Co-ordinated *cyclo*-Tetraphosphoxane and *cyclo*-Pentaphosphoxane; Two Configurations of the Co-ordinated P_4O_4 Ring

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Thermal reactions of hexacarbonyl-chromium or -tungsten with bis(di-isopropylamino)phosphine oxide or photolysis of $Mo(CO)_6$ with $[Pr^i_2NPO]_3$ afforded *cis*-$M(CO)_4[Pr^i_2NPO]_4$, which contains both chair–boat and chair–chair forms of the co-ordinated P_4O_4 ring in solution as well as in the molecular structure; additional products of the chromium reaction include the chromium cage complex, $Cr_2(CO)_8[Pr^i_2NPO]_4$, and $Cr_2(CO)_7[Pr^i_2NPO]_5$ which contains the novel *cyclo*-pentaphosphoxane P_5O_5 ring co-ordinated to one *cis*-$Cr(CO)_4$ and one *fac*-$Cr(CO)_3$ moiety.

Although cyclophosphates form a well known class of compounds,[1] cyclophosphoxanes, $[RPO]_n$, are relatively rare.[2] Through our interest in the co-ordination chemistry of bis(dialkylamino)phosphine oxides with metal carbonyls, we have isolated and characterized co-ordinated tri- and tetraphosphoxanes, apparently formed by metal-assisted amine elimination and oligomerization.[3,4] The latter formed adamantane-like cage complexes of the type $M_2(CO)_8[R_2NPO]_4$ featuring the P_4O_4 ring in a boat–boat configuration, allowing chelation of two metals in a back-to-back orientation. We

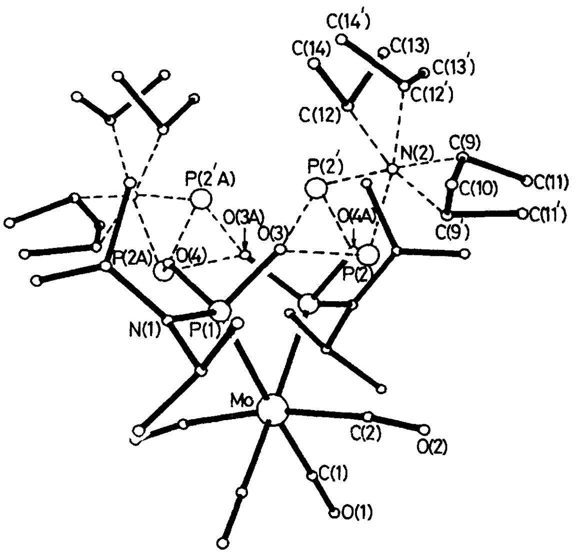

Figure 1. Molecular structure of $Mo(CO)_4[Pr^i_2NPO]_4$, (**1c**). Key bond lengths (Å) and angles (°): Mo–P(1) 2.492(2), Mo–C(1) 1.978(9), Mo–C(2) 2.007(9), P(1)–N(1) 1.660(6), P(2)–N(2) 1.667(8), P(2')–N(2) 1.74(1), P(1)–Mo–P(1A) 76.18(8), C(2)–Mo–C(2A) 168.7(4), P(1)–O(3)–P(2) 125.3(3), P(1)–O(3)–P(2') 127.1(4), P(1)–O(4)–P(2'A) 121.6(4).

report the synthesis and characterization of *cis*-$M(CO)_4[Pr^i_2NPO]_4$ (M = Cr, Mo, W), which contains both the chair–boat and the chair–chair configurations of the tetraphosphoxane heterocycle. We also report here the structure of the first pentaphosphoxane P_5O_5 ring complex, a side product of the chromium reaction.

When hexacarbonyl-chromium or -tungsten is refluxed in toluene with bis(di-isopropylamino)phosphine oxide (2 equiv.) for extended periods of time (48—60 h), the major isolated product (~50% yield) is white *cis*-$M(CO)_4[Pr^i_2NPO]_4$ [M = Cr (**1a**); M = W (**1b**)] based on elemental analyses and i.r. spectroscopy. The molybdenum analogue (**1c**) can be prepared by photolysis of $Mo(CO)_6$ with the triphosphoxane $[Pr^i_2NPO]_3$ [Hanovia 450 W medium-pressure Hg lamp, 18 h in tetrahydrofuran (THF)].[3] All three products show a mixture of 70% A_2XY and 30% AA'XX' patterns in their ^{31}P solution n.m.r. spectra. Variable temperature n.m.r. studies [*e.g.* (**1a**) in $C_2D_2Cl_4$ from 20 to 160 °C] revealed no significant temperature dependence in either the appearance or relative proportions of the two species, indicative of a substantial barrier to phosphorus inversion.

A single-crystal *X*-ray study of (**1c**) revealed a structure with the $Mo(CO)_4$ moiety 1,5-co-ordinated to a tetraphosphoxane $[Pr^i_2NPO]_4$ ring (Figure 1).† Mirroring the solution ^{31}P n.m.r. spectral results, two configurations of this P_4O_4 ring are found

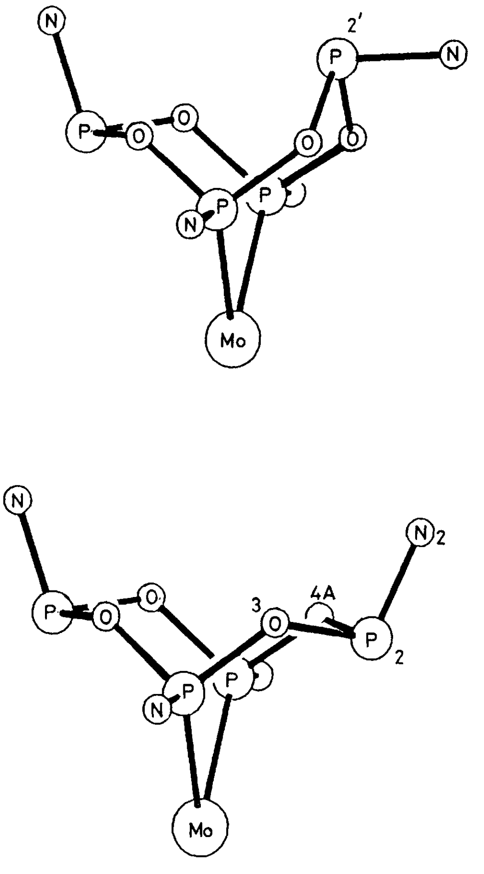

Figure 2. The chair–boat and chair–chair configurations in (**1c**). P(2) and P(2') are related by a phosphorus inversion about O(3), O(4A), and N(2).

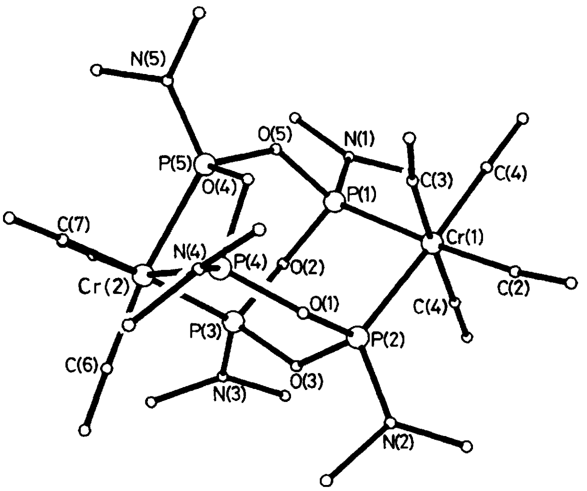

Figure 3. Molecular structure of $Cr_2(CO)_7[Pr^i_2NPO]_5$, (**3**). Key bond lengths (Å) and bond angles (°): Cr(1)–P(1) 2.352(4), Cr(1)–P(2) 2.336(5), Cr(2)–P(3) 2.288(5), Cr(2)–P(4) 2.315(4), Cr(2)–P(5) 2.312(5), P(1)–N(1) 1.67(1), P(2)–N(2) 1.69(1), P(3)–N(3) 1.67(1), P(4)–N(4) 1.65(1), P(5)–N(5) 1.66(1), P(1)–Cr(1)–P(2) 89.3(2), P(3)–Cr(2)–P(4) 92.3(2), P(3)–Cr(2)–P(5) 91.1(2), P(4)–Cr(2)–P(5) 66.4(2), P(1)–O(2)–P(3) 130.3(6), P(3)–O(1)–P(2) 129.7(6), P(2)–O(3)–P(4) 134.3(5), P(4)–O(4)–P(5) 101.0(5), P(5)–O(5)–P(1) 132.6(6).

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† *Crystal data* for (**1c**): $C_{28}H_{56}MoN_4O_8P_4$, monoclinic, $a = 18.992(1)$, $b = 11.306(1)$, $c = 19.368(1)$ Å, $\beta = 98.63(1)°$, space group $A2/a$, $Z = 4$, $D_c = 1.219$ Mg m^{-3}. Of the 2630 unique reflections measured, 2219 were used in the final refinement to give $R_f = 0.062$ and $R_w = 0.057$. P(2) and P(2') were assigned 0.7 and 0.3 occupancies, respectively, which refined to 0.697 and 0.320. For (**3**): $C_{37}Cr_2H_{70}N_5O_{12}P_5$, monoclinic, $a = 12.655(1)$, $b = 17.639(1)$, $c = 23.670(1)$ Å, $\beta = 101.82(1)°$, space group $P2_1/c$, $Z = 4$, $D_c = 1.240$ Mg m^{-3}. Of the 6667 unique reflections measured, 4337 were considered significant and used in the refinement to give $R_f = 0.088$ and $R_w = 0.081$. 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.

with relative occupancies of 2:1 (chair–boat/chair–chair, Figure 2). The disorder involves only the unco-ordinated phosphorus atom, P(2), and associated di-isopropyl groups, C(9)–C(14). A two-fold axis through the metal centre correlates the halves of its co-ordination sphere. A phosphorus inversion anchored at two phosphoxane oxygens, O(3) and O(4A), and one nitrogen, N(2), relates P(2) in the chair configuration to P(2′) in the boat form. The chair–chair ring is flattened considerably since the unco-ordinated P(2) and P(2A) are bent away from the axial metal carbonyl groups to within 0.1 Å of the phosphoxane oxygen plane [O(3), O(3A), O(4), O(4A)]. With the P(2) · · · C(2) contact at 0.5 Å below the van der Waals' radii sum, the axial carbonyl–metal–carbonyl angle is distorted away from linearity to 168.7(4)°. This molybdenum co-ordination sphere is thus quite similar to that found in the $Mo_2(CO)_8[Pr^i_2NPO]_4$ cage complex.[4] Again, the sum of bond angles around each nitrogen is consistent with planarity and multiple P–N bonding.

The reaction mixture from the synthesis of (**1a**) also contained light yellow chromium complexes (**2**) (5%) and (**3**) (10%). Complex (**2**) analysed as $Cr(CO)_4[Pr^i_2NPO]_2$. Based on its spectral properties [i.r.: ν_{CO} 2001, 1975, 1920, 1891 cm^{-1}; ν_{POP} 844 cm^{-1}; ^{31}P n.m.r.: δ +159.4 p.p.m.]; we assign it the adamantane-like cage structure previously found for its molybdenum analogue.[4] Complex (**3**) has low symmetry and exhibits six i.r. metal–carbonyl stretches at 2011, 1961, 1936, 1915, 1883, and 1871 cm^{-1}, as well as a broad ν_{POP} at 890 cm^{-1}.[5] The solution ^{31}P n.m.r. spectrum of (**3**) contains an A_2MX_2 pattern (δ_A +176.6, δ_M +175.1, δ_X +156.9 p.p.m.; J_{AM} 9, $J_{AX} \approx 0$, J_{MX} 40 Hz). Complex (**3**) analysed as $Cr_2(CO)_7[Pr^i_2NPO]_5$ and has the molecular structure shown in Figure 3.† Pertinent features include a novel pentaphosphoxane P_5O_5 heterocycle co-ordinated to one *cis*-$Cr(CO)_4$ and one *fac*-$Cr(CO)_3$ moiety. The ring angles at O(1), O(3), and O(5), are 129.7(6), 134.3(5), and 132.6(6)°, respectively. For the four-membered chelate ring [Cr(2),P(4),O(4),P(5)] included in the *fac*-Cr(2) co-ordination sphere, the P–O–P angle is only 101.0(5)°, while the P(4)–Cr(2)–P(5) angle is compressed to an unusually small value of 66.4(2)°.[6] Bond angle sums around the five nitrogens are all within 2° of planarity.

Complexes (**1**), (**2**), and (**3**) further demonstrate the compliancy of $[RPO]_n$ heterocycles in their co-ordination geometries and the ability of metal co-ordination to provide supra-structures for novel heterocycles.[7] We are currently exploring the use of (**1**) as a precursor to bimetallic cage complexes.

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