A Metal Complex of 2,4,6-Tris(*N,N*-di-isopropylamino)cyclotriphosphoxane that is an Intermediate to the $P_4O_4M_2$ Cage Complex

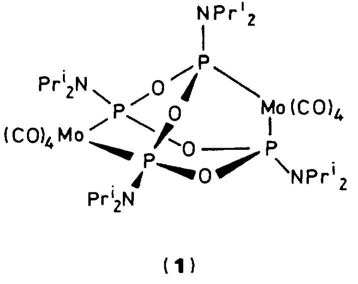
Edward H. Wong,[a]* Eric J. Gabe,[b] and Jean-Pierre Charland[b]

[a] *Department of Chemistry, University of New Hampshire, Durham, New Hampshire, U.S.A. 03824*
[b] *Chemistry Division, National Research Council of Canada, Ottawa, Canada K1A 0R9*

Reaction of $(Pr^i_2N)_2P(O)H$ with $Mo(CO)_6$ gives the title compound (**2**) identified as a $Mo(CO)_5$ complex of the six-membered $[Pr^i_2NPO]_3$ heterocycle and found to be an intermediate for the formation of the $P_4O_4M_2$ cage complex.

Cyclophosphoxanes of the type $[RPO]_3$ have been known since 1967.[1] Only the heterocycles $[Pr^i_2NPO]_3$ and $[BHTPO]_3$ [where BHT is the 2,4-bis(2,6-di-t-butyl-4-methylphenoxy) group] have been structurally characterized;[2,3] though the former structure was complicated by a disorder problem. The co-ordination chemistry of these potentially multidentate ligands has not been explored. We report here the isolation of the first metal complex of the cyclotriphosphoxane $[Pr^i_2NPO]_3$ as an intermediate from the synthesis of the $P_4O_4Mo_2$ adamantane-like cage complex. We have previously reported the quantitative synthesis of $Mo_2(CO)_8[Pr^i_2NPO]_4$, complex (**1**), from $Mo(CO)_6$ and two equivalents of $(Pr^i_2N)_2P(O)H$ in refluxing toluene, reaction (1).[4]

$$2\ Mo(CO)_6 + 4(Pr^i_2N)_2P(O)H \longrightarrow 4\ CO + 4\ Pr^i_2NH + \qquad (1)$$



(**1**)

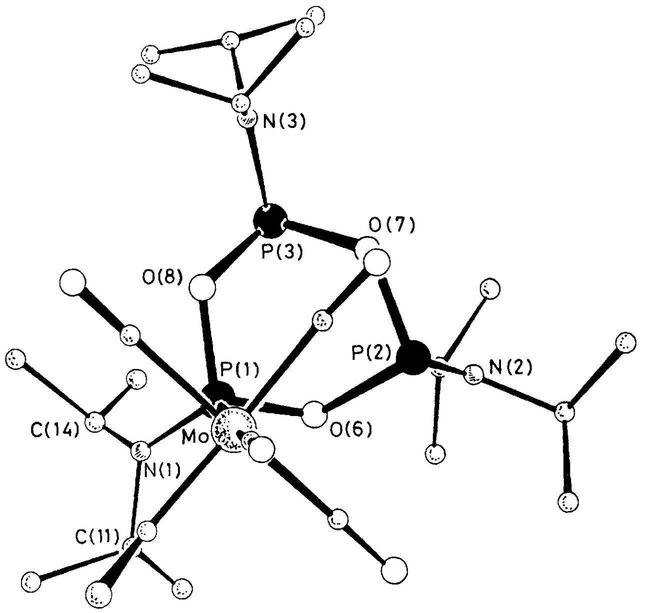


Figure 1. Molecular structure of $Mo(CO)_5[Pr^i{}_2NPO]_3$, (**2**). Key bond lengths (Å) and angles (°): Mo–P(1) 2.513(3), P(1)–O(6) 1.637(9), P(1)–O(8) 1.617(9), P(1)–N(1) 1.64(1), P(2)–O(6) 1.702(9), P(2)–O(7) 1.68(1), P(2)–N(2) 1.66(1), P(3)–O(7) 1.62(1), P(3)–O(8) 1.704(9), P(3)–N(3) 1.64(1), O(6)–P(1)–O(8) 100.3(4), P(1)–O(6)–P(2) 121.0(5), O(6)–P(2)–O(7) 94.0(5), P(2)–O(7)–P(3) 128.6(6), O(7)–P(3)–O(8) 96.9(5), P(3)–O(8)–P(1) 123.5(5), P(1)–N(1)–C(11) 120(1), P(1)–N(1)–C(14) 131(2), C(11)–N(1)–C(14) 106(2).

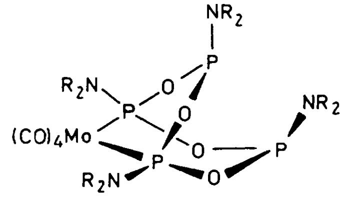


Figure 2. Proposed structure of *cis*-$Mo(CO)_4[Pr^i{}_2NPO]_4$ (**3a**).

$$\underset{(\mathbf{2})}{2\,Mo(CO)_5[Pr^i{}_2NPO]_3} \rightarrow \underset{(\mathbf{1})}{Mo_2(CO)_8[Pr^i{}_2NPO]_4} + 2CO + 2(Pr^i{}_2NPO) \quad (2)$$

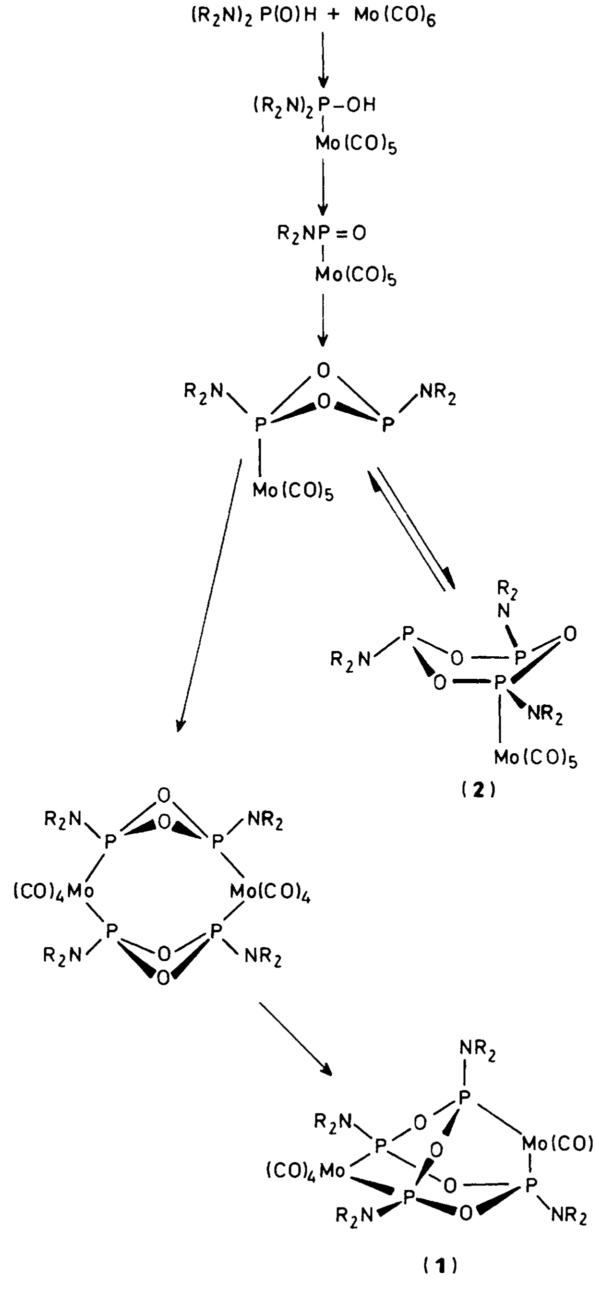
$$(Pr^i{}_2N)_2\overset{O}{\overset{\|}{P}}H \xrightarrow[i]{Mo(CO)_6} \underset{(\mathbf{2})}{Mo(CO)_5[Pr^i{}_2NPO]_3} \xrightarrow{ii} \underset{(\mathbf{1})}{Mo_2(CO)_8[Pr^i{}_2NPO]_4}$$

$$(Pr^i{}_2N)_2\overset{O}{\overset{\|}{P}}H \xrightarrow[iii]{M(CO)_6} \underset{(\mathbf{3b,c})}{cis\text{-}M(CO)_4[Pr^i{}_2NPO]_4} \ (M = Cr, W)$$

$$[Pr^i{}_2NPO]_3 \xrightarrow[iv]{Mo(CO)_6} \underset{(\mathbf{2})}{Mo(CO)_5[Pr^i{}_2NPO]_3} + \underset{(\mathbf{3a})}{cis\text{-}Mo(CO)_4[Pr^i{}_2NPO]_4}$$

$$[Pr^i{}_2NPO]_3 \xrightarrow[v]{Mo(CO)_6} \underset{(\mathbf{3a})}{cis\text{-}Mo(CO)_4[Pr^i{}_2NPO]_4}$$

Scheme 1. *Reaction conditions:* i, toluene, 100 °C, 4 h; ii, toluene, reflux, 1—2 h; iii, toluene, reflux, 48 h; iv, toluene, 100 °C, 4 h; v, THF, Hanovia 450 W Hg lamp, 18 h.



Scheme 2

When the reaction was run at 100 °C for 4—6 h, a ^{31}P n.m.r. spectrum indicated the unreacted ligand as well as an AMX multiplet among other smaller multiplets. Column chromatography yielded complex (**2**) as a white solid. A single crystal *X*-ray study† identified it as $Mo(CO)_5[Pr^i{}_2NPO]_3$.

The molecular structure of (**2**) consists of a cyclotriphosphoxane heterocycle in a distorted boat conformation with all three amino groups equatorial. The $Mo(CO)_5$ moiety is

---

† *Crystal data* for (**2**): $C_{23}H_{42}MoN_3O_8P_3$, orthorhombic, a = 11.570(2), b = 18.729(5), c = 32.056(3) Å, space group $Pbc2_1$, Z = 8, D_c = 1.241 mg m^{-3}. Of the 5272 unique reflections measured, 3469 were used in the final refinement to give R_f = 0.047 and R_w = 0.048. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

co-ordinated to the axial position of one of the two equivalent phosphoruses of the parent ligand,[2] destroying its mirror symmetry (Figure 1). Both enantiomers were found in the crystal. A short transannular P · · · O distance of 2.86 Å is observed. P–N Bond lengths at 1.64—1.66 Å conform with dπ(P)–pπ(N) bonding.[5] Angles around N(2) and N(3) approximate planarity (114—127°) while N(1) bonded to the co-ordinated P(1) is pyramidal. The observed C(11)–N(1)–C(14) angle closing to 106(2)° and C(11)–N(1)–P(1) angle opening up to 131(2)° are due to a twisting of the C(11) isopropyl group from the equatorial metal carbonyl C(5)–O(5).

Spectroscopic data for (**2**) are fully consistent with the solid-state geometry. The ^{31}P n.m.r. spectrum exhibited an AMX pattern (δ_A = 146.7, δ_M = 139.2, δ_X = 134.1 p.p.m.; $^2J_{AM}$ = 9.7, AX = 12.9, MX = 11.1 Hz; $^3J_{AH}$ = 10, MH = 11, XH = 9 Hz). This can be compared with the parent ligand's AX_2 pattern (δ_A = 140.3, δ_X = 131.3 p.p.m.; $^2J_{AX}$ = 13.5 Hz). Its i.r. (KBr disc) spectrum showed characteristic $M(CO)_5$ carbonyl stretches at 2064, 1956, 1936, and 1924 cm^{-1} as well as a POP band at 869 cm^{-1}.

Complex (**2**) can also be isolated from the thermal reaction of the parent heterocycle $[Pr^i_2NPO]_3$ with $Mo(CO)_6$. Surprisingly, photolysis of the same reagents in tetrahydrofuran (THF) afforded not (**2**) but a complex (**3a**) of stoicheiometry $Mo(CO)_4[Pr^i_2NPO]_4$ which has an A_2XY ^{31}P n.m.r. spectrum (δ_A = 154.9, δ_X = 128.7, δ_Y = 127.1 p.p.m.; $^2J_{AX}$ = 58, AY = 11, XY = 3 Hz). Its i.r. spectrum (ν_{CO} at 2012, 1926, 1915, 1920 cm^{-1}) is indicative of a *cis*-$M(CO)_4L_2$ species. A plausible structure based on a 1,5-co-ordinated tetraphosphoxane $[Pr^i_2NPO]_4$ (Figure 2) remains to be confirmed. Chromium and tungsten analogues (**3b,c**) can be synthesized by prolonged reactions of the respective hexacarbonyl with $(Pr^i_2N)_2P(O)H$ in refluxing toluene (Scheme 1).

Upon refluxing in toluene, (**2**) is smoothly converted to the cage complex (**1**) with loss of CO and Pr^i_2NPO, reaction (2). By contrast, complex (**3a**) does not appear to be a direct precursor to (**1**). Our isolation and characterization of (**2**) and its conversion to (**1**) suggest that it may be an intermediate in the original cage formation reaction. Elimination and addition of an Pr^i_2NPO unit thus appear to be facile for a metal-co-ordinated $[Pr^i_2NPO]_n$ heterocycle. A vacuum pyrolysis of $[BHTPO]_3$ at 220 °C to yield $[BHTPO]_2$ has recently been reported.[6] One speculative scheme for the formation of cage (**1**) can now be proposed (Scheme 2).

We thank the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Received, 13th September 1988; Com. 8/02633E

References

1 E. E. Nifant'ev, M. P. Koroteev, N. L. Ivanov, I. P. Gudkova, and D. A. Predvoditelev, *Acad. Sci. USSR Proc. Chem. Soc.*, 1967, **173**, 398.

2 E. Niecke, H. Zorn, B. Krebs, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 709.

3 D. W. Chasar, J. P. Fackler, A. M. Mazany, R. A. Komoroski, and W. J. Kroenke, *J. Am. Chem. Soc.*, 1986, **108**, 5956.

4 E. H. Wong, M. M. Turnbull, E. J. Gabe, F. L. Lee, and Y. Le Page, *J. Chem. Soc., Chem. Commun.*, 1983, 776.

5 J. C. Clardy, R. L. Kolpa, and J. G. Verkade, *Phosphorus*, 1974, **4**, 133.

6 D. W. Chasar, J. P. Fackler, R. A. Komorski, W. J. Kroenke, and A. M. Mazany, *J. Am. Chem. Soc.*, 1987, **109**, 5690.