Synthesis and Structure of a Molybdenum(0) Compound Containing a Stable Nine-membered Chelate Ring

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Summary *NN'*-Bis(diphenylphosphinomethyl)-*NN'*-dimethylethylenediaminetetracarbonylmolybdenum contains a stable nine-membered chelate ring with the phosphorus atoms co-ordinated to molybdenum in *cis*-positions and the nitrogen atoms unco-ordinated.

THE recently prepared ligand, *NN'*-bis(diphenylphosphinomethyl)-*NN'*-dimethylethylenediamine,[1] reacts directly with hexacarbonylmolybdenum in refluxing toluene or with tetracarbonyl(norbornadiene)molybdenum in benzene at ambient temperature to give [{$Ph_2PCH_2N(Me)CH_2CH_2N(Me)CH_2PPh_2$}$Mo(CO)_4$], m.p. 175—177 °C, *M* 691. The ^{31}P n.m.r. spectrum indicates two equivalently co-ordinated phosphorus atoms (δ −27·1 p.p.m., downfield from 85% H_3PO_4, compared to +26·9 p.p.m. for the free ligand), and the i.r. spectrum [ν_{CO} (C_6H_{12}) 1905s, 1915s, 1932m, and 2015s] is consistent with the $M(CO)_4$ group having C_{2v} local symmetry. Elemental analyses and the molecular weight support the monomeric formulation. The proposed structure of the complex based on the above data includes a rare nine-membered chelate ring.[2,3] Although there are many examples of stable small chelate rings (3—7 members) with *cis*-co-ordination and large flexible rings (11—15 members) with *trans*-co-ordination,[3-5] intermediate ring sizes (*e.g.*, 9 members) with *cis*-stereochemistry about the metal have not been investigated structurally and are expected to be unstable.[2,3]

Crystal data: space group, $P2_1/a$, $Z = 4$, $\mu = 5{\cdot}53$ cm^{-1}, $D_m = 1{\cdot}37(1)$ g cm^{-3}, $D_c = 1{\cdot}39$ g cm^{-3}, $a = 1695{\cdot}5(5)$ $b = 1957{\cdot}9(8)$, $c = 1005{\cdot}7(4)$ pm, $\beta = 96{\cdot}41(3)°$. The structure was solved by direct methods to an *R* value of 0·06. The molecule shows slight distortion from regular octahedral angles at molybdenum with ∠PMoP 100·8°.

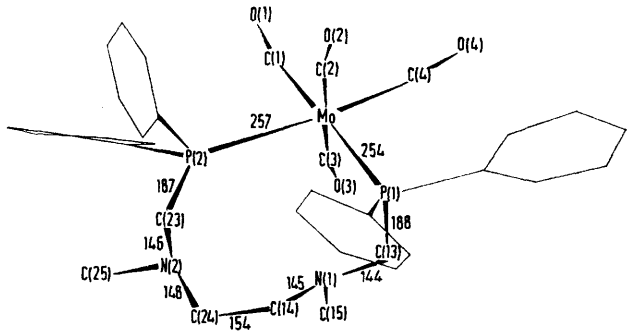

FIGURE. The molecular structure of [{$Ph_2(PCH_2N(Me)CH_2CH_2N(Me)CH_2PPh_2$}$Mo(CO)_4$]. Bond lengths are in pm.

The Mo–N distances (392 and 444 pm) are much too large for these atoms to be chemically bonded, thus corroborating the unbonded nature of the tertiary amine groups. A sketch of the molecule showing distances within the chelate ring is given in the Figure.

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