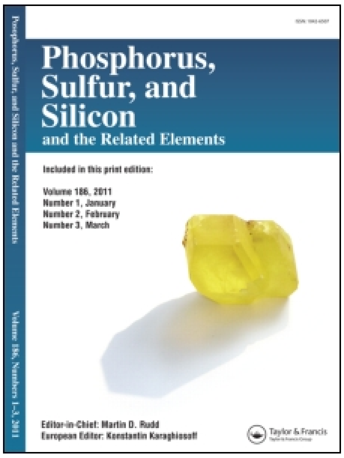

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IRON-ASSISTED REACTION OF CARBON DISULFIDE WITH TRIETHYLPHOSPHINE. SYNTHESIS AND STRUCTURE OF THE COMPOUND $[Et_3PCH_2S_2CH_2PEt_3](BPh_4)_2$.

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The reaction of carbon disulfide with triethylphosphine in the presence of hydrated iron(II) tetrafluoroborate gave white crystals of di(triethylphosphoniomethyl)disulfide tetrafluoroborate $[Et_3PCH_2S_2CH_2$-$PEt_3](BPh_4)_2$. This compound has been fully characterized by usual physical methods and X-ray analysis. The role of the iron(II) cations in the formation of the title compound is briefly discussed.

In previous papers from this Laboratory it has been extensively reported that tri(tertiary phosphines) and transition metals form moieties which are very reactive toward carbon disulfide. In the metal complexes obtained the CS_2 group has been found to act either as a simple donor ligand[1] or as the bonding fragment of more complex ligands.[2] The latter case is represented by the iron(II) complex $[(\text{etriphos})\text{-}FeZ](BF_4)_2$ (etriphos = 1,1,1-tris(diethylphosphinomethyl)ethane) which contains the cyclic zwitterion *Z* (Figure 1) formed *in-situ* by reaction of metal-activated carbon disulfide with etriphos.

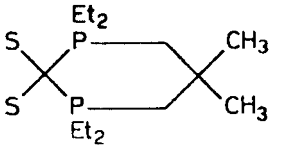

FIGURE 1

It therefore seemed to be interesting to investigate the behavior of carbon disulfide toward hydrated iron(II) tetrafluoroborate in the presence of a mono(tertiary phosphine).

When carbon disulfide reacts with a mixture of triethylphosphine and hydrated iron(II) tetrafluoroborate (ligand-metal ratio 5) in methylene chloride-alcohol, at room temperature, a white microcrystalline solid is formed. This is recrystallized as $[Et_3PCH_2S]_2(BPh_4)_2$ by treatment with sodium tetraphenylborate.

This compound is soluble in the common organic solvents in which it behaves as 1:2 electrolyte (the molar conductance value is 95 cm^2 ohm^{-1} mol^{-1} for 10^{-3} molar nitroethane solution).

The crystal and molecular structure consists of discrete $[Et_3PCH_2S_2CH_2PEt_3]^{2+}$ cations and tetraphenylborate anions. A stereoscopic view of the cation is shown in Figure 2.

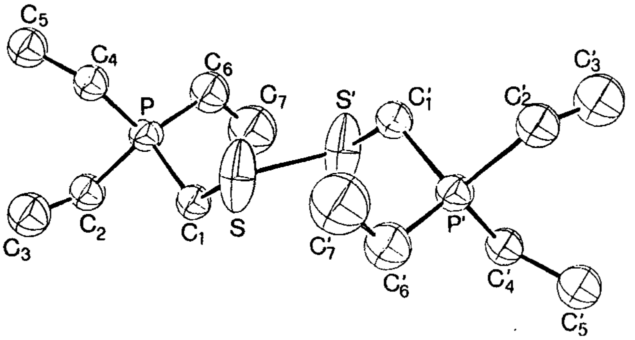

FIGURE 2 Perspective view of the cation $[Et_3PCH_2S_2CH_2PEt_3]^{2+}$. ORTEP drawing with 50% probability ellipsoids. Selected bond distances and angles: $S—S' = 2.00(1)$, $S—C_1 = 1.61(3)$, $P—C_1 = 1.92(3)$, $P—C_{Et}(av) = 1.85(4)$ Å, $S'—S—C_1 = 106.1(15)$, $S—C_1—P = 118.0(15)$, $C—P—C(av) = 109.2(15)°$.

The cation possesses C_i crystallographic symmetry, the inversion center being between the two sulphur atoms, each linked to one $—CH_2—PEt_3$ fragment. The phosphorus atom displays an almost regular tetrahedral geometry, with typical bond distances and angles. The bond distances involving the sulphur atom are somewhat shorter than expected. This is probably due to difficulties to account for the thermal motion of the sulphur atom as well as to the high disorder present in the cation.

This structure is strongly supported by ^1H NMR data. The spectrum in CD_3COCD_3 shows a doublet at 5.98, a multiplet at 7.55 and a multiplet at 8.465 τ. On the basis of their intensities and with reference to existing data, these bands are assigned to the $P—CH_2—S$ protons, to the $—CH_2—P$ protons and to the $CH_3—$ protons respectively.

Although definitive conclusions have not been reached, it is reasonable to expect that the synthesis of the title compound involves the preliminary formation of unstable iron(II) coordination species in the reaction mixture.

The basic role of the iron(II) cations in the formation of this compound is indeed confirmed by two experimental indications. The first is that in absence of any metal cations carbon disulfide reacts with triethylphosphine to give the red zwitterion Et_3PCS_2.[3] On the other hand when the reaction of carbon disulfide with triethylphosphine is carried out in the presence of other transition metal cations such as cobalt(II) or nickel(II), metal complexes are obtained as products.[4]

EXPERIMENTAL

All operations were performed under N_2 and with oxygen-free solvents. The NMR spectrum of the CD_3COCD_3 solution was recorded at 295 K with a Varian CFT 20 spectrometer equipped with a ^1H probe. Chemical shifts (τ) are relative to tetramethylsilane. Triethylphosphine (5 mmol) in dichloromethane (40 ml) was added to a solution of $Fe(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (30 ml) and carbon disulfide vapors were slowly bubbled, at room temperature, through the solution until a turquoise color was obtained (about 10 min). In a few minutes the color of the solution turned deep green and within one hour it changed further to light brown. Upon slow evaporation of the solvent a white microcrystalline solid was formed (about 4 hr). This was then dissolved in acetone and treated with a butanolic solution containing excess sodium tetraphenylborate. On concentration of the solution well shaped white crystals separated. These were filtered off and washed with ethanol and petroleum ether. They were recrystallized from acetone/butanol. From the original mother liquor only no identifiable extremely air-sensitive brown powder could be obtained. Anal. Calcd. for $C_{62}H_{74}B_2P_2S_2$: C, 77.01, H, 7.71; P, 6.41; S, 6.63. Found: C, 76.50; H, 8.07; P, 6.25; S, 6.80%. Yield, based upon triethylphosphine, ca. 20%.

The crystals are monoclinic, space group $P2_1/a$, $a = 27.816(12)$, $b = 10.203(8)$, $c = 9.791(8)$ Å, $\beta = 96.1(1)°$. $D_c = 1.162$ g/cm^3 for $Z = 4$, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 1.848 cm^{-1}. Intensity data of 1058 observed reflections ($I \geqslant 3\sigma(I)$) in the range $5° \leqslant 2\theta \leqslant 40°$ were collected on a Philips PW 1100 automatic-computer-controlled diffractometer. The structure was solved by direct methods (SHELX 76, program TANG).[5] Initial coordinates of several atoms were obtained from the E-map calculated from phases developed by weighted multi-solution tangent refinement. From successive Fourier and ΔF-Fourier maps were located all the other non-hydrogen atoms. The structure was refined by full-matrix least-squares technique applying isotropic temperature factors to carbon and boron atoms and anisotropic temperature factors to sulphur and phosphorus atoms. Throughout the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry.

The refinement of the $[PEt_3CH_2S_2CH_2PEt_3]^{2+}$ cation required some effort, for its carbon atoms showed to be highly disordered, being statistically distributed in two 50/50% positions. Hydrogen atoms of the tetraphenylborate ion were introduced in their calculated positions, but not refined. The refinement converged to $R = 0.083$ and $R_w = 0.086$ respectively.

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