Crystal Structure of Oxochlorobis-[1,2-bis(diphenylphosphino)ethane]-molybdenum(IV) Trichloro(acetone)zincate: $[\mathrm{MoOCl\{Ph_2P(CH_2)_2PPh_2\}_2}]^+[\mathrm{ZnCl_3,OC(CH_3)_2}]^-$

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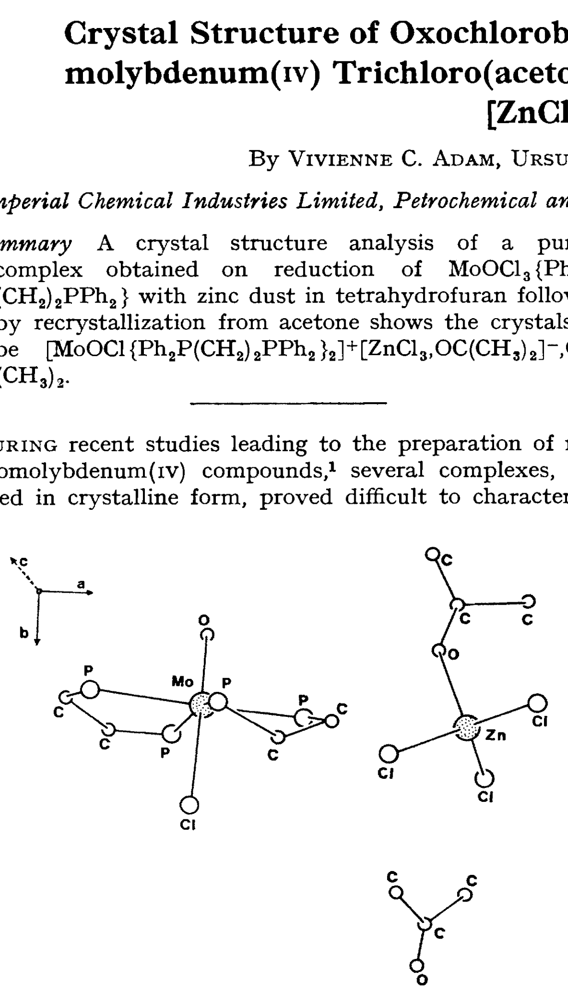
Summary A crystal structure analysis of a purple complex obtained on reduction of $\mathrm{MoOCl_3\{Ph_2P(CH_2)_2PPh_2\}}$ with zinc dust in tetrahydrofuran followed by recrystallization from acetone shows the crystals to be $[\mathrm{MoOCl\{Ph_2P(CH_2)_2PPh_2\}_2}]^+[\mathrm{ZnCl_3,OC(CH_3)_2}]^-,\mathrm{OC(CH_3)_2}$.

DURING recent studies leading to the preparation of new oxomolybdenum(IV) compounds,[1] several complexes, isolated in crystalline form, proved difficult to characterize. The crystal structure described here was undertaken to clarify the composition of one of these complexes.



FIGURE

The reaction of dppe, 1,2-bis(diphenylphosphine)ethane, with $\mathrm{MoOCl_3(thf)_2}$[2] in tetrahydrofuran (thf) yields the rust-red complex $\mathrm{Mo^VOCl_3(dppe)}$.[3] On subsequent reduction with zinc dust in thf and addition of more dppe a crystalline lilac-coloured compound could be isolated. Recrystallization of this lilac compound from acetone–pentane produced at least two purple crystalline forms, triclinic and orthorhombic, of which the latter was chosen for a full structure analysis.

Crystal data: $\mathrm{C_{58}H_{60}Cl_4MoO_3P_4Zn}$, $M = 1231$, orthorhombic, $a = 25{\cdot}38 \pm 0{\cdot}03$, $b = 18{\cdot}34 \pm 0{\cdot}01$, $c = 24{\cdot}56 \pm 0{\cdot}01$ Å, $U = 11{,}428$ Å^3, $D_m = 1{\cdot}40$ (flotation), $Z = 8$, $D_c = 1{\cdot}43$, $F(000) = 7456$, space group *Pbca*, Mo-K_α radiation (Nb filter), $\lambda = 0{\cdot}7107$ Å, $\mu = 9{\cdot}9$ cm^{-1}, diffractometer data ($-70°$).

The data were measured from a crystal cooled[4] to $-70°$; the structure solution was based on 1799 terms for which $|F_0| > 18\sigma$, where σ is the statistical standard deviation. Standard Fourier and least-squares methods were used with individual isotropic temperature factors; the phenyl rings were constrained to their known geometry and refined as rigid bodies.

One of the aims of the original work[3] was to prepare $\mathrm{MoOCl(dppe)_2}$, analogous to $\mathrm{MoOCl(H_2O)_4}$,[5] but although the isolated complex shows $\nu(\mathrm{Mo{=}O})$ at 940 and 948 cm^{-1} (Nujol), it is diamagnetic and behaves as a 1 : 1 electrolyte in nitrobenzene. The position of a single molybdenum atom could be deduced from a Patterson map. An *F*(observed) map phased on this atom showed the existence of a second heavy atom, of atomic number about two-thirds that of molybdenum. In view of the method of preparation of this complex the second atom was assumed to be zinc. The subsequent structure analysis showed the crystals to contain the cation $[\mathrm{MoOCl(dppe)_2}]^+$ and the anion $[\mathrm{ZnCl_3,OC(CH_3)_2}]^-$ with the acetone co-ordinated to the zinc. A difference map at $R = 0{\cdot}083$ revealed in addition one molecule of acetone as solvent of crystallization. The final R value for the compound $[MoOCl(dppe)_2]^+[ZnCl_3,OC(CH_3)_2]^-,(CH_3)_2CO$ was 0·066. Elemental analysis confirmed the presence of zinc in the crystals.

The structures of the three independent groups in the asymmetric unit are illustrated in the Figure in their correct orientation in the unit cell. The cation has a regular octahedral geometry with the oxygen atom *trans* to the chlorine [Mo–O, 1·69; Mo–Cl, 2·46; Mo–P(mean), 2·57 Å]; the anion is tetrahedral [Zn–O, 2·12; Zn–Cl(mean), 2·23 Å] with the co-ordinated acetone molecule having a normal geometry.

This particular complex shows the complications that can arise when carrying out apparently well recognized reactions, *e.g.* reduction with zinc. Zinc is known readily to form tetrahedral anionic entities containing neutral ligands {*e.g.* $K^+[ZnBr_3,H_2O]^-$,[6] or $[CH_3S(C_5H_{11})_2]^+[I_3Zn\text{-}CH_2S(C_5H_{11})_2]^-$ [7]} and the possibility of this happening should always be considered when this element is present during a reaction. Complexes, essentially identical to that described here, *i.e.* Mo cation and Zn anion, have been obtained with other solvents, *e.g.* thf and chloroform, present.[3]

It has also been found that reduction of $MoOCl_3(dppe)$ can lead to the formation of molecular nitrogen complexes[3] and this work will be reported subsequently.

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