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NUCLEOPHILIC ATTACK ON METAL DITHIOFORMATES BY TERTIARY PHOSPHINES: PREPARATION AND STRUCTURE OF [(dppe)Fe{S₂C(H)dppe}]BPh₄ · CH₂Cl₂

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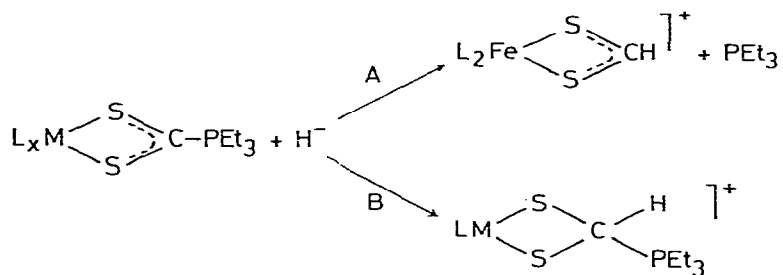
Summary

The cobalt(II) complex [(triphos)Co{S₂C(H)PEt₃}]BPh₄ containing the 1,1-dithio ligand Et₃PC(H)S₂⁻ has been obtained via nucleophilic attack by triethylphosphine on coordinated dithioformate. By reaction of potassium dithioformate with iron(II) or cobalt(II), aquocations in the presence of dppe, and NaBPh₄ the complexes [(dppe)M{S₂C(H)dppe}]BPh₄ have been synthesized. These contain the interesting tridentate zwitterion ligand Ph₂PCH₂CH₂PPh₂C(H)S₂⁻. All the products have been characterized by appropriate physical methods. The molecular structure of the iron derivative has been determined from counter diffraction data. Crystal data are: monoclinic, space group *P*2₁/*n*, *a* 23.445(7), *b* 17.837(5), *c* 16.230(5) Å, β 90.32(3)°, *Z* = 4. The structure was refined by full-matrix least-squares technique to *R* and *R_w* factors of 0.074 and 0.068, respectively. The metal atom is surrounded by the two phosphorus atoms of a dppe molecule, and by one phosphorus atom and two sulfur atoms of the Ph₂PCH₂CH₂PPh₂C(H)S₂⁻ ligand in a distorted square pyramidal geometry.

Introduction

A great variety of nucleophiles attack metal complexes containing the triethylphosphine—carbonyl disulfide adduct, Et₃P—CS₂, as a monometallic chelating ligand [1–4]. The reaction site, independent of the nucleophile used, is always the carbon atom of the CS₂ group. In particular, depending on the ancillary ligands, the attack of hydride ion from NaBH₄ on the ligand Et₃P—CS₂

can give dithioformates or phosphonium adducts of dithioformate (Scheme 1).



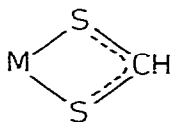
(A, L = 1,2-bis(diethylphosphino)ethane; x = 2; M = Fe;

B, L = 1,1,1-tris(diphenylphosphinomethyl)ethane,

1,1,1-tris(diethylphosphinomethyl)ethane; x = 1; M = Fe, Co)

SCHEME 1

In the light of this finding, it seemed of interest to investigate whether the carbon atom of coordinated dithioformate, behaving as an electrophilic site, undergoes nucleophilic attack by tertiary phosphines (see formula).



In this paper we describe in detail the reactions examined, the chemical and physical properties of the products, and the complete X-ray structural determination of the complex $[(dppe)Fe\{S_2C(H)dppe\}]BPh_4 \cdot CH_2Cl_2$ (dppe = 1,2-bis(diphenylphosphino)ethane).

Experimental

Triphos [5] and KS_2CH [6] were prepared by previously described methods, while dppe was purchased from Strem Chemicals Inc., Dauvers, Mass., and used without further purification. All other chemicals and solvents employed were of reagent grade quality. All 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 dry nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using Nujol mulls. All other physical measurements were carried out as previously described [7].

Preparation of $[(triphos)Co\{S_2C(H)PEt_3\}]BPh_4$ (1)

A solution of KS_2CH (1 mmol) in ethanol (10 ml) was added to a mixture of $[Co(H_2O)_6](BF_4)_2$ (1 mmol) in ethanol (10 ml) and triphos (1 mmol) in CH_2Cl_2 (20 ml). The colour of the solution turned suddenly to dark-red. When PEt_3 (1 mmol) in CH_2Cl_2 (10 ml) was then added there was a further colour change to light-brown. After addition of $NaBPh_4$ (1 mmol) in ethanol (20 ml) and slow evaporation of the solvent orange crystals separated; these were filtered off and

washed with ethanol and then with petroleum ether. They were recrystallized from acetone and butanol.

Anal. Found: C, 71.98; H, 6.25; Co, 4.85; P, 10.41. $C_{72}H_{75}BCoP_4S_2$ calcd.: C, 72.17; H, 6.31; Co, 4.91; P, 10.34%.

Preparation of [(dppe)Fe{S₂C(H)dppe}]BPh₄·CH₂Cl₂ (2)

A solution of KS_2CH (1 mmol) in ethanol (10 ml) was added to a mixture of $[Fe(H_2O)_6](BF_4)_2$ (1 mmol) in ethanol (10 ml) and dppe (2 mmol) in CH_2Cl_2 (30 ml). The solution immediately became dark-violet. $NaBPh_4$ (1 mmol) in ethanol (10 ml) was then added, and within 30 min the colour changed to red-violet. On slow evaporation of the solvent yellow-green crystals were formed, and these were collected by filtration and washed with ethanol and petroleum ether.

Anal. Found: C, 70.15; H, 5.31; Fe, 4.12; S, 4.75. $C_{78}H_{17}BCl_2FeP_4S_2$ calcd.: C, 70.22; H, 5.36; Fe, 4.18; S, 4.80%.

Preparation of [(dppe)Co{S₂C(H)dppe}]BPh₄ (3)

A mixture of $[Co(H_2O)_6](BF_4)_2$ (1 mmol) in ethanol (10 ml) and dppe (2 mmol) in CH_2Cl_2 (20 ml) was added to a solution of KS_2CH (1 mmol) in ethanol (10 ml). After addition of $NaBPh_4$ (1 mmol) in ethanol (10 ml) orange-red crystals soon separated, and these were filtered off and washed with ethanol and petroleum ether. They were recrystallized from acetone and butanol.

Anal. Found: C, 73.72; H, 5.60; Co, 4.64; S, 5.04. $C_{77}H_{69}BCoP_4S_2$ calcd.: C, 73.85; H, 5.55; Co, 4.70%.

Collection and reduction of X-ray data

The crystal used for data collection was parallelepiped shaped. The crystals are monoclinic and belong to the space group $P2_1/n$, with four $[(dppe)Fe\{S_2C(H)dppe\}]BPh_4 \cdot CH_2Cl_2$ formulae in the unit cell which has the following dimensions: a 23.445(7), b 17.837(5), c 16.230(5) Å, β 90.32(3)°. Intensity data were collected on an automatic computer-controlled diffractometer Philips PW 1100, equipped with a graphite monochromator, using Mo- K_α radiation. All reflections with $5^\circ \leq 2\theta \leq 40^\circ$ were measured using the ω - 2θ scan technique with a scan speed of $0.07^\circ s^{-1}$ in a variable range of $0.70 + 0.30 \text{ tg } \omega$ across the peak. Three standard reflections were measured every 60 min during data collection, but no significant variation was noticed. The intensity data were corrected for Lorentz and polarization effects; the standard deviations $\sigma(I)$ were estimated as described elsewhere [8] with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity I was $< 3\sigma(I)$. From the 6898 total reflection 1831 had intensity $\geq 3\sigma(I)$. The absorption correction was not applied in view of the low μ value (4.18 cm^{-1}) and the smallness of the crystal. Atomic scattering factors were taken from ref. 9. Correction from anomalous dispersion effects were also applied [10].

Solution and refinement of the structure

A three dimensional Patterson synthesis yielded the positional parameters of the iron, sulfur and phosphorus atoms. Successive F_o Fourier syntheses showed

TABLE 1
 POSITIONAL AND THERMAL PARAMETERS FOR [(dippe)Fe(S₂C(H)dippe)]₂BPPh₄·CH₂Cl₂^a

Atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Fe	6740(2)	3321(2)	4967(2)	42(2)	42(3)	39(3)	-5(3)	-6(2)	-3(2)
P(1)	6153(3)	3375(4)	3888(4)	43(5)	50(5)	50(6)	1(5)	2(4)	-13(5)
P(2)	6996(3)	2250(4)	4411(4)	52(5)	40(5)	33(6)	-3(4)	-6(4)	-2(4)
P(3)	7417(3)	4056(4)	4579(4)	46(5)	44(5)	32(5)	2(4)	-12(4)	-3(4)
P(4)	7123(3)	4597(4)	6890(4)	47(5)	58(5)	41(6)	0(5)	-9(4)	-5(5)
S(1)	6214(3)	4094(4)	5719(4)	41(5)	87(6)	51(5)	3(5)	-6(4)	-24(5)
S(2)	7057(3)	3069(4)	6242(4)	71(6)	43(5)	40(5)	-7(4)	-6(4)	1(4)

^a The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$ coordinates multiplied by 10⁴, temperature factors by 10³.

the positions of all non-hydrogen atoms including some atoms of the disordered CH_2Cl_2 solvent molecules. An accurate inspection of ΔF Fourier syntheses in the zone of CH_2Cl_2 showed the presence of various disordered arrays of this molecule. On the basis of the heights of these peaks different population parameters were assigned to the various models, i.e. 1/2 to C(78), Cl(1), and Cl(2), 1/3 to Cl(3), 1/6 to Cl(4)—Cl(7) atoms. The structure was refined by use of the full-matrix least-squares of the SHELX program [11]. The minimized function is $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values according to the expression $w = 1/\sigma^2(F_o)$. The hydrogen atoms were introduced in calculated positions, with an overall temperature factor U of 0.05 \AA^2 and were not refined. Their positions were varied in every cycle on the basis of the shift of the carbon atom (the C—H distance was fixed at 1.08 \AA). Isotropic temperature factors were used for carbon, boron and chlorine atoms, and anisotropic temperature factors for the other atoms. Phenyl groups were refined as rigid bodies, with the assumption of D_{6h} symmetry for the rings. The final conventional R factor was 0.074. The R_w factor, defined as $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.068. A final ΔF Fourier synthesis did not show any unusual features. The final values of the parameters are reported in Tables 1, 2. Lists of observed and calculated structure factors are available from the authors.

TABLE 2

THERMAL AND POSITIONAL PARAMETERS OF NON-GROUP AND GROUP ATOMS FOR $[(\text{dppe})\text{Fe}\{\text{S}_2\text{C}(\text{H})\text{dppe}\}]\text{BPh}_4 \cdot \text{CH}_2\text{Cl}_2^a$

Atom	x	y	z	$U (\text{\AA}^2)$
C(1)	6632(10)	3840(14)	6641(15)	55(9)
C(2)	6428(9)	2846(12)	3008(14)	53(8)
C(3)	6876(9)	2259(13)	3280(13)	56(8)
C(4)	7641(8)	4771(12)	6121(12)	32(7)
C(5)	7456(9)	4905(11)	5233(13)	40(7)
C(7)	5732(7)	4234(9)	2568(11)	90(10)
C(8)	5466(7)	4859(9)	2222(11)	116(12)
C(9)	5348(7)	5484(9)	2710(11)	113(12)
C(10)	5496(7)	5482(9)	3544(11)	113(12)
C(11)	5762(7)	4856(9)	3890(11)	85(10)
C(6)	5880(7)	4232(9)	3402(11)	58(8)
C(13)	5367(7)	2181(10)	3847(9)	80(9)
C(14)	4865(7)	1824(10)	4084(9)	86(10)
C(15)	4475(7)	2197(10)	4584(9)	90(10)
C(16)	4587(7)	2926(10)	4848(9)	159(15)
C(17)	5090(7)	3283(10)	4611(9)	120(12)
C(12)	5480(7)	2911(10)	4111(9)	43(7)
C(19)	7816(6)	1445(8)	5239(9)	74(9)
C(20)	8359(6)	1155(8)	5389(9)	66(8)
C(21)	8791(6)	1258(8)	4813(9)	70(9)
C(22)	8680(6)	1651(8)	4087(9)	68(8)
C(23)	8137(6)	1942(8)	3937(9)	46(7)
C(18)	7705(6)	1839(8)	4513(9)	45(7)
C(25)	6185(7)	1544(8)	5407(9)	59(8)
C(26)	5817(7)	965(8)	5630(9)	88(10)
C(27)	5815(7)	296(8)	5186(9)	81(9)
C(28)	6180(7)	206(8)	4518(9)	84(11)
C(29)	6549(7)	785(8)	4295(9)	71(9)

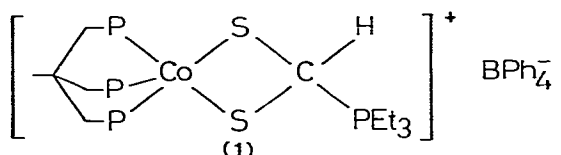
TABLE 2 (continued)

Atom	x	y	z	$U (\text{\AA}^2)$
C(24)	6551(7)	1454(8)	4739(9)	48(8)
C(31)	8563(7)	4204(7)	4190(8)	43(7)
C(32)	9146(7)	4085(7)	4301(8)	73(9)
C(33)	9338(7)	3569(7)	4887(8)	55(8)
C(34)	8945(7)	3174(7)	5362(8)	43(7)
C(35)	8362(7)	3293(7)	5251(8)	44(7)
C(30)	8171(7)	3809(7)	4665(8)	31(7)
C(37)	7124(6)	5152(9)	3415(9)	57(8)
C(38)	7061(6)	5442(9)	2621(9)	72(9)
C(39)	7251(6)	5032(9)	1945(9)	70(8)
C(40)	7504(6)	4332(9)	2062(9)	74(9)
C(41)	7567(6)	4042(9)	2855(9)	66(8)
C(36)	7377(6)	4452(9)	3532(9)	34(7)
C(43)	8056(8)	4087(10)	7791(10)	118(12)
C(44)	8306(8)	3825(10)	8517(10)	150(14)
C(45)	7995(8)	3821(10)	9248(10)	99(11)
C(46)	7434(8)	4080(10)	9252(10)	109(12)
C(47)	7183(8)	4342(10)	8526(10)	142(14)
C(42)	7494(8)	4346(10)	7795(10)	56(8)
C(49)	7084(5)	6089(10)	7274(9)	54(8)
C(50)	6829(5)	6778(10)	7442(9)	90(11)
C(51)	6236(5)	6843(10)	7438(9)	75(9)
C(52)	5898(5)	6219(10)	7267(9)	107(11)
C(53)	6153(5)	5529(10)	7099(9)	82(10)
C(48)	6746(5)	5464(10)	7102(9)	56(8)
B	6372(12)	2052(16)	182(18)	43(9)
C(54)	6045(7)	1680(10)	1007(8)	44(7)
C(55)	5494(7)	1908(10)	1208(8)	67(9)
C(56)	5196(7)	1539(10)	1829(8)	79(10)
C(57)	5449(7)	943(10)	2250(8)	91(10)
C(58)	6000(7)	715(10)	2050(8)	69(9)
C(59)	6298(7)	1084(10)	1429(8)	60(8)
C(60)	6106(8)	2925(8)	-22(13)	63(9)
C(61)	5688(8)	3007(8)	-631(13)	105(11)
C(62)	5456(8)	3712(8)	-795(13)	125(14)
C(63)	5642(8)	4335(8)	-350(13)	93(11)
C(64)	6060(8)	4254(8)	258(13)	86(10)
C(65)	6292(8)	3549(8)	422(13)	65(9)
C(66)	6242(7)	1496(9)	-682(9)	48(7)
C(67)	5948(7)	821(9)	-594(9)	71(9)
C(68)	5836(7)	376(9)	-1282(9)	78(9)
C(69)	6017(7)	606(9)	-2059(9)	61(9)
C(70)	6311(7)	1281(9)	-2148(9)	67(9)
C(71)	6424(7)	1726(9)	-1459(9)	70(9)
C(72)	7079(5)	2087(8)	354(12)	41(8)
C(73)	7482(5)	1859(8)	-222(12)	59(8)
C(74)	8062(5)	1884(8)	-25(12)	62(9)
C(75)	8238(5)	2139(8)	749(12)	64(9)
C(76)	7834(5)	2367(8)	1325(12)	61(9)
C(77)	7254(5)	2341(9)	1127(12)	55(8)
C(78)	-175(61)	2814(74)	2621(82)	195(72)
Cl(1)	195(13)	2462(16)	2025(17)	108(10)
Cl(2)	-713(14)	3577(19)	2042(19)	142(12)
Cl(3)	-791(15)	3103(21)	2306(21)	166(13)
Cl(4)	-150(25)	3205(39)	2670(39)	104(23)
Cl(5)	-173(37)	2414(47)	2185(56)	190(35)
Cl(6)	352(28)	2352(39)	1865(41)	61(28)
Cl(7)	-452(33)	3830(44)	2041(49)	160(37)

^a Coordinates multiplied by 10⁴, temperature factors by 10³.

Results and discussion

When potassium dithioformate was allowed to react with cobalt(II) aquocations, triphos (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane), and NaBPh_4 in methylene chloride-alcohol, an intense red coloration was produced. Upon addition of triethylphosphine the colour turned to light brown, and orange crystals separated. This product was shown to be the cobalt(II) complex $[(\text{triphos})\text{Co}\{\text{S}_2\text{C}(\text{H})\text{PEt}_3\}]\text{BPh}_4$ (**1**), which was recently prepared in our laboratory by reaction of NaBH_4 with the complex $[(\text{triphos})\text{Co}(\text{S}_2\text{CPEt}_3)]\text{-(BPh}_4)_2$ [**3**].



The in situ formation of 1,1-dithio ligands of the type $\text{R}_3\text{PC}(\text{H})\text{S}_2^-$ has been previously observed in the reactions of carbon disulfide with $[(\text{PMe}_2\text{Ph})_5\text{RuH}]\text{-PF}_6$ [12] and $[(\text{PR}_3)_3\text{PdH}]\text{BPh}_4$ ($\text{R} = \text{Me, Et}$) [13] to give the complexes $[(\text{PMe}_2\text{Ph})_3\text{Ru}\{\text{S}_2\text{C}(\text{H})\text{PMe}_2\text{Ph}\}]\text{PF}_6$, and $[(\text{PR}_3)_2\text{Pd}\{\text{S}_2\text{C}(\text{H})\text{PR}_3\}]\text{BPh}_4$, respectively. The formation of the zwitterionic ligand in the former complex has been reported to involve nucleophilic attack by a phosphine at the carbon atom of hydrometallated CS_2 , whereas in the latter the nucleophile is a hydridic hydrogen atom and the electrophilic site the carbon atom of the phosphonium adduct of CS_2 . In the light of our results, both the above reaction mechanism must be considered equally valid.

On reaction of potassium dithioformate with iron(II) or cobalt(II) aquocations in the presence of an excess of 1,2-bis(diphenylphosphino)ethane, dppe, and NaBPh_4 we obtained the complexes $[(\text{dppe})\text{M}\{\text{S}_2\text{C}(\text{H})\text{dppe}\}]\text{BPh}_4$ with $\text{M} = \text{Fe}$ (**2**) and $\text{M} = \text{Co}$ (**3**), respectively.

Compound **2** is reasonably air-stable in the solid state, but decomposes in solution even in an inert atmosphere, and thus has not been studied in solution. The UV reflectance spectrum with absorption maxima at 11 400, 13 000, 16 250, and 22 000 cm^{-1} , is consistent with those of distorted square-pyramidal iron(II) complexes with P_3S_2 donor set [14]. The IR spectrum in the $\nu(\text{CS})$ region shows two bands at low energies (790 and 640 cm^{-1}), thus indicating the absence of a $\text{C}=\text{S}$ bond. The crystal and molecular structure consists of discrete $[(\text{dppe})\text{Fe}\{\text{S}_2\text{C}(\text{H})\text{dppe}\}]^{2+}$ cations, BPh_4^- anions, and CH_2Cl_2 solvent molecules. Selected bond distances and angles in the complex cation are given in Table 3. The iron atom is coordinated in a distorted square-pyramidal environment to the two phosphorus atoms of a dppe molecule, to one phosphorus atom, and to two sulfur atoms of the zwitterionic ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{CHS}_2^-$, **Z**, formed in situ.

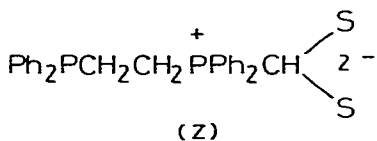


TABLE 3
SELECTED BOND DISTANCES AND BOND ANGLES

Distances (Å)			
Fe—S(1)	2.219(7)	P(3)—C(5)	1.853(19)
Fe—S(2)	2.240(7)	P(3)—C(30)	1.826(16)
Fe—P(1)	2.222(7)	P(3)—C(36)	1.842(16)
Fe—P(2)	2.199(7)	P(4)—C(1)	1.817(23)
Fe—P(3)	2.155(7)	P(4)—C(4)	1.773(19)
S(1)—C(1)	1.840(24)	P(4)—C(42)	1.761(20)
S(2)—C(1)	1.819(23)	P(4)—C(48)	1.816(17)
P(1)—C(2)	1.833(20)	C(2)—C(3)	1.546(25)
P(1)—C(6)	1.833(19)	C(4)—C(5)	1.521(24)
P(1)—C(12)	1.821(18)	B—C(54)	1.684(28)
P(2)—C(3)	1.855(21)	B—C(60)	1.710(27)
P(2)—C(18)	1.823(16)	B—C(66)	1.743(27)
P(2)—C(24)	1.842(17)	B—C(72)	1.680(27)
Angles (°)			
S(1)—Fe—S(2)	78.4(3)	Fe—P(3)—C(30)	123.1(5)
S(1)—Fe—P(1)	93.7(3)	Fe—P(3)—C(36)	118.0(5)
S(1)—Fe—P(2)	156.9(3)	C(5)—P(3)—C(30)	96.2(8)
S(1)—Fe—P(3)	101.3(3)	C(5)—P(3)—C(36)	102.5(8)
S(2)—Fe—P(1)	159.6(3)	C(30)—P(3)—C(36)	101.9(6)
S(2)—Fe—P(2)	96.6(3)	C(1)—P(4)—C(4)	114.1(10)
S(2)—Fe—P(3)	98.6(3)	C(1)—P(4)—C(42)	107.8(10)
P(1)—Fe—P(2)	83.3(3)	C(1)—P(4)—C(48)	111.5(9)
P(1)—Fe—P(3)	101.4(3)	C(4)—P(4)—C(42)	107.1(8)
P(2)—Fe—P(3)	101.8(3)	C(4)—P(4)—C(48)	108.7(8)
Fe—S(1)—C(1)	90.0(8)	C(42)—P(4)—C(48)	107.3(8)
Fe—S(2)—C(1)	89.9(8)	S(1)—C(1)—S(2)	100.7(12)
Fe—P(1)—C(2)	111.9(7)	S(1)—C(1)—P(4)	109.4(12)
Fe—P(1)—C(6)	126.0(6)	S(2)—C(1)—P(4)	107.1(12)
Fe—P(1)—C(12)	110.9(6)	P(1)—C(2)—C(3)	111.5(15)
C(2)—P(1)—C(6)	102.5(9)	P(2)—C(3)—C(2)	112.8(15)
C(2)—P(1)—C(12)	103.3(9)	P(3)—C(5)—C(4)	115.3(14)
C(6)—P(1)—C(12)	99.4(7)	P(4)—C(4)—C(5)	120.1(14)
Fe—P(2)—C(3)	111.0(7)	C(54)—B—C(60)	110.2(17)
Fe—P(2)—C(18)	124.3(5)	C(54)—B—C(66)	109.8(16)
Fe—P(2)—C(24)	113.2(5)	C(54)—B—C(72)	109.6(17)
C(3)—P(2)—C(18)	103.1(8)	C(60)—B—C(66)	107.5(17)
C(3)—P(2)—C(24)	102.1(9)	C(60)—B—C(72)	110.9(17)
C(18)—P(2)—C(24)	100.5(7)	C(66)—B—C(72)	108.8(17)
Fe—P(3)—C(5)	111.4(7)		

The distortion of the square-pyramid from the idealized geometry, which was found also in other complexes containing the $>CS_2$ fragment [4,12,14] is mainly due to the small bite of this fragment, the S(1)—Fe—S(2) angle being $78.4(3)^\circ$ (Fig. 1). The bite of the dppe ligand also does not reach the ideal value (the P(1)—Fe—P(2) angle is $83.3(3)^\circ$), so contributing to a marked distortion from a square pyramid. In this geometrical model the iron atom lies markedly away from the basal plane (0.41 \AA) toward the P(3) apical atom. The Fe—P(3) distance ($2.155(7) \text{ \AA}$) is considerably shorter than the other two basal Fe—P distances ($2.222(7)$ and $2.199(7) \text{ \AA}$). Although the hydrogen atom of the HCS_2 moiety was not located, its presence clearly results from the values of the

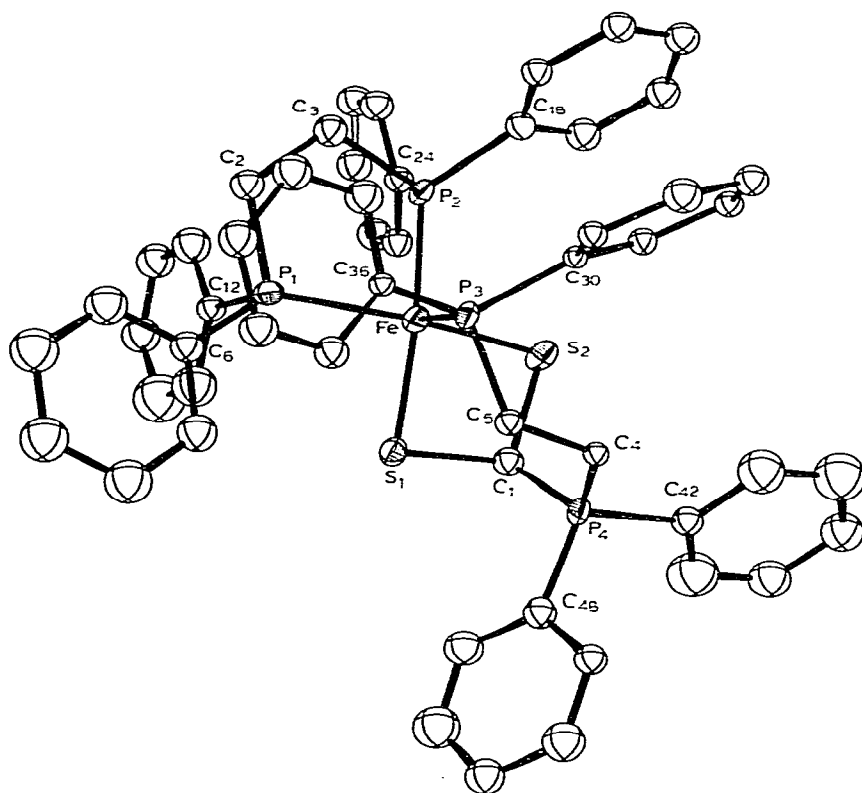


Fig. 1. Perspective view of the complex cation $[(dppe)Fe\{S_2C(H)dppe\}]^+$. ORTEP drawing with 30% probability ellipsoids.

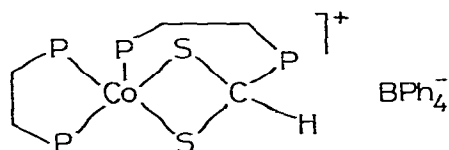
angles about the C(1) carbon atom (range $100.7\text{--}109.4^\circ$), which are indicative of a sp^3 hybridization of this carbon. The P—C and C—S distances are close to the values expected for bond order one. Bond distances and angles within the S_2CHP fragment well match the values found in other complexes containing this grouping [4,12,15].

The shortening of the apical bond in this complex seems to be electronic in nature, and in particular due to the stereochemical influence of the d electrons of the metal. A clear cut explanation of the reasons why in C_{4v} low-spin d^6 metal complexes the apical bond is expected to be shorter than the basal bonds has been given by Rossi and Hoffman in a classical paper on transition metal pentacoordination [16]. The six d electrons occupy the low b_2 and e MO orbitals, while the a_1 orbital, antibonding between d_{z^2} and the σ -donor long pair, is empty. This orbital lowers its energy as the L—M—L basal bond angles are closed and eventually becomes occupied, thus triggering a repulsion between the metal and the apical ligand. A cross-over is expected for values of these angles far removed from 180° (about 125°). In our complex, however, the angles in question average 158° , in nice agreement with the shorter M—L apical distance found in the structure.

Compound **3** is 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 1/1 electrolyte (molar conductance in 10^{-3} nitroethane solution: $44 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$). The electronic spectrum, practically identical in the solid and in 1,2-dichloroethane solution, shows absorption maxima at 8 800 ($\epsilon = 108$), 10 000 ($\epsilon = 230$), 13 350 ($\epsilon = 220$), 15 400 ($\epsilon = 290$), and 20 000 cm^{-1} ($\epsilon = 2500$), and is comparable with those of distorted square pyramidal cobalt(II) complexes with P_3S_2 donor set [4]. The room-temperature μ_{eff} is equal to $2.04 \mu_B$, as expected for a low-spin d^7 configuration. The IR spectrum is identical to that of **2**.

On the basis of these results, and of the crystal structure of **2**, a structure can be assigned to **3** in which the cobalt atom is five-coordinated by three phosphorus atoms and by two sulfur atoms in a distorted square pyramidal environment (see formula).



Metal complexes containing zwitterionic tridentate ligands of the type **Z** are very rare, and to our knowledge limited to the two complexes $[\text{M}(\text{CO})_3(\text{dpm})(\text{HCS}_2)]$ ($\text{M} = \text{Mn}, \text{Re}$; $\text{dpm} = \text{bis}(\text{diphenylphosphino})\text{methane}$), obtained by reaction of CS_2 with the corresponding $[\text{M}(\text{CO})_3(\text{dpm})\text{H}]$ compounds [15]. The crystal structure of the manganese derivative has shown the presence of the zwitterionic ligand $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{S}_2^-$, which differs from **Z** only in the length of the chain between the two phosphorus atoms. The formation of this ligand has been rationalized in terms of an insertion of CS_2 into the $\text{Mn}-\text{H}$ bond, followed by nucleophilic attack at the thiocarbonyl carbon atom by a phosphorus atom of the dpm molecule, and we reaffirm this mechanism. It is reasonable to expect nucleophilic attack by an uncoordinated phosphorus atom of a dpe molecule on the carbon atom of the dithioformate group.

The formation of the five-coordinate complex **2** instead of the possible six-coordinate complex $[(\text{dppe})_2\text{Fe}(\text{S}_2\text{CH})]\text{BPh}_4$, seems due mainly to steric factors, but the great electrophilicity of the carbon atom of the HCS_2 group is not a negligible factor.

Notwithstanding the formation of a strained seven-membered ring in compounds **2** and **3**, the six potential donor atoms rearrange themselves around the metal in square pyramidal rather than in octahedral geometry, probably because of the smaller steric crowding involved in five-coordination. These results confirm the previous suggestion that marked steric hindrance would be involved if two dppe molecules and one chelating 1,1-dithio ligand coordinated to a metal center in an octahedral arrangement [2].

The present work suggests that various interesting complexes with sulfur-containing ligands can be synthesized by nucleophilic attack on coordinated 1,1-dithioacids. Further investigation on these systems and others involving the presence of chelated disulfido ligands are in progress.

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