Journal of Organometallic Chemistry, 215 (1981) C59—C62
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS, REACTIVITY AND X-RAY STRUCTURE OF THE COMPLEX $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ (depe = 1,2-BIS(DIETHYLPHOSPHINO)ETHANE)

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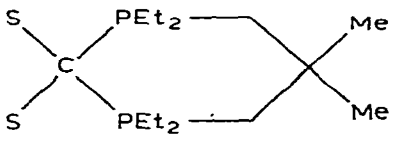
(Received May 27th, 1981)

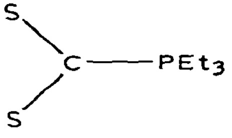
Summary

The reaction of the zwitterion Et_3PCS_2 with iron(II) tetrafluoroborate in the presence of 1,2-bis(diethylphosphino)ethane (depe) and $NaBPh_4$ gave the unusual complex $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ (I), whose structure has been determined by X-ray analysis. A dithioformatoiron(II) complex was made by treating I with $NaBH_4$.

The reactions of CS_2 and CS_2-containing molecules with metal—ligand moieties formed by 3*d*-transition metals and tris(tertiary phosphines) have been recently investigated in this laboratory. In particular a number of metal complexes containing as ligands zwitterions of the type I and II have been synthesized [1—3].



I



II

The derivatives of the zwitterion II are particularly interesting owing to the great reactivity of the coordinated zwitterion, which can be easily transformed into different disulfido ligands such as S_2CO^{2-}, S_2CS^{2-} and $S_2C(H)PEt_3^-$ [3].

By reaction of Et_3PCS_2 (Z) with iron(II) tetrafluoroborate in the presence of 1,2-bis(diethylphosphino)ethane (depe) and of $NaBPh_4$, we have now obtained the blue-green diamagnetic iron(II) complex $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ (I). Compound I, which is air stable both in the solid state and in solution, is soluble in all common organic solvents, in which it behaves as a 1/2 electrolyte (molar conductance value in 10^{-3} M nitroethane solution: 97 cm^2 ohm^{-1} mol^{-1}).

A complete X-ray structural analysis was carried out on compound I. The crystals are triclinic, space groups $P\bar{1}$, 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)°; $Z = 2$. The intensities of 4903 independent reflections with $I \geqslant 3\sigma(I)$ were measured on a Philips PW 1100 automatic diffractometer, using Mo-K_α radiation (λ 0.7107 Å). The structure was solved by the heavy atom method and refined by full-matrix least-squares cycles to R and R_w factors of 0.080 and 0.085, respectively. The crystal structure consists of complex cations $[(depe)_2FeZ]^{2+}$ and tetraphenylborate anions. The complex cation, as shown in Fig. 1, displays a distorted octahedral coordination around the metal atom. Two *cis*-positions are occupied by the sulphur atoms of the zwitterionic ligand, which chelates the metal atom to form a four-membered ring. The *trans*-positions to the two sulphur atoms are respectively occupied by two phosphorus atoms belonging to different depe molecules, the remaining phosphorus atoms being in axial sites. The distortion from the idealized octa-

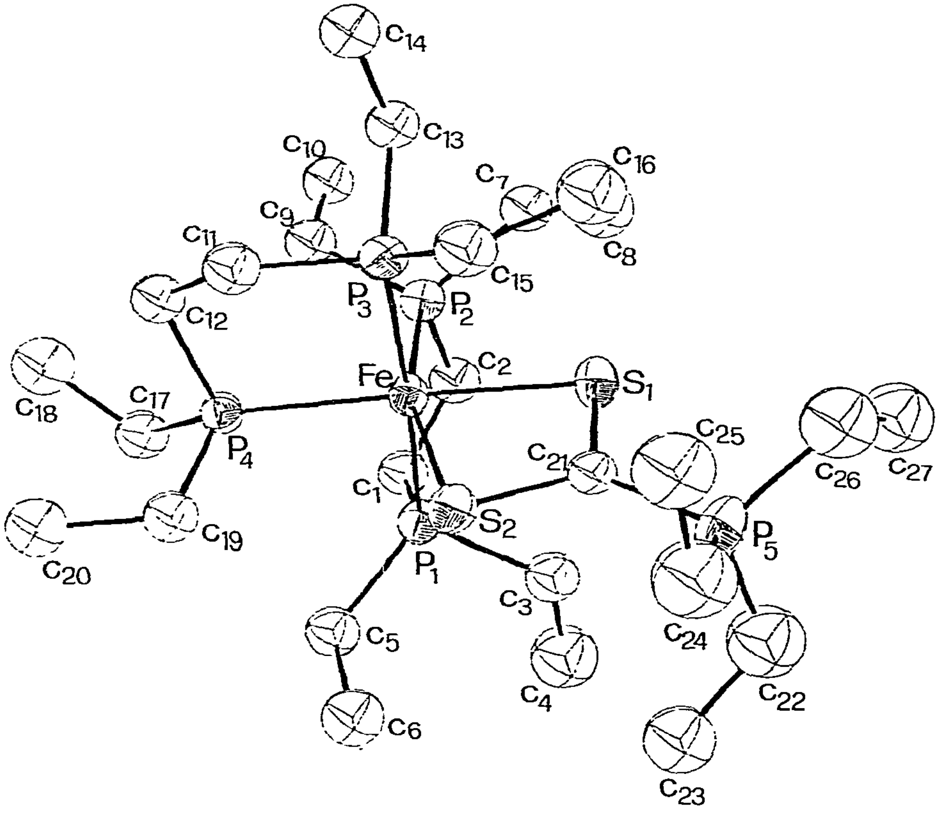


Fig. 1. Perspective view of the complex cation $[(depe)_2Fe(S_2CPEt_3)]^{2+}$. ORTEP drawing with 40% probability ellipsoids. Important bond distances and angles: Fe—P(1) 2.307(3), Fe—P(2) 2.261(3), Fe—P(3) 2.324(3), Fe—P(4) 2.285(3), Fe—S(1) 2.261(3), Fe—S(2) 2.305(3), S(1)—C(21) 1.681(9), S(2)—C(21) 1.681(9), P(5)—C(21) 1.78(1) Å; P(1)—Fe—P(3) 176.0(1), P(2)—Fe—S(2) 162.4(1), P(4)—Fe—S(1) 168.8(1), S(1)—Fe—S(2) 74.1(1), S(1)—C(2)—S(2) 109.9(5), S(1)—C(21)—P(5) 123.0(6), S(2)—C(21)—P(5) 127.0(6)°.

hedral geometry is mainly due to the bidentate nature of the zwitterionic ligand; indeed its coordination angle (S(1)—Fe—S(2)) of 74.1(1)° causes deviation from 180° of the axial angles S(2)—Fe—P(2) and S(1)—Fe—P(4), which are reduced to 168.8(1) and 162.1(1)°, respectively. The axial angle P(1)—Fe—P(3) approaches the value of 176.0(1)°, very close to the ideal 180°. The bond distances and angles within the zwitterion ligand agree very well with those reported for the similar zwitterion Ph_3PCS_2 in the iridium complex $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]BF_4$ [4], which has been obtained by insertion of carbon disulfide into the Ir—P bond. A comparison can also be made with the uncoordinated Et_3PCS_2 zwitterion [5]: whereas the S—C and C—P distances are in excellent agreement (1.68(1)(av) vs. 1.69(3)(av) and 1.78(1) vs. 1.78(3) Å, respectively) the bond angle S—C—S is not comparable as coordination causes a decrease from 127(1) to 109.9(5)°. The Fe—P and Fe—S bond distances, averaging 2.29(1) and 2.28(2) Å, respectively, are in the range previously found for a variety of hexacoordinated iron(II) complexes [6].

The ^{31}P NMR spectrum in CD_3COCD_3 shows two multiplets at 68.12 and 27.43 ppm (chemical shifts are downfield (+) from external H_3PO_4), which are assigned to the four phosphorus atoms of the phosphine ligands and to the phosphorus atom of the zwitterion, respectively.

Owing to the great reactivity of the coordinated zwitterion Z, compound I provides a convenient way of synthesising a dithioformate-iron(II) complex. When an alcoholic solution of $NaBH_4$ is allowed to react with I in acetone, violet crystals of composition $[(depe)_2Fe(S_2CH)]BPh_4$ (II) are obtained. The IR spectrum (Nujol mulls) shows two bands at 1215 and 910 cm^{-1}, attributable to δ(HCS) and $\nu(CS_2)_{asym}$, respectively, which agree very well with those found in other complexes containing dithioformate and phosphine ligands [7]. 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 $CDCl_3$ is also in agreement with the presence of a dithioformate ligand, which shows a multiplet at τ −0.94.

On the basis of these spectroscopic data, and of the preliminary results of an X-ray analysis, compound II is assigned the structure shown in Fig. 2.

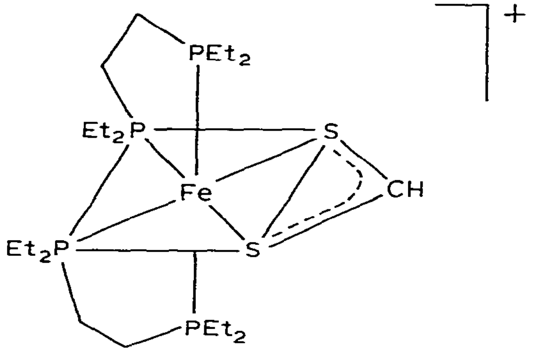


Fig. 2. Schematic drawing of the complex cation $[(depe)_2Fe(S_2CH)]^+$.

Acknowledgement

Thanks are due to Prof. L. Sacconi for helpful discussion and to Mr. P. Innocenti and Mr. F. Cecconi for technical assistance.

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