Inorganic Chemistry*; Trotman, A. F., Ed.; Pergamon Press: New York, 1973; Vol. 3, p 1026.
(13) Penfold, B. R.; Grigor, J. A. *Acta Crystallogr.* **1959**, *12*, 850−854.

Unfortunately, the attempts were unsuccessful, and therefore the infrared spectrum of the product was examined to determine the coordination mode of the sulfate ligand.[14] Sulfate can be present in a metal complex in several different ways: as a monodentate ligand, as a bidentate ligand, as a bridged bidentate complex, or as a noncoordinated counterion.[15] These coordination modes can be distinguished by the fact that the sulfate ν_3 and the ν_4 modes each give rise to two IR bands in the monodentate form, three in the bidentate form, and only one when uncoordinated.[15] The infrared data for **2**, **3**, and related complexes are summarized in Table 4. As expected from the X-ray structure, the IR spectrum of **2** is consistent with the presence of a noncoordinated sulfate ligand. (The bands at 1088 (s) and 630 (s) cm^{-1} are assigned to uncoordinated sulfate. For comparison, free sulfate in the form of Na_2SO_4 has bands around 1104 (s), 983 (w), and 613 (s) cm^{-1}. See Table 4 for additional comparisons to complexes having uncoordinated sulfate counterions.[15]) Note the IR spectrum of **3** (Table 4; Figure S2) is quite different from that of **2** and shows bands in the sulfate region at 1170, 1122, 947, 637, 607, and 584 cm^{-1}. Suggested band assignments are shown in Table 4. (The additional bands in the spectrum of **3** at 1025−1060, 981, and 890 cm^{-1} (Figure S2) are assigned to the DHBuPE ligand (Table S1 in the Supporting Information). For comparison, Figure S2 also shows the spectrum of *trans*-Fe(DHBuPE)$_2$Cl$_2$ (**1**), which also has DHBuPE bands at 1025−1060, 985, and 890 cm^{-1}. The 1025−1060 cm^{-1} absorption consists of several overlapping bands, which likely obscure the sulfate band in **3** that is also in this region. For additional reference, the uncoordinated DHBuPE ligand exhibited strong IR bands at 1025−1060 and 985 cm^{-1} (Table S1).) Comparing the IR spectrum of **3** with the other complexes in Table 4 suggests that the sulfate group is chelating or bridging. The latter possibility is unlikely because a dimer of formula (DHBuPE)$_2$Fe(μ-SO$_4$)$_2$Fe(DHBuPE)$_2$ is severely sterically congested due to the numerous hydroxy-butyl groups. For that reason a monomeric complex with a chelating sulfate ligand is proposed for **3** (eq 2).

In water, DHPrPE reacted with FeSO$_4$·7H$_2$O to yield purple *cis*-[Fe(DHPrPE)$_2$]SO$_4$ (**2**), the same product formed in methanol, as indicated by the ^{31}P NMR spectrum of the product in methanol (Table 2). DHBuPE and DHPePE also reacted with FeSO$_4$·7H$_2$O in water to initially yield purple solutions. No ^{31}P NMR signals were observed at ambient temperature for either of these products. (Again, rapid decoordination/re-coordination of one arm of the bidentate phosphine ligand or a spin state change may prevent the observation of signals for these compounds.[11b]) Each of these latter two solutions underwent additional reactions over the course of several hours to give orange solutions, the ^{31}P NMR spectra of which are characteristic of trans compounds. These reactions were thoroughly investigated and are discussed after

the sections below on solvent effects and interpretations. ^{31}P NMR data for all the products are summarized in Table 2.

Solvent Effects. With three exceptions, the reactions of FeSO$_4$·7H$_2$O or FeCl$_2$·7H$_2$O with 2 equiv of DHPrPE, DHBuPE, or DHPePE in water or methanol formed *cis*-Fe-(L$_2$)$_2$X (X = (Cl)$_2$ or SO$_4$). The three exceptions to this generalization, already discussed, are the reactions of FeCl$_2$·4H$_2$O with DHBuPE and DHPePE in methanol, both of which give the trans product, and DHPrPE, which forms a mixture of the cis and trans isomers. Note that the reaction of FeCl$_2$·4H$_2$O with DEPE in hexane gave the trans product, but the reaction of FeSO$_4$·7H$_2$O with DEPE in methanol gave the cis product.

Interpretation of the Reactivity. The results in the preceding sections are summarized and interpreted as follows.

In methanol or ethanol, the reactions of FeCl$_2$·4H$_2$O with 2 equiv of any bidentate phosphine other than DHPrPE give a trans product. This stereochemisty is suggested to be the consequence of the trans geometry of the FeCl$_2$·4H$_2$O starting material,[13] i.e., substitution of the water molecules by the phosphines retains the geometry of the starting complex (eq 3). Fe(DHPrPE)$_2$Cl$_2$ is an exception to this result; some cis

$$\text{(3)}$$
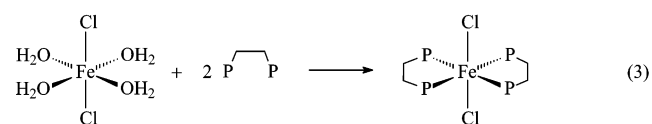
product also forms because the −OH groups on two of the ligands can coordinate to the Fe center, forming two chelating six-membered rings. The cis isomer is preferred in this molecule, probably for electronic reasons because the π-donor O atoms are trans to the π-accepting phosphines. Consistent with this interpretation, it is noted that when the −OH groups in the DHPrPE ligand are replaced with −OMe the resulting product has coordinated trans chloride ligands, analogous to the *trans*-Fe(DHBuPE)$_2$Cl$_2$ (**1**) and *trans*-Fe-(DHPePE)$_2$Cl$_2$ complexes. A crystal structure of the *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ complex (**4**) is shown in Figure 4. (The crystal structure of the isomorphous *trans*-Fe(DMeOPrPE)$_2$Br$_2$ complex (**5**) is shown in the Supporting Information.)

All of the remaining reactions initially favor products with cis stereochemistry. Thus, the bidentate ligands react with FeCl$_2$·4H$_2$O in water (where Fe(H$_2$O)$_6^{2+}$ is the predominant species) to give predominantly cis products and with FeSO$_4$·7H$_2$O in water or alcohols to give predominantly cis products. The cis isomers are the predominant product probably for several reasons. In the case of FeSO$_4$·7H$_2$O in methanol, a coordinated bidentate sulfate counterion will force the two chelating phosphines into a cis orientation (eq 4). The reasons

$$\text{(4)}$$

L = H$_2$O, CH$_3$OH, CH$_2$CH$_3$OH

for a cis geometry in water are less clear. In water, the sulfate ligand is likely not coordinated to the Fe center, and it may

(14) The infrared spectra were obtained in Nujol because the complex degraded quickly when it was mixed with KBr.
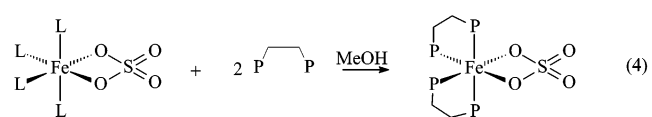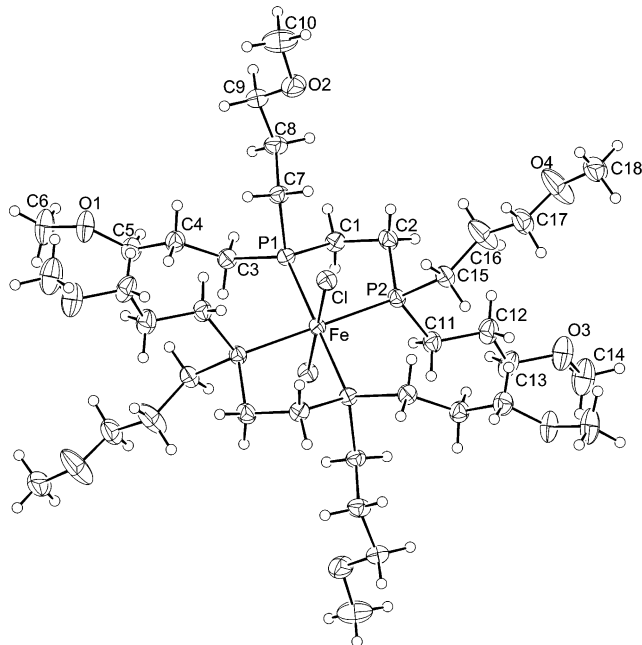
(15) Nakamoto, N. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B. Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1997; pp 79−82.

Figure 4. Molecular structure of the *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (**4**) complex.

be that the formation of the cis isomer is statistically determined. (Coordination of two bidentate ligands will result in $^5/_6$ cis and $^1/_6$ trans isomer.) Alternatively, the cis geometry may be directed by steric interactions between the hydroxy-alkyl groups on the phosphines. Note that in aqueous solution, the cis products slowly react to form trans complexes (except in the case of the DHPrPE ligands for which, as already discussed, the coordinated −OH groups stabilize the cis isomer). These reactions were studied in detail and are discussed in the next section.

Reaction of *cis*-Fe(DHBuPE)$_2$SO$_4$ with H$_2$O. Synthesis and Characterization of Fe(DHBuPE)$_2$(L)$_n$SO$_4$ (L = H$_2$O; *n* = 1 or 2). DHBuPE and DHPePE reacted with FeSO$_4$·7H$_2$O in water to initially yield *cis*-Fe(P$_2$)$_2$SO$_4$ compounds. Subsequent reactions occurred over several hours to give new products. These products were isolated for the case of P$_2$ = DHBuPE, and subsequent characterization identified the products as *trans*-Fe(DHBuPE)$_2$(H$_2$O)(SO$_4$) (**6**) and *trans*-[Fe(DHBuPE)$_2$(H$_2$O)$_2$]SO$_4$ (**7**) (Scheme 1). The complexes were synthesized and isolated pure (as indicated by elemental analysis) by stirring **3** in water at room temperature for 0.5 (**6**) or 2 h (**7**). The trans stereochemistry of each molecule was indicated by the ^{31}P{^{1}H} NMR spectra, which showed a single resonance at δ 54.6 and 55.8 for **6** and **7**, respectively. Note that the chemical shifts of these resonances are in agreement with other related trans iron chelating-phosphine complexes.[16]

The IR spectrum of **6** is consistent with the presence of a monodentate sulfate group: the sulfate bands at 1130, 638, and 604 cm^{-1} are in good agreement with other monodentate sulfate complexes reported in the literature (Table 4).[15] (The

(16) (a) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J. *J. Organomet. Chem.* **1990**, *391*, C41. (b) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872. (c) Baker, M. V.; Field, L. D. *J. Organomet. Chem.* **1988**, *354*, 351.
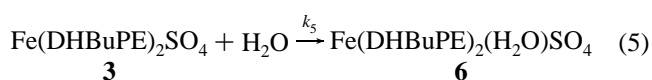
expected band in the 1050-cm^{-1} region is obscured by the broad peaks attributed to the DHBuPE ligand, Table S1.) Further support for a coordinated sulfate ligand in **6** comes from the reaction of **3** in water in the presence of added Na$_2$SO$_4$; only **6** formed and the formation of **7** was inhibited, as would be expected by the common-ion effect (mass-law retardation) for a mechanism involving the loss of a monodentate sulfate ligand.

As was the case with **3**, the ^{1}H NMR spectra of **6** and **7** were not particularly diagnostic. Both complexes exhibited a broad resonance for the alkoxybutyl groups of the phosphine ligands. Furthermore, the resonance for the H$_2$O ligand coordinated to the Fe atom in **6** was not observed, likely because of rapid H/D exchange with the CD$_3$OD solvent. Finally, note that **6** and **7** were only soluble in H$_2$O or CH$_3$OH. They did not dissolve in other common deuterated solvents such as acetone-d_6, CD$_3$Cl, or C$_6$D$_6$, and they decomposed in ethanol.

Attempts to recrystallize **6** and **7** for X-ray analysis were unsuccessful because they back-reacted to form **3** when dissolved in methanol and set aside to crystallize. For example, complex **6** reverted to **3** in about 7 days in methanol. Thus, the ^{31}P{^{1}H} NMR spectrum of this crystallization solution after 7 days showed a small residual resonance for **6** and two new resonances at δ 79.0 (t, J_{P-P} = 34 Hz) and 60.0 (t, J_{P-P} = 34 Hz), assigned to **3**. In addition, two minor peaks at 57.7 (d, J_{P-P} = 40 Hz) and 56.8 (s) were present. These peaks are conditionally assigned to the methanol-substituted complexes *trans*-[Fe(DHBuPE)$_2$(CH$_3$OH)(SO$_4$)] and *trans*-[Fe(DHBuPE)$_2$(CH$_3$OH)$_2$]SO$_4$ (Scheme 1). These complexes could not be isolated, but it is noted that the same species grew in slowly when **3** was dissolved in methanol-d_4 (Scheme 1; Figure 3), which lends credence to the suggestion that they are solvent-substituted species. Complex **7** also backreacted: when **7** was dissolved in methanol-d_4 at room temperature it initially formed **6** and then converted to **3**, as monitored by ^{31}P{^{1}H} NMR. Again, small amounts of the putative methanol-substituted complexes *trans*-[Fe(DHBuPE)$_2$(CH$_3$OH)(SO$_4$)] and *trans*-[Fe-(DHBuPE)$_2$(CH$_3$OH)$_2$]SO$_4$ also formed.
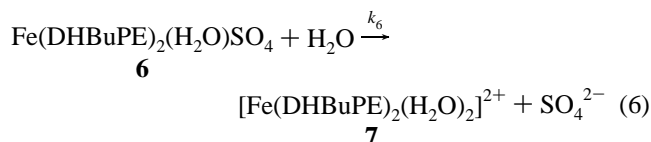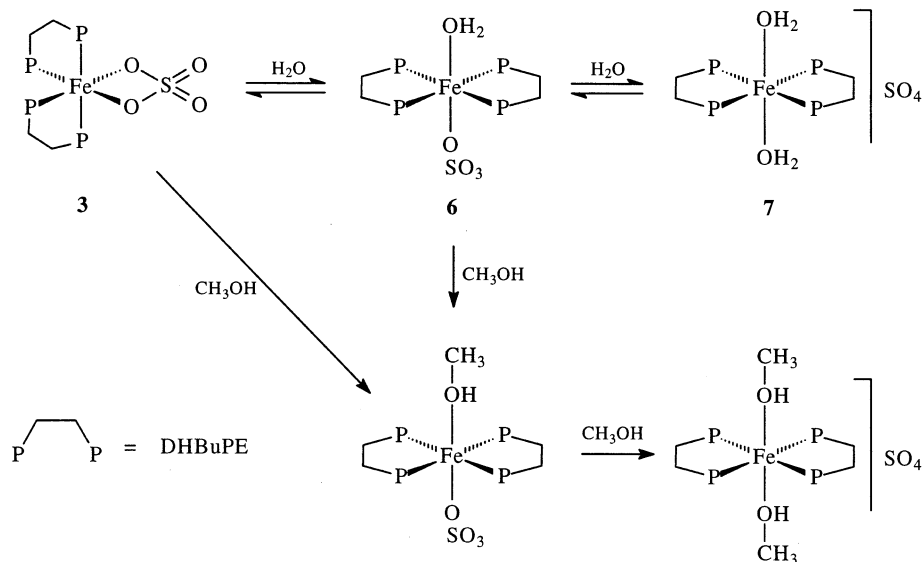
The reaction sequence **3** → **6** → **7** is also reversible in the solid state. When a solid sample of **6** (red) or **7** (orange) was heated at 363 K under vacuum for 3 h, the solid turned purple and the ^{31}P{^{1}H} NMR spectrum of the product in methanol at 233 K showed the resonances for **3** with small amounts of **6** or **7**.

Kinetics Studies of the 3 → 6 → 7 Reactions in H$_2$O. The kinetics of the reaction of **3** in water to form **6** and **7** were monitored by following the disappearance of the starting material at λ_{max} = 500 nm. The changes in absorbance with time were fit to a biexponential function. The biphasic kinetics are consistent with two successive substitution reactions that occur according to eqs 5 and 6 with k_5 = (2.79 ± 0.29) × 10^{-3} s^{-1} and k_6 = (3.99 ± 0.07) × 10^{-4} s^{-1} at 25 °C.[17,18]

$$\text{Fe(DHBuPE)}_2\text{SO}_4 + \text{H}_2\text{O} \xrightarrow{k_5} \text{Fe(DHBuPE)}_2(\text{H}_2\text{O})\text{SO}_4 \quad (5)$$
$$\mathbf{3} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{6}$$

Scheme 1. Reaction of *cis*-Fe(DHBuPE)₂SO₄ (**3**) in H₂O to Form Successively *trans*-Fe(DHBuPE)₂(H₂O)(SO₄) (**6**) and *trans*-[Fe(DHBuPE)₂(H₂O)₂]SO₄ (**7**), as Well as the Reactions of **3** and **6** in CH₃OH to Form *trans*-[Fe(DHBuPE)₂(CH₃OH)(SO₄)] and *trans*-[Fe(DHBuPE)₂(CH₃OH)₂]SO₄

$$\text{Fe(DHBuPE)}_2\text{(H}_2\text{O)SO}_4 + \text{H}_2\text{O} \xrightarrow{k_6}$$
$$\mathbf{6}$$

$$[\text{Fe(DHBuPE)}_2\text{(H}_2\text{O)}_2]^{2+} + \text{SO}_4^{2-} \quad (6)$$
$$\mathbf{7}$$

To probe the mechanisms of these aquation reactions, the effect of added Na₂SO₄ and the temperature dependences of the reaction rates were studied. The rate constants at various temperatures over the range 282−307 K are summarized in Table S2. The activation parameters, obtained from an Eyring plot of the data, are $\Delta H^{\ddagger}_5 = 15.0 \pm 1.8$ kcal mol⁻¹, $\Delta S^{\ddagger}_5 = -21.0 \pm 1.6$ cal mol⁻¹, $\Delta H^{\ddagger}_6 = 13.0 \pm 0.5$ kcal mol⁻¹, and $\Delta S^{\ddagger}_6 = -31.3 \pm 1.4$ cal mol⁻¹. In the experiments with added Na₂SO₄, the only product formed was **6**; no **7** was formed. In addition, the added SO_4^{2-} retarded the formation of **6** from **3**. For example, when $[SO_4^{2-}] = 1.50 \times 10^{-4}$ M, the rate of reaction 5 was 23 times smaller than in the absence of added SO_4^{2-} (k_5(with SO_4^{2-}) = 1.22×10^{-4} s⁻¹ vs k_5(without SO_4^{2-}) = 2.79×10^{-3} s⁻¹ at 25 °C).[18] The inhibition by added SO_4^{2-} suggests a dissociative mechanism for both substitution reactions. Although positive values of $\Delta S^{\ddagger}$ are generally expected for dissociative processes, the rather negative values for reactions 5 and 6 are likely attributable to solvent ordering as the ionic sulfate ligand

and ionic metal complex separate.[19] There are few appropriate aquation reactions of Fe(II) complexes in the literature for comparison to reactions 5 and 6, but it is noted that the activation parameters for aquation of Fe(phen)(H₂O)₄²⁺ are $\Delta H^{\ddagger} = 12.8$ kcal/mol and $\Delta S^{\ddagger} = -16$ cal/mol, both of which compare favorably to the values for reactions 5 and 6.[20]

Water Solubilities. The DHPrPE, DHBuPE, and DHPePE complexes synthesized in this study are appreciably water soluble. Selected solubilities in water at 23 °C are as follows: *cis*-Fe(DHPrPE)₂SO₄ (**2**), >0.63 M; *trans*-Fe-(DHPrPE)₂(CO)SO₄, 0.63 M; *cis*-Fe(DHBuPE)₂SO₄, 0.56 M; *trans*-Fe(DHBuPE)₂(CO)SO₄, 0.16 M; and *trans*-FeCl₂-(DHBuPE)₂, 0.43 M.

Reactions of *cis*- and *trans*-Fe(L₂)₂(X) with N₂, CO, and CH₃CN in Alcohols. The complexes synthesized above can be used to bind a variety of small molecules for possible separation purposes. In the literature it is reported that the *trans*-Fe(L₂)Cl₂ complexes (where L₂ is one of the water-insoluble chelating phosphine ligands) react with ligands such as N₂, CO, and CH₃CN in methanol or acetone[11a] to form complexes of the type *trans*-Fe(L₂)(L′)Cl⁺ or *trans*-Fe(L₂)-(L′)₂²⁺ (L′ = N₂, CO, CH₃CN, etc.). In this study, similar reactivity and products were found for the reactions of the Fe(L₂)(X) complexes (X = SO₄ or (Cl)₂; L₂ = one of the water-soluble chelating phosphines used in this study) with N₂, CO, and CH₃CN in methanol. For example, *trans*-Fe-(DHBuPE)₂Cl₂ (**2**) reacted with CO in methanol to give [*trans*-Fe(DHBuPE)₂(CO)Cl]Cl. The tetraphenylborate salt was isolated as yellow crystals (designated as compound **8**), and the X-ray structure is shown in Figure 5. Note that the trans products formed in these reactions regardless of reactant stereochemistry, reaction solvent, counterion, or alkyl chain length. The reaction of *trans*-Fe(DHBuPE)₂Cl₂ with N₂ in

(17) A small amount of an orange-yellow solid precipitated from solution after the kinetics runs were complete. A similar observation was made when **3** was dissolved in H₂O containing NaSO₄ to suppress the formation of **7**, i.e., **6** formed along with a small amount of the orange-yellow precipitate. However, the orange-yellow solid did not form when **6** reacted in H₂O to give **7**. The orange-yellow solid was not soluble in common organic solvents. The ³¹P{¹H} NMR spectra of the reaction solution in which the precipitate formed showed trace amounts of free phosphine (δ −23.4) and phosphine oxide (δ 56.6). The pH of the reaction solutions was 6.6. A decrease in pH increased the rate, and above pH 7.5, a white precipitate (perhaps Fe(OH)₂) formed quickly.

(18) As expected for mass law retardation of a rate, the retardation was dependent on the concentration of the SO_4^{2-}, as shown in the following ([Na₂SO₄]/10⁻² M, k_1/10⁻⁴ s⁻¹): 0, 27.9 ± 0.29; 0.15, 1.22 ± 0.03; 0.75, 1.00 ± 0.12; 1.50, 0.65 ± 0.08.

(19) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH Publishers: New York, 1991; pp 105−106.

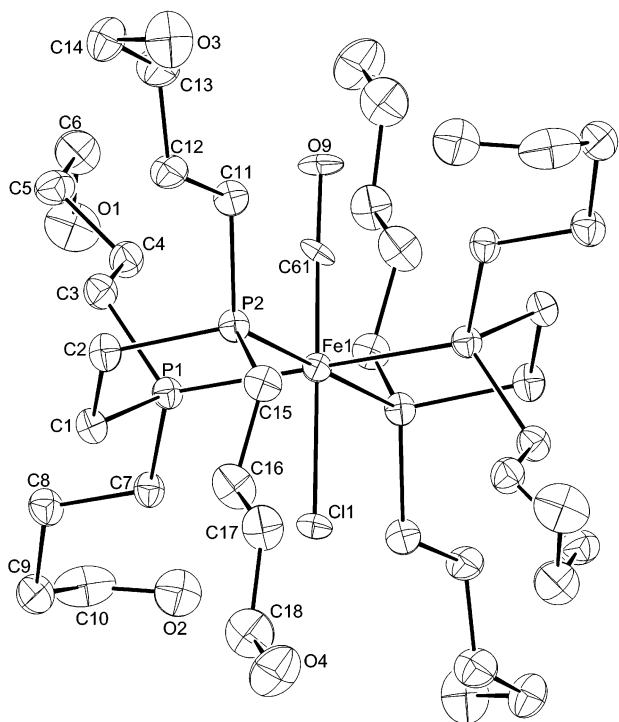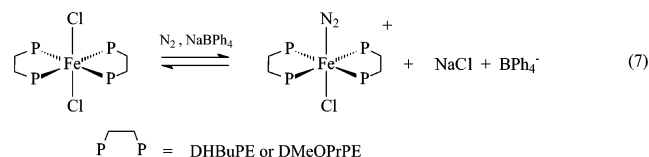(20) Bell R. S.; Sutin, N. *Inorg. Chem.* **1962**, *1*, 359.

Figure 5. Molecular structure of the *trans*-[Fe(DHBuPE)$_2$(CO)(Cl)]-[B(C$_6$H$_5$)$_4$] (**8**) complex.

the presence of NaBPh$_4$ gave [*trans*-Fe(DHBuPE)$_2$(N$_2$)Cl]-BPh$_4$. The N≡N stretch was observed at 2095 cm^{-1}.[21] The

$$\text{P}\diagdown\text{P} \;=\; \text{DHBuPE or DMeOPrPE}$$

reaction is reversible, as indicated by the decrease in the intensity of the N$_2$ peak in the IR spectrum when vacuum is applied to the reaction solution. The band increased in intensity on subsequent reexposure to N$_2$. This reversible N$_2$ binding was also observed by ^{31}P{H} NMR, which showed the reversible appearance and disappearance of a resonance at 59 ppm. The *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ complex reacted analogously with N$_2$ and CO, forming products with ν(N≡N) at 2094 cm^{-1}, ^{31}P{H} 60 ppm and ν(C≡O) at 1930 cm^{-1}, ^{31}P{H} 64 ppm, respectively.

In another example, *cis*-Fe(DHPrPE)$_2$SO$_4$ (**2**) reacted readily with CO in methanol to give a yellow solution from which *trans*-Fe(DHPrPE)$_2$(CO)SO$_4$ (**9**) was isolated (Scheme 2; for spectroscopic data see Table 2). The crystal structure of this complex is shown in Figure 6; note the monodentate coordination of the sulfate ligand. For comparison purposes, it was found that *cis*-Fe(DEPE)$_2$SO$_4$ reacted with CO in methanol to give the yellow *trans*-Fe(DEPE)$_2$(CO)(OSO$_3$) complex. (This complex was not isolated as a solid, but was characterized in solution by IR and NMR. The ^{31}P NMR spectrum showed a singlet at 69.1 ppm (23 °C) and the IR showed a single, intense carbonyl stretch at 1928 cm^{-1}.)

(21) See ref 15, pp 173−176.

Scheme 2. Reactions of **2**, **3**, and **6** with CO
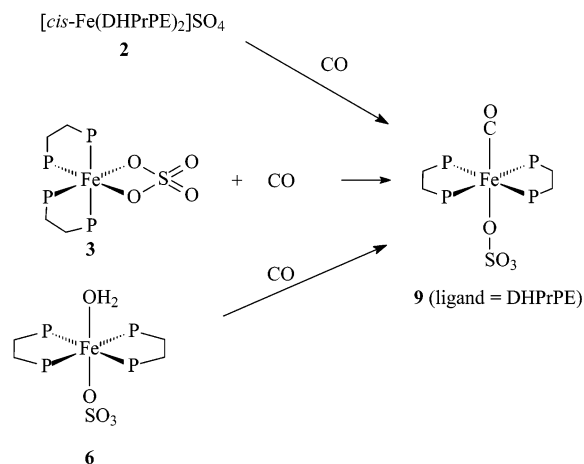
cis-Fe(DHBuPE)$_2$SO$_4$ (**3**) also reacted with 1 atm of CO at room temperature in methanol (Scheme 2). The IR spectrum of the reaction solution after 30 min showed a band at 1928 cm^{-1}, indicative of a carbonyl ligand.[22] The ^{31}P-{^{1}H} NMR exhibited only one resonance (at δ 66.4), indicative of a trans geometry. The IR spectrum of the product in Nujol showed bands corresponding to the sulfate ligand coordinated in a monodentate fashion (ν(SO$_4$) = 1154, 939, 617, and 593 cm^{-1}; the ν(CO) band was at 1917 cm^{-1} in Nujol (Figure S2)). The product is assigned the formula *trans*-Fe(DHBuPE)$_2$(CO)SO$_4$ (Scheme 2).

In a related reaction, *cis*-Fe(DHBuPE)$_2$SO$_4$ (**3**) was dissolved in methanol and two drops of CH$_3$CN were added to the solution. The starting material reacted immediately (as indicated by an immediate color change from purple to yellowish) and the IR spectrum in methanol showed a ν-(CN) band at 2257 cm^{-1} (2266 cm^{-1} in Nujol), indicative of a coordinated CH$_3$CN ligand.[23] The ^{31}P{^{1}H} NMR of the product exhibited a single resonance at δ 61.7, indicative of trans stereochemistry. *cis*-Fe(DHBuPE)$_2$SO$_4$ (**3**) is not soluble in neat CH$_3$CN, but a slurry of *cis*-Fe(DHBuPE)$_2$SO$_4$ in CH$_3$-CN reacted in the solid state to give the same complex as was formed in MeOH. Elemental analysis of the product showed the presence of two molecules of CH$_3$CN. X-ray structural analysis showed that the complex was *trans*-[Fe-(DHBuPE)$_2$(CH$_3$CN)$_2$]SO$_4$ and not the alternative [Fe-(DHBuPE)$_2$(CH$_3$CN)(SO$_4$)]·CH$_3$CN (Scheme 3).[24]

trans-Fe(DHBuPE)$_2$(H$_2$O)(SO$_4$) (**6**) also reacted with CO(g) and CH$_3$CN (Schemes 2 and 3). The reaction with

(22) See ref 15, pp 126−148.

(23) See ref 15, pp 113−115.

(24) A capillary-mounted crystal of *trans*-[Fe(DHBuPE)$_2$(CH$_3$CN)$_2$]SO$_4$ diffracted weakly with broad peaks. Data collected on a CAD 4 diffractometer sufficed to show that the Fe atom lay on a cystallographic center of symmetry in space group *C2/c* and that the composition was *trans*-[Fe(DHBuPE)$_2$(CH$_3$CN)$_2$]SO$_4$ and not the alternative [Fe(DHBuPE)$_2$(CH$_3$CN)(SO$_4$)]·CH$_3$CN. The refinement was not pursued further because of the rather poor quality of the data.

(25) (a) Nakamoto, K.; Fujita, J.; Tanaka, S.; Kobayashi, M. *J. Am. Chem. Soc.* **1957**, *79*, 4904. (b) Baldwin, M. E. *Spectrochim. Acta* **1963**, *19*, 315. (c) McWhinnie, *J. Inorg. Nucl. Chem.* **1964**, *26*, 21.

(26) (a) Eskenazi, R.; Raskovan, J.; Levitus, R. *J. Inorg. Nucl. Chem.* **1966**, *28*, 521 and references in therein. (b) Horn, R. W.; Weissberger, E.; Collman, J. P. *Inorg. Chem.* **1970**, *10*, 2367. (c) Barraclough, C. G.; Tobe, M. L. *J. Chem. Soc.* **1961**, 1993.
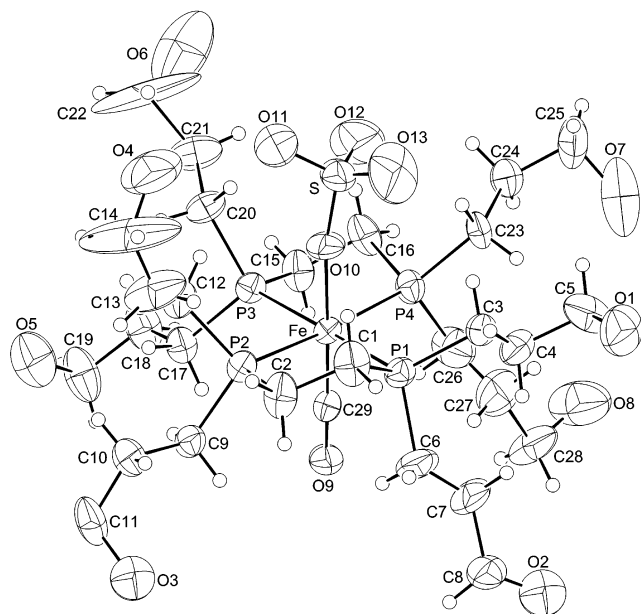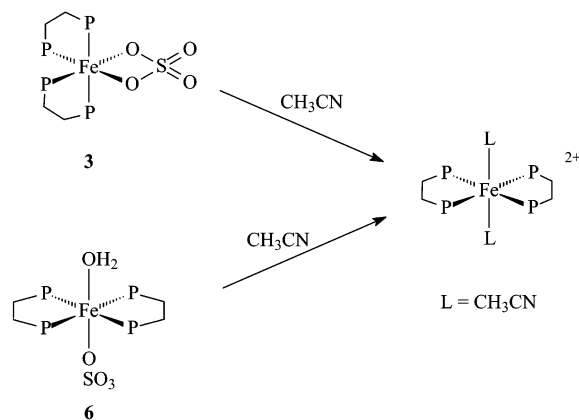
Figure 6. Molecular structure of the *trans*-Fe(DHPrPE)$_2$(CO)SO$_4$ (**9**) complex.

Scheme 3. Reactions of **3** and **6** with CH$_3$CN

CO(g) in methanol was immediate. The product was spectroscopically identical with the one formed by reaction of *cis*-Fe(DHBuPE)$_2$SO$_4$ (**3**) in methanol in the presence of CO, i.e., *trans*-Fe(DHBuPE)$_2$(CO)SO$_4$. Similarly, the reaction of *trans*-Fe(DHBuPE)$_2$(H$_2$O)(SO$_4$) (**6**) with CH$_3$CN formed a product spectroscopically identical with the one formed by reaction of *cis*-Fe(DHBuPE)$_2$SO$_4$ (**3**) in methanol with CH$_3$-CN, namely *trans*-[Fe(DHBuPE)$_2$(CH$_3$CN)$_2$]SO$_4$. The reaction of *trans*-Fe(DHBuPE)$_2$(H$_2$O)(SO$_4$) (**6**) with CH$_3$CN suggests that CH$_3$CN will substitute for coordinated water.

Finally, it is noted that reactions similar to those above also occurred in aqueous solution. For example, when the reactions of *cis*-Fe(DHPrPE)$_2$Cl$_2$ with CO and CH$_3$CN were carried out in water, the products were *trans*-Fe(L$_2$)(L′)Cl$^+$ (L′ = CO, CH$_3$CN; L′ = CO, ^{31}P{^{1}H} NMR (CD$_3$OD) δ 62.6 (s); ν(C≡O) 1930 cm^{-1}; L′ = CH$_3$CN, ^{31}P{^{1}H} NMR (CD$_3$OD) δ 61.8 (s)). Likewise, the reactions of *cis*-Fe(DHPrPE)$_2$SO$_4$ (**2**) with CO and CH$_3$CN in water gave *trans*-Fe(L$_2$)(L′)(OSO$_3$) (L′ = CO, CH$_3$CN; L′ = CO, ^{31}P{^{1}H} NMR (CD$_3$OD) δ 66.8 (s); ν(C≡O) 1927 cm^{-1}; L′ = CH$_3$-CN, ^{31}P{^{1}H} NMR (CD$_3$OD) δ 62.3 (s)).

Further Discussion of the X-ray Structures. The following additional points are noted concerning the X-ray structures of the molecules.

trans-**Fe(DHBuPE)$_2$Cl$_2$ (1).** The structure is accurately centrosymmetric. Note the hydroxybutyl side chains are extended (Figure 1). The O(1), O(2), and O(4) atoms (located in OH groups) are donors in O⋯O intramolecular hydrogen bonds (2.690−2.839(4) Å), and the O(3) atom is a donor in an O⋯Cl bond (3.087(2) Å). Thus, a full three-dimensional network is present.

trans-**[Fe(DHBuPE)$_2$(CO)Cl][B(C$_6$H$_5$)$_4$] (8).** Two independent trans-octahedral Fe(L$_2$)(CO)Cl$^+$ complexes are present. They lie on crystallographic centers of symmetry so that the trans ligands are necessarily disordered. In addition, O(2) is disordered over two positions. The hydroxyalkyl side chains are extended and all oxygen atoms have short intramolecular O⋯O contacts, attributable to hydrogen bonds.

cis-**Fe(DHPrPE)$_2$SO$_4$ (2).** Although the hydrogen atoms of the −OH groups could not be clearly located, numerous O⋯O contacts under 2.9 Å suggest there is a network of cation−cation and cation−anion hydrogen bonds. These include two short contacts (2.530, 2.576(7) Å) each involving an anion oxygen atom and a *coordinated* hydroxyl group.

trans-**Fe(DHPrPE)$_2$(CO)(SO$_4$) (9).** Despite the partial disorder, the main features of the structure are clear. The iron atom exhibits octahedral coordination, with two DHPrPE ligands in the equatorial plane and a carbonyl and a monodentate sulfate ligand in axial psoitions. The Fe−C bond length is 1.686(12) Å compared with 1.709, 1.717(16) Å for the Fe−C bonds in the two disordered cations of Fe-(DHBuPE)$_2$(CO)Cl$^+$. The Fe−C−O unit is nearly linear (178.9(8)°). The hydroxyl groups avoid the vicinity of the carbonyl oxygen, O(9). Most of the hydroxyl groups make close contacts (2.58−2.74(2) Å) with hydroxyl or noncoordinated sulfate oxygens in other molecules; in addition, an *intra*-molecular contact O(4)⋯O(11) (2.80(2) Å) may also indicate a hydrogen bond.

trans-**Fe(DMeOPrPE)$_2$Cl$_2$ (4).** The complexes lie on crystallographic centers of symmetry. The Fe−Cl and Fe−P bond lengths and chelate P−Fe−P bond angle are very similar to those in complex **1**. As was found for the latter, the extended side chains are free from disorder, although in this case there are no intermolecular contacts under 3.4 Å and no possibility of intermolecular hydrogen bonds.

trans-**Fe(DMeOPrPE)$_2$Br$_2$ (5).** The compound is isomorphous and closely isostructural with the dichloro complex, **4**.

trans-**[Fe(DHBuPE)$_2$Cl$_2$]Cl (10).** The trans-octahedral [Fe^{III}(DHBuPE)$_2$Cl$_2$]$^+$ cation lies on a crystal center of symmetry, and the ionic chlorine, Cl(2), on a crystal diad axis. Compared with the Fe^{II} complex **2**, the Fe−Cl bonds are shortened [2.361(1) Å to 2.250(1) Å] and the Fe−P bonds are lengthened [2.265, 2.284(1) Å to 2.334, 2.342(2) Å]. All side chains are extended; one is disordered, and in addition three of the four independent terminal oxygens have alternative sites. Several intermolecular O⋯O contacts [2.48−2.91-

(3) Å] and Cl(2)···O contacts [2.88−2.33(1) Å] may indicate hydrogen bonds.

Conclusions. An important consideration in removing N_2 from methane (e.g., natural gas purification) by using reversible N_2-binding to a metal complex in a homogeneous process is to use a polar solvent to enhance the separation by decreasing the solubility of methane in the carrier solvent. Because water is the best solvent for a properly designed absorbent (in that it provides the highest N_2/CH_4 selectivity), potential dinitrogen-absorbing compounds ideally are water soluble. This work showed that the water-soluble 1,2-bis-(bis(hydroxyalkyl)phosphino)ethane ligands react with $FeCl_2$ or $FeSO_4$ to form water-soluble complexes of the general type $Fe(PP)_2X$ ($X = (Cl)_2$ or SO_4). Whether the products have a cis or trans stereochemistry depends on the solvent, the counterion, and the alkyl chain length of the phosphine. Of importance to the long-range goal of finding a suitable carrier molecule, the chloride or sulfate ligands in the Fe-$(PP)_2X$ complexes are labile, and they are readily substituted by N_2, CO, or CH_3CN. Quantitative measurements of the N_2-binding in water will be reported in a subsequent paper, as will the synthesis of water-soluble complexes of the type *trans*-$Fe(PP)_2(H)(X)$, which have superior N_2-binding ability compared to the complexes reported in this paper.

With regard to the 1,2-bis(bis(hydroxyalkyl)phosphino)-ethane ligands, it is noteworthy that these ligands were originally designed to replace the more commonly used sulfonated phosphines, which in our hands were not necessarily innocent, i.e., the sulfonate group frequently bonded to the metal and prevented the coordination of small molecules. With one exception, this study found that the −OH ligands are noninterfering. (The one exception was *cis*-[Fe(DHPrPE)$_2$]SO$_4$ (**2**), in which two OH groups bonded to the metal to form two six-membered rings.)

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