# Dichromium Cage Complexes of Cyclotetra-, Cyclopenta-, and Cyclohexa-phosphoxane

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Metal-assisted assembly of *cis*-dimethylpiperidinophosphine oxide (DMP–P=O) units around chromium carbonyl at progressively higher temperatures affords dichromium complexes of cyclotetraphosphoxane (two isomers), cyclopentaphosphoxane, and ultimately, the novel cyclohexaphosphoxane.

Although cyclic polyphosphates are known in ring sizes ranging from $P_3O_3$ up to $P_{10}O_{10}$,[1] cyclopolyphosphoxanes containing rings larger than $P_5O_5$ have not been successfully synthesized. Bis(dialkylamino)phosphine oxides were found to be convenient precursors to group VI metal carbonyl complexes of cyclic polyphosphoxanes.[2,3] Chromium hexacarbonyl has been found to yield complexes of the type $Cr(CO)_4(R_2N\text{–}PO)_4$, $Cr_2(CO)_8(R_2N\text{–}PO)_4$ and $Cr_2(CO)_7(R_2N\text{–}PO)_5$ (where R = $Pr^i$ and cyclohexyl).[3] Curiously, the chromium analogue of the adamantanoid cage complex $Mo_2(CO)_8(R_2N\text{–}PO)_4$ has remained elusive. We have found that simple substitution of the dialkylamino group on the phosphorus with *cis*-2,6-dimethylpiperidine (DMP) can lead to the formation of this species as well as assembly of the first $P_6O_6$ ring within the framework of a $Cr_2P_6O_6$ cage complex.

Thermal reaction of bis(2,6-dimethylpiperidino)phosphine oxide, $(DMP)_2P(O)H$, with chromium hexacarbonyl in refluxing toluene for 24 h and subsequent workup allowed the isolation of both isomers of the dichromium tetraphosphoxane complex $Cr_2(CO)_8(DMP\text{–}PO)_4$ **1a** (yellow) and **1b** (colourless), as well as complex **2**, $Cr_2(CO)_7(DMP\text{–}PO)_5$. The structure of **2** can be readily assigned from NMR and IR spectral data to be a dichromium pentaphosphoxane cage analogous to the known $Cr_2(CO)_7(Pr^i{}_2NPO)_5$ geometry (Fig. 1).[3] Traces of a product of higher molecular symmetry, complex **3**, were also isolated.

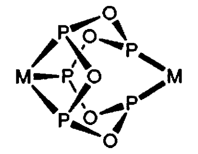


Fig. 1 Core geometry of the $Cr_2(CO)_7(Pr^i{}_2NPO)_5$ cage (ref. 3)

The two isomers of $Cr_2(CO)_8(DMP\text{–}PO)_4$ (**1a**, **1b**) have similar IR carbonyl stretching patterns; 2006(s), 1942(s) and 1892(s, br) cm$^{-1}$ for **1a** and 2004(s), 1927(sh), and 1908(s, br) cm$^{-1}$ for **1b**, consistent with a *cis*-$P_2Cr(CO)_4$ moiety. Both $^{31}P\{^1H\}$ NMR spectra contained singlets (δ +155.5 for **1a**, δ +171.1 for **1b**), but the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **1a** exhibited two distinct DMP methyl environments suggestive of a lower symmetry about the coordination plane. Their molecular structures (Figs. 2 and 3) confirmed this, showing that **1a** features two four-membered Cr–P–O–P chelate rings and is a configurational isomer of the adamantanoid complex **1b**.† Bond distances for Cr–P, P–O and Cr–C bonds are comparable in the two structures, while the intramolecular chromium–chromium separation is 5.597(1) Å for **1a** increasing slightly to 5.656(1) Å in **1b**. The P–Cr–P chelate angle in **1a** is compressed to 66.5(2)° compared to an average of 79.7(3)° in **1b**.

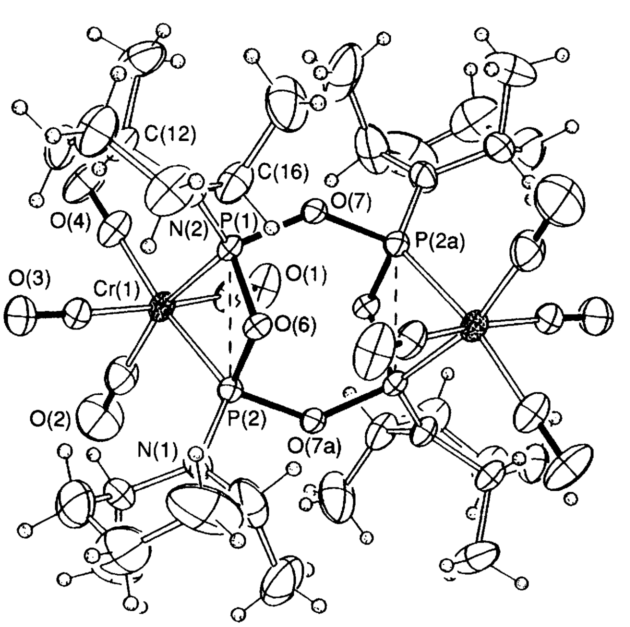


Fig. 2 Molecular structure of **1a**; key bond lengths (Å) and angles (°): Cr(1)-P(1) 2.337(1), Cr(1)-P(2)′ 2.333(1), Cr(1)-C(1) 1.884(4), Cr(1)-C(2) 1.862(6), Cr(1)-C(3) 1.875(4), Cr(1)-C(4) 1.872(5), P(1)—P(2) 2.560(1), P(1)-O(6) 1.657(3), P(1)-O(7) 1.635(3), P(2)-O(6) 1.664(3), P(2)-O(7*a*) 1.630(2); P(1)-Cr(1)-P(2) 66.5(1), P(1)-O(6)-P(2) 100.9(2), P(1)-O(7)-P(2*a*) 134.5(2), P(1)-N(2)-C(12) 121.0(3), P(1)-N(2)-C(16) 119.7(2), C(12)-N(2)-C(16) 119.2(3)

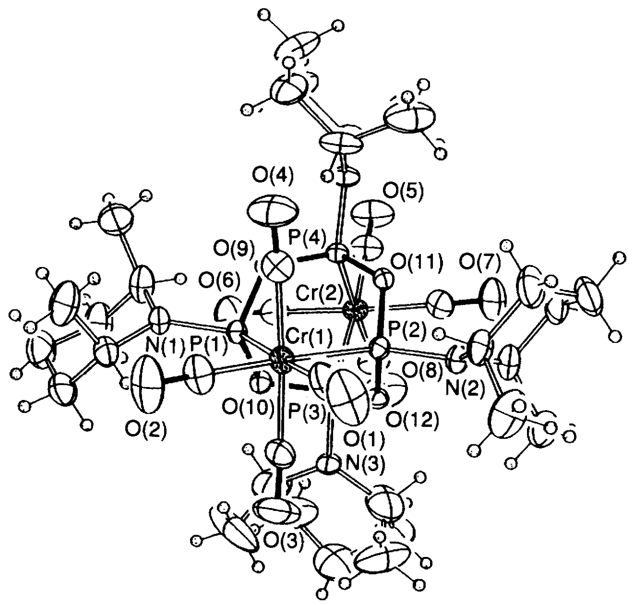


Fig. 3 Molecular structure of **1b**; key bond distances (Å) and angles (°): Cr(1)-P(1) 2.329(2), Cr(1)-P(2) 2.340(2), Cr(2)-P(3) 2.323(2), Cr(2)-P(4) 2.337(2), P(1)-O(9) 1.631(3), P(1)-O(10) 1.662(3), P(2)-O(11) 1.656(3), P(2)-O(12) 1.646(3), P(3)-O(10) 1.647(3), P(3)-O(12) 1.638(3), P(4)-O(9) 1.661(3), P(4)-O(11) 1.644(3); P(1)-Cr(1)-P(2) 80.0(1), P(3)-Cr(2)-P(4) 79.4(1), P(1)-O(9)-P(4) 128.4(2), P(1)-O(10)-P(3) 127.6(2), P(2)-O(11)-P(4) 129.6(2), P(2)-O(12)-P(3) 126.5(2), O(9)-P(1)-O(10) 99.5(2), O(9)-P(4)-O(11) 98.3(2), O(11)-P(2)-O(12) 98.8(2)

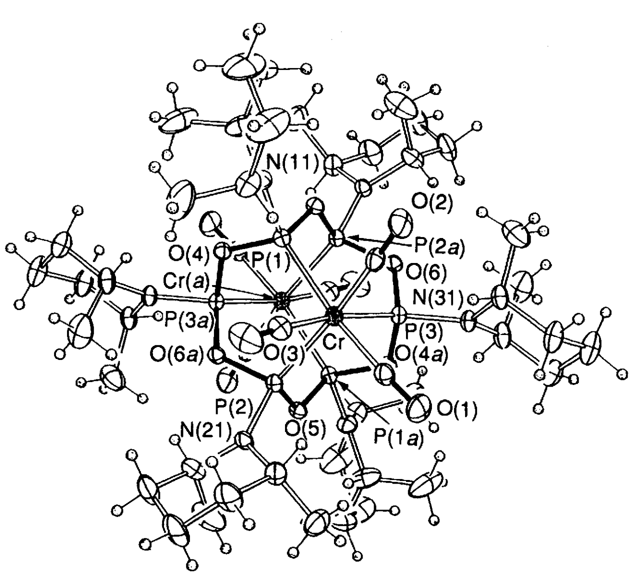


**Fig. 4** Molecular structure of **3**; key bond distances (Å) and angles (°): Cr–P(1) 2.336(2), Cr–P(2) 2.336(2), Cr–P(3), 2.334(2), Cr–C(1) 1.856(6), Cr–C(2) 1.855(6), Cr–C(3) 1.859(6), P(1)–O(4) 1.656(3), P(1)–O(5*a*) 1.628(4), P(2)–O(5) 1.658(3), P(3)–O(6) 1.653(4), P(3)–O(4*a*) 1.627(3); P(1)–Cr–P(2) 93.0(1), P(2)–Cr–P(3), 92.7(1), P(3)–Cr–P(1) 92.9(1), P(1)–O(4)–P(3*a*) 124.0(2), P(2)–O(5)–P(1*a*) 123.3(3), P(3)–O(6)–P(2*a*) 124.8(2), O(4)–P(1)–O(5*a*) 97.2(2), O(5)–P(2)–O(6*a*) 97.2(1), O(6)–P(3)–O(4*a*) 97.2(2)

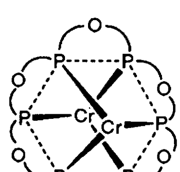
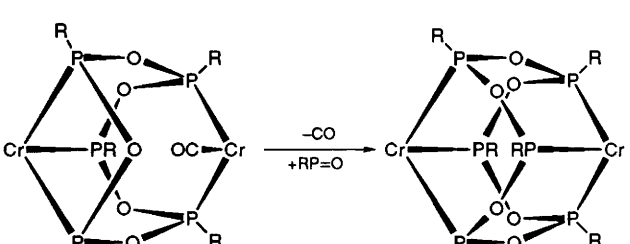


**Fig. 5** Representation of the $Cr_2P_6O_6$ core in **3**



**Scheme 1**

Complex **3** analysed as $Cr(CO)_3(DMP\text{–}PO)_3$ and has two clearly resolved IR carbonyl bands at 1949(s) and 1890(s, br) $cm^{-1}$ indicative of a *fac*-$P_3Cr(CO)_3$ vertex. Its $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at $\delta$ + 175.5 while its $^1H$ NMR also indicates high symmetry with a single DMP methyl group resonance. Confirmation of a possible $Cr_2(CO)_6(DMP\text{–}PO)_6$ cage structure was obtained from an X-ray molecular structural determination (Fig. 4). This molecule has near $D_{3d}$ symmetry with the principal axis along the metal–metal vector. The Cr–Cr intracage distance is down to 4.700(1) Å.‡ The core structure can be viewed as a $Cr_2P_6$ cube with the six oxygens bridging only the P–P edges (Fig. 5). This represents the first successful assembly of a hexaphosphoxane $P_6O_6$ ring.[4] At present, the only relative of **3** would be the previously reported $Mo_2(CO)_6(MeAsO)_6$ cage complex, formed serendipitously from the reaction of $Mo(CO)_6$ with $(MeAs)_5$ in the presence of air.[5]

An additional feature of interest common to these three structures is the *syn*-diaxial positioning of the methyl groups in all of the 2,6-dimethylpiperidine rings. The normal preference of such methyl groups for equatorial sites in substituted piperidines is apparently reversed for *N*-nitroso-, *N*-acetyl-, *N*-nitro-, and related substituents.[6] Whether the origin of this conformational reversal in our complexes is due to near-planarity at the ring nitrogens or sterical constraints of the coordination environment is under investigation.

From the clear structural relationship between complexes **2** and **3**, it is tempting to consider **2** as a precursor to **3** *via* the loss of a single CO ligand from the *cis*-$Cr(CO)_4$ vertex and incorporation of a sixth DMP–P=O unit (Scheme 1). Our expectations were realized when we discovered that refluxing of **2** with $(DMP)_2P(O)H$ in xylene indeed led to **3** in excellent yield. This stepwise build-up of polyphosphoxane rings around chromium centres supports our premise that metal templating provides an ideal strategy for the assembly of novel $P_nO_n$ rings.

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## Footnotes

† *Crystal Data* for **1a**: yellow block, $C_{36}H_{56}Cr_2N_4O_{12}P_4$, triclinic, $P\bar{1}$, $a$ = 9.905(3), $b$ = 11.668(4), $c$ = 12.189(4) Å, $\alpha$ = 96.62(2), $\beta$ = 110.81(2), $\gamma$ = 112.59(2)°, $V$ = 1162.9(5) Å$^3$, $Z$ = 1, $D_x$ = 1.378 g $cm^{-3}$, $T$ = 296 K. Of 4799 data collected (Siemens P4, Mo-K$\alpha$, $2\theta_{max}$ = 52°), 4571 were independent and 3489 were observed ($4\sigma F_0$). At convergence: $R$ = 4.81%, $R_w$ = 6.99%.

*Crystal Data* for **1b**: colourless block, $C_{36}H_{56}Cr_2N_4O_{12}P_4$, monoclinic, $I2/a$, $a$ = 27.593(8), $b$ = 18.105(7), $c$ = 18.648(5) Å, $\beta$ = 91.45(2)°, $V$ = 9313 Å$^3$, $Z$ = 8, $D_x$ = 1.376 g $cm^{-3}$, $T$ = 296 K. Of 9464 data collected, 9164 were independent and 5611 were observed. At convergence with all nonhydrogen atoms anisotropic and hydrogens idealized: R = 5.89%, $R_w$ = 6.95%.

‡ *Crystal Data* for **3**: Colourless block, $C_{48}H_{84}Cr_2N_6O_{12}P_6$, triclinic, $P\bar{1}$, $a$ = 11.882(4), $b$ = 12.112(4), $c$ = 13.219(4) Å, $\alpha$ = 62.28(2), $\beta$ = 66.18(2), $\gamma$ = 67.45(2)°, $V$ = 1494.9(5) Å$^3$, $Z$ = 1, $D_x$ = 1.36 g $cm^{-3}$, $T$ = 296 K. Of 4122 data collected, 3916 were independent and 2910 were observed. At convergence: R = 4.01%, $R_w$ = 4.42%.

Crystals of **3** were also obtained as a xylene solvate; the structures of the dichromium complex are chemically identical in these two forms with Cr—Cr separations of 4.700(1) Å and 4.692(2) Å, respectively. *Crystal Data* for **3** (xylene): colourless block, triclinic, $P\bar{1}$, $a$ = 10.650(2), $b$ = 12.407(3), $c$ = 13.064(3) Å, $\alpha$ = 106.64(3), $\beta$ = 93.60(2), $\gamma$ = 95.92(2)°, $V$ = 1637.3(6) Å$^3$, $Z$ = 1. $D_x$ = 1.352 g $cm^{-3}$, $T$ = 237 K. Of 6055 data collected, 5778 were independent and 4515 were observed. At convergence: R = 4.66%, $R_w$ = 5.19%.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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