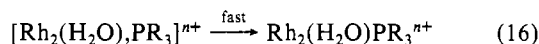
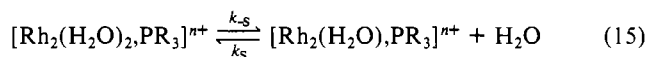
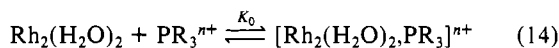


dissociative (D_{IP}) or an interchange dissociative (I_d) mechanism.



The former mechanism would seem to be unlikely in view of the overall neutrality of the dirhodium(II) complex and the lack of an ionic strength dependence of the substitution rate constants. The observed dependence of k_1 on the absolute charge of the entering ligand, however, suggests that the ligands may be involved in specifically oriented interactions with the charges distributed within the $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ complex. The latter mechanism involves the partial formation of a Rh-P bond prior to complete dissociation of the Rh-OH₂ bond. The highest occupied molecular orbitals of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ complex are the filled Rh-Rh π^* orbitals²⁵ and the electron density located in these orbitals between the Rh-O(acetate) and Rh-OH₂ bond axes would discourage the associative attack of an entering phosphine. Further kinetic studies with a wider variety of ligand types may help to clarify the nature of the interactions between the metal complex and entering ligands prior to the dissociation of the coordinated solvent. The substitution of axially coordinated solvent molecules on dirhodium(II) tetraacetate by tris(2-cyanoethyl)phosphine has now been studied in water, methanol,⁶ and acetonitrile,⁶ with rate constants (25.0 °C, $I = 0.10 \text{ M}$) of 8.5×10^5 , 2.6×10^6 , and $1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively, for the phosphine monoadduct formation. The rate constants reflect the relative σ -donor strengths of the three solvent ligands and are consistent with a dissociatively

activated substitution mechanism.

The stability constants for the formation of the mono and bis adducts (Table I) span several orders of magnitude for the ligands in this study. The ratios of K_1/K_2 for the phosphine ligands range from 7 to 275, which are higher than predicted by a statistical factor alone ($K_1/K_2 = 4$). The ratios generally increase with an increase in the magnitude of K_1 and reflect the degree of phosphine trans labilization of the axial ligand across the Rh-Rh bond. With the exception of $\text{PhP}(m\text{-SO}_3\text{Ph})^-$, the values of $\log K_1$ follow the trend in the $\text{p}K_a$ values of the protonated phosphonium species. These observations support the importance of the σ -donor strength of the phosphine ligand in the relative adduct stabilities, as seen previously.⁶

The rapid adduct formation reactions of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ with the water-soluble phosphines are followed by slower processes in which the strong absorption band in the 350-400-nm region is lost and new bands in the ultraviolet region (e.g. 270 nm for the tris(2-carboxyethyl)phosphine ligand) are formed following an induction period. The inability to regenerate the phosphine adduct upon further additions of ligand suggest that the $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ core has been altered, perhaps as a result of inter- or intramolecular electron transfer between the metals and the phosphine ligand. Further kinetic and spectroscopic studies on these secondary reactions are in progress.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada in the form of operating and equipment grants is acknowledged. We thank Queen's University for a graduate scholarship to M.A.S.A. and for a grant to D.H.M. from its Advisory Research Committee.

Registry No. $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, 29998-99-0; $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$, 4023-53-4; $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{COOH})$, 2848-01-3; $\text{Ph}_2\text{P}(m\text{-SO}_3\text{Ph})^-$, 65355-51-3; $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{COO})^-$, 115290-69-2; $\text{P}(\text{CH}_2\text{CH}_2\text{COO})_3^{3-}$, 115290-70-5; $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_3)_2)^+$, 115290-71-6; $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2^{2+}$, 115305-74-3.

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Contribution from the Departments of Organic and Inorganic Chemistry, University of Sydney, Sydney, NSW, Australia 2006

Diamagnetic \rightleftharpoons Paramagnetic Equilibria in Solutions of Bis(dialkylphosphino)ethane Complexes of Iron

Murray V. Baker,[†] Leslie D. Field,^{*,†} and Trevor W. Hambley[†]

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The X-ray structures of two iron(II) chloride complexes, $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (DEPE = 1,2-bis(diethylphosphino)ethane) and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ (DPrPE = 1,2-bis(di-*n*-propylphosphino)ethane), have been determined ($\text{Fe}(\text{DEPE})_2\text{Cl}_2$, monoclinic, space group $P2_1/c$, $a = 10.179 \text{ \AA}$, $b = 13.506 (2) \text{ \AA}$, $c = 10.674 (2) \text{ \AA}$, $\beta = 108.69 (1)^\circ$, $Z = 2$; $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$, monoclinic, space group $P2_1/c$, $a = 11.673 (1) \text{ \AA}$, $b = 11.029 (1) \text{ \AA}$, $c = 14.803 (3) \text{ \AA}$, $\beta = 106.21 (1)^\circ$, $Z = 2$). There is a small but significant increase in the Fe-P bond length in progressing from DEPE to DPrPE ligands (2.260 to 2.268 Å), and the Fe-P bond length in both complexes is markedly greater than that in the closely related complex $\text{Fe}(\text{DMPE})_2\text{Cl}_2$ (DMPE = 1,2-bis(dimethylphosphino)ethane) (2.235 Å). The complexes $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ are both diamagnetic in the solid state but give rise to paramagnetic solutions when dissolved. The solution paramagnetism varies with temperature and is ascribed to reversible dissociation (or partial dissociation) of one of the bidentate phosphine ligands from the iron. The tendency of iron(II) dichloride complexes with bis(dialkylphosphino)ethane ligands to form 6-coordinate complexes or complexes of lower coordination number is discussed in terms of the increasing steric demand of the alkyl-substituted ligands.

Introduction

During the course of our studies of iron bis(diphosphine) complexes, we have prepared a number of compounds of the general formula $\text{Fe}(\text{PP})_2\text{X}_2$ (PP = 1,2-bis(dialkylphosphino)ethane, X = Br, Cl, I). Bis(dialkylphosphino)ethanes such as DMPE (bis(dimethylphosphino)ethane), DEPE (1,2-bis(diethylphosphino)ethane), and DPrPE (1,2-bis(di-*n*-propylphosphino)ethane) are versatile bidentate ligands that form strong

complexes with a number of transition metals. The synthesis and some properties of the iron(II) complexes $\text{Fe}(\text{DMPE})_2\text{Cl}_2$ (**1**)^{1,2} and $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (**2**)^{1,3} have been previously reported; however, the anomalous magnetic behaviors of **2** and the homologous compound $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ (**3**) *in solution* have never been noted.

$\text{Fe}(\text{DMPE})_2\text{Cl}_2$, $\text{Fe}(\text{DEPE})_2\text{Cl}_2$, and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ are all green crystalline compounds that are diamagnetic in the solid state

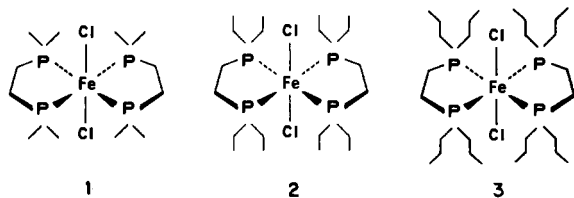
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and soluble in organic solvents (giving green solutions at room temperature). The ^{31}P NMR spectrum of **1** in solution is unremarkable, showing only a single resonance at δ 58.6 (C_6D_6 solution, 25 °C), characteristic of the trans configuration of the complex. However, neither **2** nor **3** gives rise to a high-resolution ^{31}P NMR spectrum in solution at room temperature due to the formation of paramagnetic species.⁴

For iron(II) complexes, the d^6 configuration of the metal allows the possibility for diamagnetic singlet and paramagnetic triplet or quintet spin states. A number of pseudooctahedral iron(II) complexes with a P_4Cl_2 donor set have been reported,^{1,5,6} and the majority are diamagnetic in the solid state, although magnetic properties of their solutions have not been discussed. A few paramagnetic iron complexes with the P_4Cl_2 donor set have been reported,⁵⁻⁸ but these all involve bulky phosphine ligands, and the paramagnetism has been attributed⁵ to weakened Fe-P bonds.

In this paper we report an investigation of the structures of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ in the solid state and magnetic properties of their solutions.

Experimental Section

NMR spectra were recorded on a Bruker WM400 NMR spectrometer (superconducting magnet) operating at 400.1 MHz for ^1H observation and 162.0 MHz for ^{31}P observation. ^1H NMR spectra were referenced to residual solvent resonances, and ^{31}P NMR spectra were referenced to external, neat trimethyl phosphite (taken to be 140.85 ppm at the temperature quoted).

Synthesis of Compounds. All solvents were of reagent quality and were rigorously dried and degassed before use. The ligands DEPE and DPrPE were synthesized from bis(1,2-dichlorophosphino)ethane by following the procedure of Chatt et al.⁹ DHPE (DHPE = 1,2-diphosphinoethane) was synthesized by following the procedure of Taylor and Walters.¹⁰ $\text{Fe}(\text{DMPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ were prepared by literature methods.¹

$\text{Fe}(\text{DPrPE})_2\text{Cl}_2$. DPrPE (5.03 g, 19.2 mol) was added to a stirred suspension of anhydrous iron(II) chloride (1.21 g, 9.55 mmol) in dry ether (100 mL). The mixture was stirred overnight at room temperature, and the solvent was removed under reduced pressure. The residue was recrystallized from light petroleum to give $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ as a green crystalline solid (yield 5.06 g, 81%), mp 153.5–156.5 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_6 , -50 °C): δ 58.1. $^1\text{H}\{^{31}\text{P}\}$ NMR (toluene- d_6 , -50 °C): δ 1.00 (dd, 24 H, $J = 7.2, 7.2$ Hz, CH_3), 1.64 (dddq, 8 H, $J = 4.3, 13.3, 12.9, 7.2$ Hz, CH_2CHH), 1.76 (dddq, 8 H, $J = 13.3, 4.0, 12.9, 7.2$ Hz, CH_2CHH), 1.92 (ddd, 8 H, $J = 13.9, 4.0, 13.3$ Hz, $\text{CH}_2\text{CH}_2\text{CHH}$), 2.19 (s, 8 H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.35 (ddd, 8 H, $J = 13.9, 13.3, 4.3$ Hz, $\text{CH}_2\text{CH}_2\text{CHH}$). Anal. Found: C, 51.9; H, 9.3; P, 19.3. Calcd for $\text{FeC}_{28}\text{Cl}_2\text{H}_{64}\text{P}_4$: C, 51.6; H, 9.9; P, 19.0.

$\text{Fe}(\text{DMPE})_2\text{Br}_2$. DMPE (0.649 g, 4.32 mmol) was added to a solution of anhydrous iron(II) bromide (0.465 g, 2.16 mmol) in THF (50 mL), and the mixture was stirred for 6 h at room temperature. The solvent was removed under vacuum, and the residue was recrystallized from benzene/light petroleum to give $\text{Fe}(\text{DMPE})_2\text{Br}_2$ as pale green plates (yield 0.581 g, 77%), which decomposed without melting at temperatures above 300 °C. $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6 , 25 °C): δ 58.1. $^1\text{H}\{^{31}\text{P}\}$ NMR (benzene- d_6 , 25 °C): 1.48 (s, 24 H, CH_3), 2.02 (s, 8 H,

Table I. Crystal Data

	$\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (2)	$\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ (3)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
<i>a</i> , Å	10.179 (2)	11.673 (1)
<i>b</i> , Å	13.506 (2)	11.029 (2)
<i>c</i> , Å	10.674 (2)	14.803 (3)
β , deg	108.69 (1)	106.21 (1)
cell vol, Å ³	1390.2	1830.0
calcd density, g·cm ⁻³	1.288	1.182
mol wt	539.2	651.4
<i>Z</i>	2	2
<i>F</i> (000), e	576	704
abs coeff, cm ⁻¹	9.23	7.04
cryst dims, mm	0.10 × 0.18 × 0.30	0.08 × 0.14 × 0.14
faces	±100, ±011, ±011	±100, ±011, ±011
transmission factors	0.91, 0.85	0.95, 0.92
temp, °C	21	21
radiation (λ , Å)	Mo K α (0.71069)	Mo K α (0.71069)
monochromator	graphite	graphite
scan mode	ω - θ	ω -0.67 θ
2 θ range, deg	2.0–50.0	2.0–45.0
no. of rflns measd	2712	2680
<i>hkl</i> ranges	0 → 12, 0 → 15, -12 → 12	0 → 12, 0 → 11, -15 → 15
no. of nonequiv rflns	2076	1951
merging <i>R</i>	0.017	0.018
no. of rflns used	1532	1243
no. of variables	126	169
<i>R</i>	0.054	0.049
<i>R</i> _w	0.063	0.053
weighting constants <i>k</i> , <i>g</i> ($w = k/(\sigma^2 F_o + g F_o^2)$)	3.93, 0.0048	1.62, 0.00063
shift/esd	0.05 σ	0.05 σ
resid extrema in final diff map, e·Å ⁻³	±0.4	±0.3

Table II. Positional Parameters ($\times 10^4$) for $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (**2**)

	<i>x</i>	<i>y</i>	<i>z</i>	occ
Fe(1)	0	0	0	
Cl(1)	220 (2)	1232 (1)	1601 (2)	
P(1)	1837 (2)	-836 (1)	1330 (2)	
P(2)	1573 (2)	781 (1)	-744 (2)	
C(1)	3387 (14)	-398 (12)	1220 (15)	0.47
C(2)	3383 (17)	506 (13)	806 (17)	0.47
C(1')	3127 (19)	-778 (13)	296 (20)	0.53
C(2')	3141 (13)	163 (9)	-316 (14)	0.53
C(3)	1854 (9)	-2205 (6)	1362 (10)	
C(4)	3244 (11)	-2713 (7)	1985 (12)	
C(5)	2391 (23)	-470 (18)	3303 (19)	0.42
C(6)	3745 (23)	-508 (19)	3991 (23)	0.42
C(5')	3046 (30)	-358 (22)	2729 (28)	0.26
C(5'')	1894 (31)	-898 (22)	3179 (28)	0.32
C(6'')	2987 (51)	-872 (32)	4152 (44)	0.32
C(7)	1938 (17)	2090 (11)	-255 (29)	0.51
C(8)	3152 (18)	2610 (14)	-333 (30)	0.51
C(7')	1802 (18)	2074 (12)	-764 (32)	0.49
C(8')	3224 (19)	2438 (16)	-883 (31)	0.49
C(9)	1150 (15)	864 (12)	-2635 (13)	0.58
C(10)	2294 (21)	819 (16)	-3150 (20)	0.58
C(9')	2306 (26)	346 (22)	-1821 (25)	0.42
C(10')	1189 (36)	370 (28)	-3348 (31)	0.42

$\text{PCH}_2\text{CH}_2\text{P}$). Anal. Found: C, 28.2; H, 6.4; P, 24.3. Calcd for $\text{FeBr}_2\text{C}_{12}\text{H}_{32}\text{P}_4$: C, 27.9; H, 6.2; P, 24.3.

X-ray Crystallography. Crystals suitable for study by X-ray diffraction were obtained by recrystallization from light petroleum and were mounted on glass fibers with epoxy resin. A light coating of the resin was used to preclude aerial oxidation.

Lattice parameters were determined by a least-squares fit to the setting angles of 25 independent reflections. Crystal data and data collection parameters are listed in Table I. Data were collected on a Enraf-Nonius CAD4F four-circle diffractometer, employing graphite-monochromated Mo K α radiation.

The structures were solved by heavy-atom methods; the calculated value of 2 for *Z* indicated that the iron atom must lie at a center of symmetry. In both structures many of the carbon atoms of the phosphine ligands are disordered, in some cases over three sites. In the structure of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$, C(6) is disordered over at least three sites but only two could be located. Disordered atoms were refined isotropically with

- Similarly $\text{Fe}(\text{DMPE})_2\text{Br}_2$ is diamagnetic in solution whereas the corresponding $\text{Fe}(\text{DEPE})_2\text{Br}_2$ ¹⁸ complex gives rise to paramagnetic species when dissolved. The behavior of these compounds has not been examined in detail.
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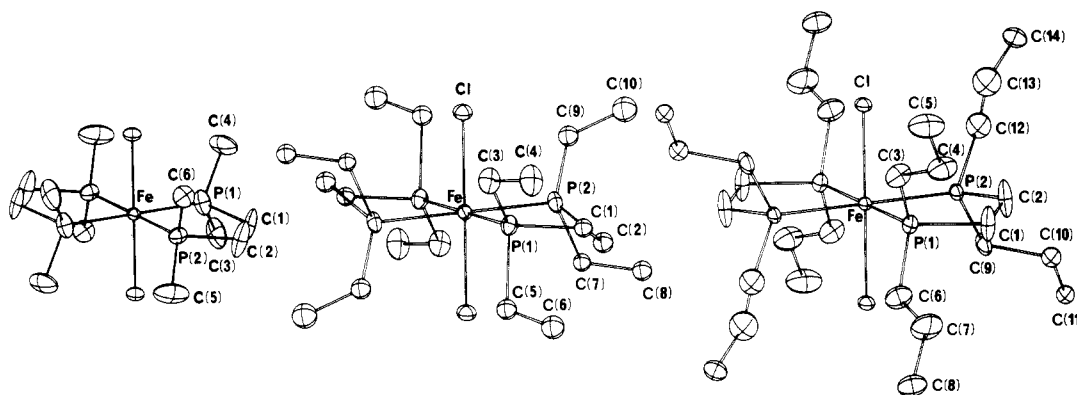


Figure 1. ORTEP plots of Fe(DMPE)₂Cl₂ (1,⁵ left), Fe(DEPE)₂Cl₂ (2,¹⁶ middle), and Fe(DPrPE)₂Cl₂ (3, right).

Table III. Positional Parameters ($\times 10^4$) for Fe(DPrPE)₂Cl₂ (3)

	x	y	z	occ
Fe(1)	0	5000	5000	
Cl(1)	-75 (2)	3545 (2)	3830 (1)	
P(1)	1887 (2)	4423 (2)	5743 (2)	
P(2)	-532 (2)	3578 (2)	5920 (1)	
C(1)	1835 (11)	3175 (13)	6535 (10)	
C(2)	831 (12)	3022 (14)	6725 (10)	
C(3)	2877 (9)	5538 (10)	6469 (8)	
C(4)	3854 (12)	5167 (13)	7274 (10)	
C(5)	4544 (11)	6190 (14)	7805 (10)	
C(6)	2824 (13)	3782 (14)	5035 (12)	
C(7)	3730 (15)	3126 (17)	5229 (15)	
C(8)	4353 (11)	2658 (12)	4562 (10)	
C(9)	-1277 (11)	2218 (8)	5384 (6)	
C(10)	-985 (16)	1022 (13)	6008 (10)	0.65
C(11)	-1903 (27)	48 (24)	5460 (16)	0.40
C(10')	-1728 (23)	1219 (21)	5861 (16)	0.35
C(11')	-2685 (34)	374 (32)	5386 (24)	0.35
C(11'')	-1255 (34)	-166 (31)	5535 (22)	0.25
C(12)	-1756 (29)	3888 (24)	6589 (23)	0.64
C(13)	-1618 (30)	4413 (38)	7230 (22)	0.64
C(14)	-2630 (12)	4363 (12)	7762 (9)	
C(12')	-926 (26)	3857 (19)	6937 (15)	0.36
C(13')	-2302 (39)	3608 (33)	6934 (27)	0.36

complementary occupancy factors. All other non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at calculated sites (C-H = 0.97 Å) with group isotropic thermal parameters. Full-matrix least-squares refinement converged with all shifts less than 0.05σ in both cases.

Positional parameters are listed in Tables II and III. Anisotropic thermal parameters, hydrogen atom parameters, bond lengths, and observed and calculated structure factors have been deposited as supplementary material. Programs used were SUSCAD¹¹ for data reduction, ABSORB¹¹ for absorption corrections, SHELX 76¹² for refinement, and ORTEP¹³ for plotting. Scattering factors and anomalous dispersion terms were taken from Ref 14 for Fe and from SHELX 76¹² for all other atoms.

Magnetic Measurements in Solution. Magnetic susceptibilities of solutions were determined by NMR spectroscopy using the Evans method¹⁵ according to eq 1 with tetramethylsilane, cyclododecane, or cyclopentane as internal reference. m_0 is the mass of the paramagnetic

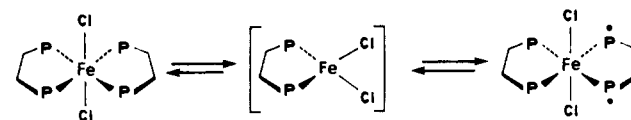
$$\frac{\Delta\nu}{\nu_0} = S_f m_0 \chi_0 - \frac{S_f m_0 \chi_D}{MW} - \frac{S_f m_0}{MW} \left[\frac{\mu}{2.828} \right]^2 \frac{1}{T} \quad (1)$$

Table IV. Bond Lengths (Å) and Angles (deg) about the Iron Atom

atoms	Fe(DMPE) ₂ Cl ₂ ^a	Fe(DEPE) ₂ Cl ₂ ^b	Fe(DPrPE) ₂ Cl ₂ ^b
Fe-Cl	2.352 (1)	2.344 (1)	2.345 (2)
Fe-P(1)	2.241 (1)	2.256 (2)	2.261 (2)
Fe-P(2)	2.230 (1)	2.264 (2)	2.275 (2)
Fe-P(av)	2.235	2.260	2.268
Cl-Fe-P(1)	88.9 (1)	91.8 (1)	89.9 (1)
Cl-Fe-P(2)	88.1 (1)	90.7 (1)	90.6 (1)
P(1)-Fe-P(2)	85.8 (1)	85.3 (1)	84.6 (1)

^a Taken from ref 5. ^b This work.

Scheme I



solute (g) dissolved in 1 mL of solution. $\Delta\nu$ is the chemical shift difference (Hz) between the resonances of the reference compound in the presence of the paramagnetic solute and in the absence of the paramagnetic solute. ν_0 is the operating frequency of the NMR spectrometer. χ_0 is the mass susceptibility of the solvent. χ_D is the molar magnetic susceptibility of the ligands. MW is the molecular weight of the paramagnetic solute. μ is the magnetic moment of the metal (μ_B). T is the absolute temperature (K). S_f is a shape factor, which is $-2\pi/3$ for a cylindrical sample in an iron core magnet (sample axis perpendicular to magnetic field) and $4\pi/3$ for a cylindrical sample in a superconducting magnet (sample axis parallel to magnetic field).

Results and Discussion

Solid-State Structure. ORTEP plots of Fe(DEPE)₂Cl₂¹⁶ and Fe(DPrPE)₂Cl₂ with the atom-numbering schemes used are shown in Figure 1. The two structures are close to being isostructural, and the structures are also closely related to that of Fe(DMPE)₂Cl₂,⁵ which is included in Figure 1 for comparison. The degree of disorder severely limits the precision of the determination, particularly in the parameters relating to the carbon atoms. Therefore, only bond lengths and angles about the iron atom are listed in Table IV.

The iron to phosphorus bond lengths show a small but significant trend of increasing with increasing bulk of the substituents bonded to phosphorus. The intraligand P-Fe-P bond angle concomitantly decreases with the increase in bulk, indicating that steric interactions between the ligands are significant. A number of close contacts between the ligands are observed in both complexes, the shortest being between hydrogen atoms attached to C(3) and C(7) (2.24 (1) Å) in Fe(DEPE)₂Cl₂ and between hydrogen atoms attached to C(6) and C(12) (1.91 (2) Å) in Fe(DPrPE)₂Cl₂.

The Fe-Cl bond distances are apparently unaffected by the change in ligand from DEPE to DPrPE but are slightly shorter

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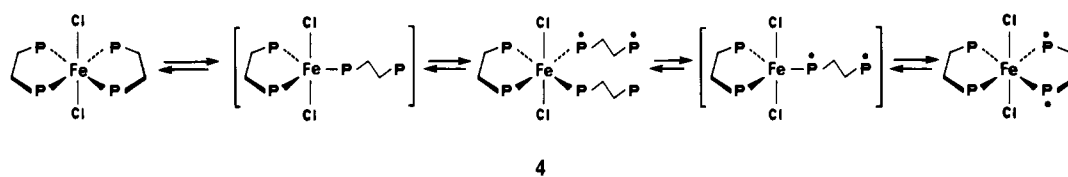
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(16) The structure of Fe(DEPE)₂Cl₂ has been noted previously, but details of the analysis have not been reported. See footnote 13 in ref 5.

Scheme II



4

Table V. ^{31}P NMR Data for the AA'XX' Spectra of the Mixed-Ligand Unsymmetrical *trans*-Dichloride Complexes^a

complex	$\delta(\text{P}_{\text{AA}'})$ (ligand)	$\delta(\text{P}_{\text{XX}'})$ (ligand)	$J_{\text{AA}'}, J_{\text{XX}'}$	$J_{\text{AX}} = J_{\text{A'X'}}$	$J_{\text{AX'}} = J_{\text{A'X}}$
$\text{FeCl}_2(\text{DEPE})(\text{DHPE})$	80.61 (DEPE)	9.59 (DHPE)	+37.9 (3), +44.5 (3)	+57.3 (2)	-150.8 (2)
$\text{FeCl}_2(\text{DPrPE})(\text{DHPE})$	75.05 (DPrPE)	9.41 (DHPE)	+37.7 (3), +44.0 (3)	+56.5 (3)	-151.6 (3)
$\text{FeCl}_2(\text{DMPE})(\text{DEPE})$	67.74 (DEPE)	55.78 (DMPE)	+40.0 (7), +40.2 (6)	+50.4 (5)	-132.3 (7)
$\text{FeCl}_2(\text{DMPE})(\text{DPrPE})$	63.25 (DPrPE)	55.99 (DMPE)	+39.8 (2), +39.9 (2)	+50.2 (2)	-132.5 (2)
$\text{FeCl}_2(\text{DEPE})(\text{DPrPE})^b$	63.06 (DEPE)	57.96 (DPrPE)	+40.1 (3), +40.4 (2)	+47.5 (2)	-121.4 (2)
$\text{FeCl}_2(\text{DMPE})_2$ (1)	58.64 ^c (DMPE)				
$\text{FeCl}_2(\text{DEPE})_2$ (2)	62.47 (DEPE)				
$\text{FeCl}_2(\text{DPrPE})_2$ (3)	58.08 (DPrPE)				

^aData for the symmetrical $\text{Fe}(\text{PP})\text{Cl}_2$ complexes are included for comparison. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 162 MHz and -50°C , in toluene unless otherwise stated. Chemical shifts (δ) are referenced to external, neat trimethyl phosphite (taken as δ 140.85). Coupling constants (in Hz, with uncertainties in parentheses) were determined by computer simulation. $J_{\text{AA}'}$ and $J_{\text{XX}'}$ could not be individually assigned with the available data. ^bIn THF. ^cIn benzene- d_6 at 25°C .

Table VI. Effective Magnetic Moments (μ_{eff}^a) of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (2) and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ (3) in Various Solvents

complex	$\text{C}_6\text{D}_5\text{Br}$	toluene- d_8	THF- d_8
$\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (2)	0.90	0.59	0.73
$\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ (3)	1.20	0.69	1.23

^a μ_{eff} in μ_{B} at 26°C .

than that observed for $\text{Fe}(\text{DMPE})_2\text{Cl}_2$.⁵ The greatest change in Fe-P bond length is observed on going from the DMPE complex to the DEPE complex, and it may be that as the Fe-P bonds weaken the π -bonding between the iron and chlorine increases, leading to a shortening of the Fe-Cl bond.

In the solid state, $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ is essentially diamagnetic (Gouy balance) up to temperatures of ca. 100°C .

Ligand Exchange in Solution. In solution, $\text{Fe}(\text{DMPE})_2\text{Cl}_2$ shows no tendency to exchange DMPE ligands for DEPE, DPrPE, or DHPE ligands on addition of the free diphosphines. However, in solution $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ rapidly and reversibly exchange their respective ligands for added free diphosphines. The ligand exchange can be monitored by ^{31}P NMR spectroscopy since the singlet resonance of the symmetrical *trans*-dihalides is transformed to the characteristic AA'XX' coupling pattern of the mixed-ligand *trans*-dichlorocomplexes¹⁷ on addition of different free diphosphine ligands (Table V). Ligand exchange presumably proceeds via the total loss (Scheme I) or partial dissociation (Scheme II) of one of the bidentate ligands, i.e. through a four- or five-coordinate species.

Solution Paramagnetism. Solutions of $\text{Fe}(\text{DMPE})_2\text{Cl}_2$ were diamagnetic at all temperatures examined; however, at room temperature, ^{31}P NMR spectra could not be observed for solutions of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ or $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ due to the formation of paramagnetic species. The effective magnetic moments of both 2 and 3 varied from solvent to solvent (Table VI), and in all cases examined, $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ had a larger μ_{eff} value than the corresponding $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ complex under the same experimental conditions.

Solutions containing 2 or 3 are essentially diamagnetic at -60°C but become increasingly paramagnetic as the temperature is raised (figure 2); the changes are fully reversible, and cooling the sample reestablishes the diamagnetic condition.

The temperature dependence of μ_{eff} for 2 or 3 in solution can be rationalized in terms of equilibria between diamagnetic and paramagnetic species where the equilibria favor the diamagnetic species at low temperature. For 2 and 3, a number of possible

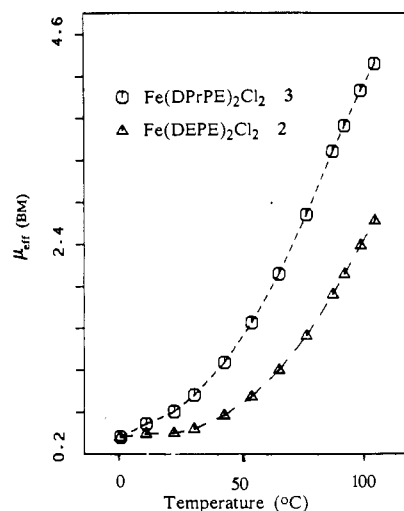


Figure 2. Experimental temperature dependences of the effective magnetic moments (μ_{eff}) of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ (2) and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ (3) in toluene- d_8 solution.

high-spin \rightleftharpoons low-spin equilibria can be envisaged and these would include the following.

(i) A spin-state equilibrium between high-spin and low-spin states of the iron atom (i.e. a magnetic spin-state crossover) could exist. Spin equilibria are well documented for octahedral iron(II) complexes and are expected in the regime of intermediate ligand field strength. Mössbauer studies¹⁸ of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DEPE})_2\text{Br}_2$ suggest that although these compounds are diamagnetic in the solid state (at 22°C), the ligand field strengths are such that the complexes are on the verge of a spin-state transition. Solid-state magnetic susceptibility studies have shown that the complex $\text{Fe}(\text{DPPEN})_2\text{Cl}_2$ (DPPEN = *cis*-1,2-bis(diphenylphosphino)ethylene)^{6,7} and its acetone solvate $\text{Fe}(\text{DPPEN})_2\text{Cl}_2 \cdot 2\text{Me}_2\text{CO}$ ⁷ exist in temperature-dependent equilibria between high-spin (quintet) and low-spin forms. Two related complexes containing a P_4X_2 donor set, $\text{Fe}(\text{DPPEN})_2\text{Br}_2$ ⁶ and $\text{Fe}(\text{PPP})_2\text{Cl}_2 \cdot 2\text{Me}_2\text{CO}$ (PPP = bis[2-(diphenylphosphino)ethyl]phenylphosphine)⁵ have notably long Fe-P bonds (ca. 2.7 Å) and have been shown to be high spin in the solid state. The majority of iron complexes with a P_4X_2 donor set are diamagnetic in the solid state, and complexes that have been studied include

(17) See for example: Baker, M. V.; Field, L. D. *Inorg. Chem.* **1987**, *26*, 2010.

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$\text{Fe}(\text{DMPE})_2\text{Cl}_2$,^{1,20} $\text{Fe}(\text{DEPE})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$),^{1,18} and $\text{Fe}(\text{DEPB})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{DEPB} = 1,2\text{-bis}(\text{diethylphosphino})\text{-benzene}$).^{1,18}

(ii) Reversible loss of one or both halide ligands may occur, leading to a 5- or 4-coordinate species with a P_4Cl or simply P_4 donor set. Mays et al.¹⁹ have demonstrated that the halides in $\text{Fe}(\text{DMPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ are labile and can be substituted easily by methanol or acetonitrile solvents. In less coordinating solvents, the reversible loss of a halide could give rise to paramagnetic species. A number of 5-coordinate iron(II) complexes with P_4X donor sets and a variety of geometries have been reported,²⁰ and none are diamagnetic.

(iii) Reversible *total* loss of one bidentate ligand may occur, leading to a 4-coordinate species with a P_2Cl_2 donor set as depicted as the intermediate species in Scheme I. A number of stable paramagnetic 4-coordinate iron(II) complexes (with distorted-tetrahedral geometries) and a P_2Cl_2 donor set are known, and cases of equilibria between octahedral P_4Cl_2 and tetrahedral P_2Cl_2 species in solution have been reported.^{6,21} The electronic spectra of solutions of $\text{Fe}(\text{DPPEN})_2\text{Cl}_2$ and $\text{Fe}(\text{DPPEN})_2\text{Br}_2$ indicate⁶ that, in solution, the octahedral six-coordinate complexes are in equilibrium with tetrahedral species and free DPPEN. A similar equilibrium has been proposed for solutions containing $\text{Fe}(\text{PP-P})_2\text{Cl}_2$.⁵

Equilibria between octahedral and tetrahedral complexes are not restricted to systems involving bidentate diphosphine ligands. In the presence of excess PMe_3 , the paramagnetic tetrahedral complexes $\text{Fe}(\text{PMe}_3)_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are in equilibrium with the corresponding diamagnetic octahedral complexes $\text{Fe}(\text{PMe}_3)_4\text{X}_2$, the octahedral complexes being favored at lower temperatures.²²

(iv) Reversible dissociation of one arm of a bidentate ligand may occur, leading to a paramagnetic 5-coordinate species with a P_3Cl_2 donor set as depicted as the intermediates in Scheme II. Although Muettterties et al.²³ have reported the paramagnetic phosphite complexes $\text{Fe}[\text{P}(\text{OMe})_3]_3\text{Cl}_2$ and $\text{Fe}[\text{P}(\text{OEt})_3]_3\text{Cl}_2$, there are as yet no examples of 5-coordinate iron phosphine complexes with the P_3Cl_2 donor set.

Two experimental observations eliminate some possibilities from the list above. First, at all temperatures, highly paramagnetic solutions of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ or $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ are homogeneous, even in nonpolar solvents such as toluene, with no evidence for insolubility of the paramagnetic complex. This eliminates possibility ii since any species formed by loss of Cl^- would be ionic and insoluble in nonpolar solvents.

Second, the observed paramagnetism of solutions of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ or $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ is suppressed dramatically by the addition of excess diphosphine ligand. In THF solution at 50 °C, μ_{eff} for $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ is reduced from 1.13 to 0.46 μ_{B} in the

presence of 2.1 equiv of free DEPE ligand. Alternative i above is inconsistent with this observation, since there is no conceivable mechanism by which the addition of excess ligand could significantly alter an equilibrium between high-spin and low-spin forms of an octahedral $\text{Fe}(\text{PP})_2\text{Cl}_2$ complex.

Alternatives iii and iv above (or a combination of the two) provide reasonable mechanisms that rationalize the paramagnetism in solutions of $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$. In the case of alternative iv, the formation of a diamagnetic species such as **4** could account for the suppression of paramagnetism in solutions of **2** or **3** on addition of excess diphosphine ligand.

The trend of values for μ_{eff} observed for $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ in toluene- d_8 (Figure 2) over the temperature range -10 to +100 °C indicates that paramagnetic species with quintet spin states must be involved (since μ_{eff} is significantly greater than 3–3.2 μ_{B} , the value expected for a triplet spin state²⁰), although contributions from triplet species cannot be excluded. In a mixed, high-boiling-point solvent (bromobenzene- d_5 /cyclododecane, 70:30 w/w) μ_{eff} for $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ increases to a plateau at ca. 130 °C. If the data are fitted to a simple 4-coordinate \rightleftharpoons 6-coordinate equilibrium model (as depicted in Scheme I), values of $\mu = 4.5 \mu_{\text{B}}$, $\Delta H = 89 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta S = 240 \pm 5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ provide a good fit to the observed data. However, without knowledge of the precise nature of the equilibrium little quantitative significance can be attached to these values.

Conclusions

Although the structures of $\text{Fe}(\text{DMPE})_2\text{Cl}_2$, $\text{Fe}(\text{DEPE})_2\text{Cl}_2$, and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ in the solid state are similar, the complexes exhibit different stabilities in solution. In the solid state the complexes show a small but significant increase in the Fe–P bond lengths as the bulkiness of the ligand substituents increases.

In solution, $\text{Fe}(\text{DMPE})_2\text{Cl}_2$ is a stable complex that shows no tendency for ligand loss or exchange whereas both $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ freely exchange ligands in the presence of other phosphine donors. In solution, $\text{Fe}(\text{DEPE})_2\text{Cl}_2$ and $\text{Fe}(\text{DPrPE})_2\text{Cl}_2$ are in equilibrium with paramagnetic species although there is no evidence for paramagnetism in the solid state. From the available data it is not possible to assign structures to the paramagnetic species formed in solution and it is possible that a number of equilibrating complexes may be responsible for the observed paramagnetism.

Ligand lability increases in the sequence



which follows the trend of increasing steric demand of the ligands. With still bulkier ligands (e.g., two Me_3P ligands) stable 4-coordinate tetrahedral complexes are known to be favored over their octahedral counterparts.²²

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Registry No. **2**, 22920-46-3; **3**, 114860-51-4; $\text{Fe}(\text{DMPE})_2\text{Br}_2$, 101566-81-8.

Supplementary Material Available: Tables of bond lengths, thermal parameters, and hydrogen positional and thermal parameters for **2** and **3** (6 pages); tables of calculated and observed structure factors for **2** and **3** (17 pages). Ordering information is given on any current masthead page.

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- (21) For examples of iron(II) complexes containing a P_2X_2 donor set, see: Issleib, K.; Doll, G. Z. *Anorg. Allg. Chem.* **1960**, *305*, 1. Naldini, L. *Gazz. Chim. Ital.* **1960**, *80*, 391. Issleib, K.; Hohlfeld, G. Z. *Anorg. Allg. Chem.* **1961**, *312*, 169. Karsch, H. H. *Inorg. Synth.* **1980**, *20*, 69. Mays, M. J.; Sears, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1873. Baker, W. A.; Lutz, P. M. *Inorg. Chim. Acta* **1976**, *16*, 5.
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