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REACTIVITY OF THE TRIETHYLPHOSPHINECARBON DISULFIDE ADDUCT Et_3PCS_2 TOWARD IRON(II) CATIONS IN THE PRESENCE OF THE BIS(TERTIARY PHOSPHINES), depe, AND diphos. X-RAY CRYSTAL STRUCTURES OF THE COMPLEXES $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ AND $[(depe)_2Fe(S_2CH)](BPh_4)$

C. BIANCHINI, P. INNOCENTI, A. MELI, A. ORLANDINI and G. SCAPACCI

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del C.N.R., Via F.D. Guerrazzi 27, 50132 Florence (Italy)

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Summary

Reaction of the triethylphosphinecarbon disulfide adduct Et_3PCS_2 with iron(II) aquocations in the presence of the bis(tertiary phosphines) depe or diphos, and $NaBPh_4$ has given the monomeric complexes $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$, **1**, and $[(diphos)Fe(S_2CPEt_3)_2](BPh_4)_2 \cdot 0.5\,(CH_3)_2CO$, **3** (depe = 1,2-bis(diethylphosphino)ethane; diphos = 1,2-bis(diphenylphosphino)ethane). Compound **1** undergoes nucleophilic attack by hydride ion on the coordinated Et_3PCS_2 ligand to give the dithioformato derivative $[(depe)_2Fe(S_2CH)](BPh_4)$, **2**. The structures of compounds **1** and **2** have been determined from counter diffraction X-ray data. Crystal data for **1** are: triclinic, space group $P\bar{1}$, a 18.583(8), b 14.836(7), c 14.019(7) Å, α 94.38(4), β 102.56(4), γ 103.34(4)°, $Z = 2$, $R = 0.080$. Crystal data for **2** are: monoclinic, space group $P2_1/a$, a 28.912(10), b 11.949(6), c 13.386(7) Å, β 94.35(5)°, $Z = 4$, $R = 0.076$. In both structures the iron atom displays a distorted octahedral geometry, being linked to the phosphorus atoms of two depe molecules and to the two sulfur atoms of the zwitterion in compound **1** or of the dithioformato group in compound **2**.

Introduction

In the course of recent investigations of the reactivity of CS_2 and CS_2-containing molecules towards transition metals, it has been found that zwitterions of the types I and II form complexes with the metals in various oxidation states [1—5].

In particular the triethylphosphinecarbon disulfide adduct II can function either as a monodentate or bidentate σ donor through its electron-rich sulfur

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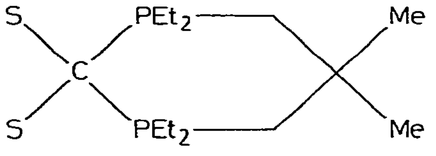

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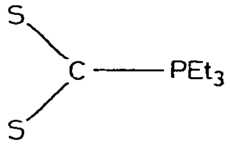
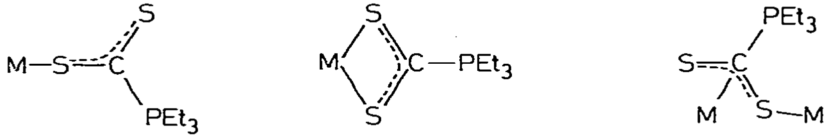


II

atoms or as a π donor through the conjugated CS_2 pseudoallylic system (Scheme 1).



SCHEME 1

The metal complexes containing the ligand Et_3PCS_2 are particularly interesting owing to the high reactivity of the coordinated zwitterion. This can be attacked by a great variety of nucleophiles to give various disulfido ligands such as S_2CO^{2-}, S_2CS^{2-}, and $S_2C(H)PEt_3^-$ [3]. In order to obtain further information on the coordinative behaviour and on the reactivity of adduct II, the latter was treated with iron(II) aquocations in the presence of the diphosphine ligands 1,2-bis(diethylphosphino)ethane (depe) or 1,2-bis(diphenylphosphino)-ethane (diphos), and this led to isolation of the mononuclear iron(II) complexes $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$, **1**, and $[(diphos)Fe(S_2CPEt_3)_2](BPh_4)_2 \cdot 0.5(CH_3)_2CO$, **3**. The reactivity of both compounds **1** and **3** toward various nucleophiles has been also examined. We describe below the reactions performed, the chemical and physical properties of the products, and the complete X-ray structural determination of the complexes **1** and $[(depe)_2Fe(S_2CH)](BPh_4)$, **2**. A preliminary account of the results has already appeared [5].

Experimental

The ligands Et_3PCS_2 [6] and depe [7] were prepared by previously described methods; the diphos ligand was purchased from Strem Chemicals Inc., Dauvers, Mass, and used without further purification. All other chemicals employed were of reagent grade quality. All the reactions were carried out under nitrogen, using deoxygenated solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin—Elmer 283 spectrophotometer using samples mulled in Nujol. The ^1H and ^{31}P NMR spectra were recorded on a CFT 20 Varian spectrometer. Phosphorus chemical shifts are downfield (+) from external H_3PO_4. Conductivity measurements were carried out as previously described [8].

Preparation of $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ (1)

A mixture of $Fe(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (10 ml) and depe (2 mmol) in acetone (20 ml) was added at room temperature to a solution of Et_3PCS_2 (1 mmol) in acetone (10 ml). After addition of $NaBPh_4$ (2 mmol) in butanol

(20 ml) and slow evaporation of the solvent, blue-green crystals separated. These were filtered off, washed with ethanol and petroleum ether, and recrystallized from DMF/Butanol.

Anal. Found: C, 69.18; H, 7.98; Fe, 4.12; P, 12.09. $C_{75}H_{103}B_2FeP_5S_2$ calcd.: C, 69.23; H, 7.98; Fe, 4.29; P, 11.90%.

Preparation of [(depe)$_2$Fe(S$_2$CH)](BPh$_4$) (2)

A solution of **1** (0.5 mmol) in acetone (20 ml) was treated with a solution of $NaBH_4$ (0.5 mmol) in ethanol (10 ml). There was an immediate color change from dark blue to violet. After addition of butanol (20 ml) and slow evaporation of the solvent violet crystal were formed, and these were filtered off and washed with ethanol and petroleum ether. Compound **2** was also prepared by using sodium methoxide or sodium naphthalenide instead of $NaBH_4$.

Anal. Found: C, 61.84; H, 8.64; Fe, 6.49; P, 14.08. $C_{45}H_{69}BFeP_4S_2$ calcd.: C, 62.50; H, 8.04; Fe, 6.45; P, 14.32%.

Preparation of [(diphos)Fe(S$_2$CPEt$_3$)$_2$](BPh$_4$)$_2$·0.5(CH$_3$)$_2$CO (3)

Et_3PCS_2 (2 mmol) was added to a mixture of $Fe(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (10 ml) and diphos (1 mmol) in acetone (20 ml). $NaBPh_4$ (2 mmol) in butanol (20 ml) was then added. Slow evaporation of the resulting dark blue

TABLE 1

CRYSTAL DATA AND DATA COLLECTIONS DETAILS

	$[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$	$[(depe)_2Fe(S_2CH)](BPh_4)$
Mol. formula	$C_{75}H_{103}B_2FeP_5S_2$	$C_{45}H_{69}BFeP_4S_2$
Mol. wt	1301.12	864.73
a (Å)	18.583(8)	28.912(10)
b (Å)	14.836(7)	11.949(6)
c (Å)	14.019(7)	13.386(7)
α (deg)	94.38(4)	
β (deg)	102.56(4)	94.35(5)
γ (deg)	103.34(4)	
d_{calcd} (g cm^{-3})	1.187	1.245
U (Å^3)	3638.0	4611.3
Space group	$P\bar{1}$	$P2_1/a$
Z	2	4
μ(Mo-K_α) (cm^{-1})	4.08	5.79
Colour	blue-green	violet
Habit	parallelepiped	irregular prism
Dimensions (mm)	0.25×0.5×0.5	0.20×0.20×0.25
Diffractometer	Philips PW 1100	Philips PW 1100
λ(Mo-K_α) (Å)	0.7107	0.7107
Monochromator	flat graphite crystal	flat graphite crystal
Method	ω-2θ scan technique	ω-2θ scan technique
Scan speed (deg/s)	0.08	0.06
Scan width	0.8	0.8
Bkgd time	half scan time	half scan time
Standards	3 every 120 min	3 every 120 min
2θ limits (deg)	$5 \leqslant 2\theta \leqslant 40$	$5 \leqslant 2\theta \leqslant 40$
No. of total data	6402	4802
No. of data with $I \geqslant 3\sigma(I)$	4920	2031
No. final of variables	286	202

solution gave turquoise crystals, which were filtered off and washed with ethanol and petroleum ether.

Anal. Found: C, 71.23; H, 6.49; Fe, 3.80; S, 8.27. $C_{89.5}H_{97}B_2FeO_{0.5}P_4S_4$ calcd: C, 71.17; H, 6.47; Fe, 3.69; S, 8.49%.

Collection and reduction of X-ray data

The crystals of both compounds were mounted on a Philips PW 1100 automatic computer-controlled diffractometer. The crystal of compound **1**, a parallelepiped of approximate dimensions 0.5×0.5×0.25 mm, belongs to triclinic system, space group $P\bar{1}$. Crystal **2**, an irregular prism with approximate dimensions 0.2×0.2×0.25 mm, belongs to monoclinic system, with extinctions $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$, characteristic of space group $P2_1/a$. Cell dimensions and orientation matrix for data collection were determined by least-squares refinement of the angular settings of 20 and 22 reflections for compounds **1** and **2** respectively. Crystal data and data collection details for both the compounds are given in Table 1. The intensities (I) as well as the standard deviations $\sigma(I)$ of the intensities were calculated as described elsewhere [9], using the value of 0.03 for the instability factor k for both the structures. Intensities were corrected for Lorentz and polarization effects, but no for absorption, in view of the small values of the linear absorption coefficients (μ(Mo-K_α) 4.08 and 5.79 cm^{-1} for compounds **1** and **2** respectively).

Atomic scattering factors were taken from ref. 10 for non-hydrogen atoms and from ref. 11 for hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms [12]. The refinement was based on F_o, the function minimizing being $\Sigma w(|F_o| - |F_c|)^2$; the assigned weights are given as $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ (g was set 0 and 0.001 for complexes **1** and **2**, respectively). The calculations were carried out on a SEL 32/70 computer using the SHELX76 crystallographic system of programs [13].

Solution and refinement of the structures

[(depe)$_2$Fe(S$_2$CPEt$_3$)](BPh$_4$)$_2$. The position of the iron atom was revealed by inspection of a Patterson map. All the other non-hydrogen atoms were

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	2175(1)	2985(1)	2484(1)	44(1)	36(1)	41(1)	10(1)	19(1)	5(1)
P(1)	1927(2)	2110(2)	3721(2)	56(2)	44(2)	47(2)	13(1)	21(1)	11(1)
P(2)	894(1)	2653(2)	1925(2)	44(2)	46(2)	53(2)	8(1)	17(1)	7(1)
P(3)	2446(2)	3961(2)	1319(2)	49(2)	51(2)	47(2)	14(1)	22(1)	13(1)
P(4)	2390(2)	4345(2)	3506(2)	58(2)	40(2)	41(2)	13(1)	16(1)	4(1)
P(5)	3684(2)	1146(2)	1718(3)	72(2)	56(2)	92(3)	30(2)	40(2)	11(2)
S(1)	2201(2)	1747(2)	1458(2)	61(2)	49(2)	60(2)	16(1)	26(1)	−2(1)
S(2)	3411(1)	2845(2)	2887(2)	51(2)	50(2)	59(2)	15(1)	20(1)	7(1)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^\star b^\star + 2U_{13}hla^\star c^\star + 2U_{23}klb^\star c^\star)]$ coordinates multiplied by 10^4, temperature factors by 10^3.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS FOR $[(\text{depe})_2\text{Fe}(\text{S}_2\text{CPEt}_3)](\text{BPh}_4)_2$ [a]

Atom	x	y	z	U (Å^2)
C(1)	915(5)	1906(7)	3695(7)	65(3)
C(2)	465(6)	1755(7)	2642(7)	65(3)
C(3)	2022(6)	918(7)	3532(8)	68(3)
C(4)	1851(8)	261(10)	4325(10)	111(5)
C(5)	2390(6)	2467(7)	5036(7)	69(3)
C(6)	3220(6)	2380(8)	5394(6)	87(4)
C(7)	508(6)	2147(8)	628(6)	63(3)
C(8)	—139(7)	1195(9)	375(9)	97(4)
C(9)	389(5)	3542(7)	2078(8)	65(3)
C(10)	—486(6)	3288(7)	1625(8)	69(3)
C(11)	2865(6)	5148(7)	1999(7)	67(3)
C(12)	2431(6)	5326(7)	2754(7)	60(3)
C(13)	1684(5)	4118(7)	320(7)	60(3)
C(14)	1920(6)	4934(7)	—306(8)	71(3)
C(15)	3195(6)	3851(7)	680(8)	73(3)
C(16)	2936(7)	3146(8)	—268(9)	88(4)
C(17)	1791(6)	4543(7)	4348(8)	64(3)
C(18)	1500(7)	5460(8)	4302(9)	90(4)
C(19)	3355(5)	4700(7)	4318(7)	62(3)
C(20)	3578(6)	5679(8)	4945(8)	76(3)
C(21)	3128(5)	1912(6)	2010(7)	50(3)
C(22)	3633(8)	219(10)	2486(11)	122(5)
C(23)	4048(8)	585(9)	3611(10)	104(4)
C(24)	4681(10)	1794(12)	1924(13)	151(6)
C(25)	4764(8)	2498(10)	1134(11)	116(5)
C(26)	3330(10)	658(12)	405(13)	147(6)
C(27)	2607(8)	—226(10)	242(11)	116(5)
B(1)	358(7)	2799(8)	6901(8)	52(3)
B(2)	5305(7)	2215(8)	7928(9)	57(3)

[a] Coordinates multiplied by 10^4, temperature factors by 10^3.

detected from successive Fourier syntheses. The refinement of the trial structure was undertaken by block-diagonal least-squares procedures, by assigning isotropic temperature factors to all non-hydrogen atoms. Then further refinement was carried out with the assignment of anisotropic temperature factors to iron, phosphorus and sulfur atoms and isotropic factors to carbon and boron atoms. Throughout the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms of the phenyl rings as well as those belonging to methylenic carbons were placed in their calculation positions, but not refined. A final full-matrix least-squares cycle converged to R and R_w factors 0.080 and 0.085 respectively. The refined positional and thermal parameters are given in Tables 2—4.

$[(depe)_2Fe(S_2CH)](BPh_4)$. A three dimensional Patterson function map revealed the positions of the iron and two phosphorus atoms in the asymmetric unit. A series of Fourier maps, least-squares refinement and difference-Fourier maps were calculated and the full structure was determined. The refinement, undertaken by block-diagonal least-squares cycles, was performed with full-matrix least-squares techniques. Iron, phosphorus and sulfur atoms were assigned anisotropic temperature factors, while carbon and boron were assigned

TABLE 4

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS FOR $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ [a]

Atom	x	y	z	U (Å²)
C(1) 1	1171(3)	3629(4)	7044(5)	56(3)
C(2) 1	1146(3)	4554(4)	6964(5)	61(3)
C(3) 1	1819(3)	5245(4)	7063(5)	72(3)
C(4) 1	2518(3)	5011(4)	7240(5)	71(3)
C(5) 1	2543(3)	4086(4)	7320(5)	69(3)
C(6) 1	1870(3)	3396(4)	7221(5)	60(3)
C(1) 2	—224(4)	2726(4)	5777(5)	51(3)
C(2) 2	—905(4)	2028(4)	5528(5)	84(4)
C(3) 2	—1407(4)	1941(4)	4608(5)	85(4)
C(4) 2	—1228(4)	2554(4)	3938(5)	68(3)
C(5) 2	—547(4)	3253(4)	4187(5)	67(3)
C(6) 2	—45(4)	3339(4)	5107(5)	55(3)
C(1) 3	579(4)	1765(4)	7064(4)	48(3)
C(2) 3	863(4)	1602(4)	8024(4)	65(3)
C(3) 3	1100(4)	788(4)	8184(4)	77(3)
C(4) 3	1053(4)	138(4)	7385(4)	73(3)
C(5) 3	769(4)	302(4)	6426(4)	75(3)
C(6) 3	532(4)	1115(4)	6265(4)	68(3)
C(1) 4	—164(4)	2959(4)	7751(5)	57(3)
C(2) 4	—115(4)	3846(4)	8211(5)	72(3)
C(3) 4	—596(4)	3957(4)	8825(5)	82(4)
C(4) 4	—1125(4)	3181(4)	8979(5)	87(4)
C(5) 4	—1173(4)	2294(4)	8519(5)	85(4)
C(6) 4	—693(4)	2183(4)	7905(5)	79(4)
C(1) 5	5841(4)	2035(4)	7123(4)	55(3)
C(2) 5	6630(4)	2195(4)	7446(4)	53(3)
C(3) 5	7067(4)	2110(4)	6768(4)	70(3)
C(4) 5	6715(4)	1864(4)	5766(4)	85(4)
C(5) 5	5926(4)	1703(4)	5442(4)	94(4)
C(6) 5	5489(4)	1789(4)	6121(4)	75(3)
C(1) 6	5147(4)	3273(5)	7844(4)	58(3)
C(2) 6	4994(4)	3760(5)	8636(4)	80(4)
C(3) 6	4789(4)	4601(5)	8528(4)	96(4)
C(4) 6	4738(4)	4955(5)	7629(4)	94(4)
C(5) 6	4891(4)	4467(5)	6837(4)	93(4)
C(6) 6	5095(4)	3627(5)	6944(4)	72(3)
C(1) 7	5758(3)	2110(4)	9100(4)	54(3)
C(2) 7	5580(3)	1276(4)	9496(4)	55(3)
C(3) 7	5982(3)	1195(4)	10436(4)	64(3)
C(4) 7	6562(3)	1948(4)	10979(4)	71(3)
C(5) 7	6740(3)	2782(4)	10582(4)	80(4)
C(6) 7	6338(3)	2863(4)	9643(4)	69(3)
C(1) 8	4449(3)	1416(5)	7642(5)	53(3)
C(2) 8	4368(3)	513(5)	7196(5)	72(3)
C(3) 8	3664(3)	—142(5)	6998(5)	79(4)
C(4) 8	3041(3)	107(5)	7245(5)	76(3)
C(5) 8	3123(3)	1010(5)	7692(5)	76(3)
C(6) 8	3827(3)	1664(5)	7890(5)	63(3)

[a] Coordinates multiplied by 10^4, temperature factors by 10^3.

isotropic ones. Rigid bodies of D_{6h} symmetry were used to refine the phenyl rings of the tetraphenylborate ions. The hydrogen atoms, which have been introduced in their geometrical positions, were not refined. The discrepancy

(Continued on p. 241)

TABLE 5

POSITIONAL AND THERMAL PARAMETERS FOR $[(\mathrm{depe})_2\mathrm{Fe}(\mathrm{S_2CH})](\mathrm{BPh_4})$ [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	848(1)	369(2)	7514(2)	54(1)	51(1)	42(1)	0(1)	−1(1)	1(1)
P(1)	1206(2)	−733(4)	6434(4)	63(3)	72(3)	67(3)	−3(3)	5(3)	−16(3)
P(2)	1090(2)	1807(4)	6606(3)	77(4)	59(3)	44(3)	14(3)	6(3)	5(3)
P(3)	473(2)	1470(4)	8600(4)	62(3)	59(3)	60(3)	−2(3)	8(3)	2(3)
P(4)	1440(2)	293(4)	8710(3)	63(3)	53(3)	51(3)	0(3)	−7(2)	4(2)
S(1)	144(2)	161(4)	6592(3)	64(3)	106(4)	60(3)	−5(3)	−10(3)	1(3)
S(2)	488(2)	−1204(4)	8124(4)	75(3)	61(3)	76(3)	−18(3)	5(3)	1(3)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ coordinates multiplied by 10^4, temperature factors by 10^3.

TABLE 6

POSITIONAL AND THERMAL PARAMETERS FOR [(depe)$_2$Fe(S$_2$CH)](BPh$_4$) [a]

Atom	x	y	z	U (Å^2)
C(1)	1594(8)	105(19)	5777(20)	165(10)
C(2)	1425(7)	1300(16)	5574(15)	106(7)
C(3)	1602(7)	−1812(16)	6776(17)	125(8)
C(4)	1317(8)	−2986(20)	6933(18)	143(9)
C(5)	855(7)	−1315(19)	5356(16)	138(9)
C(6)	1083(8)	−1904(20)	4494(19)	134(8)
C(7)	1500(7)	2810(17)	7172(16)	120(8)
C(8)	1708(7)	3769(19)	6602(17)	125(8)
C(9)	668(7)	2717(17)	5919(16)	121(8)
C(10)	438(7)	2367(18)	4984(17)	119(8)
C(11)	788(5)	1286(14)	9834(12)	81(6)
C(12)	1321(6)	1280(15)	9717(14)	87(6)
C(13)	457(6)	3000(14)	8484(14)	96(6)
C(14)	250(7)	3681(17)	9380(17)	114(7)
C(15)	−116(6)	1180(15)	8896(14)	89(6)
C(16)	−525(7)	1712(16)	8259(15)	102(7)
C(17)	1456(6)	−982(14)	9444(13)	82(6)
C(18)	1836(7)	−1152(16)	10312(15)	103(7)
C(19)	2043(6)	510(15)	8506(14)	102(7)
C(20)	2335(6)	1286(15)	9307(14)	87(6)
C(21)	45(6)	−989(14)	7280(13)	71(5)
B	1437(7)	4241(16)	2430(15)	63(6)

[a] Coordinates multiplied by 10^4, temperature factors by 10^3.

TABLE 7

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS FOR [(depe)$_2$Fe(S$_2$CH)](BPh$_4$)

Atom	x	y	z	U (Å^2)
C(1) 1	1445(3)	4598(7)	1234(8)	61(5)
C(2) 1	1738(3)	4067(7)	600(8)	67(5)
C(3) 1	1750(3)	4423(7)	−391(8)	89(6)
C(4) 1	1470(3)	5308(7)	−747(8)	98(6)
C(5) 1	1177(3)	5838(7)	−113(8)	93(6)
C(6) 1	1165(3)	5483(7)	877(8)	87(6)
C(1) 2	897(4)	4433(8)	2781(7)	67(5)
C(2) 2	534(4)	3951(8)	2184(7)	80(6)
C(3) 2	78(4)	4076(8)	2438(7)	84(6)
C(4) 2	−15(4)	4683(8)	3291(7)	89(6)
C(5) 2	348(4)	5164(8)	3889(7)	97(6)
C(6) 2	804(4)	5039(8)	3634(7)	76(6)
C(1) 3	1795(4)	5106(8)	3137(10)	74(5)
C(2) 3	1984(4)	4753(8)	4074(10)	103(7)
C(3) 3	2235(4)	5501(8)	4704(10)	113(7)
C(4) 3	2296(4)	6604(8)	4398(10)	110(7)
C(5) 3	2107(4)	6957(8)	3461(10)	105(7)
C(6) 3	1856(4)	6208(8)	2830(10)	90(6)
C(1) 4	1606(3)	2910(10)	2588(8)	72(5)
C(2) 4	1284(3)	2054(10)	2678(8)	74(5)
C(3) 4	1432(3)	944(10)	2754(8)	101(7)
C(4) 4	1902(3)	690(10)	2740(8)	106(7)
C(5) 4	2225(3)	1546(10)	2650(8)	114(7)
C(6) 4	2077(3)	2656(10)	2574(8)	99(7)

[a] Coordinates multiplied by 10^4, temperature factors by 10^3.

indices R and R_w converged to 0.076 and 0.079 respectively. Tables 5—7 report final positional and thermal parameters.

Results and discussion

Depe complexes

When a solution of depe and iron(II) tetrafluoroborate in acetone/ethanol reacts with the triethylphosphinecarbon disulfide adduct Et_3PCS_2, an intense blue colour appears. Upon addition of $NaBPh_4$ blue-green crystals of empirical formula $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$, **1**, are precipitated. This compound is diamagnetic and air-stable both in the solid state and in solution. It is very soluble in common organic solvents in which it behaves as a 1/2 electrolyte (molar conductance in 10^{-3} nitroethane solution: 99 cm^2 ohm^{-1} mol^{-1}). The IR spectrum shows bands in the $—CS_2$ stretching region at 1010, 990, 980, and 960 cm^{-1}. Recently bands at 1115 and 995 cm^{-1} have been observed in the IR spectrum of a ruthenium(II) complex containing the zwitterion $EtPh_2PCS_2$ as a bidentate ligand, and have been attributed to the $\nu(CS_2)_{asym}$ stretching vibrational mode of this ligand [14]. The ^{31}P NMR spectrum in acetone at 295 K shows two multiplets centered at 68.12 and 27.43 ppm, which are assigned to the four phosphorus atoms of the phosphine ligands and to the phosphorus

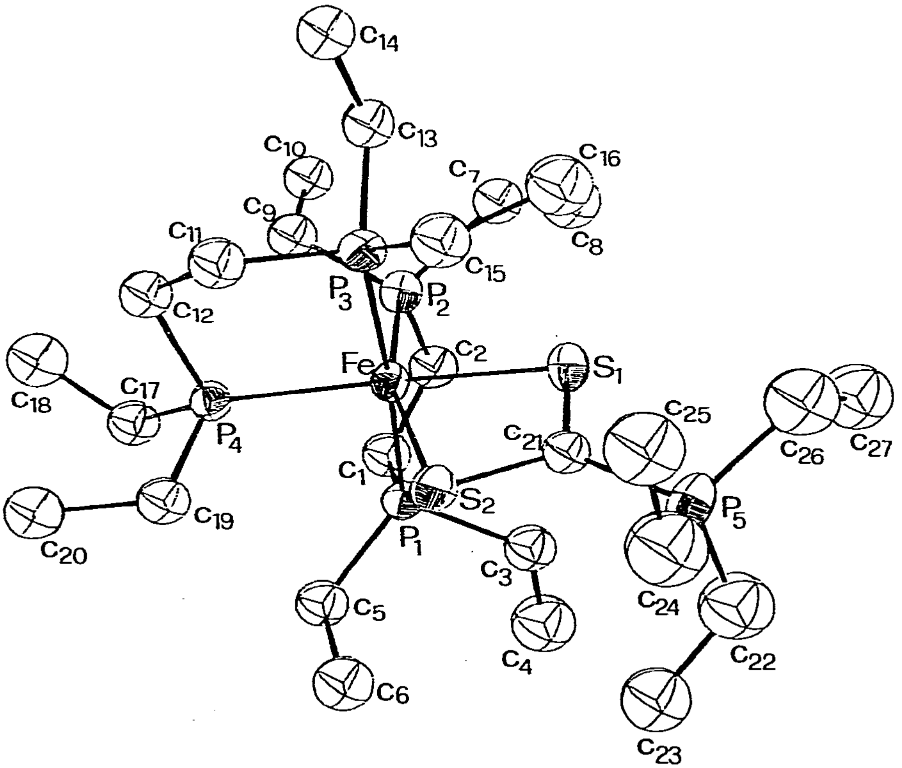


Fig. 1. Perspective view of the complex cation $[(depe)_2Fe(S_2CPEt_3)]^{2+}$. Ortep drawing with 40% probability ellipsoids.

TABLE 8

SELECTED BOND DISTANCES (Å) AND ANGLES (deg)

	$[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$	$[(depe)_2Fe(S_2CH)](BPh_4)$
Fe—P(1)	2.307(3)	2.264(5)
Fe—P(2)	2.261(3)	2.248(5)
Fe—P(3)	2.324(3)	2.292(5)
Fe—P(4)	2.285(3)	2.255(5)
Fe—S(1)	2.261(3)	2.312(5)
Fe—S(2)	2.305(3)	2.326(5)
S(1)—C(21)	1.68(1)	1.69(2)
S(2)—C(21)	1.68(1)	1.66(2)
P(5)—C(21)	1.78(3)	
P(1)—Fe—P(2)	85.4(1)	85.5(2)
P(1)—Fe—P(3)	176.0(1)	179.0(2)
P(1)—Fe—P(4)	91.3(1)	94.1(2)
P(1)—Fe—S(1)	94.1(1)	91.3(2)
P(1)—Fe—S(2)	88.6(1)	89.6(2)
P(2)—Fe—P(3)	95.6(1)	94.9(2)
P(2)—Fe—P(4)	100.4(1)	99.5(2)
P(2)—Fe—S(1)	89.8(1)	95.2(2)
P(2)—Fe—S(2)	162.4(1)	166.8(2)
P(3)—Fe—P(4)	84.7(1)	86.7(2)
P(3)—Fe—S(1)	89.8(1)	87.8(2)
P(3)—Fe—S(2)	91.6(1)	89.8(2)
P(4)—Fe—S(1)	168.8(1)	164.7(2)
P(4)—Fe—S(2)	96.3(1)	93.1(2)
S(1)—Fe—S(2)	74.1(1)	72.6(2)
Fe—S(1)—C(21)	88.7(3)	88.6(6)
Fe—S(2)—C(21)	87.2(3)	88.8(6)
S(1)—C(21)—S(2)	109.9(5)	110.0(9)
S(1)—C(21)—P(5)	123.0(6)	
S(2)—C(21)—P(5)	127.0(6)	

atom of the zwitterion, respectively. Assignment of the peaks was made on the basis of their intensities and by reference to previous data on R_3PCS_2 complexes [2,4,15].

The crystal structure of the compound 1 consists of $[(depe)_2Fe(S_2CPEt_3)]^{2+}$ cations and BPh_4^- anions. Fig. 1 shows a perspective view of the cation, which displays a distorted octahedral coordination around the metal atom. Table 8 lists selected bond distances and angles. The zwitterion ligand, which chelates the metal forming a four-membered ring, occupies two *cis* positions through both the sulfur atoms. The positions *trans* to the sulfur atoms are occupied by two phosphorus atoms of two different depe molecules, the remaining phosphorus atoms being at axial sites. The distortion of the octahedron from the limit geometry, evidenced by the values of the axial angles S(2)—Fe—P(2) and S(1)—Fe—P(4) (162.4(1) and 168.8(1)° respectively), seems mainly due to the bidentate nature of the zwitterionic ligand: indeed its coordination angle of 74.1(1)° causes deviation from 180° of the axial angles involving the sulfur atoms. The axial angle P(1)—Fe—P(3) approaching the value of 176.0(1)°, is very close to the ideal 180°. It is interesting to note that the Fe—P bond distances involving phosphorus atoms *trans* to the sulfur atoms are somewhat shorter than the others (2.261(3)—2.285(3) vs. 2.307(3)—2.324(3) Å), suggesting probable trans effects. However all the values of the Fe—P bond distances (averaging 2.29(1) Å) as well as the those of the Fe—S bond distances (averaging 2.28(2) Å) fall in the range of values previously reported for a variety of hexacoordinated iron(II) complexes [16].

Inspection of the bond distances and angles within the zwitterion ligand reveals very close agreement with the values reported for the Ph_3PCS_2 containing iridium complex $[Ir(S_2CPPh_3)(CO)(PPh_3)_2](BF_4)$, which was obtained by insertion of carbon disulfide into the Ir—P bond [17]. A comparison with the uncoordinated Et_3PCS_2 zwitterion shows that the C—S and the C—P bond distances are in good agreement, being 1.68(1)av vs. 1.69(3)av Å and 1.78(1) vs. 1.78(3) Å, respectively, while the S—C—S bond angle is very different because coordination causes a decrease from 127(1) to 109.9(5)° [18].

It has been recently reported that metal complexes containing the zwitterion Et_3PCS_2 as a monometallic chelating ligand coordinated via both sulfur atoms exhibit a high reactivity toward nucleophilic reagents. In these reactions the carbon atom of the CS_2 group has been always observed to be the reactive site, independent of the nucleophile used. The nucleophilic attack can lead either to the replacement of the PEt_3 group with other groups or to addition of the nucleophile itself to the carbon atom [3].

Thus we investigated the reactivity of **1** toward sodium tetrahydroborate, sodium methoxide, or sodium naphthalenide. All the reactions gave violet crystals of empirical formula $[(depe)_2Fe(S_2CH)](BPh_4)$, **2**. Compound **2** is diamagnetic and air-stable only in the solid state. It is soluble in common organic solvents, in which it behaves as a 1/1 electrolyte (molar conductance in 10^{-3} nitroethane solution: 45 cm^2 ohm^{-1} mol^{-1}). The IR spectrum shows two bands at 1215 and 910 cm^{-1} attributable to $\delta(HCS)$ and $\nu(CS_2)_{asym}$, respectively, which are in exact agreement with those found in other complexes containing dithioformato and phosphine ligands [19]. A positive assignment for $\nu(CS_2)_{sym}$ is not possible because the region 800—700 cm^{-1} is partially masked by vibrations associated with the phosphine ligands. The ^1H NMR spectrum in $CHCl_3$ is also consistent with the presence of a dithioformato ligand, showing a multiplet at τ −0.94 [19].

An X-ray determination has shown that the crystal and molecular structure of the compound **2** consists of discrete complex $[(depe)_2Fe(S_2CH)]^+$ cations and BPh_4^- anions. Figure 2 shows a perspective view of the cation, which displays a distorted octahedral coordination around the metal atom. The geometrical environment of the metal atom closely resembles that in compound **1**, the only difference consisting in the presence of an hydrogen atom in place of one phosphine on the S_2C group. Although in the final Fourier difference map there is no peak to be attributed at hydrogen atom linked to the carbon atom of the CS_2 group, nevertheless the substantial equivalence of the C—S and Fe—S bond distances suggests a delocalized bond system similar to that in the dithioformate compounds. The bond distances and angles involving the dithioformato group match very well the values previously reported for a variety of dithioacids. Excellent agreement for example is found for the dithioformato containing complex $Re(CO)_2(S_2CH)(PPh_3)_2$ [20].

Formation of compound **2** from the reaction of compound **1** with different reagents such as BH_4^-, CH_3O^-, or $C_{10}H_8^-$ is not surprising since all these reagents

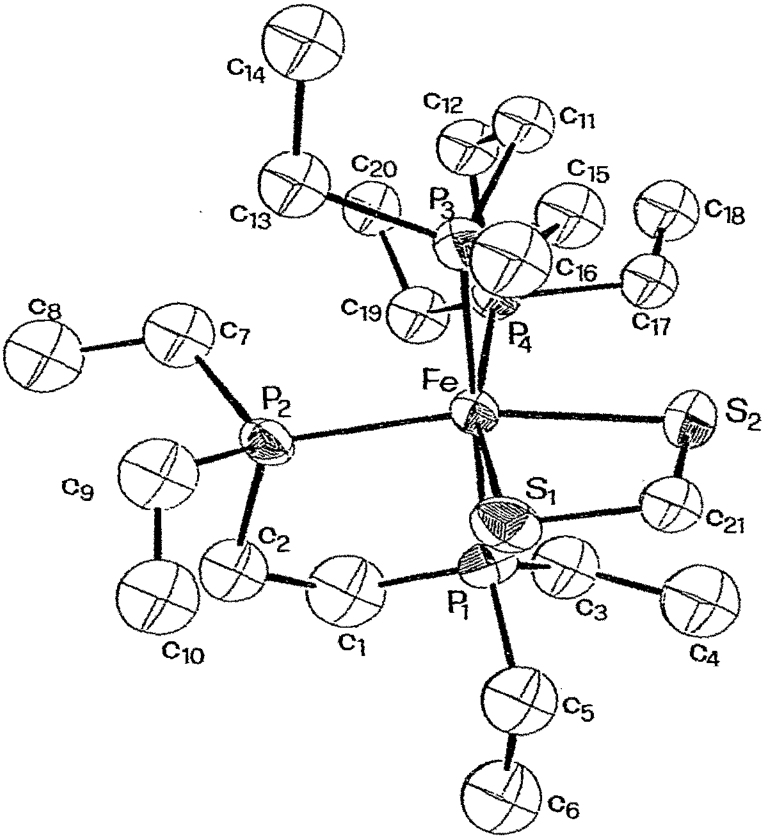


Fig. 2. Perspective view of the complex cation $[(\text{depe})_2\text{Fe}(S_2CH)]^+$. Ortep drawing with 40% probability ellipsoids.

are a potential source of hydride ions [21]. Nucleophilic attack by hydride ion on coordinated Et_3PCS_2 has been previously observed in the reaction of the complex $[(\text{triphos})Co(S_2CPEt_3)](BPh_4)_2$, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, with $NaBH_4$, and resulted in isolation of the five-coordinate complex $[(\text{triphos})Co\{S_2C(H)PEt_3\}](BPh_4)$ containing a phosphonium adduct of a dithioformato ligand [3]. On the other hand it has been reported that the square-pyramidal complex $[(PMe_2Ph)_3Ru\{S_2C(H)PMe_2Ph\}](PF_6)$ is obtained by a sterically-controlled rearrangement of the octahedral dithioformato complex $[(PMe_2Ph)_4Ru(S_2CH)](PF_6)$. The former compound undergoes substitution reactions with small phosphines to give square-pyramidal $S_2C(H)PR_3$ complexes, while with larger phosphines octahedral S_2CH complexes are obtained [22].

The results suggest that the most likely path for the formation of compound **2** involves hydride attack on the carbon atom of the PCS_2 group, and that the subsequent expulsion of the PEt_3 group is mainly due to steric factors. In particular the coordination of the $S_2C(H)PEt_3$ group as a chelate ligand seems to be allowed in five-coordinate metal complexes, while it is forbidden in octahedral complexes, probably on account of the steric hindrance between the PEt_3 group attached to the sp^3 hybridised carbon atom and the other four donor groups.

Diphos complexes

It is well known that the nature of the substituents at the phosphorus atoms can be extremely important in determining the chemical behaviour of phosphine ligands [23]. With this in mind we investigated the reactivity of Et_3PCS_2 toward iron(II) cations in the presence of diphos, which differs from depe in having phenyl substituents in place of ethyl on the phosphorus atoms. Iron(II) tetrafluoroborate reacts with Et_3PCS_2 and diphos in acetone/butanol to give a blue solution. Upon addition of $NaBPh_4$, turquoise crystals of composition $[(diphos)Fe(S_2CPEt_3)_2](BPh_4)_2 \cdot 0.5(CH_3)_2CO$, **3**, are precipitated. Compound **3** is diamagnetic, air-stable, and soluble in common organic solvents in which it behaves as 1/2 electrolyte (molar conductance in 10^{-3} nitroethane solution: 101 cm^2 ohm^{-1} mol^{-1}). The formation of this compound does not depend on the ratio between the phosphine and Et_3PCS_2 ligands. The IR spectrum in the CS_2 stretching region is very similar to that of compound **1**, showing absorptions at 1010(sh), 995, 980(sh), and 970 cm^{-1}. The ^{31}P NMR spectrum in CD_2Cl_2 at 295 K consists of two doublets at 81.52 ppm (*J*(PP) 5.3 Hz) and 29.01 ppm (*J*(PP) 5.3 Hz) (relative intensity 1/1), which are assigned to the phosphorus atoms of diphos and to the phosphorus atoms of two Et_3PCS_2 zwitterions, respectively. On the basis of analytical, spectroscopic, magnetic, and conductivity measurements a structure can be assigned to compound **3** where the iron atom is six coordinated by the two phosphorus atoms of diphos and by the four sulfur atoms of two Et_3PCS_2 molecules (Fig. 3).

According to two recent reviews dealing with the behaviour of tertiary phosphine ligands the steric effects due to the substituents at the phosphorus atoms are at least as important as the electronic effects [24]. As regards the formation of iron(II) complexes with Et_3PCS_2 in the presence of depe or diphos, the dominant effect seems to be the steric hindrance of the phosphorus substituents. In particular, only one phenylated diphosphine can coordinate to the metal.

Compound **3** reacted with sodium borohydride, sodium naphthalenide, or sodium methoxide to give intensely coloured solutions, but no products could be isolated.

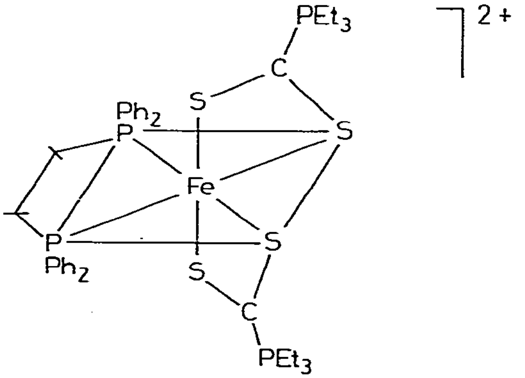


Fig. 3. Schematic drawing of the complex cation $[(diphos)Fe(S_2CPEt_3)_2]^{2+}$.

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