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METAL-ASSISTED REACTION OF CARBON DISULFIDE WITH THE TRIS(TERTIARY PHOSPHINE) 1,1,1-TRIS(DIETHYLPHOSPHINOMETHYL)ETHANE. SYNTHESIS AND STRUCTURE OF THE COMPLEX $[MeC(CH_2PEt_2)_3Fe\{S_2C(PEt_2CH_2)_2CMe_2\}](BF_4)_2$

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Summary

Carbon disulfide reacts with iron(II) tetrafluoroborate in the presence of 1,1,1-tris(diethylphosphinomethyl)ethane, etriphos, to give the complex $[MeC(CH_2PEt_2)_3Fe\{S_2C(PEt_2CH_2)_2CMe_2\}](BF_4)_2$. This is the first example of a diamagnetic five-coordinate iron(II) complex. Its molecular structure has been determined from counter diffraction data. The crystals are monoclinic belonging to space group $P2_1/c$ with four molecules in the unit cell of dimensions a 18.964(7), b 18.016(7), c 14.033(5) Å, β 109.1(1)°. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to final R and R_w factors of 0.074 and 0.073, respectively. The iron atom is five-coordinated by the three phosphorus atoms of the etriphos ligand and the two sulfur atoms of the zwitterionic ligand in a distorted square pyramidal geometry.

Introduction

The activation of carbon disulfide by metal-ligand moieties of the type (triphos)M (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, M = Co, Ni) has been widely investigated in this laboratory. In particular, several mononuclear and homo- and heterometal dinuclear complexes have been described [1,2]. In these complexes carbon disulfide has been found to act either as a η^2-bonded ligand or as a bridging ligand between two metal centers (Fig. 1).

It therefore seemed of interest to investigate the behaviour of carbon disulfide toward iron(II) salts in the presence of 1,1,1-tris(diethylphosphinomethyl)ethane, etriphos, whose coordinating capability toward iron(II) cations has

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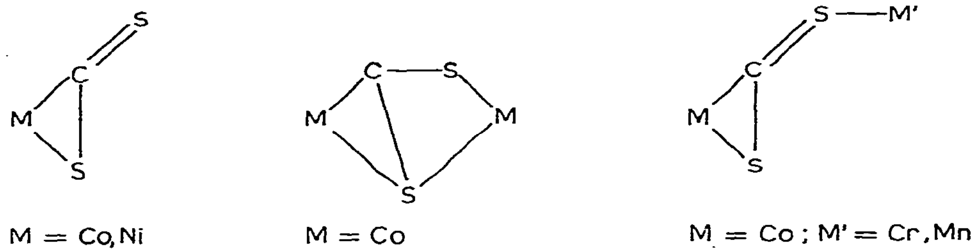

Fig. 1. Binding modes of carbon disulfide in mono- and dinuclear metal complexes.

been previously reported [3]. We have used the reaction of carbon disulfide with iron(II) tetrafluoroborate in the presence of an excess of etriphos to prepare the iron(II) complex [(etriphos)FeZ]$(BF_4)_2$, where Z is the unprecedented six-membered heterocyclic zwitterion 1,1,3,3-tetraethyl-5,5-dimethyl-1,3-diphosphonia-2,2-cyclohexane dithiolate.

Few metal complexes with disulfido ligands containing quaternary phosphonium atoms are known and only two structures of such complexes have been determined by X-ray analysis [4,5]. The title compound seems to be the first example of a metal complex with a disulfido ligand in the form of a cyclic zwitterion containing two phosphonium atoms. A complete X-ray structural analysis has been carried out on this compound.

A preliminary account of part of this work has already appeared [6].

Experimental

All materials and solvents were of reagent grade quality and were used without further purification. The ligand etriphos was prepared by a published procedure [7]. The physical measurements were executed by methods previously described [8]. The ^{31}P NMR spectra of the CH_2Cl_2 solutions were recorded at 295 K with a Varian CFT 20 spectrometer. Chemical shifts are downfield (+) from external H_3PO_4. The reactions were carried out using oxygen-free solvents under nitrogen.

Preparation of the complex

Carbon disulfide vapors were bubbled for 30 min into a hot mixture of etriphos (2 mmol) in methylene chloride (40 ml) and $[Fe(H_2O)_6](BF_4)_2$ (1 mmol) in ethanol (30 ml). The mixture was mantained at reflux temperature for one hour. Upon slow evaporation of the resulting dark green solution green crystals were formed, and these were filtered off and washed with ethanol and the petroleum ether and dried in a stream of dry nitrogen. They were recrystallized from methylene chloride/ethanol. Anal. Found: C, 41.32; H, 7.88; Fe, 6.15; P, 17.47; S, 7.00. Calcd. for $C_{31}H_{69}B_2F_8FeP_5S_2$: C, 41.82; H, 7.81; Fe, 6.27; P, 17.39; S, 7.20%.

Crystal data and data collection

Diffraction data were collected on a Philips PW 1100 automated diffractometer using graphite-monochromated Mo-K_α radiation. Lattice constants were determined by least-squares refinement of the angular positions of 20 reflections carefully centered on the diffractometry. The crystals are monoclinic and belong to space group $P2_1/c$ with four molecules in the unit cell of dimensions a 18.964(7), b 18.016(7), c 14.033(5) Å, β 109.1(1)°. The calculated density 1.305 g/cm^3 for four formulae per unit cell is in good agreement with the measured density 1.30 g/cm^3 obtained by flotation. The green crystal used for data collection, rombohedral shaped, had dimensions 0.17 × 0.17 × 0.22 mm. Intensity data for the unique set of reflections with $2\theta \leqslant 40°$ were collected by using the ω—2θ scan technique, with the scan variable with θ, according to the expression $A + B$ tg θ, where $A = 0.8°$ and $B = 0.69$ at the scan speed of 0.06°/s. Backgrounds counts were made for one half of the scan time at each end of the scan. Three control reflections monitored every 200 reflections did not change significantly during the course of data collection. Intensity data were reduced to a set of F_0's by application of Lorentz and polarization corrections (Lp). Standard deviations of the intensity I were calculated as described elsewhere [9] using for the instability factor K the value of 0.04. In view of the equidimensional shape of the crystal and of the small linear absorption coefficient ($\mu = 6.47$ cm^{-1}) no absorption correction was applied (it was estimated to introduce a maximum error of ±1% in intensity). Reflections were taken as observed if $I \geqslant 3\sigma(I)$. This amounts to 1936 data from the 4620 total measurements. Scattering factors for neutral atoms were taken from ref. 10 and were modified for both the real and imaginary components of anomalous dispersion.

Structure solution and refinement

The calculations were carried out using the SHELX76 crystallographic system [11] on a SEL 32/70 computer installed in our Institute. A three-dimensional Patterson synthesis showed the position of the iron atom. All the other non-hydrogen atoms were located from successive Fourier maps. Refinement was performed by using full-matrix least-squares techniques, the function minimized being $\Sigma w(|F_0| - |F_c|)^2$, where w is $w = 1/\sigma^2(F_0)$. Some cycles with isotropic thermal motion on all non-hydrogen atoms were followed by some mixed cycles, where anisotropic thermal vibration was assigned to iron, phosphorus and sulfur atoms. Hydrogen atoms were introduced, but not refined. The location and refinement of the two tetrafluoroborate ions required much effort, and either disorder or large vibrational motion strongly affect the two anions. For one of the two BF_4^- ions it was possible to discern from a difference Fourier map two different models with the B(1)—F(1) bond superimposed and six peaks lying on a circle, at the same distance from the F(1) atom. The two distinct BF_4^- models were refined as rigid tetrahedral groups (F—B = 1.372 Å) with an overall temperature factor. While the B(1) and F(1) atoms were assigned a population parameter of 1, the two groups F(2), F(3), F(4) and F(21), F(31), F(41) were given multiplicities of α and $1 - \alpha$, respectively, and the parameter α was allowed to vary (it converged to 0.56, i.e. there is approximately 50—60% disorder in this group). For the other tetrafluoroborate anion a delta F Fourier map indicated considerable anisotropy of thermal motion, but only one model on unconstrained refinement gave reasonable bond distances and bond angles. Some disorder was detected also in the regions of the terminal carbon atoms of the ethylenic chains, whenever possible, two distinct positions

TABLE 1

POSITIONAL ($\times 10^4$) AND THERMAL [a] ($\times 10^3$) PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	7141(1)	5283(1)	2869(2)	44(2)	41(2)	39(1)	2(2)	16(1)	0(2)
P(1)	6155(3)	4736(3)	2950(4)	56(3)	47(3)	56(3)	−5(3)	29(3)	−4(3)
P(2)	7637(3)	5232(3)	4515(4)	58(3)	56(4)	45(3)	0(3)	20(3)	3(3)
P(3)	6595(3)	6332(3)	2967(4)	53(3)	39(3)	51(3)	−2(3)	20(3)	1(3)
P(4)	7671(3)	4002(3)	661(4)	71(4)	52(4)	56(4)	1(3)	30(3)	3(3)
P(5)	8485(3)	5458(3)	1061(4)	49(3)	74(4)	53(3)	2(3)	21(3)	−8(3)
S(1)	8122(3)	4663(3)	2749(4)	52(3)	69(4)	48(3)	9(3)	18(3)	15(3)
S(2)	6973(2)	5356(3)	1194(3)	45(3)	56(3)	41(3)	5(3)	15(2)	11(3)
F(5)	5656(8)	2172(8)	1322(12)	129(13)	134(13)	154(13)	33(11)	30(11)	38(11)
F(6)	5938(8)	1238(10)	2351(13)	138(14)	193(16)	175(16)	77(14)	47(12)	−42(12)
F(7)	6800(8)	1956(9)	2307(15)	91(12)	160(15)	244(20)	36(14)	−12(13)	−43(11)
F(8)	6254(12)	1248(12)	1047(14)	286(25)	259(22)	138(15)	−28(15)	71(16)	150(20)

[a] The form of the ellipsoid is: $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots))$.

TABLE 2

POSITIONAL ($\times 10^4$) AND THERMAL ($\times 10^3$) PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS

Atom	x/a	y/b	z/c	U	
C(1)	5814(11)	5869(11)	5373(15)	86(7)	
C(2)	6230(10)	5701(10)	4607(14)	57(5)	
C(3)	5736(10)	5159(10)	3826(13)	63(6)	
C(4)	6942(9)	5339(10)	5188(13)	59(5)	
C(5)	6300(10)	6432(10)	4103(13)	60(6)	
C(6)	6302(11)	3739(10)	3353(15)	74(6)	
C(7)	5625(13)	3306(13)	3280(18)	121(9)	
C(8)	5385(9)	4657(11)	1715(13)	70(6)	
C(9)	4599(12)	4569(13)	1720(17)	110(8)	
C(10)	8133(12)	4378(11)	5006(14)	79(7)	
C(11)	8270(13)	4214(13)	6111(16)	110(8)	
C(12)	8334(10)	5917(11)	5152(14)	72(6)	
C(13)	8997(12)	5971(12)	4816(16)	99(8)	
C(14)	7223(10)	7120(9)	3056(15)	64(6)	
C(15)	6902(13)	7895(12)	3199(18)	113(9)	
C(16)	5728(11)	6632(11)	1980(14)	74(6)	
C(17)	5792(13)	6791(12)	947(17)	108(8)	
C(18)	7852(9)	4849(9)	1416(12)	44(5)	
C(19)	7470(10)	5111(10)	—2022(14)	74(6)	
C(20)	7925(10)	4859(10)	—956(14)	64(6)	
C(21)	8648(11)	4472(11)	—987(15)	81(7)	
C(22)	7418(10)	4312(10)	—634(13)	56(6)	
C(23)	8104(10)	5557(9)	—287(13)	57(6)	
C(24)	8461(12)	3378(12)	1022(17)	90(7)	
C(25)	8234(23)	2671(25)	244(34)	136(22)	(P.P. 0.62(4))
C(251)	8497(35)	2857(33)	2016(37)	107(21)	(P.P. 0.38(4))
C(26)	6904(11)	3510(11)	831(15)	75(7)	
C(27)	6199(19)	3506(20)	81(27)	236(18)	
C(28)	8508(11)	6358(11)	1655(15)	73(6)	
C(29)	8133(25)	6985(19)	1038(28)	96(18)	(P.P. 0.63(5))
C(291)	8846(32)	6949(26)	1129(35)	57(14)	(P.P. 0.37(5))
C(30)	9420(10)	5171(12)	1406(15)	85(7)	
C(31)	9860(15)	5146(15)	2486(20)	147(10)	
F(1)	304(10)	3696(10)	712(13)	195(10)	
F(2)	968(29)	2653(19)	1176(20)	195(10)	(P.P. 0.56(2))
F(3)	143(13)	2983(27)	1930(31)	195(10)	(P.P. 0.56(2))
F(4)	1199(23)	3630(15)	2216(24)	195(10)	(P.P. 0.56(2))
F(21)	1386(13)	3152(34)	1575(37)	195(10)	(P.P. 0.44(2))
F(31)	307(28)	2562(15)	1365(31)	195(10)	(P.P. 0.44(2))
F(41)	617(37)	3551(23)	2382(14)	195(10)	(P.P. 0.44(2))
B(1)	653(8)	3240(8)	1509(11)	195(10)	
B(2)	6191(20)	1683(20)	1761(26)	84(9)	

were located, and were assigned refined population parameters α and $1-\alpha$, respectively. Refinement converged at $R = 0.074$ and $R_w = 0.073$, R_w being defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The final positional and thermal parameters appear in Tables 1 and 2. A list of the observed and calculated structure amplitudes is available from the authors.

Results and discussion

Reaction of carbon disulfide with iron(II) tetrafluoroborate and etriphos in methylene chloride/ethanol gave green crystals of the composition [(etriphos)-

$Fe\{S_2C(Et_2PCH_2)_2CMe_2\}](BF_4)_2$. This compound is reasonably air stable in the solid state but decomposes rapidly in solution unless air is excluded. It is soluble in all common organic solvents, in which it behaves as a 1 : 2 electrolyte (molar conductance in 10^{-3} nitroethane solution: 143 cm^2 ohm^{-1} mol^{-1}). The UV reflectance and solution spectrum (in CH_3NO_2) of this diamagnetic compound are similar to each other and show absorption maxima at 14100 (ϵ = 620), 17800 (ϵ = 190), and 22900 cm^{-1} (ϵ = 460), respectively.

The crystal and molecular structure consists of discrete $[(etriphos)Fe\{S_2C(PCH_2)_2C(CH_3)_2\}]^{2+}$ cations and of BF_4^- anions. A schematic representation of the formula unit is given in Fig. 2. Figure 3 shows a perspective view of the complex cation.

The metal atom is surrounded by the three phosphorus atoms of the etriphos ligand and by the two sulfur atoms of the Z zwitterion in a distorted square pyramidal geometry. Selected bond distances and angles in the complex cation are given in Table 3. The distortion of the square pyramid from the idealized geometry is evidenced by the values of the basal bond angles P(2)—Fe—S(2) and P(3)—Fe—S(1) which are 163.7(2) and 150.1(2)°, respectively, instead of 180°. The displacements of the four basal atoms from their basal least-squares plane range from 0.15 to 0.18 Å with the metal lying 0.40 Å from that plane.

The mean value of the Fe—P distances, 2.174(13) Å, is somewhat shorter than those of 2.221 and 2.236 Å found for the confacial bioctahedral complex $[Fe_2H_3(triphos)_2]PF_6$ [12] and for the five-coordinate complex $[Fe(P_4)Br]BPh_4$ ($P_4 = PH_2P(CH_2)_2PPh(CH_2)_2PPh(CH_2)_2PPh_2$) [13], respectively. On the other hand, the mean value of the Fe—S distances, 2.247(23) Å, in the present compound agrees well with those found in the dinuclear iron complexes $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ [14] and $[Fe(\eta^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$ [15].

The coordination geometry around the carbon atom of the CS_2 group is close to tetrahedral, as shown by the values of the C—P and C—S distances (range 1.80—1.82 Å) and by the angles about the carbon atom (range 101.7—114.0°). These values are clearly indicative of sp^3 hybridization, and are in excellent agreement with those reported for the zwitterionic moiety $S_2C(H)PMe_2Ph$, Z_w, present in the ruthenium complex $[Ru(Z_w)(PMe_2Ph)_3]PF_6$ [4], in which a hydrogen atom and a phsohine are attached to the carbon atom in a tetrahedral arrangement. A correlation can be made also with the distances and angles found for the zwitterionic ligand Ph_3PCS_2 in the iridium complex $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]BF_4$ [5] and with those reported in the uncoordi-

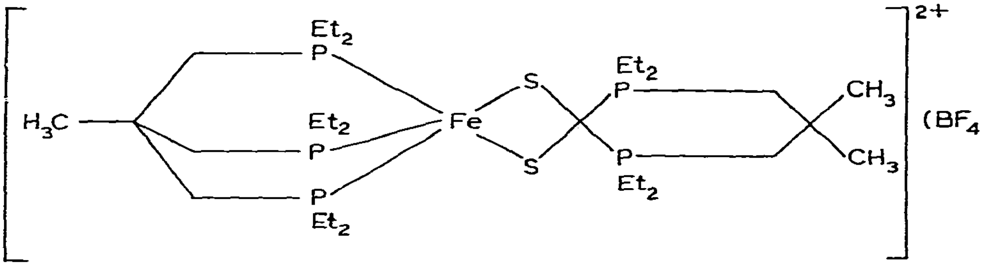

Fig. 2. Schematic representation of the $[(etriphos)FeZ](BF_4)_2$ compound.

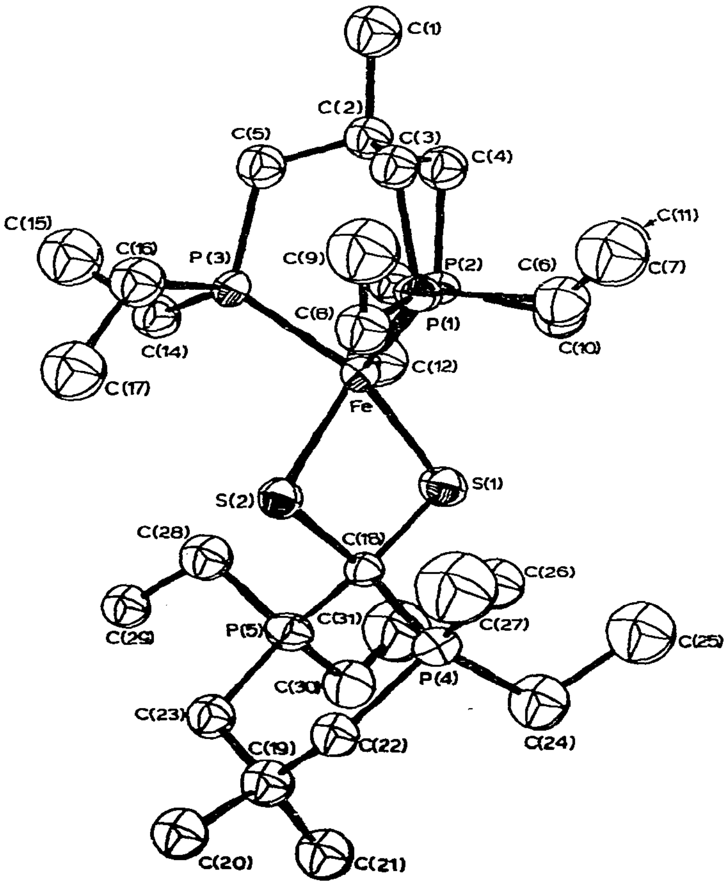

Fig. 3. Perspective view of the complex cation [(etriphos)FeZ]$^{2+}$. ORTEP drawing with 50% probability ellipsoids.

nated Et_3PCS_2 molecule [16] in which, however, the central carbon atom of the zwitterion, bearing only one phosphine substituent, is sp^2 hybridized.

The ^{31}P NMR spectrum of the [(etriphos)FeZ]$(BF_4)_2$ complex shows three peaks, centered at 56.92, 34.89 and 34.80 ppm, which, on the basis of their intensities, are assigned to the three phosphorus atoms of etriphos and the two phosphorus atoms of Z, respectively.

The formation of zwitterions of the type R_3PCS_2 is not uncommon in the reactions of carbon disulfide with tertiary phosphines [17]. In the case of our complex the in-situ formation of a zwitterion with two phosphonium atoms attached to the carbon atom of the CS_2 group may be accounted for by the enhancement of the electrophilic character of carbon disulfide when linked to the metal [18].

Definitive conclusions have not been reached about the cleavage of a carbon—phosphorus bond in the third chain of the etriphos entity; nevertheless it is reasonable to expect that carbon disulfide, whose high reactivity toward phosphorus compounds is well known, plays a determinant role in such

TABLE 3

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (deg)

Fe—P(1)	2.149(5)	P(4)—C(24)	1.81(2)
Fe—P(2)	2.192(5)	P(4)—C(26)	1.78(2)
Fe—P(3)	2.181(5)	P(5)—C(18)	1.81(2)
Fe—S(1)	2.224(5)	P(5)—C(23)	1.80(2)
Fe—S(2)	2.270(5)	P(5)—C(28)	1.82(2)
P(1)—C(3)	1.83(2)	P(5)—C(30)	1.76(2)
P(1)—C(6)	1.88(2)	S(1)—C(18)	1.80(2)
P(1)—C(8)	1.87(2)	S(2)—C(18)	1.83(2)
P(2)—C(4)	1.87(2)	C(1)—C(2)	1.56(2)
P(2)—C(10)	1.82(2)	C(2)—C(3)	1.54(2)
P(2)—C(12)	1.81(2)	C(2)—C(4)	1.48(2)
P(3)—C(5)	1.86(2)	C(2)—C(5)	1.52(2)
P(3)—C(14)	1.83(2)	C(19)—C(20)	1.53(2)
P(3)—C(16)	1.85(2)	C(20)—C(21)	1.55(2)
P(4)—C(18)	1.83(2)	C(20)—C(22)	1.54(2)
P(4)—C(22)	1.81(2)	C(20)—C(23)	1.54(2)
P(1)—Fe—P(2)	90.3(2)	C(18)—P(4)—C(26)	110.2(9)
P(1)—Fe—P(3)	87.4(2)	C(22)—P(4)—C(24)	113.3(9)
P(1)—Fe—S(1)	122.6(2)	C(22)—P(4)—C(26)	109.2(9)
P(1)—Fe—S(2)	104.6(2)	C(24)—P(4)—C(26)	107.0(10)
P(2)—Fe—P(3)	91.0(2)	C(18)—P(5)—C(23)	106.0(8)
P(2)—Fe—S(1)	88.8(2)	C(18)—P(5)—C(28)	109.4(8)
P(2)—Fe—S(2)	163.7(2)	C(18)—P(5)—C(30)	116.5(9)
P(3)—Fe—S(1)	150.1(2)	C(23)—P(5)—C(28)	109.6(9)
P(3)—Fe—S(2)	96.1(2)	C(23)—P(5)—C(30)	109.9(9)
S(1)—Fe—S(2)	77.8(2)	C(28)—P(5)—C(30)	105.4(10)
Fe—P(1)—C(3)	114.9(6)	Fe—S(1)—C(18)	91.4(5)
Fe—P(1)—C(6)	114.1(6)	Fe—S(2)—C(18)	89.1(5)
Fe—P(1)—C(8)	114.5(6)	C(1)—C(2)—C(3)	106.7(15)
C(3)—P(1)—C(6)	104.5(9)	C(1)—C(2)—C(4)	106.4(15)
C(3)—P(1)—C(8)	106.0(8)	C(1)—C(2)—C(5)	107.1(15)
C(6)—P(1)—C(8)	101.5(9)	C(3)—C(2)—C(4)	110.2(15)
Fe—P(2)—C(4)	113.5(6)	C(3)—C(2)—C(5)	110.2(15)
Fe—P(2)—C(10)	115.1(7)	C(4)—C(2)—C(5)	115.7(16)
Fe—P(2)—C(12)	118.9(7)	S(1)—C(18)—S(2)	101.7(8)
C(4)—P(2)—C(10)	105.0(9)	S(1)—C(18)—P(4)	112.4(9)
C(4)—P(2)—C(12)	101.6(8)	S(1)—C(18)—P(5)	114.1(9)
C(10)—P(2)—C(12)	100.7(9)	S(2)—C(18)—P(4)	109.3(8)
Fe—P(3)—C(5)	114.8(6)	S(2)—C(18)—P(5)	107.4(8)
Fe—P(3)—C(14)	111.3(6)	P(4)—C(18)—P(5)	111.2(8)
Fe—P(3)—C(16)	122.1(7)	C(19)—C(20)—C(21)	109.0(15)
C(5)—P(3)—C(14)	103.7(9)	C(19)—C(20)—C(22)	105.6(14)
C(5)—P(3)—C(16)	99.8(9)	C(19)—C(20)—C(23)	107.1(15)
C(14)—P(3)—C(16)	102.9(9)	C(21)—C(20)—C(22)	111.2(16)
C(18)—P(4)—C(22)	105.2(8)	C(21)—C(20)—C(23)	111.3(16)
C(18)—P(4)—C(24)	112.1(9)	C(22)—C(20)—C(23)	112.2(15)

cleavage. Facile phosphorus—carbon bond cleavages of this type, followed by replacement of the phosphorus atom by an hydrogen atom, have previously been reported for the reactions of the triphosphine Tdppm, tris(diphenylphosphino)methane, and of its derivatives $TdppmS_2$ and $TdppmSe_2$ with sulfur and selenium [19].

To our knowledge the title compound is the first example of a five-coordinate iron(II) complex with a singlet ground state. Although values of the nucleophilic reactivity constant, n^0, have not been established for sulfur atoms in zwitterions of the type we are referring to, the Σn^0 value for the P_3S_2 donor set in this compound is expected to be very high [20]. In particular it would be expected to be higher than that of the P_4Br set in the complex [Fe(P_4)Br]BPh_4, which shows a singlet—triplet spin state equilibrium [13].

The diamagnetism of the complex [(etriphos)FeZ]$(BF_4)_2$, therefore, is in agreement with the prediction [21] that five-coordinate iron(II) complexes can exist only in a square-pyramidal geometry and with a donor atom set of high Σn^0.

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