C7'—P1'	1.808 (6)	C8'—P2'	1.830 (5)
C9'—P2'	1.830 (5)	C10'—P2'	1.830 (5)
C11'—C1'	1.464 (6)	C12'—C11'	1.379 (7)
C13'—C12'	1.382 (8)	C14'—C13'	1.352 (10)
C15'—C14'	1.406 (10)	C16'—C11'	1.386 (7)
C16'—C15'	1.391 (8)	C21'—C2'	1.464 (6)
C22'—C21'	1.379 (7)	C23'—C22'	1.382 (8)
C24'—C23'	1.352 (10)	C25'—C24'	1.406 (10)
C26'—C21'	1.386 (7)	C26'—C25'	1.391 (8)
Cl1''—W''	2.443 (2)	Cl2''—W''	2.489 (2)
P1''—W''	2.548 (2)	P2''—W''	2.548 (2)
C1''—W''	2.033 (5)	C2''—W''	2.033 (5)
C2''—C1''	1.330 (10)	C3''—W''	2.248 (5)
C4''—W''	2.248 (5)	C4''—C3''	1.399 (13)
C5''—P1''	1.808 (6)	C6''—P1''	1.808 (6)
C7''—P1''	1.808 (6)	C8''—P2''	1.830 (5)
C9''—P2''	1.830 (5)	C10''—P2''	1.830 (5)
C11''—C1''	1.464 (6)	C12''—C11''	1.379 (7)
C13''—C12''	1.382 (8)	C14''—C13''	1.352 (10)
C15''—C14''	1.406 (10)	C16''—C11''	1.386 (7)
C16''—C15''	1.391 (8)	C21''—C2''	1.464 (6)
C22''—C21''	1.379 (7)	C23''—C22''	1.382 (8)
C24''—C23''	1.352 (10)	C25''—C24''	1.406 (10)
C26''—C21''	1.386 (7)	C26''—C25''	1.391 (8)

$[WCl_2(PhC{\equiv}CPh)_2(PMe_3)_2]$

Cl1—W	2.504 (2)	Cl2—W	2.503 (1)
P1—W	2.594 (2)	P2—W	2.581 (2)
C5—P1	1.816 (7)	C6—P1	1.819 (8)
C7—P1	1.818 (7)	C8—P2	1.796 (8)
C9—P2	1.794 (9)	C10—P2	1.800 (8)
C1—W	2.075 (4)	C2—W	2.066 (5)
C2—C1	1.296 (8)	C3—W	2.076 (7)
C4—W	2.068 (6)	C4—C3	1.295 (7)
C11—C1	1.470 (4)	C12—C11	1.371 (8)
C13—C12	1.410 (9)	C14—C13	1.359 (11)
C15—C14	1.365 (12)	C16—C11	1.386 (8)
C16—C15	1.408 (10)	C21—C2	1.471 (4)
C22—C21	1.397 (9)	C23—C22	1.397 (10)
C24—C23	1.363 (13)	C25—C24	1.356 (14)
C26—C21	1.366 (9)	C26—C25	1.413 (9)
C31—C3	1.470 (5)	C32—C31	1.395 (10)
C33—C32	1.377 (12)	C34—C33	1.367 (16)
C35—C34	1.389 (14)	C36—C31	1.388 (10)
C36—C35	1.402 (11)	C41—C4	1.470 (5)
C42—C41	1.391 (9)	C43—C42	1.382 (10)
C44—C43	1.368 (10)	C45—C44	1.377 (11)
C46—C41	1.384 (9)	C46—C45	1.390 (11)

Absorption corrections for both compounds were applied using ψ scans at χ near 90° to derive empirical absorption curves (North, Phillips & Mathews, 1968).

For dichloro(η^2-ethylene)(diphenyl-η^2-acetylene)bis(trimethylphosphine)tungsten(IV), 379 parameters were varied but the effective degrees of freedom is less since restraints were imposed so that the differences between certain chemically equivalent distances approach zero. This involved 28 degrees of freedom using 42 intermolecular restraints and 27 degrees of freedom using 33 intramolecular restraints.

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Structure of *trans*-Aquadichloro(triphenylphosphine)platinum(II)

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Abstract

The title complex (1) was obtained as yellow crystals after workup of the reaction of $[Pt_2(\mu\text{-Cl})_2Cl_2(PPh_3)_2]$ with MeLi, PhLi or MeMgBr. The molecular structure of (1) is approximately square planar with two chloride ligands in the *trans* positions. This is only the second example of a platinum(II) complex containing phosphine and water ligands in mutually *trans* positions.

Comment

Although tertiary phosphines are ubiquitous ligands in platinum chemistry, and complexes containing at least one coordinated water molecule are numerous, few complexes containing both have been structurally characterized (Ferguson, Ruhl & Hampden-Smith, 1986; Siedle, Gleason, Newmark & Pignolet, 1986; Dema, Lukehart, McPhail & McPhail, 1989; Lukehart, McPhail, McPhail & Owen, 1990; Chen, Yeh, Lee & Wang, 1991; Fallis, Anderson & Rath, 1991), and only one of these contains PR_3 and H_2O ligands in mutually *trans* positions (Fallis *et al.*, 1991). During a study of the reactions of $[Pt_2(\mu\text{-Cl})_2Cl_2(PPh_3)_2]$ with organolithium and Grignard reagents we isolated *trans*-$[PtCl_2(H_2O)(PPh_3)]$ (1) as a crystalline solid.

The molecular structure of (1) reveals that it contains two crystallographically distinct molecules within the unit cell. Each molecule is approximately square planar with a *trans* disposition of the two chloride ligands (Fig. 1). The bulky PPh_3 groups

produce P—Pt—Cl angles greater than 90°, whereas the O—Pt—Cl angles are less than 90°, in each molecule. The Cl—Pt—Cl angles are 172.0 (4) and 171.0 (4)°, respectively. One molecule exhibits virtually identical Pt—Cl bond distances [average = 2.343 (5) Å] and a P—Pt—O angle of 178.6 (4)°, whereas in the other molecule the Pt—Cl distances are 2.308 (4) and 2.359 (4) Å and the P—Pt—O angle is distorted a little further from linearity [176.1 (4)°]. The reason for this distortion is unclear. It might be expected that hydrogen bonding would exist between the chlorines of one molecule and the coordinated water molecules of another, but all the chlorine–oxygen distances exceed the sums of the van der Waals radii (3.2 Å). The Pt—O distances of 2.12 (2) and 2.13 (2) Å are equal within experimental error to those found in the $[Pt(H_2O)_2(dppe)]^{2+}$ cation, whereas the Pt—P bonds are 0.02–0.03 Å longer [2.238 (5) and 2.251 (4) Å] in this case, suggesting that these bond lengths are close to optimum and are rather insensitive to the nature of the cis ligands and the charge on the complex.

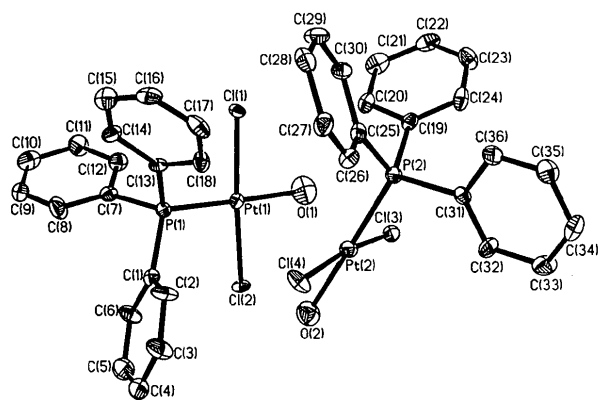Fig. 1. Projection view of the molecular structure of trans-[PtCl₂(PPh₃)(H₂O)] (1) showing the atom-labeling scheme. Thermal ellipsoids are scaled to enclose 25% probability.

Experimental

Crystal data

[PtCl₂(C₁₈H₁₅P)(H₂O)]
$M_r = 546.3$
Triclinic
$P\bar{1}$
$a = 9.355$ (2) Å
$b = 14.678$ (2) Å
$c = 14.685$ (4) Å
$\alpha = 101.82$ (2)°
$\beta = 93.01$ (2)°
$\gamma = 108.36$ (2)°
$V = 1858.1$ (7) Å³
$Z = 4$

$D_x = 1.953$ Mg m⁻³
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 12.5$–$17.5°$
$\mu = 7.925$ mm⁻¹
$T = 298$ K
Plate
$0.5 \times 0.4 \times 0.1$ mm
Yellow

Data collection

Siemens R3m/V diffractometer
θ–2θ scans
Absorption correction:
  empirical
  $T_{min} = 0.4224$, $T_{max} = 0.9597$
11 670 measured reflections
10 824 independent reflections

5786 observed reflections
  $[F > 4.0\sigma(F)]$
$R_{int} = 0.040$
$\theta_{max} = 30.0°$
$h = -4 \rightarrow 13$
$k = -20 \rightarrow 19$
$l = -20 \rightarrow 20$
3 standard reflections
  monitored every 50 reflections
  intensity variation: 5%

Refinement

Refinement on F
$R = 0.0713$
$wR = 0.0884$
$S = 1.09$
5786 reflections
415 parameters
H-atom parameters not refined

$w = 1/(\sigma^2 F + 0.0035F^2)$
$(\Delta/\sigma)_{max} = 0.044$
$\Delta\rho_{max} = 4.56$ e Å⁻³
$\Delta\rho_{min} = 2.95$ e Å⁻³
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Pt(1)	0.2035 (1)	0.1038 (1)	0.1930 (1)	0.030 (1)
Pt(2)	0.6168 (1)	0.3185 (1)	0.1321 (1)	0.036 (1)
Cl(1)	0.1427 (4)	0.2130 (3)	0.3085 (3)	0.033 (1)
Cl(2)	0.2328 (4)	−0.0106 (3)	0.0632 (3)	0.034 (1)
Cl(3)	0.4111 (5)	0.3093 (3)	0.0299 (3)	0.035 (1)
Cl(4)	0.8265 (4)	0.3066 (3)	0.2170 (4)	0.045 (2)
P(1)	0.3216 (4)	0.0561 (3)	0.3015 (3)	0.029 (1)
P(2)	0.6547 (4)	0.4770 (3)	0.2020 (3)	0.030 (1)
O(1)	0.1015 (19)	0.1589 (13)	0.0943 (12)	0.090 (9)
O(2)	0.5788 (16)	0.1679 (11)	0.0662 (12)	0.070 (7)
C(1)	0.4643 (17)	0.0040 (11)	0.2598 (11)	0.032 (6)
C(2)	0.6136 (19)	0.0609 (13)	0.2703 (15)	0.055 (8)
C(3)	0.723 (2)	0.0250 (14)	0.2325 (17)	0.062 (9)
C(4)	0.682 (3)	−0.0740 (18)	0.1836 (17)	0.064 (11)
C(5)	0.530 (3)	−0.1353 (16)	0.1767 (17)	0.067 (10)
C(6)	0.422 (2)	−0.0949 (12)	0.2147 (15)	0.050 (7)
C(7)	0.1927 (17)	−0.0346 (11)	0.3515 (12)	0.035 (6)
C(8)	0.239 (2)	−0.0920 (15)	0.4019 (17)	0.061 (10)
C(9)	0.142 (3)	−0.1525 (18)	0.4444 (17)	0.074 (12)
C(10)	−0.007 (3)	−0.1596 (14)	0.4431 (17)	0.075 (11)
C(11)	−0.061 (2)	−0.1011 (16)	0.3926 (17)	0.062 (10)
C(12)	0.0419 (19)	−0.0386 (14)	0.3466 (14)	0.047 (7)
C(13)	0.4249 (15)	0.1573 (10)	0.4001 (10)	0.028 (5)
C(14)	0.4186 (19)	0.1503 (13)	0.4921 (12)	0.041 (7)
C(15)	0.501 (2)	0.2249 (16)	0.5640 (14)	0.050 (8)
C(16)	0.599 (2)	0.3095 (15)	0.5472 (13)	0.047 (7)
C(17)	0.6069 (19)	0.3221 (12)	0.4597 (15)	0.048 (7)
C(18)	0.5162 (18)	0.2435 (11)	0.3840 (13)	0.040 (6)
C(19)	0.4786 (16)	0.5042 (12)	0.1995 (11)	0.032 (6)
C(20)	0.3532 (18)	0.4416 (14)	0.2338 (13)	0.043 (7)
C(21)	0.2192 (18)	0.4638 (16)	0.2360 (14)	0.055 (8)
C(22)	0.2087 (18)	0.5466 (16)	0.2060 (13)	0.050 (8)
C(23)	0.325 (2)	0.6039 (14)	0.1733 (16)	0.055 (9)
C(24)	0.461 (2)	0.5831 (14)	0.1688 (13)	0.046 (7)
C(25)	0.7321 (17)	0.5200 (12)	0.3225 (12)	0.035 (6)
C(26)	0.8857 (19)	0.5327 (13)	0.3496 (13)	0.041 (7)
C(27)	0.955 (2)	0.5723 (13)	0.4393 (13)	0.044 (7)
C(28)	0.870 (2)	0.6001 (13)	0.5089 (14)	0.055 (8)
C(29)	0.720 (2)	0.5910 (15)	0.4845 (13)	0.051 (9)
C(30)	0.6511 (17)	0.5522 (12)	0.3958 (12)	0.034 (6)
C(31)	0.7883 (16)	0.5659 (11)	0.1490 (11)	0.032 (5)

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 [Pt$_2$(μ-Cl)$_2$Cl$_2$(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 NH$_4$Cl solution (5 ml). The ether layer was separated and the solvent was removed to leave a yellow powder. ^{31}P{^{1}H} NMR (CDCl$_3$): δP 4.3, ^1J(Pt, P) 3740 Hz. ^{1}H NMR: δH 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 (2θ) 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 ψ-scan curves with $\chi > 83°$. 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.

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Structure of a Dichromium Octacarbonyl Complex of Cyclotetrakis[bis(diisopropyl-amino)phosphoxane]

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Abstract

The molecule, μ-2,4,6,8-tetrakis(N,N-diisopropylamino)-cyclotetraphosphoxane-1$\kappa^2 P^2, P^4$:2$\kappa^2 P^6, P^8$-bis[tetra-carbonylchromium(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 P$_4$O$_4$ heterocycle [^{i}Pr$_2$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