Oligophosphine Ligands.
XI.* Hexacoordinate Halogenoiron Complexes $FeX_2[P(CH_2CH_2CH_2PMe_2)_3]$ (X = Cl, Br, I)

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Abstract

The reaction of anhydrous iron(II) halides with the tripod tetra(tertiary) phosphine $P(CH_2CH_2CH_2PMe_2)_3$ gave the complexes *cis*-$FeX_2[P(CH_2CH_2CH_2PMe_2)_3]$ with X = Cl (**I**), Br (**II**), and I (**III**). Crystals of **I**–**III** are monoclinic, space group $P2_1/n$ (Z = 4) with a = 946.5(3), b = 1416.8(5), c = 1682.9(8) pm, and β = 104.85(3)° for the chloride **I**, a = 952.9(4), b = 1456.3(8), c = 1671(1) pm, and β = 104.89(4)° for the bromide **II**, and a = 959.8(9), b = 1510.1(7), c = 1688(2) pm, and β = 104.29(9)° for the iodide **III**, respectively. The X-ray structures were solved by conventional methods and refined to the following discrepancy indexes: **I**, R = 0.062, R_w = 0.067 (1109 data); **II**, R = 0.088, R_w = 0.080 (972 data); **III**, R = 0.097, R_w = 0.102 (799 data). The coordination geometry of the complexes corresponds to distorted octahedral. Selected bond lengths are (in pm): Fe–PMe_2 (*trans*-atom P); 233.8(5) and 230.6(5) for **I**, 230(1) and 229(1) for **II**, and 2 × 233(2) for **III**. Fe–PMe_2 (*trans*-atom X); 223.1(5) for **I**, 225(1) for **II**, and 228(2) for **III**. Fe–P; 220.2(5) for **I**, 223(1) for **II**, and 223(2) for **III**. Fe–X; 241.0(4) and 238.8(4) for **I**, 255.5(6) and 255.0(6) for **II**, and 273.9(8) and 272.5(8) for **III**.

Introduction

This work reports the preparation and structural characterization of three halide complexes of iron(II) derived from the novel tripod tetra(tertiary) phosphine $P(CH_2CH_2CH_2PMe_2)_3$, recently prepared in our laboratory [2]. The compounds *cis*-$FeX_2[P(CH_2CH_2CH_2PMe_2)_3]$, where X = Cl (**I**), Br (**II**), and I (**III**), described hereafter were synthesized with the principal objective of obtaining suitable precursors of hydro and alkyl complexes containing reactive *cis*-Fe(H)(X), *cis*-Fe(H)(R), *cis*-FeH_2, and *cis*-FeR_2 fragments [3].

Experimental

All manipulations were carried out under nitrogen atmosphere as described previously [4].

Preparation of Complexes

$FeCl_2[P(CH_2CH_2CH_2PMe_2)_3]$ (I)

A mixture of 1.02 g (8.05 mmol) of anhydrous $FeCl_2$, 100 ml of toluene and 10 ml of ethanol was heated to 60 °C. Addition of the tetra(tertiary) phosphine ligand (2.75 g, 8.08 mmol) caused the rapid formation of a violet solution which was kept at 60 °C for 2 h and subsequently refluxed for an additional 15 min. The mixture was then concentrated under reduced pressure to give a final volume of approximately 50 ml, to which hexane (80 ml) was added in portions. Oily deposits which were occasionally observed were removed by filtration and the filtrate was allowed to stand at –30 °C overnight, during which time complex **I** separated as violet needles. Yield: 3.24 g (86%). Found: C, 38.22; H, 7.87; Cl, 15.20; Fe, 11.63; calcd. for $C_{15}H_{36}Cl_2FeP_4$ (467.10): C, 38.57; H, 7.77; Cl, 15.18; Fe, 11.96%.

$FeBr_2[P(CH_2CH_2CH_2PMe_2)_3]$ (II)

By analogy to **I** from 3.80 g (17.62 mmol) of $FeBr_2$ and 6.00 g (17.63 mmol) of the ligand. Yield: 6.80 g (69%) of violet complex **II**. Found: C, 32.91; H, 6.82; Br, 29.31; Fe, 9.50; calcd. for $C_{15}H_{36}Br_2FeP_4$ (556.01): C, 32.40; H, 6.53; Br, 28.74; Fe, 10.04%.

$FeI_2[P(CH_2CH_2CH_2PMe_2)_3]$ (III)

As described above from 1.80 g (5.81 mmol) of FeI_2 and 1.95 g (5.73 mmol) of $P(CH_2CH_2CH_2$-

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*For Part X, see ref. 1.

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$PMe_2)_3$. Yield: 2.61 g (69%) of complex **III** (partly as violet-black needles, partly as a grey powder). Found: C, 27.59; H, 5.35; Fe, 8.58; I. 38.96; calcd. for $C_{15}H_{36}FeI_2P_4$ (650.01): C, 27.72; H, 5.58; Fe, 8.59; I, 39.06%.

X-ray Studies

Weakly-diffracting needle-shaped crystals of the complexes grew from the toluene/hexane mother liquors of the above preparations. Since attempts at recrystallization failed, the crystal quality of the specimens chosen for X-ray work was poor. However, even with these reservations, the salient features of the structures were revealed and it therefore was deemed unnecessary to repeat the diffraction experiments.

X-ray measurements were made at 20 ± 2 °C on a Syntex $P2_1$ instrument using Mo-Kα radiation (λ = 71.069 pm). Details of data collection ($\theta/2\theta$ scan) and processing, and of programs used, have been described previously [4]. Absorption corrections were not applied. The structures were solved by conventional Patterson, Fourier and least-squares refinement techniques.

Crystallographic Data

I: M = 467.10; monoclinic, space group $P2_1/n$; a = 946.5(3), b = 1416.8(5), c = 1682.9(8) pm, β = 104.85(3)°; $V = 2181 \times 10^6$ pm^3, $Z = 4$, D = 1.42 g cm^{-3}, μ = 11.5 cm^{-1}. Anisotropic refinement converged at R = 0.062 and R_w = 0.067 (1109 reflections with $|F_o| > 3\sigma(F_o)$ and $2\theta_{max}$ = 36°; unit weights).

II: M = 556.01; monoclinic; space group $P2_1/n$; a = 952.9(4), b = 1456.3(8), c = 1671(1) pm, β = 104.89(4)°; $V = 2241 \times 10^6$ pm^3, $Z = 4$, D = 1.65 g cm^{-3}, μ = 43.9 cm^{-1}. Final R values were R =

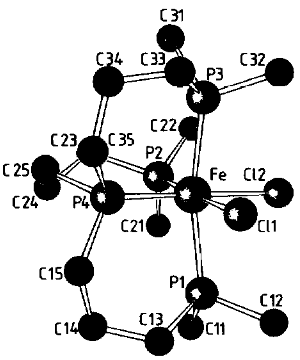

Fig. 1. The structure of $FeCl_2[P(CH_2CH_2CH_2PMe_2)_3]$ (I). Important bond lengths (pm) and angles (°) are: Cl1–Fe, 238.8(4); Cl2–Fe, 241.0(4); P1–Fe, 233.8(5); P2–Fe, 223.1(5); P3–Fe, 230.6(5); P4–Fe, 220.2(5). Cl2–Fe–Cl1, 93.6(2); P1–Fe–Cl1, 81.5(2); P1–Fe–Cl2, 83.9(2); P2–Fe–Cl1, 176.9(2); P2–Fe–Cl2, 83.7(2); P2–Fe–P1, 99.7(2); P3–Fe–Cl1, 83.2(2); P3–Fe–Cl2, 91.5(2); P3–Fe–P1, 163.8(2); P3–Fe–P2, 95.3(2); P4–Fe–Cl1, 85.6(2); P4–Fe–Cl2, 179.0(2); P4–Fe–P1, 95.4(2); P4–Fe–P2, 97.1(2); P4–Fe–P3, 88.9(2).

TABLE I. Fractional Atomic Coordinates with e.s.d.s for I–III.

Atom	I (X = Cl)			II (X = Br)			III (X = I)		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Fe	−0.0640(2)	0.8057(2)	0.2165(1)	−0.0710(5)	0.8057(3)	0.2130(3)	−0.0771(8)	0.8051(5)	0.2092(5)
X1	0.0839(4)	0.6869(3)	0.2983(3)	0.0836(4)	0.6807(3)	0.3000(2)	0.0774(6)	0.6736(3)	0.3015(3)
X2	−0.2828(4)	0.7113(3)	0.1908(3)	−0.2991(4)	0.7060(3)	0.1844(3)	−0.3195(5)	0.7023(3)	0.1690(4)
P1	−0.1185(5)	0.8384(3)	0.3416(3)	−0.1246(11)	0.8389(7)	0.3368(6)	−0.1406(21)	0.8398(12)	0.3302(13)
P2	−0.2097(5)	0.9105(3)	0.1362(3)	−0.2142(10)	0.9108(7)	0.1334(6)	−0.2120(18)	0.9118(11)	0.1306(10)
P3	0.0089(5)	0.7330(3)	0.1110(3)	0.0046(9)	0.7333(6)	0.1096(6)	0.0018(20)	0.7342(12)	0.1057(12)
P4	0.1373(4)	0.8908(3)	0.2422(3)	0.1286(9)	0.8924(7)	0.2405(6)	0.1176(19)	0.8908(12)	0.2404(12)
C11	−0.259(2)	0.916(1)	0.358(1)	−0.272(4)	0.914(3)	0.351(2)	−0.274(6)	0.920(4)	0.337(3)
C12	−0.171(2)	0.736(1)	0.393(1)	−0.170(4)	0.744(3)	0.394(2)	−0.192(6)	0.752(4)	0.392(4)
C13	0.038(2)	0.878(1)	0.424(1)	0.026(4)	0.888(2)	0.422(2)	0.003(6)	0.891(4)	0.415(3)
C14	0.116(2)	0.964(1)	0.401(1)	0.102(4)	0.963(3)	0.394(2)	0.104(6)	0.954(4)	0.396(3)
C15	0.219(2)	0.932(1)	0.349(1)	0.195(4)	0.934(3)	0.346(2)	0.190(6)	0.919(4)	0.339(3)
C21	−0.347(2)	0.975(1)	0.174(1)	−0.353(4)	0.968(3)	0.163(2)	−0.368(6)	0.957(4)	0.150(3)
C22	−0.337(2)	0.867(1)	0.041(1)	−0.332(4)	0.877(3)	0.036(2)	−0.297(6)	0.890(4)	0.032(3)
C23	−0.124(2)	1.008(1)	0.095(1)	−0.133(4)	1.012(3)	0.095(2)	−0.132(6)	1.014(4)	0.117(4)
C24	−0.001(2)	1.055(1)	0.163(1)	−0.012(4)	1.051(3)	0.166(2)	−0.003(6)	1.052(4)	0.171(4)
C25	0.138(2)	0.997(1)	0.181(1)	0.126(4)	0.999(2)	0.178(2)	0.115(6)	0.997(4)	0.181(4)
C31	−0.022(2)	0.779(1)	0.004(1)	−0.038(4)	0.777(2)	0.003(2)	−0.031(6)	0.771(4)	0.004(3)
C32	−0.066(2)	0.616(1)	0.087(1)	−0.054(4)	0.619(2)	0.091(2)	−0.050(6)	0.622(3)	0.084(3)
C33	0.207(2)	0.706(1)	0.132(1)	0.206(3)	0.713(2)	0.123(2)	0.186(6)	0.723(4)	0.114(4)
C34	0.304(2)	0.794(1)	0.146(1)	0.286(4)	0.800(3)	0.135(2)	0.267(6)	0.815(4)	0.128(3)
C35	0.309(2)	0.839(1)	0.228(1)	0.299(4)	0.838(3)	0.221(2)	0.292(6)	0.848(4)	0.216(3)

0.088 and R_w = 0.080 (mixed thermal model assigning anisotropic behaviour to the metal, bromine, and phosphorus atoms; 972 data with $|F_o| > 4\sigma(F_o)$ collected out to a maximum 2θ of 40°; weighting scheme $w = [\sigma^2(F_o) + 0.00042(F_o)^2]^{-1}$).

III: M = 650.01; monoclinic; space group $P2_1/n$; a = 959.8(9), b = 1510.1(7), c = 1688(2) pm, β = 104.29(9)°; $V = 2371 \times 10^6$ pm^3, $Z = 4, D = 1.82$ g cm^{-3}, $\mu = 32.8$ cm^{-1}. Refinement resulted in convergence at R = 0.097 and R_w = 0.102 (Fe, I, and P anisotropic, C isotropic; 799 structure factors with $|F_o| > 4\sigma(F_o)$ and $2\theta_{max}$ = 37°; weights w given by $w = [\sigma^2(F_o) + 0.00108(F_o)^2]^{-1}$).

Final atomic positions are presented in Table I. Relevant bond distances and angles are given in the captions to Figs. 1–3.*

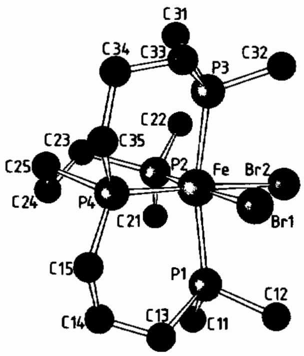

Fig. 2. Perspective view of the molecule $FeBr_2[P(CH_2CH_2CH_2PMe_2)_3]$ (II). Selected bond lengths (pm) and angles (°) are: Br1–Fe, 255.0(6); Br2–Fe, 255.5(6); P1–Fe, 230(1); P2–Fe, 225(1); P3–Fe, 229(1); P4–Fe, 223(1). Br2–Fe–Br1, 92.3(2); P1–Fe–Br1, 82.4(3); P1–Fe–Br2, 85.0(3); P2–Fe–Br1, 177.4(3); P2–Fe–Br2, 85.3(3); P2–Fe–P1, 98.5(4); P3–Fe–Br1, 81.6(3); P3–Fe–Br2, 90.8(3); P3–Fe–P1, 163.2(4); P3–Fe–P2, 97.3(4); P4–Fe–Br1, 87.1(3); P4–Fe–Br2, 178.9(4); P4–Fe–P1, 94.1(4); P4–Fe–P2, 95.3(4); P4–Fe–P3, 89.9(4).

Results and Discussion

The tripod tetra(tertiary) phosphine $P(CH_2CH_2CH_2PMe_2)_3$ [2] reacts rapidly with anhydrous ferrous halides to give deeply colored solutions, which upon working-up deposited violet crystals of composition $FeX_2[P(CH_2CH_2CH_2PMe_2)_3]$ (X = Cl (I), Br (II), I (III)]. These complexes are diamagnetic, electrolytically non-conducting materials.

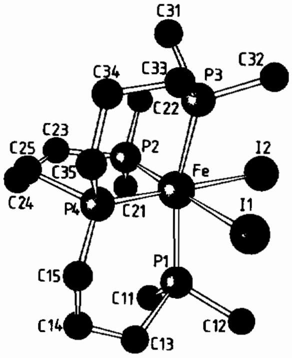

Fig. 3. Molecular structure of $FeI_2[P(CH_2CH_2CH_2PMe_2)_3]$ (III). Metal–ligand bond distances (pm) and angles (°) are: I1–Fe, 272.5(8); I2–Fe, 273.9(8); P1–Fe, 233(2); P2–Fe, 228(2); P3–Fe, 233(2); P4–Fe, 223(2). I2–Fe–I1, 92.2(3); P1–Fe–I1, 83.5(5); P1–Fe–I2, 87.4(5); P2–Fe–I1, 178.2(5); P2–Fe–I2, 86.0(5); P2–Fe–P1, 96.7(7); P3–Fe–I1, 82.1(5); P3–Fe–I2, 88.1(5); P3–Fe–P1, 164.7(7); P3–Fe–P2, 97.5(7); P4–Fe–I1, 89.0(5); P4–Fe–I2, 178.9(6); P4–Fe–P1, 92.7(7); P4–Fe–P2, 92.9(6); P4–Fe–P3, 92.0(7).

They are thus very different from the purple, low-spin paramagnetic salts [FeX(QP)]X (X = Cl, Br, I) [5] and $[FeCl(PP_3)]_2[FeCl_4]$ [6] which have previously been obtained from iron(II) halides and the tetradentate ligands $P(o\text{-}C_6H_4PPh_2)_3$ (QP) and $P(CH_2CH_2PPh_2)_3$ (PP_3). In view of the steric constraints of the $-o\text{-}C_6H_4-$ and $-CH_2CH_2-$ bridged chelates, the pentacoordinate cations of the latter complexes have been assigned trigonal-bipyramidal C_{3v} structures. This also accounts for the triplet ground states observed for these species [5–7], established by an X-ray study of the $[FeBr(PP_3)]^+$ cation [8].

The diamagnetism of compounds I–III, their lack of electrolytic conductivity as well as their failure to react with methyl iodide [5] lead us to assume that the title complexes are hexacoordinate and have an octahedral structure similar to that found in $RuBr_2[As(o\text{-}C_6H_4AsPh_2)_3]$ [9]. This assumption has been confirmed by three X-ray diffraction analyses performed on the complexes.

As indicated in Figs. 1–3, the overall molecular geometry about the central iron atom corresponds to distorted octahedral with the halide ions occupying *cis* positions.

The phosphorus-to-iron bonds of I–III measure *ca.* 229–234 ppm within the *trans*-P–Fe–P units and range from 220 to 228 pm within the Fe–P moieties *trans* to the respective halide ligands. It has been shown [10, 11] that pseudo-octahedral halide complexes of iron(II) containing coordinated oligophosphines will possess singlet ground states if the Fe–P bond lengths are normal, *i.e.* if they amount to *ca.* 230 pm or less. Alternatively, such

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*Further crystallographic information including tables of thermal parameters and F_o/F_c listings is available from the Fachinformationszentrum Energie, Physik, Mathematik GmbH (cooperating with the Cambridge Crystallographic Data Centre), D-7514 Eggenstein-Leopoldshafen 2 (F.R.G.). Any request should be accompanied by the registration number CSD-51147, as well as the full literature citation for this communication.

compounds will be in the high-spin quintet ground state if the metal-to-phosphorus bonds are abnormally long, *i.e.* if they measure *ca.* 260 pm or more. Despite the limited accuracy of the structure determinations, the Fe–P distances of **I–III** thus may be regarded as consistent with the diamagnetic behaviour of the three species.

A possible explanation for the change of the coordination geometry from five- to six-coordinate, observed on passing from the halide complexes of iron(II) with the more rigid QP and PP_3 ligands [5–8] to those with the $P(CH_2CH_2CH_2PMe_2)_3$ tetradentate, may be put forward in terms of the conformational flexibility of the C_3 backbones of the latter phosphine: compared to the constrained $-o\text{-}C_6H_4-$ and $-CH_2CH_2-$ linkages of the QP and PP_3 ligands which permit chelate bite angles of 84 ± 2 ℃ only, the trimethylene connecting chains of $P(CH_2CH_2CH_2PMe_2)_3$ can provide increased metal–P overlap. The $-CH_2CH_2CH_2-$ linked chelate thus ensures that the ligand field about the central iron is enforced, which in turn favours hexacoordination at the expense of pentacoordination [12].

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References

1 E. Arpac and L. Dahlenburg, *Chem. Ber.,* in press.
2 M. Antberg, C. Prengel and L. Dahlenburg, *Inorg. Chem.,* in press.
3 M. Antberg, *Dissertation,* Universität Hamburg, in preparation.
4 L. Dahlenburg, A. Yardimcioglu and N. Höck, *Inorg. Chim. Acta, 89,* 213 (1984).
5 M. T. Halfpenny, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc. A:,* 627 (1967).
6 R. B. King, R. N. Kapoor, M. S. Saran and P. N. Kapoor, *Inorg. Chem., 10,* 1851 (1971).
7 P. Stoppioni, F. Mani and L. Sacconi, *Inorg. Chim. Acta, 11,* 227 (1974).
8 L. Sacconi and M. DiVaira, *Inorg. Chem., 17,* 810 (1978).
9 R. H. B. Mais, H. M. Powell and L. Venanzi, *Chem. Ind.,* 1204 (1963).
10 F. Cecconi, M. DiVaira, S. Midollini, A. Orlandini and L. Sacconi, *Inorg. Chem., 20,* 3423 (1981).
11 M. DiVaira, S. Midollini and L. Sacconi, *Inorg. Chem., 20,* 3430 (1981).
12 L. M. Venanzi, *Angew. Chem., 76,* 621 (1964); *Angew. Chem., Int. Ed. Engl., 3,* 453 (1964).