

**Preliminary communication**

**Preparation and some reactions of  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$ , a useful precursor for new dimolybdenum (II) complexes. Crystal structure of  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]_2\text{[Mo}_6\text{O}_{19}] \cdot 4\text{C}_4\text{H}_8\text{O}$**

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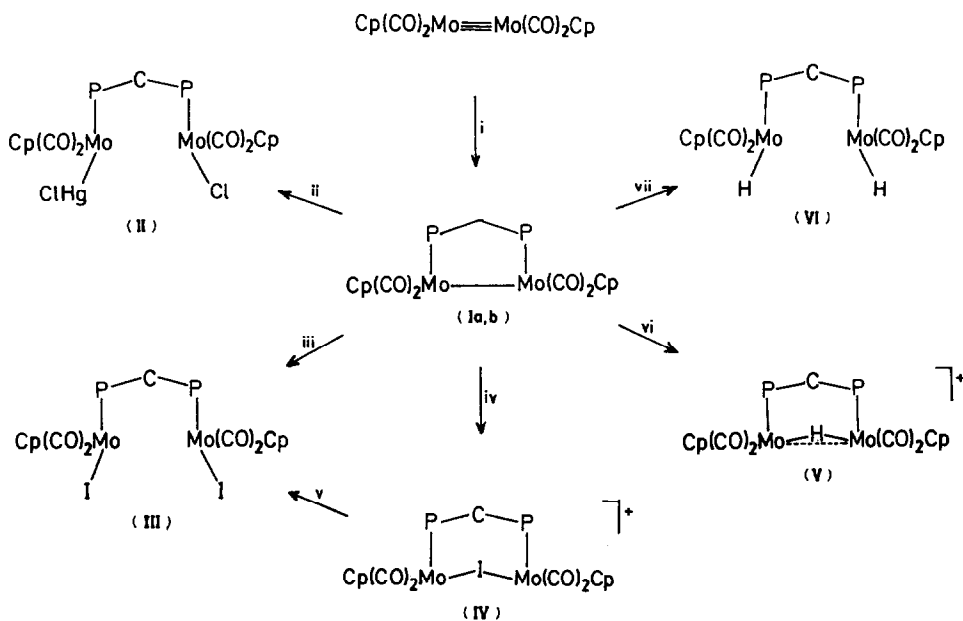
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**Abstract**

The new compounds  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu\text{-P} \cap \text{P})]$ , ( $\text{P} \cap \text{P} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ , dppm; or  $(\text{EtO})_2\text{POP}(\text{OEt})_2$ , tedip) have been prepared from  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4](\text{Mo} \equiv \text{Mo})$  and dppm or tedip respectively; the dppm bridged compound reacts with the electrophilic reagents  $\text{HgCl}_2$ ,  $\text{I}_2$ ,  $[\text{I}(\text{C}_5\text{H}_5\text{N})_2]\text{BF}_4$ , or  $\text{HBF}_4$  to give either  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\text{X})(\text{Y})(\mu\text{-dppm})]$ , ( $\text{X} = \text{Cl}$ ,  $\text{Y} = \text{HgCl}$ ;  $\text{X} = \text{Y} = \text{I}$ ) or  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu\text{-X})(\mu\text{-dppm})]\text{BF}_4$ , ( $\text{X} = \text{I}$ ,  $\text{H}$ ) species, and with Na amalgam to give, after acidification, the dihydrido compound  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4\text{H}_2(\mu\text{-dppm})]$ . The crystal structure of the  $[\text{Mo}_6\text{O}_{19}]^{2-}$  salt of the cation  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\mu\text{-H})(\mu\text{-dppm})]^+$  has been determined.

Reactions of dinuclear transition metal carbonyl species containing a single metal-metal bond frequently give mononuclear compounds [1]. Bridging phosphorus donor ligands of the type  $\text{A}_2\text{PBPA}_2$  ( $\text{A} = \text{R}$ ,  $\text{OR}$ ;  $\text{B} = \text{CH}_2$ ,  $\text{N}(\text{R}')$ ,  $\text{O}$ ;  $\text{R}$ ,  $\text{R}' = \text{alkyl}$ ,  $\text{aryl}$ ) have proved to be useful in preventing dimer degradation [2–4] and, moreover, can be used to introduce steric and electronic changes at the dimetallic centre. We report briefly here the preparation of the compounds  $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-P} \cap \text{P})]$  (Ia,b) ( $\text{Cp} = \eta\text{-C}_5\text{H}_5$ ; a:  $\text{P} \cap \text{P} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ , dppm; b:  $\text{P} \cap \text{P} = (\text{EtO})_2\text{POP}(\text{OEt})_2$ , tedip), which can be used as precursors for a variety of new dimolybdenum (II) species.



Scheme 1. (i) 1 equiv.  $\text{P} \sim \text{P}$  (dppm or tedip), diglyme, r.t., 15 min. (ii) excess  $\text{HgCl}_2$ ,  $\text{Et}_2\text{O}$ , r.t., 30 min. (iii) 1 equiv.  $\text{I}_2$ ,  $\text{CH}_2\text{Cl}_2$ , r.t., 12 h. (iv) 1 equiv.  $[\text{I}(\text{py})_2]\text{BF}_4$  and 2 equiv.  $\text{HBF}_4 \cdot \text{OEt}_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 15 min. (v)  $\text{BF}_4^-$  salt and excess  $\text{KI}$ ,  $\text{CH}_2\text{Cl}_2$ , r.t., 12 h.  $\text{I}^-$  salt,  $\text{CH}_2\text{Cl}_2$ , r.t., 12 h. (vi) excess  $\text{HBF}_4 \cdot \text{OEt}_2$ , toluene, r.t., 2 h. (vii)  $\text{Na}/\text{Hg}$ , THF, 30 min. Then 2 equiv.  $\text{NH}_4\text{PF}_6$ , r.t., 15 min.

Reaction of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_4]$  ( $\text{Mo}\equiv\text{Mo}$ ) with dppm or tedip gives the red compounds Ia and Ib in 60–80% yield (i in Scheme 1); for both compounds spectroscopic data indicate the presence in solution of two isomers. Compared with that in  $[\text{Mo}_2\text{Cp}_2(\text{CO})_6]$ , the electron density at the dimetallic centre should be enhanced in compounds Ia,b owing to the presence of the  $\text{P} \sim \text{P}$  bridging ligand, and this allows the study of a broader range of reactions in which the metal–metal bond acts as a nucleophilic site. Thus, reaction of Ia with  $\text{HgCl}_2$  occurs at room temperature (r.t.) and involves oxidative addition of a  $\text{Hg}-\text{Cl}$  bond across the  $\text{Mo}-\text{Mo}$  bond, to give  $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\text{Cl})(\text{HgCl})(\mu\text{-dppm})]$  (II, ii in Scheme 1); this contrasts with the related reactions of binuclear Fe [5] and Rh [6] species, which have been reported to result in the symmetrical insertion of the  $\text{HgCl}_2$  molecule (“via” the Hg atom) into the metal–metal bond.

Iodine reacts with compound Ia in  $\text{CH}_2\text{Cl}_2$  at r.t. to give  $[\text{Mo}_2\text{Cp}_2(\text{CO})_4\text{I}_2(\mu\text{-dppm})]$  (III, iii in Scheme 1). Iodination of single metal–metal bond dimers has been observed to go “via” cationic “ $\text{M}_2(\mu\text{-I})^+$ ” intermediates in a number of examples [7]; in our case, the cation  $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-I})(\mu\text{-dppm})]^+$  (IV) was isolated in high yield just by carrying out the reaction in  $\text{Et}_2\text{O}$  (giving the  $\text{I}^-$  salt) or by treating Ia with  $[\text{I}(\text{C}_5\text{H}_5\text{N})_2]\text{BF}_4$  [7a] (iv in Scheme 1). As expected, nucleophilic attack of  $\text{I}^-$  on compound IV affords the neutral III (v in Scheme 1).

The metal–metal bond present in Ia is basic enough to be protonated with  $\text{HBF}_4$  to yield the hydrido compound  $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-dppm})]\text{BF}_4$  (V, vi in Scheme 1), which is moderately stable; as expected, the proton takes up a bridging position. Analogous results have been found in the reactions of related Fe [8a], Co [8b], Rh

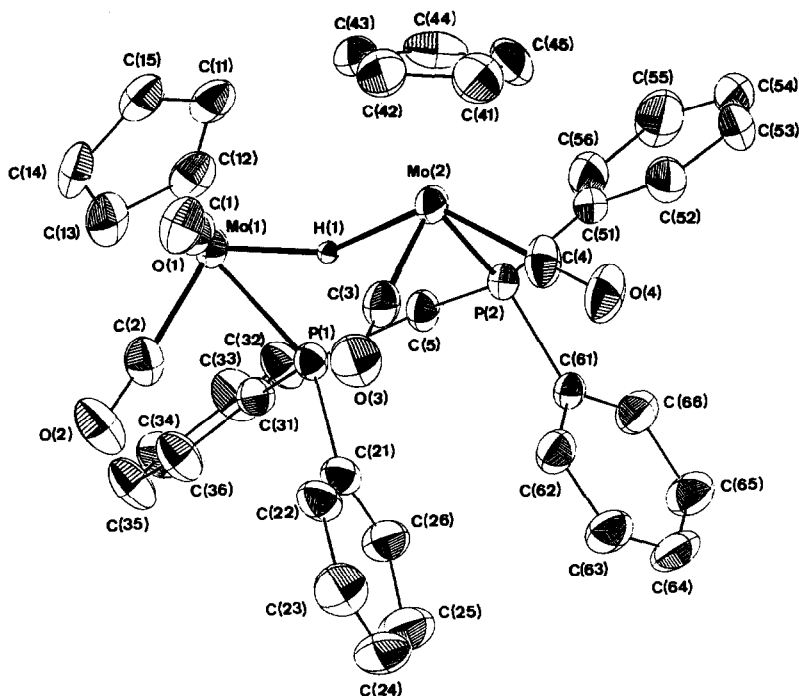


Fig. 1. View of the cation with the atom numbering scheme. Selected distances (Å) and bond angles (°): Mo(1)···Mo(2) 3.566(1), Mo(1)–H(1) 1.69(6), Mo(2)–H(1) 2.05(6), Mo(1)–P(1) 2.479(1), Mo(2)–P(2) 2.477(1), Mo(1)–C(1) 2.008(5), Mo(1)–C(2) 1.944(5), Mo(2)–C(3) 1.962(5) Å, Mo(2)–C(4) 1.977(5); Mo(1)–H(1)–Mo(2) 145(4), H(1)–Mo(1)–P(1) 61(2), H(1)–Mo(2)–P(2) 71(2), P(1)–C(5)–P(2) 113.9(2)°.

[8c] and MoMn [8d] bridged dimetallic species with strong acids, although earlier studies on the protonation of  $[M_2Cp_2(CO)_{2n}]$  ( $n = 3$  for  $M = Mo, W$ ;  $n = 2$  for  $M = Fe$ ) were less conclusive [8a]. However, NMR data for compound V showed the presence of an equilibrium mixture of the three isomers in solution, and so an X-ray study was undertaken in order to gain more precise structural information for this compound. Unexpectedly, the counter anion of the  $[Mo_2(\eta-C_5H_5)_2(CO)_4(\mu-H)(\mu-Ph_2PCH_2PPh_2)]^+$  cation in the crystal turned out to be the Linqvist polymolybdate  $[Mo_6O_{19}]^{2-}$ , formed probably by partial oxidation of the sample during crystal growing.

The geometry of the cation (Fig. 1) shows two features worthy of comment. First, the Mo–Mo distance (3.566(1) Å) is markedly longer than those reported for related compounds (viz., 3.27 Å for  $[Mo_2Cp_2(CO)_4(\mu-H)(\mu-PMe_2)]$  [9] and 3.31 Å for  $[Mo_2Cp_2(CO)_4(\mu-H)(\mu-I)]$  [10]), and the degree of direct metal–metal interaction is thus uncertain. Second, the hydrido ligand, clearly seen on a difference Fourier map, bridges the two metal atoms in an apparent asymmetric fashion (Mo–H: 1.69(6) and 2.05(6) Å); this observation, however, should be regarded with caution because not only is the accuracy in the position of the hydrogen atom relatively low, but also other factors, such as the nature of the counterion [11], might have a significant structural influence.

Reaction of compound Ia with Na amalgam gave a yellow solution which, after protonation, gave the dihydrido compound  $[Mo_2Cp_2(CO)_4H_2(\mu-dppm)]$  (VI, vii in

Scheme 1) in ca. 60% yield. This strongly suggests the initial formation of the anionic species  $\text{Na}_2[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-dppm})]$  through a classical reduction of metal-metal bonded carbonyl complexes. The dianionic nature of our proposed intermediate makes it valuable from a synthetic point of view, and we are currently carrying out studies in that direction.

*Selected spectroscopic data:* Compound Ia:  $\nu_{\text{max}}(\text{CO})$ : 1916s, 1878vs, 1844m and 1825m  $\text{cm}^{-1}$  in toluene;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $-20^\circ\text{C}$ ):  $\delta$  5.23 (s,  $\text{C}_5\text{H}_5$ , isomer A) and 4.51 ppm (s,  $\text{C}_5\text{H}_5$ , isomer B);  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  ( $\text{CDCl}_3$ ,  $-20^\circ\text{C}$ ):  $\delta$  47.3 (s, MoP, isomer B) and 33.1 ppm (s, MoP, isomer A). Compound Ib:  $\nu_{\text{max}}(\text{CO})$ : 1943s, 1907vs, 1874m and 1858m  $\text{cm}^{-1}$  in hexane;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , r.t.):  $\delta$  5.13 (s,  $\text{C}_5\text{H}_5$ , isomer A) and 5.21 ppm (s,  $\text{C}_5\text{H}_5$ , isomer B);  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  ( $\text{CDCl}_3$ , r.t.):  $\delta$  174.7 (s, MoP, isomer B) and 163.8 ppm (s, MoP, isomer A). Compound II:  $\nu_{\text{max}}(\text{CO})$ : 1967vs, 1919s, 1876s and 1841vs  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , r.t.):  $\delta$  5.23 (s,  $\text{C}_5\text{H}_5$ , 5H) and 4.84 ppm (d,  $J(\text{PH})$  1,  $\text{C}_5\text{H}_5$ , 5H);  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  ( $\text{CDCl}_3$ , r.t.):  $\delta$  48.8 (d,  $J(\text{PP})$  42, MoP) and 62.7 ppm (d,  $J(\text{HgP})$  415,  $J(\text{PP})$  42, HgMoP). Compound III:  $\nu_{\text{max}}(\text{CO})$ : 1958vs and 1873s  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , r.t.):  $\delta$  5.21 ppm (s,  $\text{C}_5\text{H}_5$ );  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  ( $\text{CDCl}_3$ , r.t.):  $\delta$  45.2 ppm (s, MoP). Compound IV:  $\nu_{\text{max}}(\text{CO})$ : 1974sh, 1967vs, 1894s and 1884sh  $\text{cm}^{-1}$  in THF;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , r.t.):  $\delta$  5.25 (s,  $\text{C}_5\text{H}_5$ , isomer A) and 5.00 ppm (s,  $\text{C}_5\text{H}_5$ , isomer B);  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  ( $\text{CD}_2\text{Cl}_2$ , r.t.):  $\delta$  43.1 (br, MoP, isomer B) and 37.0 ppm (s, MoP, isomer A). Compound V:  $\nu_{\text{max}}(\text{CO})$ : 1985vs, 1966s, 1903sh, and 1890s  $\text{cm}^{-1}$  in THF;  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , r.t.):  $\delta$  5.22 (s,  $\text{C}_5\text{H}_5$ , isomers A and B), 4.98 (s,  $\text{C}_5\text{H}_5$ , isomer C),  $-18.26$  (t,  $J(\text{PH})$  31, MoHMo, isomer A),  $-18.31$  (t,  $J(\text{PH})$  31, MoHMo, isomer B) and  $-18.52$  ppm (t,  $J(\text{PH})$  35, MoHMo, isomer C);  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  ( $\text{CD}_2\text{Cl}_2$ , r.t.):  $\delta$  53.8 (s, MoP, isomer C) and 48.1 ppm (s, MoP, isomers A and B). Compound VI:  $\nu_{\text{max}}(\text{CO})$ : 1933vs and 1850s  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ;  $^1\text{H NMR}$  ( $\text{Me}_2\text{CO}-d_6$ , r.t.):  $\delta$  4.99 (s,  $\text{C}_5\text{H}_5$ , 10H) and  $-5.18$  ppm (d,  $J(\text{PH})$  61, MoH, 2H);  $^{31}\text{P}\{^1\text{H}\}\text{NMR}$  ( $\text{Me}_2\text{CO}-d_6$ , r.t.):  $\delta$  62.7 ppm (s, MoP).

*Crystal data* \*.  $\text{C}_{47}\text{H}_{49}\text{Mo}_5\text{O}_{15.5}\text{P}_2$ ,  $M = 1371.5$ . Monoclinic;  $a$  20.156(3),  $b$  12.638(3),  $c$  21.704(6) Å,  $\beta$  112.78(2)°,  $V = 5097$  Å<sup>3</sup>. Space group  $P2_1/n$ ,  $Z = 4$ .  $D_{\text{calc}}$  1.78  $\text{g cm}^{-3}$ .  $F(000) = 679$ . CAD4 Enraf-Nonius.  $\omega$ - $2\theta$  mode with scan width  $1.0 + 0.35 \tan \theta$ . Mo- $K_\alpha$  radiation and graphite monochromator.  $\theta$  range 1–25° C. 9602 reflections recorded at room temperature; 5896 with  $F > 5\sigma(F)$  used for refinement. Two standard reflections measured every two hours showed no decay. Absorption correction applied with min–max = 1.0–1.16.

Structure analysis and refinement: Molybdenum atoms located by direct methods. All other atoms found from Fourier maps. Refinements with CRYSTALS [14] by block diagonal matrix least squares (757 parameters). Difference map revealed two THF molecules, which were refined isotropically. Hydrogen atoms were found from a difference map except those for THF. Final  $R$  0.032,  $R_w$  0.048.

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\* The authors will deposit a table of atomic coordinates and a full list of bond lengths and angles with the Cambridge Crystallographic Data Centre.

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