A Possible Carbon Dioxide Complex of Molybdenum and its Rearrangement Product Di-μ-carbonato-bis{carbonyltris(dimethylphenylphosphine)molybdenum}: *X*-Ray Crystal Structure

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Summary Carbon dioxide reacts with *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] to form a complex [$Mo(CO_2)_2(PMe_2Ph)_4$] which changes spontaneously in solution into a carbonato-bridged complex, [$(PMe_2Ph)_3(CO)Mo(CO_3)_2Mo(CO)(PMe_2Ph)_3$], the structure of which has been determined; the planar carbonate ions bridge in an unusual manner, each being bidentate to one molybdenum atom and monodentate to the other.

There are several claims in the literature to compounds containing ligating carbon dioxide, but in no case has the presence of carbon dioxide as a ligand been unambiguously demonstrated. In the majority of cases carbon dioxide reacts with other ligands to give products such as carbonyl, phosphine oxide, formate, carbonate, carboxylate.[1]

We have found that the complex [$Mo(N_2)_2(PMe_2Ph)_4$], but neither [$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$] nor [$W(N_2)_2(PMe_2Ph)_4$], reacts rapidly with carbon dioxide in toluene at room temperature to give a dark brown solution from which small monoclinic crystals analysing as [$Mo(CO_2)_2(PMe_2Ph)_4$] (I) are obtained. These crystals were only weakly diffracting and decomposed in the *X*-ray beam so that a complete diffraction analysis was not possible. I.r. bands at 1760, 1510, and 1335 cm^{-1} are assigned to the co-ordinated group or groups derived from the carbon dioxide.

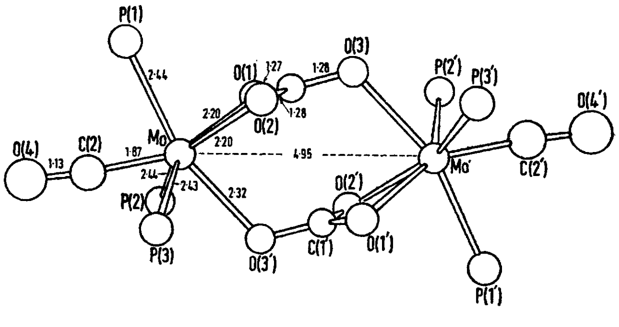

Figure. [{$Mo(CO_3)(CO)(PMe_2Ph)_3$}$_2$]: metal–ligand bonds and essential stereochemistry. Standard deviations in the bond lengths average 0·003 (Mo ··· Mo), 0·01 (Mo–P), $0{\cdot}10_5$ (Mo–C and Mo–O), and 0·03 Å (C–O).

When (I) is dissolved in tetrahydrofuran (thf) the i.r. spectrum slowly changes; the band at 1760 cm^{-1} loses intensity and broadens and a new band appears at 1835 cm^{-1}. After two weeks, triclinic crystals analysing for $Mo(CO_2)_2(PMe_2Ph)_3(thf)$ (II), were obtained from thf. These showed the new band at 1835 cm^{-1}, but the bands at 1510 and 1335 cm^{-1} had disappeared. Great difficulty was experienced in cleanly recrystallising (I) because of the ready loss of a phosphine ligand.

The structure of (II) was obtained by standard diffraction analysis methods based on 5506 independent reflections (Mo-K_α diffractometry), convergence to $R = 0{\cdot}079$ being based on the refinement of atomic positional and isotropic temperature parameters only.

There are two crystallographically independent, structurally identical, centrosymmetric dimeric molecules in the triclinic cell; the structure of the dimer is shown schematically in the Figure. The molybdenum atoms are bridged by planar carbonate ions each of which acts as a bidentate ligand to one metal atom and as a monodentate ligand to the other. This is an unusual mode of binding for the carbonate ion.[2] Each molybdenum atom is 7-co-ordinate, and has approximately C_3 symmetry. The oxygen and phosphorus atoms co-ordinating each molybdenum ion take up an approximately facial, octahedral configuration, with the additional carbonyl co-ordinated to the centre of the face of the octahedron defined by the three phosphorus atoms, *i.e.*, along the pseudo-C_3 axis.

It is tempting to assume that a disproportionation of carbon dioxide has occurred as in equation (1) but we have no evidence that this is so. The reaction could equally well

$$2CO_2 + 2e \rightarrow CO_3^{2-} + CO \qquad (1)$$

involve the reduction of one molecule of ligating carbon dioxide to carbon monoxide by the displaced tertiary phosphine,[3] and the reaction of the remaining carbon dioxide with adventitious dioxygen to form carbonate as has been observed in some platinum(0) species.[4]

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[1] There is no recent review on this topic. The best general review is by M. E. Volpin, *Zeit. Chem.*, 1972, **12**, 361; a plausible carbon dioxide complex has been reported by P. W. Jolly, K. Jonas, C. Krüger, and Y. H. Tsay, *J. Organometallic Chem.*, 1971, **33**, 109; and by B. R. Flynn and L. Vaska, *J.C.S. Chem. Comm.*, 1974, 703.

[2] But see M. H. Meyer, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Acta. Cryst.*, 1972, **28B**, 1607; and G. Ferguson and D. M. Hawley, *ibid.*, 1974, **30B**, 103 for similar binding of mono-μ-carbonato ligands.

[3] T. Ito, T. Kokuto, T. Yamamoto, A. Yamamoto, and S. Ikeda, *J.C.S. Chem. Comm.*, 1974, **136**.

[4] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Comm.*, 1967, 408.