INVESTIGATION OF THE INTERMEDIATES IN THE OXIDATION OF A BULKY ARYLPHOSPHINE LIGAND WITH FERRIC CHLORIDE

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(Received 10 July 1992; accepted 22 October 1992)

Abstract—The syntheses, spectroscopic properties and structures of iron(II) and iron(III) complexes prepared by reactions of ferric chloride with the tertiary phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) are described. The novel diferrous chloride salt $[H-TMPP]_2[Fe_2Cl_6]$ (1) was prepared by the reaction of anhydrous ferric chloride with 1 equivalent of TMPP in benzene or diethyl ether. This redox reaction also produces $[TMPP-Cl][FeCl_4]$ (2) as the oxidized by-product. The structure of 1, determined by single-crystal X-ray diffraction, revealed that the $[Fe_2Cl_6]^{2-}$ anion consists of two edge-sharing tetrahedra with two terminal and two bridging chlorides per metal atom. Dissolution of complex 1 in ethanol produces $[H-TMPP]_2[Fe^{II}Cl_4]$ (3), which was identified on the basis of a preliminary X-ray investigation. Compound 3, independently prepared by the reaction of [Fe(NCCH₃)₆][AlCl₄]₂ with 2 equivalents of TMPP in methanol, reacts with molecular oxygen to initially form [H-TMPP][Fe^{III}Cl₄] (4) and finally the phosphine oxide species $FeCl_3(O=TMPP)$ (5). The structure of 4 was determined by single-crystal X-ray diffraction. To test the importance of compound 4 as an intermediate in the production of TMPP=O, it was prepared directly by reaction of $[Fe(NCCH_3)_6][SbCl_6]_2$ with 2 equivalents of TMPP in methanol and reacted with oxygen to give 5 in high yield. Compounds 1-5were further characterized by IR and electronic spectroscopies, as well as by elemental analyses. The reactions of the salts 1, 3 and 4 suggest that the oxidation of tertiary arylphosphines with FeCl₁ in alcohols does not proceed via the formation of dioxygen complexes, but rather via quaternarization of the phosphine ligand.

Phosphine oxides are important reagents for a variety of applications, including the extraction of transition elements and lanthanides from acidic solutions.¹ A considerable body of research has been devoted to the study of the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide by a variety of transition metal complexes including those containing iron, ruthenium, cobalt, iridium, nickel and palladium.^{2–7} Recently, Ondrejovic and co-workers investigated the catalytic oxidation of triphenylphosphine by FeCl₃ and the phosphine complex FeCl₃(PPh₃)₂, and in the course of their investigation isolated bis-phosphine oxide adducts of the type FeX₃(Ph₃P=O)₂ (X = Br, Cl, NCS).

which are themselves catalysts for the reaction.⁸ The reaction proceeds too rapidly to allow for the detection of intermediates, thus it is not possible to obtain detailed mechanistic information. One way to approach this dilemma is to use bulkier arylphosphine ligands to lend kinetic stability to compounds along the reaction pathway. To this end, we undertook an investigation of the ferric chloride chemistry of the bulky triphenylphosphine derivative tris(2,4,6-trimethoxyphenyl)phosphine (TMPP).9 This phosphine ligand has a cone angle of 184° as compared to that of 145° for triphenylphosphine. In the course of this work we were successful at isolating three key intermediates in the pathway leading to the thermodynamically stable product FeCl₃(O=TMPP), which is a catalyst for the production of O=TMPP. Our results suggest that O₂ adducts of transition metal phosphine complexes are not responsible for catalytic oxidation of

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this particular phosphine ligand. A portion of this work was the subject of a previous report.¹⁰

EXPERIMENTAL

Starting materials

Anhydrous FeCl₃ was purchased from Strem Chemicals and used as received. The starting materials [Fe(NCCH₃)₆][AlCl₄]₂ and [Fe(NCCH₃)₆] [SbCl₆]₂ were prepared as described in the literature.¹¹ Tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) was prepared by a modification of the reported method; the corresponding phosphine oxide was synthesized in our laboratories.¹² All solvents were dried over 4 Å molecular sieves. Benzene, diethyl ether and THF were distilled from sodium/potassium benzophenone ketvl radical, whereas methylene chloride, acetonitrile and methanol were distilled under nitrogen from P_2O_5 , CaH₂ and Mg(OCH₃)₂, respectively.

Reaction procedures

All reactions were carried out under argon using standard Schlenk and dry-box techniques, unless otherwise specified.

(a) Preparation of $[H-TMPP]_2[Fe_2^{II,II}Cl_6]$ (1).

(i) Preparation of $[H-TMPP]_2[Fe_2^{II,II}Cl_6]$ (1) in benzene. A quantity (0.162 g, 0.999 mmol) of anhydrous FeCl₃ was added to 1 equivalent of TMPP (0.532 g, 0.999 mmol) in deoxygenated benzene (30 cm³). The resulting suspension was stirred at room temperature for 24 h, after which time the solvent was decanted from a yellow solid. The product was washed with several aliquots of benzene (3×10) cm^3) and THF (3 × 10 cm³) until the washings were colourless. The resulting pale yellow product was dried in vacuo; yield: 0.456 g (65% relative to FeCl₃). Found: Cl, 15.3; C, 46.0; H, 4.9. Calc. for $Fe_2Cl_6PC_{54}O_{18}H_{68}$: Cl, 15.3; C, 46.6; H, 4.9%. Slow diffusion of hexanes into an acetone solution of 1 resulted in the formation of X-ray quality yellow crystals of 1. Four v(Fe-Cl) stretches were observed in the far-IR spectrum at 360(s), 300(m), 280(m) and 230(w) cm⁻¹. The ¹H NMR spectrum exhibited the characteristic resonances attributed to the protonated phosphine ligand [H-TMPP]⁺ $(CD_3CN, \delta ppm)$: 3.67 (s, 18, *o*-OCH₃), 3.85 (s, 9, p-OCH₃), 6.24 (d, 6, m-H), 8.37 (d, 1, P-H). The electronic spectrum consists of three features [CHCl₃, λ_{max} (nm); ε M⁻¹ cm⁻¹]: 377(1.80 × 10³), 287(sh) and 260(6.80×10^4). The decanted brownred reaction solution was evaporated to dryness; yield of [TMPP-Cl][FeCl₄] (2): 0.078 g (11% relative to FeCl₃). ¹H NMR (CD₃CN, δ ppm): 3.35 (s,

18H), 3.64 (s, 9H), 5.95 (d, 6H). ³¹P NMR (CD₃CN, δ ppm): -1.56. IR (CsI, Nujol): v(Fe—Cl) = 380 cm⁻¹. FAB mass spectrum: m/z = 567 (corresponding to [TMPP-Cl]⁺).

(ii) Preparation of $[\text{H-TMPP}]_2[\text{Fe}_2^{II,II}\text{Cl}_6]$ (1) in diethyl ether. A quantity of FeCl₃ (0.062 g, 0.380 mmol) was dissolved in diethyl ether (15 cm³) and filtered into a diethyl ether solution (25 cm³) of TMPP (0.203 g, 0.380 mmol). The resulting yellow suspension was stirred at room temperature for 24 h. The reaction was treated in a manner identical to that described in (i) above; yield: 0.148 g (56%).

(b) Preparation of $[H-TMPP]_2[Fe^{II}Cl_4]$ (3).

(i) From decomposition of $[H-TMPP]_2[Fe_2Cl_6]$ (1) in alcohols. An amount of 1 (0.050 g, 0.036 mmol) was dissolved in EtOH or MeOH (40 cm³). The resulting yellow solution slowly became colourless over the period of 1 week under an argon atmosphere. Careful evaporation of the solvent by purging the solution with a strong flow of argon yielded a crop of pale yellow crystals suitable for a single-crystal X-ray study.

(ii) From reaction of $[Fe^{II}(NCCH_3)_6][AlCl_4]_2$ with TMPP. An amount of [Fe(NCCH₃)₆][AlCl₄]₂ (0.303 g, 0.474 mmol) was reacted with 2 equivalents of TMPP (0.505 g, 0.949 mmol) in MeOH (20 cm^3) . The bright yellow solution was stirred at room temperature for 0.5 h. A pale yellow solid, isolated after reduction of the volume, was dried under a dynamic vacuum and recrystallized from an acetone/hexanes mixture (v/v 1:1); yield: 0.240 g (40%). Found : C, 51.9; H, 4.9. Calc. for $FeCl_4P_2$ $C_{54}O_{18}H_{68}$: C, 51.3; H, 5.4%. Pale yellow microcrystals were grown by slow diffusion of diethyl ether into a THF solution of 3, or by diffusion of toluene into a CH₂Cl₂ solution. IR (CsI, Nujol, cm⁻¹): v(Fe--Cl) = 280(s). UV-vis [CHCl₃, λ_{max} (nm); $\varepsilon (M^{-1} cm^{-1})$]: 361(4.6 × 10³), 309(4.9 × 10³), 287(sh), 261(7.2×10^4). ¹H NMR (CD₃CN, δ ppm): 3.68(s, 18), 3.88(s, 9), 6.25(d, 6), 8.40(d, 1). Cyclic voltammetry: $(E_{1/2})_{ox} = +0.04 \text{ V}; \ \mu_{eff} = 5.29 \ \mu_{B}.$

(c) Preparation of $[H-TMPP][Fe^{III}Cl_4]$ (4).

(i) From oxidation of [H-TMPP]₂[Fe^{II}Cl₄] (3) with molecular oxygen. An amount of **3** (0.050 g, 0.039 mmol) was dissolved in MeOH (20 cm³). Upon bubbling dry oxygen into the solution the colour changed from yellow to orange. Evaporation of the solution produced long orange needles that were of a quality suitable for an X-ray study. Found : C, 44.3; H, 4.7. Calc. for FeCl₄PC₂₇O₉H₃₄: C, 44.3; H, 4.6%. IR (CsI, Nujol, cm⁻¹): ν (Fe—Cl) = 380(s). ¹H NMR (CD₃CN, δ ppm): 3.70(s, 18), 3.88(s, 9), 6.26(d, 6), 8.38(d, 1). UV-vis [CHCl₃, λ_{max} (nm); ε (M⁻¹ cm⁻¹)]: 365(5.05 × 10³), 315(4.9 × 10³), 289(sh) and 261(7.54 × 10⁴). Cyclic voltammetry: ($E_{1/2}$)_{red} = +0.03 V; μ_{eff} = 6.11 μ_{B} .

(ii) From reaction of [Fe^{II}(NCCH₃)₆][SbCl₆]₂ with TMPP. A quantity of [Fe(NCCH₃)₆][SbCl₆]₂ (0.173 g, 0.179 mmol) was added to 2 equivalents of TMPP (0.190 g, 0.357 mmol) in MeOH (10 cm³). Upon addition of the solvent a bright yellow solid rapidly precipitated from an orange solution. The orange filtrate was decanted from the solid and subjected to a dynamic vacuum to yield a residue which was washed with diethyl ether $(2 \times 10 \text{ cm}^3)$ and dried in vacuo; yield: 0.0642 g (51% relative to Fe^{2+}). The resulting orange compound was identified by a comparison of its IR and ¹H NMR properties to those of an authentic, structurally characterized sample of [H-TMPP][Fe^{III}Cl₄]. The yellow solid was characterized as [H-TMPP] $[SbCl_6]$; yield: 0.089 g (40% relative to TMPP). Found: Cl, 24.5; C, 37.3; H, 3.9. Calc. for SbCl₆P C₂₇O₉H₃₄: Cl, 24.1; C, 36.7; H, 3.9%. IR (CsI, Nujol): $v(Sb--Cl) = 345 \text{ cm}^{-1}$. ¹H NMR (CDCl₃, δ ppm): 3.69(s, 18), 3.87(s, 9), 6.11(d, 6) and 8.33(d, 1). The identical compound was independently prepared from the reaction of Na⁺SbCl₆⁻ with 1 equivalent of TMPP in MeOH.

(d) Oxygen reactions to yield Fe^{III}Cl₃(O=TMPP) (5).

(i) From [H-TMPP]₂[Fe₂Cl₆] (1). An amount of 1 (0.050 g, 0.036 mmol) was dissolved in EtOH (30 cm³). The resulting yellow solution was bubbled with dry oxygen for 10 min, during which time it turned to a dark orange colour. The reaction solution was then left to evaporate under a purge of oxygen gas which produced red-orange crystals of 5; yield: 0.041 g (80% relative to 1). Found: C, 45.9; H, 4.7. Calc. for FeCl₃PO₁₀C₂₇H₃₃: C, 45.6; H, 4.6%. IR (CsI, Nujol, cm⁻¹): 380(s) and 320(w). Electronic spectrum [CHCl₃, λ_{max} (nm); ε (M⁻¹ cm⁻¹)]: 342(4.3 × 10³), 287(sh), 258(4.0 × 10⁴). FAB-mass spectrum: m/z = 548 (corresponding to TMPP=O); ¹H NMR (CD₃CN): very broad. Cyclic voltammetry: $(E_{1/2})_{red} = -0.02$ V, $\mu_{eff} = 6.31 \mu_{B}$.

An anaerobic EtOH solution of 1, as described above, became colourless during a period of standing for 1 week. After bubbling oxygen through this solution for 5 min, a yellow colour ensued, which converted to dark orange within 10 min. Red-orange crystals of 5 formed under an oxygen atmosphere after several days.

An amount of 1 (0.050 g, 0.036 mmol) was dissolved in acetonitrile (20 cm^3) and a stream of oxygen gas was passed through the solution for ca 1 h. The resulting orange solution was layered with hexanes and diethyl ether. Crystals of 5 were isolated from this solvent mixture after 1 day; yield 0.040 g (78% relative to 1).

(ii) From $[H-TMPP]_2[Fe^{II}Cl_4]$ (3) with molecular oxygen. An amount of 3 (0.100 g, 0.079 mmol) was

dissolved in MeOH (20 cm³), treated with oxygen for 4 h and layered with hexanes and diethyl ether. Red-orange crystals of 5 were isolated after 1 day; yield : 0.030 g (53% relative to 3).

(iii) From [H-TMPP][Fe^{III}Cl₄] (4). A quantity of 4 (0.100 g, 0.137 mmol) was dissolved in MeOH (30 cm³), whereupon the solution was bubbled with oxygen for 3–4 days. During this time, the solvent was replenished regularly to avoid complete evaporation. Red-orange crystals of 5 were eventually deposited at the bottom of the flask; yield: 0.058 g (60% relative to 4).

(iv) From FeCl₃, TMPP and O₂ mixtures. An amount of FeCl₃ (0.142 g, 0.874 mmol) was treated with 1 equivalent of TMPP (0.465 g, 0.874 mmol) in EtOH (20 cm³) under a slow stream of oxygen for 3 h. The resulting orange solution was evaporated under reduced pressure to yield a dark orange solid, which was then recrystallized from EtOH and diethyl ether; yield: 0.345 g (54%).

(v) From FeCl₃ and TMPP=O. A quantity of FeCl₃ (0.119 g, 0.736 mmol) was treated with 1 equivalent of TMPP oxide (0.404 g, 0.736 mmol) in EtOH (12 cm³). The resulting orange suspension was stirred at room temperature for *ca* 1 h until all of the FeCl₃ had dissolved. The suspension was then filtered in air and washed with EtOH (3×10 cm³), followed by diethyl ether (1×10 cm³) and finally dried *in vacuo*; yield: 0.423 g (81% relative to FeCl₃).

(e) Preparation of TMPP=O. A quantity of FeCl₃(O=TMPP) (5) (0.067 g, 0.094 mmol) was reacted with a 10-fold excess of TMPP (0.500 g, 0.939 mmol) in acetone (20 cm³) under a stream of dry oxygen. The solution was stirred at room temperature for 1-2 h, during which time a significant quantity of white solid precipitated from solution. The orange solution was decanted from the solid, which was washed with diethyl ether $(3 \times 10 \text{ cm}^3)$ and dried *in vacuo*. Chilling the orange filtrate produced more white product, characterized as TMPP=O; yield: 0.325 g (63% relative to TMPP). Work-up of the remaining orange solution consisted of successive extractions by CH₂Cl₂ and EtOH, which yielded crystals of FeCl₃(O=TMPP); total recovered yield: 0.062 g (93% of the initial mass). ¹H NMR of TMPP=O (CD₃CN, δ ppm): 3.48(s, 18), 3.79(s, 9), 6.10(d, 6).

(f) Reaction of [TMPP-Cl]Cl with FeCl₃. A solution of TMPP (0.461 g, 0.867 mmol) in benzene (20 cm³) was bubbled with chlorine gas for 1–2 min until it had turned bright yellow, thereby signifying the formation of the oxidized compound TMPP-Cl⁺Cl⁻. The reaction solution was then pumped down to a sticky residue, but since no solid could be isolated it was redissolved in benzene (20 cm³)

and added to FeCl₃ (0.141 g, 0.867 mmol). A colour change from yellow to dark brown-red immediately ensued. The solvent was removed under dynamic vacuum to produce a brown residue that was recrystallized from an acetone/hexanes mixture (v/v 1:1); yield: 0.020 g. The properties of this solid were identical to those described for [TMPP-Cl] [FeCl₄] (2) (vide supra).

Physical measurements

IR spectra were recorded on a Perkin-Elmer 599 or a Nicolet 740 FT-IR spectrophotometer. ¹H NMR spectra were measured on a Varian-Gemini 300 MHz spectrometer. Chemical shifts were referenced relative to the residual proton impurity of d_3 -acetonitrile (1.93 ppm with respect to TMS). Electronic absorption spectra were measured on a Hitachi U-2000 spectrophotometer. Electrochemical measurements were performed using an EG&G Princeton Applied Research Model 362 scanning potentiostat in conjunction with a BAS Model RXY recorder. Cyclic voltammetry experiments were carried out at $22 \pm 2^{\circ}C$ in methylene chloride containing 0.1 M tetra-n-butylammonium tetrafluoroborate (TBABF₄) as the supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode and are uncorrected for junction potentials. The Cp₂Fe/ Cp_2Fe^+ couple occurs at $E_{1/2} = +0.51$ V under the same experimental conditions. Variable-temperature magnetic susceptibility measurements were carried out on a Quantum Design MPMS susceptometer in the Physics and Astronomy Department at Michigan State University. Data points were collected over a temperature range from 5 to 300 K at 20° intervals in a field of 500 G. Elemental analyses were performed at Galbraith Laboratories, Inc.

X-ray crystallographic procedures

The structures of complexes 1, 3 and 4 were determined by applications of general procedures described elsewhere.¹³ Geometric and intensity data were collected on a Nicolet P3/F diffractometer for 3 and on a Rigaku AFC6S diffractometer for 1 and 4; both instruments were equipped with graphite monochromated Mo- K_{α} ($\lambda_{\bar{\alpha}} = 0.71073$ and 0.71069 Å, respectively) radiation. The data were corrected for Lorentz and polarization effects. Calculations for 1, 3 and 4 were performed on a VAXSTATION 2000 computer using programs from the TEXSAN Crystallographic Package of the Molecular Structure Corporation.¹⁴ A summary of crystallographic data for compounds 1 and 4 is listed in Table 1,

whereas data for compound 3 have been deposited as supplementary material.

[H-TMPP]₂[Fe₂Cl₆] (1). A yellow parallelepiped of approximate dimensions $0.31 \times 0.47 \times 0.52$ mm³ was mounted at the end of a glass fibre with Dow Corning silicone grease and placed into a nitrogen cold stream at $-100 \pm 2^{\circ}$ C. A preliminary monoclinic cell was determined by centring and indexing 20 reflections. The cell was then refined by a least-squares fit of 21 reflections in the range $23 \le 2\theta \le 30^{\circ}$. Intensity data were collected from 4 to 47° in 2θ , by using the θ - 2θ scan mode. Three standard reflections were measured at regular intervals during data collection and showed no significant decay in crystal quality. After averaging equivalent reflections, 4952 unique data remained, of which 3440 were observed with $F_0^{2} \ge 3\sigma(F_0)^2$.

The position of the metal atom was determined by a solution provided by the direct methods program in SHELXS-86.15 The positions of the remaining non-hydrogen atoms and of H(1) bound to the phosphorus atom were located by use of the program DIRDIF.¹⁶ An empirical absorption correction based on the program DIFABS was applied after isotropic convergence had been achieved.¹⁷ The positions of the hydrogen atoms that were not directly located were generated by a program in the TEXSAN package. These were included in the structure factor calculation but not refined. The final full-matrix refinement involved 3440 data and 370 parameters and converged with residuals $R(R_w) = 0.046(0.079)$ and a quality-of-fit of 2.84. The final difference-Fourier map showed a highest peak of 0.96 e $Å^{-3}$.

 $[H-TMPP]_2[Fe^{II}Cl_4]$ (3). The structure of this compound is of a poor quality and is mentioned only in a preliminary form to confirm the identity of the salt as an intermediate in the chemistry of FeCl₃ with TMPP. Lack of data and problems with refining the solvent molecule precluded a full refinement of the structure to a satisfactory point. A full listing of data and a description of the structure solution have been deposited in the supplementary material.

[H-TMPP][Fe^{III}Cl₄] (4). An orange platelet of approximate dimensions $0.10 \times 0.21 \times 0.52$ mm³ was selected and mounted on the end of a glass fibre with epoxy cement. Intensity and geometric data were collected at room temperature. A preliminary orthorhombic unit cell was determined by centring and indexing on 20 reflections. The cell was then refined by a least-squares determination of 24 reflections with $9 \le 2\theta \le 23$. Intensity data were collected by the θ -2 θ scan mode over the range 4– 45° in 2θ . Three standard reflections were measured at regular intervals during data collection and

Formula	$Fe_2Cl_6P_2C_{54}O_{18}H_{68}$	FeCl ₄ PO ₉ C ₂₇ H ₃₄	
Formula weight	1391.48	731.19	
Space group	$P2_1/n$	Pbca	
Systematic absences	$h0l: h+l \neq 2n; 0k0: k \neq 2n$	0kl: k = 2n; h0l: l = 2n; hk0: h = 2n	
$a(\mathbf{A})$	14.294(8)	19.952(5)	
$b(\mathbf{A})$	10.140(9)	19.352(7)	
<i>c</i> (Å)	22.543(8)	17.821(4)	
α (°)	90.0	90.0	
β (°)	105.76(4)	90.0	
γ (°)	90.0	90.0	
$V(\text{\AA}^3)$	3144(3)	6881(6)	
Ζ	2	8	
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.469	1.411	
Crystal size (mm)	$0.31 \times 0.47 \times 0.52$	$0.10 \times 0.21 \times 0.52$	
$\mu (\mathrm{Mo-}K_{\alpha}) (\mathrm{cm}^{-1})$	8.32	8.40	
Data collection instrument	Rigaku AFC6S	Rigaku AFC6S	
Radiation (monochromated	Mo- K_{α} ($\lambda_{\alpha} = 0.71073$ Å)	$Mo-K_{\alpha} (\lambda_{\alpha} = 0.71073 \text{ Å})$	
in incident beam)	Graphite monochromated	Graphite monochromated	
Orientation reflections number, range (2θ)	21, 23–30	25, 8–25	
Temperature (°C)	-100	23 + 2	
Scan method	θ –2 θ	$\theta - 2\overline{\theta}$	
Data collection, 2θ (°)	4-47	4-45	
No. of unique data	4952	3612	
Total with $F_0^2 > 3\sigma(F_0^2)$	3440	1472	
Number of parameters refined	370	379	
Transmission factors, max., min.	0.82-1.26	0.79–1.00	
R ^a	0.046	0.051	
R _w ^b	0.079	0.066	
Quality-of-fit indicator ^c	2.84	1.457	
Largest shift/e.s.d. final cycle	0.00	0.066	
Largest peak (e Å ⁻³)	0.96	0.494	

^{*a*} $R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$

$${}^{\sigma}R_{w} = [\Sigma(w|F_{o}| - |F_{c}|)^{2}/\Sigma w|F_{o}|^{2}]^{1/2}; w = 1/\sigma^{2}(|F_{o}|).$$

Quality-of-fit =
$$[\Sigma(w|F_o| - |F_c|)^2 / (N_{obs} - N_{para})]^{1/2}$$

showed no decay over time. An empirical absorption correction was applied using the PSI-scan program within the TEXSAN package. After averaging equivalent reflections 3612 unique data remained, of which 1472 were observed with $F_{0}^{2} \ge 3\sigma(F_{0})^{2}$. The position of the metal atom was determined from a solution provided by the direct methods program MITHRIL.¹⁸ The positions of the remaining non-hydrogen atoms and of H(1) were located by the program DIRDIF. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and were included in the structure factor calculations, but not refined. The final full-matrix refinement involved 1472 data and 379 parameters. The refinement converged with residuals R and R_{w} of 0.051 and 0.066, respectively, and a quality-offit indicator of 1.457. The final difference-Fourier map showed a highest peak of 0.49 e Å⁻³.

RESULTS

Synthesis

Several years ago we reported that the reaction of anhydrous FeCl₃ with 1 equivalent of tris(2,4,6trimethoxyphenyl)phosphine in benzene yields a pale yellow compound, formulated as Fe^{III}Cl₃ (η^3 -TMPP) on the basis of elemental analyses. Although no X-ray study of the compound was available at the time, its structure was proposed to be octahedral from the number of observed ν (Fe—Cl) modes in the IR spectrum.¹⁰ Although we realized that hard first-row transition metals are not particularly compatible with a soft donor atom such as phosphorus,¹⁹ we argued that this particular phosphine would be rendered more compatible with a hard Lewis acid such as FeCl₃ by the presence of the oxygen donors, which we expected to participate in the bonding to the iron centre. Precedence for the assignment of a tridentate mode for the phosphine (i.e. η^3 -TMPP) existed in the form of the structurally characterized species Mo(CO)₃(η^3 -TMPP)^{9c} and [Rh(η^3 -TMPP)₂][BF₄]_x (x = 2, 3), ^{9a,b} wherein the ligand is coordinated to the metal centre through the phosphorus atom and two oxygen atoms from the pendent methoxy groups on the phenyl rings. At the time, this picture was the most reasonable structure that fit the available data for the iron compound.

Since the earlier report Mössbauer and EPR studies were performed, the results of which did not support this formulation.²⁰ Most importantly, we finally managed to crystallize compound 1 from acetone and the single-crystal X-ray study revealed that the complex is actually [H-TMPP]2[Fe2Cl6], in which Fe^{III} has been reduced to Fe^{II} and the tertiary phosphine has become protonated. The empirical formula for this salt differs by only one H⁺ from the earlier molecule, thus it was not possible to distinguish between the two designations on the basis of elemental composition. Three v(Fe-Cl) bands are observed in the IR spectrum of [H- $TMPP_{2}[Fe_{2}Cl_{6}]$, one of which is split which accounts for the four bands expected for a D_{2h} symmetry.

Facile reduction of FeCl₃ is not uncommon, as in the synthesis of $Fe^{II}Cl_2(HPyS)_2$ from the reaction of $FeCl_3$ and HPyS (HPyS = 2-mercaptopyridine),²¹ furthermore, TMPP is known to be quite sensitive to quaternarization in the presence of metal halides. In fact, similar chemistry was seen to occur earlier, with alcoholic cobalt(II) solutions giving rise to [H-TMPP]₂[Co^{II}Cl₄] and TMPP reactions of CoCl₂ in benzene yielding [CH₃-TMPP]₂ [Co₂Cl₆].^{22a,b} To our knowledge, however, there is no documentation in the literature of the $[Fe_2Cl_6]^{2-1}$ moiety,^{22d} although the cobalt(II) and copper(II) analogues are known and $[Fe_2I_6]^{2-}$ has been documented.^{22b,c} It is interesting to note that when the reaction is carried out in acetonitrile small amounts of 1 are isolated, but if other solvents such as chloroform or ethanol are used [H-TMPP][FeCl₄] is obtained, indicating that no reduction of the metal centre occurs in these solvents.

Upon slow dissolution of $[H-TMPP]_2[Fe_2Cl_6]$ in ethanol under anaerobic conditions, the phosphonium salt $[H-TMPP]_2[Fe^{II}Cl_4]$ (3) is observed to form. In an effort to study the reactions of this salt as they pertain to the overall reaction to form TMPP=O, the compound was prepared deliberately by the reaction of $[Fe^{II}(NCCH_3)_6][AlCl_4]_2$ with 2 equivalents of TMPP in methanol. Redissolution of 3 in methanol followed by rapid evaporation in air or treatment with a stream of oxygen

gas yields the oxidized form of the anion, viz. [H-TMPP][Fe^{III}Cl₄] (4). The conversion of Fe^{II} to Fe^{III} was monitored by IR spectroscopy in the far-IR region, according to the Fe-Cl stretching frequency which occurs at 280 cm⁻¹ for v(Fe^{II}—Cl) and 380 cm⁻¹ for v(Fe^{III}—Cl). Compound 4 was, in turn, independently prepared by the reaction of [Fe^{II}(NCCH₃)₆][SbCl₆]₂ with 2 equivalents of TMPP in methanol. Approximately 50% of the original phosphine is consumed to form [H-TMPP] [SbCl₆], as determined by NMR and IR spectroscopies as well as elemental analysis. Antimony(V) is a good oxidizing agent²³ and, therefore, it is not surprising to observe a conversion from Fe^{II} to Fe^{III} in this reaction. In a similar fashion as for 3 protonation of the phosphine occurs with the formation of the very stable $[Fe^{III}Cl_4]^-$ anion, which is quite a common phenomenon.^{24,25} The spectroscopic and electrochemical properties of 3 and 4 are in excellent agreement with the reported literature values for various salts of [Fe^{III}Cl₄]⁻ and [Fe^{II} $Cl_4]^{2-.26}$

Lastly, $FeCl_3(O=TMPP)$ (5) can be obtained quantitatively, *inter alia*, from the reaction of 4 with oxygen in methanol over a period of 1–2 days. The stability of $FeCl_3(O=TMPP)$ is evidenced by the extreme facility with which this compound is formed from 1, 3 or 4. Scheme 1 summarizes the different synthetic routes to 5 that we have encountered in this work.

Molecular structures

 $[H-TMPP]_2[Fe_2Cl_6]$ (1). The X-ray structure unequivocally established the identity of 1 as an $[Fe_2Cl_6]^{2-}$ salt, for which two protonated phosphines serve as counter-ions. An ORTEP representation of [H-TMPP]₂[Fe₂Cl₆] is shown in Fig. 1, while pertinent bond distances and angles are summarized in Table 2. The $[Fe_2Cl_6]^{2-}$ anion consists of two edge-sharing tetrahedra, with two bridging and two terminal chlorides per metal atom, and an inversion centre situated at the mid-point of the $Fe(1) \cdots Fe(1)'$ axis, as was previously observed in the isomorphous structure of [CH₃-TMPP]₂[Co₂ Cl_6 ^{22b} The Fe(1) ··· Fe(1)' separation of 3.350(4) Å, much larger than the sum of the covalent radii, precludes the assignment of a direct metal-metal bond, and is comparable to the distances of 3.32 Å found in $[Fe_2(\mu-OH)(OAc)_2(Me_3TACN)_2](ClO_4)^{27}$ and 3.35 Å in [Fe₂(BPMP)₂] (BPh₄),²⁸ but considerably longer than the corresponding distances reported for the two closely related structures $[Fe_2(SEt)_6]^{2-}$ and $[Fe_2Cl_4(OPh)_2]^{2-}$, these being 2.978(1) and 3.177(3) Å, respectively.²⁹ The average Fe^{II}—Cl bond distance for the terminal chloride



Scheme 1. Synthetic routes to FeCl₃(O=TMPP) (5).

[2.231(2) Å] is somewhat intermediate between the reported range for Fe^{II} —Cl (2.25–2.35 Å)³⁰ and Fe^{III} —Cl (2.15–2.20 Å).³¹ As expected, the average distance for the bridging chlorides is longer [2.397(2) Å] than the terminal chlorides. The Cl—Fe—Cl bond angles fall in the range expected for tctrahedral geometry [108.02(9)– 120.5(1)°], but the Cl(2)—Fe(1)—Cl(2)' and the Fe(1)—Cl(2)—Fe(1)' angles of 91.36(8) and 88.64(8)°, respectively, are considerably distorted from ideal geometry. A three-dimensional packing diagram of [H-TMPP]₂[Fe₂Cl₆] is presented in Fig. 2 and clearly shows the segregated packing of cations and anions when viewed down the *b*-axis. The structural features of the protonated phosphine are similar to those of previously reported examples. Related polynuclear iron chloride salts are $[Fe_2Cl_9]^{3-}$, $[Fe_2Cl_6(\mu-O)]^{2-}$, $[Fe_2Cl_6(\mu-OR)_2]^{2-}$ and $Fe_4Cl_8(THF)_{6}$.^{26,32}

 $[H-TMPP]_2[Fe^{II}Cl_4]$ (3). The structure of this salt is reported only for the purpose of positively identifying the species and is without remarkable



Fig. 1. ORTEP diagram showing the constituent ions in the salt $[H-TMPP]_2[Fe_2Cl_6]$ (1). Phenyl group atoms are represented as small circles for clarity, whereas all other atoms are represented as their 50% probability thermal ellipsoids.

Compound	1			4
Fe—Cl	Fe(1) - Cl(1) Fe(1) - Cl(2) Fe(1) - Cl(3) Fe(1) - Cl(2)' Fe(1) - Cl(2) Fe(1) Fe(1) Fe(1) - Cl(2) Fe(1) Fe(2.235(2) 2.385(2) 2.227(2) 2.409(2) 2.350(4)	$\begin{array}{c} Fe(1) & -Cl(1) \\ Fc(1) & -Cl(2) \\ Fe(1) & -Cl(3) \\ Fe(1) & -Cl(4) \end{array}$	2.161(4) 2.155(4) 2.168(4) 2.182(5)
Р—С	P(1)C(1) P(1)C(10) P(1)C(19)	1.773(6) 1.782(6) 1.793(6)	P(1)—C(1) P(1)—C(10) P(1)—C(19)	1.76(1) 1.76(1) 1.79(1)
Cl—Fe—Cl	$\begin{array}{c} Cl(1) & - Fe(1) Cl(2) \\ Cl(1) & - Fe(1) Cl(2) \\ Cl(2) & - Fe(1) Cl(2) \\ Cl(2) & - Fe(1) Cl(2) \\ Cl(3) & - Fe(1) Cl(2) \\ Fe(1) Cl(2) Fe(1) \\ \end{array}$	$\begin{array}{cccc} 2) & 108.02(9) \\ 2)' & 110.57(8) \\ 3) & 120.5(1) \\ 2)' & 91.36(8) \\ 3) & 110.96(9) \\ 2)' & 111.50(8) \\ 1)' & 88.64(8) \end{array}$	Cl(1)—Fe(1)—C Cl(1)—Fe(1)—C Cl(1)—Fe(1)—C Cl(2)—Fe(1)—C Cl(2)—Fe(1)—C Cl(3)—Fe(1)—C	$\begin{array}{llllllllllllllllllllllllllllllllllll$
С—Р—С	$\begin{array}{c} C(1) \longrightarrow P(1) \longrightarrow C(10) \\ C(1) \longrightarrow P(1) \longrightarrow C(19) \\ C(10) \longrightarrow P(1) \longrightarrow C(19) \end{array}$	115.3(3) 109.2(3) 2) 114.4(3)	C(1)—P(1)—C(C(1)—P(1)—C(C(10)—P(1)—C	10)114.5(7)19)116.0(6)2(19)112.4(7)

Table 2. Selected bond distances (Å) and angles (°) for compounds 1 and 4

features. The metal atom lies on a two-fold axis and is ligated by four chlorine atoms to form the $[FeCl_4]^{2-}$ anion. Two protonated phosphines, [H-TMPP]⁺, serve as the cations in this structure. The structural features of the cation are similar to those of the free phosphine and other phosphonium salts.²⁴ It is noteworthy that the $[FeCl_4]^{2-}$ anion has been observed to crystallize only with very large cations, such as quaternary ammonium or phosphonium ions.²⁶



Fig. 2. Packing diagram of [H-TMPP]₂[Fe₂Cl₆] (1) viewed down the b-axis.



Fig. 3. ORTEP diagram for $[H-TMPP][FeCl_4]$ (4). Phenyl group atoms are represented as small circles for clarity, whereas all other atoms are represented as their 50% probability thermal ellipsoids.

[H-TMPP][Fe^{III}Cl₄] (4). An ORTEP diagram of the two constituent ions in the asymmetric unit of 3 is shown in Fig. 3. Pertinent bond angles and distances are summarized in Table 2. The metal atom is surrounded by four chlorine atoms to form the well-known [FeCl₄]⁻ anion. The Fe—Cl bond distances are in the range 2.161(4)–2.182(5) Å, which is in excellent agreement with the literature.^{31,32} The Cl—Fe—Cl bond angles fall between 106.2(2) and 112.6(2)°, which deviates very little from ideal tetrahedral geometry. The phosphonium cation is similar to that found in other structures.²⁴

DISCUSSION

Chemistry of FeCl₃ with TMPP.

The compound $[\text{H-TMPP}]_2[\text{Fe}_2\text{Cl}_6]$ is the first reported example of a compound containing the unit $[\text{Fe}_2\text{Cl}_6]^{2-.22d,33}$ Whereas the molecule Fe_2Cl_6 is known to be the stable form of FeCl_3 in the gas phase, and similar di-Fe^{III} compounds of the type $[\text{Fe}_2\text{Cl}_9]^{3-}$ or $[\text{Fe}_2\text{Cl}_6(\mu\text{-O})]^{2-}$, $[\text{Fe}_2\text{Cl}_6(\mu\text{-OEt})_2]^{2-}$ and $\text{Fe}_4\text{Cl}_8(\text{THF})_6$ have been structurally characterized, ^{26,32} no such analogous di-ferrous chloride complexes have been reported. There are more examples of the $[M_2X_6]^{2-}$ unit with the heavier halogens, for example the anions $[\text{Fe}_2\text{I}_6]^{2-}$ and $[\text{Mn}_2X_6]^{2-}$ (X = Br, I) are known.³⁴ The isolation of [H-TMPP]_2[\text{Fe}_2\text{Cl}_6] from the 1: 1 stoichiometric reaction of FeCl₃ with TMPP casts some doubt on

the proposed formulations of stable yellow compounds, such as FeCl₃(PCy₃)³⁵ and FeCl₃(PPh₃).³⁶ Actually, neutral four-coordinate adducts of FeCl₃ are quite rare in general; among them only $FeCl_3(S_4N_4)^{37}$ and $FeCl_3(THF)^{31d}$ have been structurally characterized. Most neutral "FeX₃L" species have actually proven to be of the type [FeCl₄] [FeCl₂L₂]. A more common stoichiometry for this type of complex is $FeCl_3(PR_3)_2$ (R = Me, Ph),³⁸ as in the recently reported FeBr₃(PMePh₂)₂.³⁹ Further supporting our contention that the mono-adducts $FeCl_3(PR_3)$ are not likely to be particularly stable is the work of Poli et al., who report the synthesis and isolation of FeCl₃(PCy₃) and crystallization of FeCl₃(PBu^t₃),^{32a} but only the detection of FeCl₃(PMe₃) and FeCl₃(PPh₃) as elusive dark red species by low-temperature EPR experiments.³⁸ In the same work, the eventual formation of unidentified iron(II) species from the FeCl₃/PPh₃ reaction in toluene was noted, along with the concomitant production of chloro-substituted toluene as the oxidized by-product. In the present case, work-up of the benzene reaction filtrate produced a redbrown solid, whose mass-spectrometry, ¹H and ³¹P NMR and IR data collectively point to the salt [Cl-TMPP][FeCl₄]. A rational synthesis of this species involved the use of [Cl-TMPP]⁺Cl⁻, prepared by reacting TMPP with chlorine gas in benzene, which was then reacted with FeCl₃ to give a compound whose properties are in agreement with those of the by-product. Consequently, we propose the following mechanism for the formation of 1:

$$\begin{array}{ccc} 3FeCl_3 + 3TMPP \xrightarrow{2HCl} [H-TMPP]_2[Fe_2Cl_6] \\ Fe^{III} & P^{III} & Fe^{II}, P^{III} \\ & + [Cl-TMPP][FeCl_4]. \\ Fe^{III} & P^V \end{array}$$

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As the equation clearly indicates, the source of the protons and the extra chloride ions is postulated to be adventitious HCl, which is a ubiquitous contaminant in metal halides. In order to test the general nature of this reaction, and to isolate the iron(II) species previously mentioned by Poli et al., we set out to re-investigate the chemistry of PPh₃ and $FeCl_3$. The reactions of $FeCl_3$ with 1 equivalent of $PR_3(R = Cy, Ph)$ in benzene produce dark red solutions instantaneously, from which red solids can be isolated. The spectroscopic properties of the products are in agreement with those of the reported mononuclear FeCl₃(PR₃) complexes.^{32a,38} However, if the reaction is allowed to progress further, the solution turns yellow. The yellow solids isolated from these solutions exhibit far-IR spectra that are very similar to that of 1 $[v(\text{Fe}-\text{Cl}) = 380(\text{s}), 360(\text{m}), 315(\text{m}), 300(\text{w}) \text{ cm}^{-1}]$ for R = Cy and 380(s), 330(m), 320(m), 300(w) cm^{-1} for R = Ph]. In addition, the highest peaks in the FAB mass spectrum of these complexes are m/z = 281 and m/z = 263, corresponding to [H-PCy₃]⁺ and [H-PPh₃]⁺, respectively, and in the case of the tricyclohexylphosphonium compound, the characteristic P—H stretch at 2400 cm⁻¹ was observed in the IR spectrum.

The final oxidized product FeCl₃(O=TMPP) (5) is a very stable compound and quite unique in itself, since it is atypical for a mono-phosphine oxide adduct of FeCl₃ to be more stable than the corresponding bis-adduct. To date, only two analogous compounds have been reported to our knowledge; these are FeCl₃(O=PPh₃) by Lindner *et al.* in 1967⁴⁰ and FeCl₃(O=PCy₃) by Issleib *et al.* in 1954,³⁵ but neither have been structurally characterized. A much more commonly encountered stoichiometry is FeX₃L₂ or FeL₄ⁿ⁺, where L is a phosphine oxide ligand.⁴¹

Oxidation chemistry of $[Fe_2Cl_6]^{2-}$

We now discuss the reaction pathway that leads to the formation of complex 5, summarized in Scheme 2. In order to understand the present results, one must first take note of previous work in this area, particularly with respect to the solvent dependence of this chemistry. Let us first consider the reactions of FeCl₃ and PR₃ ligands that have been performed in CH₃CN. In this solvent the oxidation of triphenylphosphine to triphenyl-



Scheme 2. Major products isolated from the reaction of $[H-TMPP]_2[Fe_2Cl_6]$ with O_2 in alcohols.

phosphine oxide by iron(III) complexes in the presence of molecular oxygen was reported by Ondrejovic and co-workers to yield complexes of empirical formula $FeX_3(O=PPh_3)_2$ (X = Cl, NCS, Br),^{8a} among which "FeCl₃(O=PPh₃)₂" was structurally characterized and proven to actually be [FeCl₄][FeCl₂(O=PPh₃)₄].⁴² When identical chemistry was performed in a protic solvent such as methanol, the compound [CH3-PPh3][FeCl4] was isolated.^{31a} Ondrejovic proposes that protic solvents induce the quaternarization of the phosphine, by methylation in this case, which is then oxidized to Ph₃P=O.^{31a} In the 1970s Sutin et al. also investigated the oxidation of PPh3 in the presence of iron(III) and iron(IV) dithiolate complexes of the type $[Fe(mnt)_2]^-$, where $[mnt]^{2-}$ is maleonitriledithiolate.43 In this work, only the stable bis-phosphine oxide complex $[Fe(mnt)_2(O=PPh_3)_2]^-$ was observed, however, with no evidence of intermediate species such as the previously postulated dioxygen adducts.^{5,44} Recently, McAuliffe and coworkers reported that oxygen decomposes $FeBr_3(PMePh_2)_2$ to an orange product that exhibits a strong P=O stretching frequency in the IR spectrum, but no molecular oxygen species were detected or isolated. These results, like ours, disfavour the hypothesis that stable dioxygen complexes are important intermediates in the oxidation of PR₃ to $O = PR_3$.³⁹

As in the aforementioned chemistry, the reaction between $FeCl_3/TMPP$ and oxygen is also solventdependent. The reaction of $[H-TMPP]_2[Fe_2Cl_6]$ (1) with oxygen in CH₃CN leads to the rapid formation of $FeCl_3(O=TMPP)$ (5) with no detection of phosphonium intermediates. The reaction pathway is dramatically different in alcohol solvents in which protic phosphonium salts of tetrachloroferrate(II) and (III) are formed. A suspension of [H-TMPP]2 $[Fe_2Cl_6]$ (1) reacts with molecular oxygen in ethanol or methanol to form [H-TMPP][FeCl₄] (4), as determined by IR spectroscopy and confirmed by X-ray crystallography. One must bear in mind, however, that this reaction is not quantitative, since some [H- $TMPP_{2}[Fe_{2}Cl_{6}]$ must be sacrificed to yield extra chloride ions for [FeCl₄]⁻. The salt [H-TMPP] [FeCl₄] further reacts with oxygen in alcohols to form FeCl₃(O=TMPP) (5). Scheme 2 also points out that if [H-TMPP]₂[Fe₂Cl₆] is suspended in ethanol (but without the addition of oxygen) for a period of time in excess of 1 week, the compound eventually dissolves, with reaction, to yield the iron(II) species [H-TMPP]₂[FeCl₄] (3). Compound 3 can, in turn, be reacted with oxygen in methanol or ethanol to form compound 4, and subsequently, compound 5. We have independently prepared complexes 3 and 4 and demonstrated that they indeed react as proposed in the scheme.

Two years ago we reported the formation of a green intermediate during the reaction of [H- $TMPP_{2}[Fe_{2}Cl_{6}]$ (1) with molecular oxygen in CH_2Cl_2 .¹⁰ At that time we hypothesized that the species was a dioxygen adduct, but subsequent IR studies of the behaviour of 1 in CH₂Cl₂ revealed only the appearance of $[FeCl_4]^-$ and $[ClCH_2^-$ TMPP]⁺ ions over time. Facile decomposition of free TMPP in CH₂Cl₂ to give [ClCH₂-TMPP]Cl is well-known.^{12a} Thus, we conclude that the TMPP ligand in [H-TMPP]₂[Fe₂Cl₆] is reacting with CH_2Cl_2 . We note that photochemically induced reactions of similar FeCl₃/PR₃ compounds in chlorinated solvents are documented as in the formation of [FeCl₄][FeCl₂(dmpe)₂] from the photochemical oxidation of FeCl₂(dmpe)₂ in chlorinated solvents such as CH₂Cl₂, CHCl₃ or CCl₄.⁴⁵

Catalytic formation of TMPP=O

Finally, in view of Ondrejovic's work and the demonstrated catalytic nature of the $FeCl_3/PR_3/O_2$ systems, it was relevant to ask whether $FeCl_3$ (O=TMPP) (5) could act as a catalyst for the oxidation of TMPP to TMPP=O. Indeed, when $FeCl_3(O=TMPP)$ is reacted with an excess of the phosphine (from 10- to 100-fold) in acetone, acetonitrile or ethanol in the presence of oxygen, TMPP=O is formed in high yield with essentially complete recovery of $FeCl_3(O=TMPP)$.

CONCLUSIONS

In summary, the chemistry of 1:1 mixtures of FeCl₃/TMPP with oxygen appears to be dominated by the formation of $[Fe^{II}Cl_4]^{2-}$, $[Fe^{III}Cl_4]^{-}$ and [H-

TMPP⁺ species. In accord with this observation is the demonstrated role of quaternary onium tetrachloroferrate salts in numerous catalysed reactions such as hydrosilylation,⁴⁶ polymerization of ε caprolactone⁴⁷ and polymerization of α -oxides.⁴⁸ The present work has also established the existence of a hitherto unknown di-ferrous chloride, namely [Fe₂Cl₆]^{2-,22d} Collectively, the results of this investigation support the conclusion that the stable and unprecedented mono-phosphine oxide adduct FeCl₃(O=TMPP) does not form via the formation of metal-oxygen adducts, but via quaternarization of the phosphine. Finally, we did not observe the formation of bis-phosphine oxide complexes, a result that is in contrast to previously reported work.

Acknowledgements-We gratefully acknowledge the National Science Foundation (Grant CHE-8914915 to K.R.D.) and the Camille and Henry Dreyfus Foundation for financial support. The X-ray equipment was purchased with grants provided by the National Science Foundation (Grants CHE-8403823 and CHE-8908088). The NMR equipment was supported by grants from the National Science Foundation (Grant CHE-88-00770) and the National Institutes of Health (Grant No. 1-510-RR04750-01). The SQUID instrument is housed in the Physics and Astronomy Department and was purchased by The Center for Fundamental Materials Research, Michigan State University. The authors would like to thank Dr Sue-Jane Chen for help with the data collection of compound 3 and Dr Steven C. Haefner for assistance with the crystallographic procedures and helpful discussions.

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