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Preliminary communication

TRIETHYLPHOSPHINE—CARBON DISULFIDE ZWITTERION AS A BRIDGING SIX-ELECTRON DONOR LIGAND IN $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3$ SYNTHESIS AND X-RAY CRYSTAL STRUCTURE

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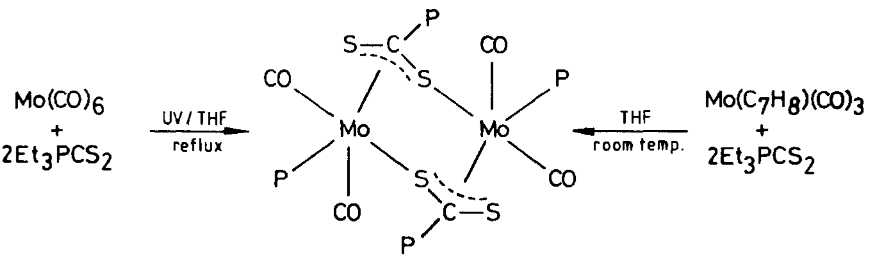
Summary

The zwitterion Et_3PCS_2 reacts with $Mo(CO)_6$ or $Mo(C_7H_8)(CO)_3$ to give the dinuclear complex $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$. An X-ray crystal structure determination has showed that both zwitterions coordinate one metal through an η^3-S_2C linkage and the second metal through a single sulphur atom.

Recently several metal complexes containing zwitterions of the type R_3PCS_2 as monometallic chelating ligands coordinated via both sulphur atoms have been prepared [1—3]. We now describe the synthesis and the structural characterization of the dinuclear complex $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$ in which two zwitterionic Et_3PCS_2 molecules, showing an unprecedented bridging capability, cement together two metal centres. The complex exhibits a new bonding mode for Et_3PCS_2, which coordinates to the metal through all three atoms of the S_2C fragment.

A mixture of $Mo(CO)_6$ and Et_3PCS_2 (molar ratio 1/2) in THF was irradiated for ca. 30 min. under reflux and butanol was added to the resulting dark red solution. Slow evaporation of the solvent gave red crystals (yield ca. 20%). The compound was obtained in higher yield (ca. 60%) by treating $Mo(C_7H_8)(CO)_3$ with Et_3PCS_2 (molar ratio 1/2) in THF, at room temperature. The complex, which is soluble in most organic solvents, slowly decomposes in the air (IR Nujol $\nu(CO)$ 1890 and 1760 cm^{-1}; ^{31}P NMR [4] (CD_2Cl_2) δ 44.45 (t, M-PEt_3, $^3J(P—P)$ 1.4 Hz) and 28.93 ppm (t, C-PEt_3, $^3J(P—P)$ 1.4 Hz)).

A complete X-ray structural analysis was carried out on this compound. The crystals are orthorhombic, space group *Pbca*, a 14.132(5), b 23.693(9), c 12.667(4) Å, U 4241.3 Å^3, $Z = 4$, D_c 1.454 g cm^{-3}, μ(Mo-K_α) 9.45 cm^{-1}.



Data collection was carried out on a Philips PW 1100 automatic diffractometer using a monochromatized Mo-K_α radiation. The structure was solved by the heavy atom method and refined by full-matrix least-squares cycles until R and R_w factors of 0.056 and 0.056, respectively, using 1826 independent observed reflections ($2\vartheta \leqslant 50°$) with $I \geqslant 3\sigma(I)$. Molybdenum, phosphorus and sulphur atoms were assigned anisotropic temperature factors. Two terminal carbon atoms of two ethylenic chains, affected by disorder, were assumed to be statistically distributed over two positions with p.p. 0.5.

The crystal and molecular structure consists of dimeric centrosymmetric complex molecules $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$. A perspective view of the complex molecule is given in Fig. 1. The two molybdenum atoms are linked together by two zwitterion ligands; each zwitterion coordinates to one metal through an η^3-S_2C linkage and to the other metal through only one sulphur atom. The pseudo-octahedral coordination about each metal atom is com-

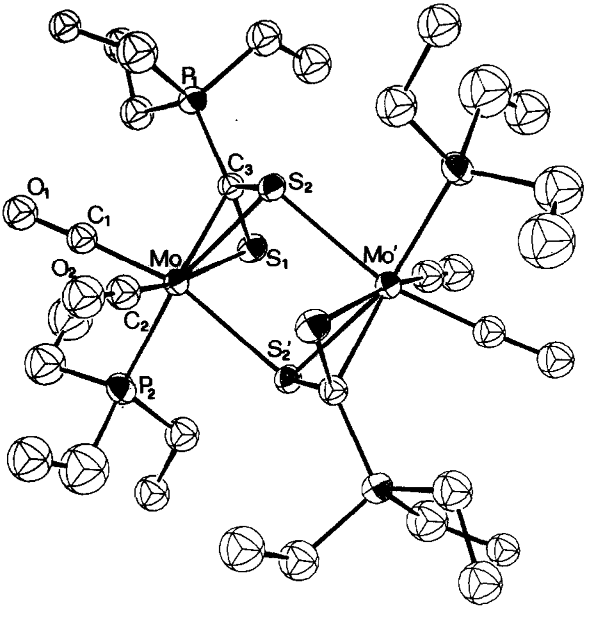


Fig. 1. Perspective view of the complex molecule $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$. ORTEP drawing with 30% probability ellipsoids. Important bond distances (Å) and bond angles (deg): Mo—S(1) 2.551(3), Mo—S(2) 2.520(3), Mo—S(2′) 2.631(3), Mo—P(2) 2.489(4), Mo—C(1) 1.89(1), Mo—C(2) 1.94(1), Mo—C(3) 2.14(1), Mo...Mo′ 3.866(2), C(3)—S(1) 1.76(1), C(3)—S(2) 1.75(1); S(1)—Mo—C(2) 167.3(4), S(2)—Mo—P(2) 162.7(1), S(2′)—Mo—C(1) 164.6(4), S(1)—Mo—S(2) 75.2(1), S(2)—Mo—S(2′) 82.7(1), S(1)—C(3)—S(2) 123.8(6), S(1)—C(3)—P(1) 118.9(6), S(2)—C(3)—P(1) 114.2(6).

pleted by two carbonyl groups and a triethylphosphine molecule derived from the cleavage of the P—C bond in a zwitterion Et_3PCS_2. The zwitterion Et_3PCS_2 exhibits a new bonding mode, the molybdenum atom being markedly displaced from the S_2C plane with a dihedral angle between the MoS(1)S(2) and C(3)S(1)S(2) planes of 87.5°. It follows that the central carbon atom is clearly within a bonding distance of the metal atom (2.14(1) Å). Moreover the S_2CP group is planar and the two CS bonds are equivalent, so that the S_2C fragment can be regarded as an η^3-coordinated pseudoallylic ligand. The Mo—S bond lengths, ranging from 2.520(3) to 2.631(3) Å, are much longer than the corresponding bond lengths in the monomeric $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ complex containing a thioxanthate η^3-S_2C coordinated [5]. A structural *trans* influence as well as steric requirements (larger coordination number) can be invoked to explain this difference.

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