

C(32)	0.8242 (17)	0.5387 (14)	0.0613 (13)	0.042 (7)
C(33)	0.929 (2)	0.6077 (14)	0.0205 (14)	0.052 (8)
C(34)	0.991 (2)	0.7015 (16)	0.0694 (14)	0.052 (8)
C(35)	0.953 (2)	0.7295 (13)	0.1577 (15)	0.055 (8)
C(36)	0.852 (2)	0.6650 (13)	0.1967 (13)	0.045 (7)

Table 2. Geometric parameters (Å, °)

Pt(1)—Cl(1)	2.308 (4)	Pt(1)—Cl(2)	2.359 (4)
Pt(1)—P(1)	2.238 (5)	Pt(1)—O(1)	2.12 (2)
Pt(2)—Cl(3)	2.341 (4)	Pt(2)—Cl(4)	2.344 (5)
Pt(2)—P(2)	2.251 (4)	Pt(2)—O(2)	2.129 (15)
P(1)—C(1)	1.811 (18)	P(1)—C(7)	1.802 (16)
P(1)—C(13)	1.818 (12)	P(2)—C(19)	1.813 (17)
P(2)—C(25)	1.782 (17)	P(2)—C(31)	1.833 (16)
Cl(1)—Pt(1)—Cl(2)	172.0 (4)	C(34)—C(35)—C(36)	121.8 (16)
Cl(2)—Pt(1)—P(1)	96.0 (2)	Cl(1)—Pt(1)—P(1)	90.7 (2)
Cl(2)—Pt(1)—O(1)	86.4 (5)	Cl(1)—Pt(1)—O(1)	87.2 (5)
Cl(3)—Pt(2)—Cl(4)	171.0 (4)	P(1)—Pt(1)—O(1)	176.1 (4)
Cl(4)—Pt(2)—P(2)	96.2 (1)	Cl(3)—Pt(2)—P(2)	92.2 (2)
Cl(4)—Pt(2)—O(2)	84.8 (4)	Cl(3)—Pt(2)—O(2)	86.9 (5)
Pt(1)—P(1)—C(1)	114.5 (6)	P(2)—Pt(2)—O(2)	178.6 (4)
C(1)—P(1)—C(7)	106.3 (8)	Pt(1)—P(1)—C(7)	112.8 (6)
C(1)—P(1)—C(13)	103.7 (7)	Pt(1)—P(1)—C(13)	113.0 (6)
Pt(2)—P(2)—C(19)	111.9 (5)	C(7)—P(1)—C(13)	105.7 (7)
C(19)—P(2)—C(25)	103.5 (8)	Pt(2)—P(2)—C(25)	118.0 (6)
C(19)—P(2)—C(31)	107.2 (8)	Pt(2)—P(2)—C(31)	113.5 (5)

The title compound was obtained by adding PhMgBr (0.115 ml, 3.0 M, 2.1 eq.) dropwise to a stirred ethereal suspension of  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2]$  (0.174 g) at 273 K. The solution was allowed to warm to room temperature over a period of 3 h, then it was hydrolysed with 1 M  $\text{NH}_4\text{Cl}$  solution (5 ml). The ether layer was separated and the solvent was removed to leave a yellow powder.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta\text{P}$  4.3,  $^1J(\text{Pt}, \text{P})$  3740 Hz.  $^1\text{H}$  NMR:  $\delta\text{H}$  2.95 br, 7.3–7.8 m. A crystal suitable for diffraction studies was mounted on a glass fiber in random orientation. Indexing 15 automatically centered reflections from the photograph resulted in a triclinic cell. Axial photographs were taken to confirm the Laue symmetry and cell lengths. A set of high-angle data ( $2\theta$ ) was obtained using the initial orientation matrix. Final cell constants and orientation matrix for data collection were calculated by least-squares refinement. Data were collected with a variable scan rate. The intensities of the standards remained constant within experimental error and therefore no decay correction was applied.

Data reduction, structure solution and refinement were carried out using the *SHELXTL-Plus* software package (Sheldrick, 1991). A semi-empirical absorption correction was applied to the data using nine  $\psi$ -scan curves with  $\chi > 83^\circ$ . The structure was solved by the Patterson method and refined successfully in the space group  $P\bar{1}$ . Full-matrix least-squares refinement was carried out by minimizing  $w(F_o - F_c)^2$ . The non-H atoms were refined anisotropically. The H atoms were added in idealized calculated positions and were held fixed.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete bond distances and angles, along with a structure-determination summary have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71348 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1054]

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*Acta Cryst.* (1993). **C49**, 2081–2083

## Structure of a Dichromium Octacarbonyl Complex of Cyclotetrakis[bis(diisopropylamino)phosphoxane]

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(Received 13 November 1992; accepted 23 April 1993)

## Abstract

The molecule,  $\mu$ -2,4,6,8-tetrakis(*N,N*-diisopropylamino)-cyclotetraphosphoxane- $1\kappa^2\text{P}^2, \text{P}^4:2\kappa^2\text{P}^6, \text{P}^8$ -bis[tetracarbonylchromium(0)], has an inversion center that relates the two chromium coordination spheres. Each metal atom is *cis*-coordinated to two P atoms of the tetraphosphoxane ring to form a four-membered Cr—P—O—P chelate ring. The eight-membered phosphoxane heterocycle is a novel twist-boat-twist-boat configurational isomer of the alternative adamantanoid cage. Average distances are Cr—C 1.869 (3), Cr—P 2.337 (4) and P—O 1.65 (2) Å.

## Comment

The  $\text{P}_4\text{O}_4$  heterocycle  $[\text{Pr}_2\text{NPO}]_4$  has been shown to be a versatile tetradentate ligand in a number of transition-metal complexes (Wong *et al.*, 1988; Wong, Gabe & Lee, 1989). X-ray as well as solution NMR data have established that it can be 1,3,5,7-tetradentate adopting a boat-boat conformation in an adamantanoid bimetallic cage complex or 1,5-bidentate for a single metal in either a chair-boat or chair-chair form. In addition, a

1,3-chelating mode is also feasible for first-row transition metals (Wong, Sun, Gabe & Lee, 1991). We report here a dichromium complex that has this ligand in a novel twist-boat-twist-boat form, which is a configurational isomer of the adamantanoid cage complex.

The molecule has a crystallographic center of symmetry relating its two chromium coordination spheres, which are distorted octahedral. Cr—P distances of 2.3393 (9) and 2.3353 (9) Å are comparable to other reported values (Wong, Prasad, Gabe & Bradley, 1982; Wong *et al.*, 1989). Carbonyls (C2 and C4) *trans* to the P atoms have slightly shorter Cr—C distances [1.856 (3) Å average] than those *trans* to each other [C1 and C3, 1.882 (3) Å average] as is observed commonly (Cheung, Lai & Mok, 1971; Payne, Mokuolu & Speakman, 1965). The axial C1—Cr—C3 angle deviates somewhat from linearity at 171.7 (1)°. The four-membered Cr—P1—O2—P2 chelate ring contains a compressed P—Cr—P angle of 66.16 (3)° and a P—O—P angle of only 100.56 (10)°, similar to two previously reported chelate rings of this type (Wong *et al.*, 1982, 1989). The P<sub>4</sub>O<sub>4</sub> ring is in a twist-boat-twist-boat conformation (Fig. 2) orienting the two chromium moieties away from each other. Average ring P—O distances [1.65 (2) Å] are unchanged from the boat-boat form values [1.65 (4) Å (Wong *et al.*, 1989)]. Not surprisingly, the ring P—O—P angles differ severely from the 131.0 (2)° angle observed for the latter conformation because of the two four-membered Cr—P—O—P chelate rings. Two P—O—P angles are compressed to 100.56 (10)°, while the remaining two open up to 135.6 (1)°. The nitrogen bonding sphere is nearly planar with the sum of the bond angles equal to 359.4 (3)°.

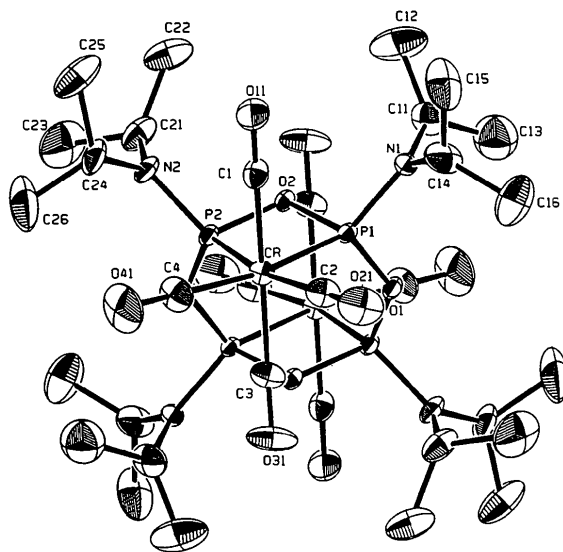


Fig. 1. ORTEP (Johnson, 1976) drawing and numbering scheme of the title compound. Thermal ellipsoids are drawn at the 50% probability level.

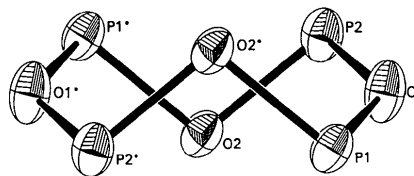


Fig. 2. ORTEP (Johnson, 1976) drawing of the P<sub>4</sub>O<sub>4</sub> ring only, showing the twist-boat conformation. Thermal ellipsoids are drawn at the 50% probability level.

## Experimental

### Crystal data

[Cr<sub>2</sub>(C<sub>24</sub>H<sub>56</sub>N<sub>4</sub>O<sub>4</sub>P<sub>4</sub>)(CO)<sub>8</sub>]  
*M<sub>r</sub>* = 916.4  
 Triclinic  
 P1  
*a* = 11.634 (2) Å  
*b* = 12.172 (1) Å  
*c* = 10.056 (2) Å  
 $\alpha$  = 114.099 (9)°  
 $\beta$  = 115.05 (1)°  
 $\gamma$  = 92.81 (1)°  
*V* = 1134.5 (9) Å<sup>3</sup>  
*Z* = 2.00

*D<sub>x</sub>* = 1.34 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 $\lambda$  = 0.7107 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 48.92–49.93°  
 $\mu$  = 0.6598 mm<sup>-1</sup>  
*T* = 296.1 K  
 Prism  
 0.75 × 0.65 × 0.45 mm  
 Clear

### Data collection

AFC-6S diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 refined from  $\Delta F$   
*T<sub>min</sub>* = 0.924, *T<sub>max</sub>* = 1.066  
 4211 measured reflections  
 3994 independent reflections  
 3241 observed reflections  
 [*I* > 3.00 $\sigma$ (*I*)]

*R<sub>int</sub>* = 0.021  
 $\theta_{\max}$  = 25°  
*h* = 0 → 14  
*k* = -14 → 14  
*l* = -12 → 12  
 3 standard reflections  
 monitored every 150 reflections  
 intensity variation:  
 -0.60%

### Refinement

Refinement on *F*  
*R* = 0.0423  
*wR* = 0.0518  
*S* = 2.239  
 3241 reflections  
 329 parameters  
 Only coordinates of H atoms refined  
 Weighting scheme based on measured e.s.d.'s  
 ( $\Delta/\sigma$ )<sub>max</sub> = 2.02

$\Delta\rho_{\max}$  = 0.49487 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.75714 e Å<sup>-3</sup>  
 Extinction correction:  
 Zachariasen type 2 Gaussian isotropic  
 Extinction coefficient:  
 3.52111 × 10<sup>-5</sup>  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Cr	0.88507 (4)	0.26373 (3)	0.47640 (4)	0.0314
P1	0.83161 (6)	0.37183 (5)	0.32166 (7)	0.0234
P2	1.06227 (6)	0.34698 (5)	0.46241 (7)	0.0259
O2	0.9733 (1)	0.3896 (1)	0.3212 (2)	0.0247
O31	0.9271 (3)	0.4657 (2)	0.8062 (2)	0.0790
O11	0.8125 (2)	0.0277 (2)	0.1586 (3)	0.0705
O21	0.6229 (2)	0.1708 (3)	0.4383 (3)	0.0866
O41	1.0236 (3)	0.1366 (3)	0.6746 (3)	0.1100
O1	0.8286 (2)	0.5183 (1)	0.3954 (2)	0.0298
N2	1.1501 (2)	0.2675 (2)	0.3888 (3)	0.0392
N1	0.7192 (2)	0.3118 (2)	0.1256 (2)	0.0323
C3	0.9156 (3)	0.3944 (3)	0.6808 (3)	0.0455
C1	0.8416 (3)	0.1179 (2)	0.2781 (3)	0.0425
C21	1.2217 (3)	0.3214 (3)	0.3302 (4)	0.0629
C23	1.3708 (4)	0.3464 (5)	0.4283 (7)	0.1188
C2	0.7229 (3)	0.2060 (3)	0.4516 (3)	0.0504
C4	0.9702 (3)	0.1843 (3)	0.5981 (4)	0.0607
C22	1.1639 (4)	0.2583 (4)	0.1428 (5)	0.0978
C24	1.1689 (3)	0.1547 (3)	0.4086 (4)	0.0583
C25	1.1632 (5)	0.0481 (4)	0.2610 (6)	0.1061
C26	1.2885 (5)	0.1802 (5)	0.5712 (7)	0.1244
C11	0.7366 (4)	0.3582 (3)	0.0176 (4)	0.0651
C12	0.7660 (5)	0.2726 (4)	-0.1050 (5)	0.1110
C13	0.6753 (6)	0.4534 (5)	-0.0050 (6)	0.1211
C15	0.5461 (4)	0.1097 (4)	-0.0804 (6)	0.1006
C16	0.4923 (4)	0.2941 (6)	0.0894 (7)	0.1186
C14	0.5937 (3)	0.2273 (4)	0.0701 (4)	0.0769

The complex was isolated in small yields as crystals from the thermal reaction of  $\text{Cr}(\text{CO})_6$  with  $({}^t\text{Pr}_2\text{N})_2\text{P}(\text{O})\text{H}$ . It was recrystallized from hexane by slow cooling of a saturated solution. Analysis: calculated for  $\text{C}_{32}\text{Cr}_2\text{H}_{56}\text{N}_4\text{O}_{12}\text{P}_4$  C 41.92, H 6.11, N 6.11%; found C 41.90, H 6.02, N 5.91%. A crystal of the title compound was mounted on a glass fiber. Weak reflections [ $I < 10.0\sigma(I)$ ] were rescanned (maximum of two rescans) and the counts accumulated to ensure good counting statistics. An empirical absorption correction, using the program *DIFABS* (Walker & Stuart, 1983), and *Lp* and secondary-extinction corrections applied; no decay correction was made. Refinement minimized  $\sum w(|F_o| - |F_c|)^2$  and  $\sigma^2(F_o^2)$ , where  $\sigma^2(F_o^2) = [S^2(C + 4B) + pF_o^2]/Lp^2$  ( $S$  = scan count,  $B$  = normalized background); the weighting scheme was based on counting statistics and included a factor ( $p = 0.03$ ) to downweight the intense reflections. Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order,  $\sin \theta/\lambda$  and various classes of indices showed no unusual trends. All calculations were performed on a VAXstation 3520 minicomputer. The enantiomorphs are indistinguishable from the X-ray data.

The authors acknowledge the financial support of the donors to the Petroleum Research Fund, administered by the American Chemical Society and National Science Foundation Research in Undergraduate Institutions Instrumentation Program (grant No. 8818397) for creation of the New England Molecular Structure Center at Keene State College.

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cr—P1	2.3393 (9)	O21—C2	1.151 (4)
Cr—P2	2.3353 (9)	O41—C4	1.144 (4)
Cr—C3	1.881 (3)	N2—C21	1.466 (5)
Cr—C1	1.884 (3)	N2—C24	1.480 (4)
Cr—C2	1.856 (3)	N1—C11	1.488 (4)
Cr—C4	1.857 (4)	N1—C14	1.482 (4)
P1—O2	1.655 (2)	C21—C23	1.526 (5)
P1—O1	1.636 (2)	C21—C22	1.513 (5)
P1—N1	1.637 (2)	C24—C25	1.492 (5)
P2—O2	1.663 (2)	C24—C26	1.524 (6)
P2—O1	1.640 (2)	C11—C12	1.437 (6)
P2—N2	1.637 (2)	C11—C13	1.436 (7)
O31—C3	1.146 (3)	C15—C14	1.445 (5)
O11—C1	1.143 (3)	C16—C14	1.500 (7)
P1—Cr—P2	66.16 (3)	O2—P2—N2	104.8 (1)
P1—Cr—C3	98.09 (10)	O1—P2—N2	101.4 (1)
P1—Cr—C1	88.10 (10)	P1—O2—P2	100.56 (10)
P1—Cr—C2	101.7 (1)	P1—O1—P2	135.6 (1)
P1—Cr—C4	164.4 (1)	P2—N2—C21	118.4 (2)
P2—Cr—C3	98.57 (9)	P2—N2—C24	117.8 (2)
P2—Cr—C1	89.0 (1)	C21—N2—C24	123.1 (3)
P2—Cr—C2	167.6 (1)	P1—N1—C11	119.7 (2)
P2—Cr—C4	98.4 (1)	P1—N1—C14	117.5 (2)
C3—Cr—C1	171.7 (1)	C11—N1—C14	122.1 (2)
C3—Cr—C2	85.2 (1)	Cr—C3—O31	173.3 (3)
C3—Cr—C4	86.1 (1)	Cr—C1—O11	177.9 (3)
C1—Cr—C2	88.1 (1)	N2—C21—C23	113.4 (4)
C1—Cr—C4	89.4 (1)	N2—C21—C22	114.4 (3)
C2—Cr—C4	93.6 (2)	C23—C21—C22	115.0 (4)
Cr—P1—O2	95.77 (7)	Cr—C2—O21	179.1 (3)
Cr—P1—O1	124.65 (7)	Cr—C4—O41	179.2 (3)
Cr—P1—N1	125.02 (9)	N2—C24—C25	114.0 (4)
O2—P1—O1	98.49 (9)	N2—C24—C26	114.0 (3)
O2—P1—N1	104.7 (1)	C25—C24—C26	112.2 (4)
O1—P1—N1	102.2 (1)	N1—C11—C12	115.1 (3)
Cr—P2—O2	95.70 (6)	N1—C11—C13	118.6 (4)
Cr—P2—O1	124.68 (8)	C12—C11—C13	121.6 (4)
Cr—P2—N2	125.77 (9)	N1—C14—C15	116.9 (4)
O2—P2—O1	98.54 (9)	N1—C14—C16	113.4 (4)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71269 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1030]

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