The Crystal Structures of Pentaethylcyclopentaphosphinemolybdenum Tetracarbonyl, $(EtP)_5Mo(CO)_4$, and Tetraethylcyclotetraphosphinetungsten Tetracarbonyl, $(EtP)_4W(CO)_4$

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COMPLEXES obtained from cyclic polyphosphines and metal carbonyls have two points of structural interest: the size and configuration of the polyphosphine ring; and the mode of attachment of the ring to the metal.[1,2] We have now completed a structural analysis of the orange-yellow crystals obtained by reaction of $(EtP)_4$ with $Mo(CO)_6$ in tetrahydrofuran[3] and have thereby shown that the molecular formula for the product is $(EtP)_5Mo(CO)_4$ and that the pentaphosphine ring is 1 : 3-co-ordinated to the Mo atom. This result substantiates a suggestion put forward earlier for compounds of this type.[3]

The *X*-ray analysis of $(EtP)_5Mo(CO)_4$ was based on 3300 Weissenberg data and has led to a present discrepancy index $R = 8{\cdot}8\%$ by Fourier synthesis and block-diagonal refinement.[4] The crystals are triclinic ($P\bar{1}$) and contain two crystallographically distinct molecules in the asymmetric unit. Within experimental error, however, these molecules are identical in conformation. A full-matrix refinement and further crystallographic details will be published elsewhere later.

The pentaphosphine ring is 1 : 3-co-ordinated to the molybdenum atom, resulting in a bond angle at Mo of 66° (see Figure). The Mo valencies

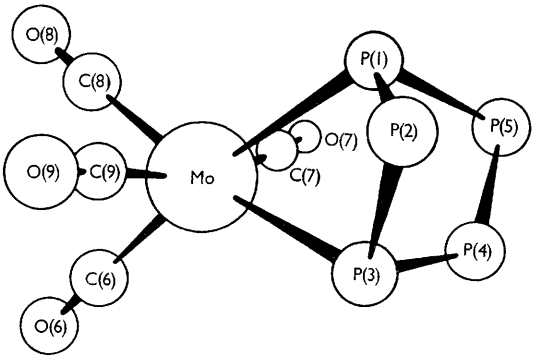

FIGURE. *The configuration of* $(EtP)_5Mo(CO)_4$; *the ethyl groups are not shown.*

consequently show distortion from a regular octahedral configuration, although the atoms Mo,

C(6), C(8), P(1), and P(3) are nearly coplanar. Indeed, if the other phosphorus atoms are disregarded, the group as a whole possesses approximate C_{2v} (*mm*) symmetry. The polyphosphine ring is very puckered; its angles are not equal, the most acute (77°) being at P(2) which bridges the two co-ordinated phosphorus atoms. Bond lengths and the more important bond angles are given below; these are mean values for the two independent molecules, the mean standard deviations, based on the least-square residuals, being given in parentheses:—

Mo–P, 2·52 (0·02) Å; P–P, 2·21 (0·03) Å;
Mo–C, 1·96 (0·03) Å; P–C, 1·84 (0·03) Å;
C–C, 1·53 (0·04) Å; C–O, 1·17 (0·04) Å;
P(1)–Mo–P(3), 66 (1)°; C(6)–Mo–C(8), 92 (2)°;
P(1)–Mo–C(8), 101 (2)°; P(3)–Mo–C(6), 101 (2)°;
C(8)–Mo–C(9), 88 (2)°; C(8)–Mo–C(7), 87 (2)°;
C(6)–Mo–C(9), 84 (2)°; C(6)–Mo–C(7), 86 (2)°;
P(1)–Mo–C(9), 92 (2)°; P(1)–Mo–C(7), 99 (2)°;
P(3)–Mo–C(9), 94 (2)°; P(3)–Mo–C(7), 94 (2)°;
Mo–P(1)–P(2), 91 (1)°; Mo–P(3)–P(2), 91 (1)°;
P(1)–P(2)–P(3), 77 (2)°; P(2)–P(3)–P(4), 109 (2)°;
P(3)–P(4)–P(5), 95 (2)°; P(4)–P(5)–P(1), 96 (2)°;
P(5)–P(1)–P(2), 99 (2)°.

We have also made a preliminary *X*-ray study of the yellow crystals obtained by reaction of $(EtP)_4$ with $(MeCN)_3W(CO)_3$ in cyclohexane.[3] The triclinic unit cell here contains four formula weights corresponding to a $(EtP)_4W(CO)_4$ composition, strongly suggesting that in this compound the polyphosphine ring is four-membered.

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