2,4,6,8-Tetrakis(*N,N*,-di-isopropylamino)cyclotetraphosphoxane (Pr$^i_2$NPO)$_4$, a Tetradentate Ligand that chelates two Metals: Assemblage of a $P_4O_4Mo_2$ Cage Structure

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Reaction of $(Pr^i_2N)_2P(O)H$ with $Mo(CO)_6$ resulted in deamination and formation of complex (**1**) which was characterized by *X*-ray analysis as $[Pr^i_2NPO]_4Mo_2(CO)_8$, a *closo*-$P_4O_4Mo_2$ cage structure featuring a novel tetradentate phosphoxane ligand.

Chelating and bridging ligands based on the diphosphoxane, P–O–P, unit have been used to co-ordinate a variety of transition metals.[1] Multidentate ligands of this type may be amenable to self-assemblage by condensation or elimination reactions. We report here the first example of a cyclotetraphosphoxane ligand that chelates two metals in an adamantane-like cage complex. This ligand, 2,4,6,8-tetrakis(*N,N*-di-isopropylamino)cyclotetraphosphoxane, was formed from the reaction of molybdenum hexacarbonyl with bis-(*N,N*-di-isopropylamino)phosphine oxide, $(Pr^i_2N)_2P(O)H$, in refluxing toluene, as shown in equation(1). Work-up and recrystallization gave clear prisms of the product $[Pr^i_2NPO]_4Mo_2(CO)_8$ (**1**) in >90% yield.

$$2\,Mo(CO)_6 + 4\,(Pr^i_2N)_2P(O)H \rightarrow 4\,CO + 4\,Pr^i_2NH + \underset{(\mathbf{1})}{[Pr^i_2NPO]_4Mo_2(CO)_8} \quad (1)$$

The structure of (**1**) was determined by a single-crystal *X*-ray study. *Crystal data:* crystals of (**1**) $C_{32}H_{56}Mo_2N_4O_{12}P_4$, are tetragonal, $a = 13.441(1)$, $c = 12.469(1)$ Å, space group $P4_2/n$, $Z = 2$, $D_c = 1.481\ g\,cm^{-3}$. Of the 3294 unique reflections measured, 2174 were used in the final refinement. The structure was solved by heavy-atom methods and refined anisotropically to $R_F = 0.044$ and $R_{wF} = 0.054$.† The title compound (**1**) has the structure of a highly distorted $P_4O_4Mo_2$ adamantane-like cage (Figure 1). Each of the *cis*-$Mo(CO)_4$ moieties is chelated by a pair of P-atoms from the cyclic tetraphosphoxane ligand in the boat conformation. The molecule has $\bar{4}$ crystallographic symmetry and is close to $42m$ symmetry. The P–O distances of 1.650(4) and 1.642(4) Å, OPO angles of 99.1(2)°, and POP angles of 131.0(2)° are surprisingly similar to the corresponding P–O distances of 1.66 Å, OPO angles of 100°, and POP angles of 127° in the cage structure of P_4O_6 (Figure 2).[2]

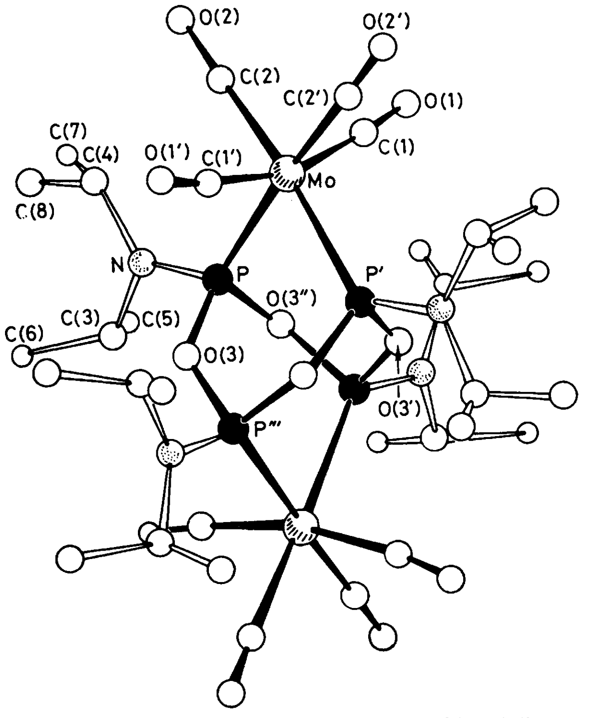
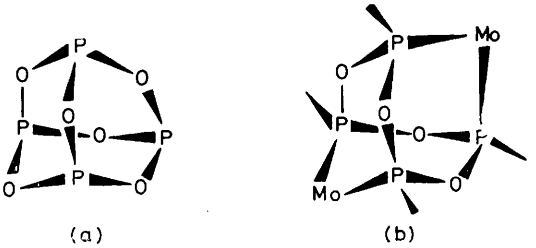


Figure 1. The molecular structure of (**1**). Selected bond distances: Mo–P 2.501(1), Mo–C(1) 2.039(6), Mo–C(2) 1.986(6), P–N 1.665(4), P–O(3) 1.650(4), P–O(3") 1.642(4), N–C(3) 1.506(7), N–C(4) 1.471(7), C(1)–O(1) 1.146(7), C(2)–O(2) 1.154(7), C(3)–C(5) 1.550(9), C(3)–C(6) 1.553(9), C(4)–C(7) 1.538(10), C(4)–C(8) 1.475(11) Å. Selected bond angles: P–Mo–P′ 75.96(5)°, C(1)–Mo–C(1′) 167.3(2)°, C(2)–Mo–C(2′) 85.3(2)°, O(3)–P–O(3″) 99.1(2)°, C(3)–N–C(4) 125.9(4)°, P–O(3)–P‴ 131.0(2)°.

The co-ordination geometry around each Mo is pseudo-octahedral with a compressed P–Mo–P angle of 76.0(1)°. The four carbonyls are all tilted away from the cage with *cis*-C–Mo–C angles of 85.9(3), 84.7(2), and 85.3(2)°. The C(1)–Mo–C(1′) angle is only 167.3(2)°. Carbonyls *cis* to the P-donors have Mo–C distances of 2.039(6) Å and C–O distances of 1.146(7) Å. Corresponding values for *trans*-carbonyls are 1.986(6) and 1.154(7) Å, consistent with known trends in *cis*-$Mo(CO)_4(PR_3)_2$ complexes.[3]

Spectroscopic data on (**1**) are in agreement with the structure. The proton-decoupled ^{31}P n.m.r. spectrum exhibited a single resonance at +150.3 p.p.m. Its ^1H n.m.r. spectrum showed the expected isopropyl signals at δ 4.32 and 1.36. Its i.r. spectrum exhibited strong carbonyl stretches at 2017, 1941, 1926, and 1902 cm^{-1}(KBr).

The overall stoicheiometry of the reaction can be represented as in equation (1). While details of the reaction are still under investigation, we expect initial formation of a co-ordinated bis(*N,N*-di-isopropylamino)phosphinous acid (equation 2). Subsequent elimination of Pr^i_2NH with additional phosphine oxide to give co-ordinated P–O–P units and



(a) (b)

Figure 2. Cage structures of (a) P_4O_6 and (b) $P_4O_4Mo_2$.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

cage formation appears to be quite favourable, since no other ^{31}P resonances were observed during the reaction. Interestingly, use of a large deficiency of ligand also led to (**1**) as the only product while heating of the ligand alone yielded various oligomeric species.

$$Mo(CO)_6 + (Pr^i_2N)_2P(O)H \rightarrow CO + (Pr^i_2N)_2P(OH)Mo(CO)_5 \qquad (2)$$

We thank the National Science Foundation for an instrument grant towards the purchase of the Fourier-transform n.m.r. spectrometer used.

Received, 18th April 1983; Com. 479

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