

C(1)—C(2)	1.502 (23)	B—C(43)	1.694 (18)
C(3)—C(4)	1.533 (22)	B—C(49)	1.715 (20)
P(1)—Pt(1)—Pt(2)	93.4 (1)	Pt(2)—P(4)—C(23)	115.4 (7)
P(2)—Pt(1)—Pt(2)	93.1 (1)	C(19)—P(4)—C(21)	102.5 (8)
C(25)—Pt(1)—Pt(2)	164.3 (4)	C(19)—P(4)—C(23)	102.2 (8)
P(1)—Pt(1)—P(2)	169.5 (1)	C(21)—P(4)—C(23)	104.1 (8)
P(1)—Pt(1)—C(25)	88.3 (3)	P(1)—C(1)—C(2)	116.3 (11)
P(2)—Pt(1)—C(25)	87.6 (3)	P(1)—C(3)—C(4)	116.2 (11)
Pt(1)—Pt(2)—P(3)	91.3 (1)	P(1)—C(5)—C(6)	115.6 (10)
Pt(1)—Pt(2)—P(4)	112.0 (1)	P(2)—C(7)—C(8)	116.7 (18)
P(3)—Pt(2)—P(4)	156.6 (2)	P(2)—C(9)—C(10)	104.1
Pt(1)—P(1)—C(1)	118.0 (5)	P(2)—C(11)—C(12)	121.2 (23)
Pt(1)—P(1)—C(3)	114.5 (5)	P(3)—C(13)—C(14)	116.7 (10)
Pt(1)—P(1)—C(5)	110.7 (5)	P(3)—C(15)—C(16)	113.7 (10)
C(1)—P(1)—C(3)	106.1 (6)	P(3)—C(17)—C(18)	113.9 (11)
C(1)—P(1)—C(5)	100.5 (6)	P(4)—C(19)—C(20)	118.1 (14)
C(3)—P(1)—C(5)	105.4 (7)	P(4)—C(21)—C(22)	113.3 (12)
Pt(1)—P(2)—C(7)	114.8 (7)	P(4)—C(23)—C(24)	112.5 (13)
Pt(1)—P(2)—C(9)	110.7	C(25)—C(26)—C(27)	124.7 (13)
Pt(1)—P(2)—C(11)	118.2 (10)	C(26)—C(27)—C(28)	118.5 (13)
C(7)—P(2)—C(9)	103.0	C(27)—C(28)—C(29)	122.4 (13)
C(7)—P(2)—C(11)	101.9 (16)	C(28)—C(29)—C(30)	117.0 (14)
C(9)—P(2)—C(11)	106.7	C(29)—C(30)—C(25)	123.5 (13)
Pt(2)—P(3)—C(13)	118.1 (5)	C(30)—C(25)—C(26)	113.8 (1)
Pt(2)—P(3)—C(15)	113.3 (5)	C(31)—B—C(37)	109.4 (10)
Pt(2)—P(3)—C(17)	112.6 (5)	C(31)—B—C(43)	109.9 (10)
C(13)—P(3)—C(15)	103.7 (7)	C(31)—B—C(49)	108.9 (10)
C(13)—P(3)—C(17)	103.0 (7)	C(37)—B—C(43)	110.1 (10)
C(15)—P(3)—C(17)	104.9 (7)	C(37)—B—C(49)	108.9 (9)
Pt(2)—P(4)—C(19)	114.7 (5)	C(43)—B—C(49)	109.5 (10)
Pt(2)—P(4)—C(21)	116.2 (6)		

The structure was solved by Patterson and Fourier techniques and refined by least-squares methods. The thermal parameters of the P(2) ethyl groups were very high and some rotational disorder around the Pt(1)—P(2) bond was suspected. Difference Fourier maps revealed only two other peaks in the vicinities of C(9) and C(10). Thus, the ethyl group C(9)—C(10) was introduced in the refinement with two orientations [C(9), C(10), C(9'), C(10')] having occupancy factors (0.66, 0.33) based on the relative heights of the Fourier peaks; the positions were not refined. The refinement was carried out with the phenyl rings of the tetraphenylborate anion treated as rigid groups and with the H atoms included at calculated positions.

All calculations were performed on a Data General Eclipse MV800011 computer, using local programs (Cerrini & Spagna, 1977). Probable hydride-ligand positions were calculated at the minima of the potential energy by the program *HYDEX* (Orpen, 1980).

The authors wish to thank Professor L. M. Venanzi for providing the crystals and for helpful discussions.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and rigid-group parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71351 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1031]

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The Faulted Structures of [WCl₂(PhC₂Ph)(CH₂=CH₂)(PMe₃)₂] and [WCl₂(PhC₂Ph)₂(PMe₃)₂]

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Abstract

The crystal structures of dichloro(diphenyl- η^2 -acetylene)(η^2 -ethylene)bis(trimethylphosphine)tungsten(IV) and dichlorobis(diphenyl- η^2 -acetylene)-bis(trimethylphosphine)tungsten(IV) are described. The crystal structures are unusual in that they contain stacking faults leading to disordered structures. This has necessitated constrained restrained least-squares refinement.

Introduction

Details of the preparation and preliminary structural details for [WCl₂(PhC₂Ph)(CH₂=CH₂)(PMe₃)₂] have been published recently (Clark, Nielson, Rae & Rickard, 1992). During the initial structure solution and attempted refinement the presence of a stacking fault, in the crystal studied, became apparent. Preliminary investigations of the structure of [WCl₂(PhC₂Ph)₂(PMe₃)₂] also indicated the presence of a stacking-fault. It was necessary to carry out a constrained restrained refinement of both structures to obtain a satisfactory convergence. Full details of the stacking-fault mechanisms and the refinement processes are presented.

The asymmetric unit of [WCl₂(PhC₂Ph)(CH₂=CH₂)(PMe₃)₂] contains three molecules. These three

molecules are related by a pseudo translation operation $x + \frac{1}{3}$, y , $z - \frac{2}{3}$ and the pseudo-equivalent atoms have been labelled W , W' and W'' , etc. to show this relationship. The structure may be regarded as being built up in sections. The molecules almost have twofold rotation symmetry and this pseudo symmetry axis aligns with the b axis of the crystal. The c glide creates one-molecule-wide strips of approximate $P2/c$ symmetry parallel to c within the $y = 0$ to $\frac{1}{2}$ region of the unit cell. Three parallel strips translated by $\pm(\frac{1}{3}, 0, -\frac{2}{3})$ create the contents for the $y = 0$ to $\frac{1}{2}$ region of the unit cell. The arrangement of W atoms is depicted in Fig. 1. The 2_1 and $\bar{1}$ symmetry operations relate these molecules to those in the $y = \frac{1}{2}$ to 1 region of the unit cell.

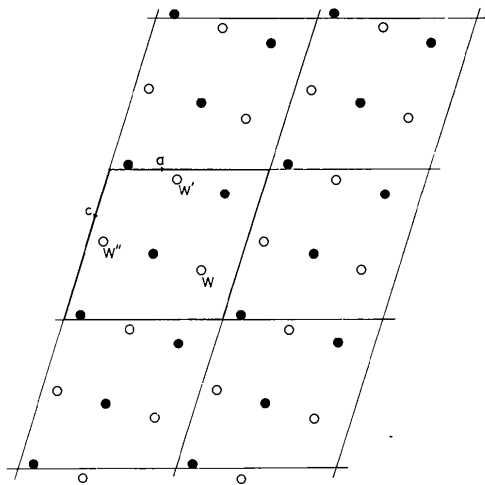


Fig. 1. A projection down the b axis for the region $y = 0 \rightarrow 0.5$ in $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$. Open circles represent independent W atoms (all at $y = 0.18$), solid circles represent W atoms after operation of the c glide (all at $y = 0.32$).

Alternatively, the structure can be described as adjacent layers of molecules (approximately in the bc plane) of approximate $P2_1/c$ symmetry. The symmetry operations of the true $P2_1/c$ spacegroup acting on the molecule (W' etc.) creates one such layer. Two c -glide related positions of the molecule (W etc.) and two c -glide related equivalent positions of the molecule (W'' etc.) make up the adjacent layers translated by $\pm(\frac{1}{3}, 0, -\frac{2}{3})$. A perfect crystal would appear to be an ordered array of these tri-layers, having a translational repeat of $\frac{1}{3}, 0, -\frac{2}{3}$ between nearest layers of adjacent tri-layers. The crystal studied would appear to have a stacking fault in that very occasionally four rather than three layers are related by the $\frac{1}{3}, 0, -\frac{2}{3}$ translation. Difference maps show two peaks consistent with such a displacement of the W atom. This is confirmed by the Patterson map.

The structure factor, $F'(\mathbf{h})$, for the faulted structure can be described in terms of the structure factor

$F(\mathbf{h})$ for the unfaulted structure as

$$F'(\mathbf{h}) = K(\mathbf{h})F(\mathbf{h}),$$

where

$$K(\mathbf{h}) = \sum_m a_m \exp(2\pi i \mathbf{h} \cdot \mathbf{d}_m)$$

and a_m is the fraction of the structure displaced by \mathbf{d}_m .

By making $\mathbf{d}_m = m(\mathbf{a}/3 - 2\mathbf{c}/5)$ exactly, only 15 non-equivalent values of m result, i.e. $m = -7$ to $+7$, and as a consequence there are only 15 different values for $K(\mathbf{h})$, i.e. K_n , where $n = -7$ to $+7$, depending on the value of $n = 5h - 6l$, modulo 15. Now,

$$\begin{aligned} K_n &= \sum_m a_m \exp(2\pi i \mathbf{h} \cdot \mathbf{d}_m) \\ &= \sum_{|m|} [(a_m + a_{-m}) \cos(2\pi mn/15) \\ &\quad + i(a_m - a_{-m}) \sin(2\pi mn/15)] \end{aligned}$$

and we see that $K_{-n} = K_n^*$ and, since only the magnitude of K_n can be refined, it follows that only eight scale-variables can be refined. If it is assumed that the K_n are real then this implies that $a_m = a_{-m}$ for every value of m .

Data were allotted scale constants according to the value of $|n|$ and these scale constants were related for refinement purposes to extra parameters $|a_m|$, where $m = 0$ to 7. Only the first three values of m were used and only the first gave a significant value, indicating that the fraction 0.178 (1) of the structure was stacking-fault related to the remaining fraction 0.822. The effect of the assumption that the scale constants are real indicates that there are 5, not 3, W atoms in a row with occupancies of 0.089, 0.911, 1.00, 0.911 and 0.089, respectively.

Because of the implicit overlap of atoms in a scattering density map, it was necessary to use constraints and restraints in the least-squares refinement which used the program *RAELS89* (Rae, 1989). The difference between pseudo translationally equivalent bond lengths (but not bond angles) was restrained to approach zero and all phenyl groups were constrained to have identical planar geometry. The PMe_3 and $\text{C}-\text{Ph}$ groups were constrained to have rigid-body thermal motion using a **TL** model (12 parameters per group) (Rae, 1975). For the PMe_3 groups, the bonds were restrained to approach equality within a group and the centres of libration were located on the W atom to which they were attached. The remaining centres of libration were the C atoms to which the phenyl groups were attached. Individual anisotropic thermal parameters were used for the remaining non-H atoms. H atoms were reinserted at chemically sensible positions after each refinement cycle and were included in rigid groups for the evaluation of anisotropic thermal parameters.

A 3% error in F in excess of counting statistic error was assumed for the evaluation of weights.

Errors were evaluated from the inverse of the matrix of the least-squares equations that included the constraints and restraints mentioned above. Accordingly, some of the tabulated errors are smaller than they would be if calculated solely from errors in the atomic coordinates. The restraints reduced differences between values of certain parameters but had no effect on average values. Thermal parameters U_{ij} are defined relative to orthonormal axes parallel to \mathbf{a} , \mathbf{b} , \mathbf{c}^* .

For $[\text{WCl}_2(\text{PhC}_2\text{Ph})_2(\text{PMe}_3)_2]$, the structure may be described as a disordering of an ordered structure in $P2_1/c$. The nature of this disorder causes the $l = 2n + 1$ data to be unobserved. A data collection of the $l = 2n + 1$ reflections confirmed that all were indeed absent. The Fourier transform of the $l = 2n$ data produces an ordered structure of apparent $P2_1/m$ symmetry. The W atom lies at approximately $y = \frac{1}{4}$ and should the tungsten be at exactly $y = \frac{1}{4}$ then it would make no contribution to the $l = 2n + 1$ data. That this $P2_1/m$ structure cannot be ordered to form spacegroup $P2_1$ is apparent from intermolecular contacts. Ordering of the two PMe_3 groups and the phenyl rings C31–C36 and C41–C46 in the only intramolecularly sensible way, implied that a c glide must be used to relate adjacent molecules and thus that $l = 2n + 1$ data were unobserved because of a stacking fault. Further consideration of intra- and intermolecular contacts revealed that the molecule could be sensibly positioned relative to the symmetry operations of spacegroup $P2_1/c$. Maximizing intramolecular contact distances selected between options for the other two phenyl rings and equivalences of distances and angles within the molecule, determined on which side of $y = \frac{1}{4}$ the W, Cl2, C1 and C2 atoms were for a single molecule. Certain atoms lie near to $y = \pm \frac{1}{4}$ causing difficulties for unconstrained refinement. As a consequence, constrained refinement was carried out, again using the program *RAELS89*. From the coordinates it is seen that no disorder should occur about the centres of inversion and 2_1 screw axes at $y = \frac{1}{2}$. However, the symmetry operations at $x = 0$ could easily be displaced by $\frac{1}{4}c$ because of the stacking fault (a $\frac{1}{2}c$ translation) without disrupting the structure very much.

The following constraints and restraints were used in the least-squares refinement. Atoms in the phenyl rings were constrained to be coplanar and each phenyl ring and the C atom attached was constrained to have a rigid-body thermal parameterization of the TLX type (Rae, 1975). The two PMe_3 groups were also constrained to have this form of thermal parameterization. H atoms were unrefined but relocated in physically sensible positions at the end of each refinement cycle. Their thermal parameters were imposed by the rigid-group parameters appropriate to the atoms to which they were

attached. The remaining W and Cl atoms were allowed anisotropic thermal parameterization, though in the initial cycle, $U_{12} = U_{13} = 0$ was imposed for the W and Cl2 atoms near the mirror plane of disorder. In an initial cycle, certain differences in bond lengths and bond angles were restrained to approach zero in order to define the y coordinates of W, Cl2, C1 and C2, but these restraints were subsequently removed when refinement behaved. Atom C44 lies almost on $y = -\frac{1}{4}$ and so the C41...C44 distance had to be restrained to approach the C11...C14, C21...C24 and C31...C34 distances. Weak restraints were also used to make the C1–C2 distances match the C3–C4 distance and to match the C1–C11, C2–C21, C3–C31 and C4–C41 distances. A 2% error in F in excess of counting statistic error was assumed for the evaluation of weights. Reflection data for $l = 2n$ is the Fourier transform of the apparent electron density $[\rho(\mathbf{r}) + \rho(\mathbf{r} + \frac{1}{2}\mathbf{c})]/2$ and reflection data for $l = 2n + 1$ is the Fourier transform of the apparent electron density $[\rho(\mathbf{r}) - \rho(\mathbf{r} + \frac{1}{2}\mathbf{c})]/2$. Consequently, when an atom is close to the glide planes at $y = \pm \frac{1}{4}$, the atom and its glide-related equivalent make very little contribution to data with $l = 2n + 1$, making y for this atom (and to a lesser extent the correlated thermal parameters U_{22} , U_{12} and U_{23}) poorly determined. It was necessary to decide which side of the glide plane such atoms are on since unconstrained refinement will not shift the atoms from one side of the glide plane to the other no matter on which side of the glide plane the atom is initially located. This is because the $l = 2n + 1$ data are absent. Errors were evaluated from the inverse of the least-squares matrix that included the effects of the constraints used to impose such decisions. This makes the errors in poorly determined parameters

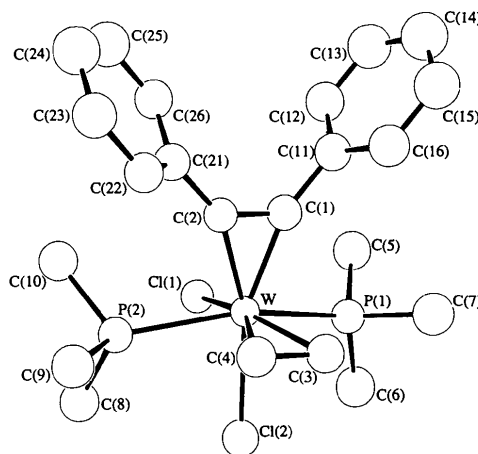


Fig. 2. Perspective view of one independent molecule of $[\text{WCl}_2-(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$ showing the numbering scheme. Each of the three independent molecules has the same numbering.

appear to be acceptable but assumes the appropriateness of the constraint. Of the hard-to-refine parameters only the y coordinate of the C1 atom was not involved in some constraint. Refinement with bond length and angle constraints applied to other atoms created sufficient certainty from comparative geometry to decide that its value was greater than 0.25.

The molecular geometry and numbering for $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$ are shown in Fig. 2; the other two molecules use the same numbering. The structure shows a distorted octahedral geometry about tungsten with *cis*-chloro and *trans*-phosphine ligands. The diphenylacetylene and ethylene ligands are mutually *cis*. Interatomic distances are within the expected range. The metal-carbon distances are consistent with the proposed formulation as a $d^2\text{W}^{\text{IV}}$ complex.

The molecular geometry for $[\text{WCl}_2(\text{PhC}_2\text{Ph})_2(\text{PMe}_3)_2]$ is shown in Fig. 3. The PMe_3 groups are *trans* and the diphenylacetylene groups are in *cis* positions. Interatomic distances are within the expected range.

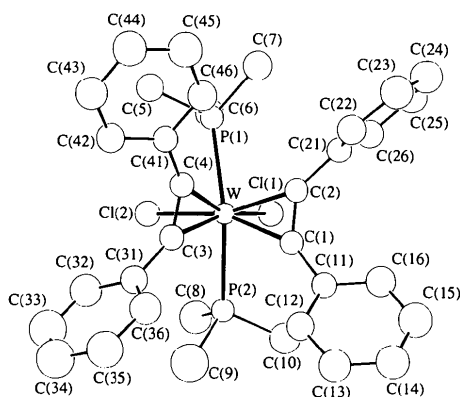


Fig. 3. Perspective view of $[\text{WCl}_2(\text{PhC}_2\text{Ph})_2(\text{PMe}_3)_2]$ showing the numbering.

Experimental

$[\text{WCl}_2(\text{PhC}\equiv\text{CPh})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$

Crystal data

$[\text{WCl}_2(\text{C}_3\text{H}_9\text{P})_2(\text{C}_{14}\text{H}_{10})\text{-}(\text{C}_2\text{H}_4)]$

$M_r = 613.2$

Monoclinic

$P2_1/c$

$a = 21.143 (11) \text{ \AA}$

$b = 17.911 (2) \text{ \AA}$

$c = 20.415 (3) \text{ \AA}$

$\beta = 107.83 (2)^\circ$

$V = 7359.5 (8) \text{ \AA}^3$

$Z = 12$

$D_x = 1.660 \text{ Mg m}^{-3}$

$D_m = 1.64 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 11.5\text{--}13.4^\circ$

$\mu = 5.33 \text{ mm}^{-1}$

$T = 295 (1) \text{ K}$

Needle

$1.09 \times 0.20 \times 0.16 \text{ mm}$

Yellow

Crystal source: crystallized from toluene

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical

$T_{\min} = 0.65$, $T_{\max} = 0.99$

12 266 measured reflections

9917 independent reflections

5958 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 25^\circ$

$h = -26 \rightarrow 26$

$k = 0 \rightarrow 21$

$l = 0 \rightarrow 26$

3 standard reflections

frequency: 60 min

intensity variation: <3%

Refinement

Refinement on F

$R = 0.048$

$wR = 0.061$

$S = 1.35$

5958 reflections

379 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0009F^2]$

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

$[\text{WCl}_2(\text{PhC}\equiv\text{CPh})_2(\text{PMe}_3)_2]$

Crystal data

$[\text{WCl}_2(\text{C}_3\text{H}_9\text{P})_2(\text{C}_{14}\text{H}_{10})_2]$

$M_r = 763.38$

Monoclinic

$P2_1/c$

$a = 12.208 (2) \text{ \AA}$

$b = 12.270 (2) \text{ \AA}$

$c = 21.498 (6) \text{ \AA}$

$\beta = 94.81 (2)^\circ$

$V = 3208.9 (1.0) \text{ \AA}^3$

$Z = 4$

$D_x = 1.58 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, Zr filter

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 14.4\text{--}17.5^\circ$

$\mu = 4.09 \text{ mm}^{-1}$

$T = 295 (1) \text{ K}$

Tablets

$0.17 \times 0.16 \times 0.10 \text{ mm}$

Lemon

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical

$T_{\min} = 0.906$, $T_{\max} =$

0.998

6587 measured reflections

6310 independent reflections

4410 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 33^\circ$

$h = 0 \rightarrow 18$

$k = 0 \rightarrow 18$

$l = -32 \rightarrow 32$

3 standard reflections

frequency: 60 min

intensity variation: <3%

Refinement

Refinement on F

$R = 0.028$

$wR = 0.033$

$S = 1.04$

4410 reflections

210 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0004F^2]$

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$				
	x	y	z	U_{eq}
[WCl₂(PhC≡CPh)(CH₂=CH₂)(PMe₃)₂]				
W	0.76564 (4)	0.18597 (4)	0.66951 (4)	0.035
Cl1	0.6455 (1)	0.1663 (2)	0.6305 (2)	0.049
Cl2	0.7743 (3)	0.0484 (1)	0.6870 (3)	0.055
P1	0.7486 (3)	0.1501 (3)	0.5445 (1)	0.049
P2	0.7394 (2)	0.1777 (3)	0.7831 (1)	0.045
C1	0.7716 (7)	0.2882 (4)	0.6286 (6)	0.047
C2	0.7703 (7)	0.2966 (3)	0.6929 (5)	0.042
C3	0.8720 (3)	0.1691 (9)	0.6731 (8)	0.051
C4	0.8705 (4)	0.1805 (10)	0.7404 (7)	0.054
C5	0.6832 (8)	0.2007 (10)	0.4823 (8)	0.066
C6	0.7270 (12)	0.0543 (5)	0.5196 (10)	0.070
C7	0.8149 (8)	0.1614 (12)	0.5066 (10)	0.072
C8	0.6965 (9)	0.0929 (7)	0.7963 (10)	0.061
C9	0.8037 (7)	0.1802 (12)	0.8668 (6)	0.061
C10	0.6815 (8)	0.2478 (8)	0.7961 (10)	0.059
C11	0.7779 (5)	0.3463 (3)	0.5805 (4)	0.051
C12	0.7239 (6)	0.3871 (6)	0.5421 (6)	0.060
C13	0.7317 (8)	0.4430 (7)	0.4986 (6)	0.076
C14	0.7923 (9)	0.4587 (6)	0.4928 (6)	0.084
C15	0.8481 (7)	0.4180 (8)	0.5314 (7)	0.076
C16	0.8404 (6)	0.3617 (6)	0.5753 (6)	0.060
C21	0.7726 (5)	0.3598 (3)	0.7391 (4)	0.046
C22	0.8224 (6)	0.3672 (6)	0.8008 (5)	0.049
C23	0.8243 (7)	0.4286 (7)	0.8424 (5)	0.060
C24	0.7773 (8)	0.4823 (6)	0.8233 (6)	0.070
C25	0.7259 (7)	0.4761 (6)	0.7607 (7)	0.068
C26	0.7240 (6)	0.4143 (5)	0.7188 (6)	0.054
W'	0.4324 (1)	0.1800	0.0689	0.034
Cl1'	0.3125 (1)	0.1594 (3)	0.0343 (2)	0.050
Cl2'	0.4410 (3)	0.0421 (1)	0.0840 (3)	0.056
P1'	0.4128 (3)	0.1480 (3)	-0.0574 (1)	0.051
P2'	0.4093 (3)	0.1696 (2)	0.1840 (1)	0.044
C1'	0.4345 (8)	0.2832 (4)	0.0283 (5)	0.040
C2'	0.4379 (7)	0.2901 (3)	0.0941 (5)	0.037
C3'	0.5375 (4)	0.1638 (10)	0.0676 (9)	0.051
C4'	0.5383 (4)	0.1695 (10)	0.1362 (8)	0.054
C5'	0.3422 (9)	0.1932 (13)	-0.1176 (9)	0.090
C6'	0.3969 (14)	0.0509 (6)	-0.0806 (12)	0.097
C7'	0.4785 (8)	0.1721 (13)	-0.0930 (11)	0.084
C8'	0.3684 (9)	0.0836 (7)	0.1977 (10)	0.059
C9'	0.4760 (8)	0.1767 (11)	0.2658 (6)	0.066
C10'	0.3527 (9)	0.2406 (8)	0.1981 (11)	0.063
C11'	0.4369 (5)	0.3440 (3)	-0.0189 (4)	0.043
C12'	0.3800 (6)	0.3784 (6)	-0.0595 (7)	0.064
C13'	0.3839 (8)	0.4370 (7)	-0.1021 (7)	0.079
C14'	0.4435 (10)	0.4616 (6)	-0.1048 (6)	0.073
C15'	0.5022 (8)	0.4276 (8)	-0.0639 (7)	0.077
C16'	0.4984 (6)	0.3685 (7)	-0.0210 (6)	0.062
C21'	0.4425 (5)	0.3522 (3)	0.1420 (4)	0.042
C22'	0.4948 (6)	0.3589 (6)	0.2018 (6)	0.052
C23'	0.4988 (8)	0.4193 (8)	0.2450 (6)	0.070
C24'	0.4515 (9)	0.4728 (6)	0.2295 (7)	0.080
C25'	0.3976 (8)	0.4674 (6)	0.1688 (8)	0.074
C26'	0.3935 (6)	0.4066 (5)	0.1252 (6)	0.054
W''	0.1005	0.1853	0.4768	0.032
Cl1''	-0.0198 (1)	0.1680 (3)	0.4340 (3)	0.073
Cl2''	0.1095 (3)	0.0472 (1)	0.4899 (3)	0.065
P1''	0.0920 (2)	0.1544 (2)	0.3526 (1)	0.044
P2''	0.0716 (2)	0.1698 (3)	0.5885 (1)	0.045
C1''	0.1033 (6)	0.2900 (3)	0.4394 (5)	0.031
C2''	0.1058 (7)	0.2945 (3)	0.5052 (5)	0.045
C3''	0.2074 (3)	0.1707 (9)	0.4817 (8)	0.051
C4''	0.2043 (4)	0.1739 (10)	0.5491 (7)	0.054
C5''	0.0219 (9)	0.1927 (13)	0.2864 (8)	0.084
C6''	0.0805 (12)	0.0569 (5)	0.3293 (10)	0.077
C7''	0.1578 (8)	0.1814 (13)	0.3179 (10)	0.079
C8''	0.0322 (11)	0.0812 (7)	0.5979 (11)	0.074
C9''	0.1376 (8)	0.1749 (13)	0.6708 (6)	0.078
C10''	0.0099 (9)	0.2363 (10)	0.5995 (12)	0.075
C11''	0.1011 (5)	0.3491 (3)	0.3893 (4)	0.036
[WCl₂(PhC≡CPh)₂(PMe₃)₂]				
W	0.22108 (2)	0.24471 (7)	0.10349 (1)	0.030
Cl1	0.2020 (2)	0.4288 (1)	0.1517 (1)	0.048
Cl2	0.0265 (1)	0.2726 (1)	0.0599 (1)	0.046
P1	0.1003 (1)	0.1985 (2)	0.1936 (1)	0.041
P2	0.2485 (2)	0.3805 (2)	0.0144 (1)	0.038
C5	0.0029 (6)	0.0887 (7)	0.1761 (3)	0.052
C6	0.0073 (7)	0.3067 (7)	0.2132 (4)	0.064
C7	0.1605 (7)	0.1625 (8)	0.2711 (3)	0.061
C8	0.1363 (7)	0.4725 (8)	-0.0045 (5)	0.080
C9	0.2713 (13)	0.3347 (8)	-0.0627 (4)	0.097
C10	0.3616 (7)	0.4732 (7)	0.0305 (4)	0.068
C1	0.3911 (3)	0.2580 (23)	0.1132 (2)	0.036
C2	0.3576 (4)	0.2288 (5)	0.1664 (2)	0.037
C3	0.2224 (7)	0.1220 (6)	0.0370 (3)	0.040
C4	0.2110 (5)	0.0778 (4)	0.0908 (3)	0.037
C11	0.5006 (3)	0.2664 (5)	0.0899 (2)	0.039
C12	0.5218 (5)	0.2253 (4)	0.0329 (3)	0.047
C13	0.6300 (6)	0.2256 (5)	0.0145 (4)	0.059
C14	0.7136 (5)	0.2667 (6)	0.0533 (4)	0.065
C15	0.6931 (6)	0.3078 (6)	0.1101 (4)	0.069
C16	0.5857 (5)	0.3084 (5)	0.1295 (3)	0.055
C21	0.4118 (4)	0.2079 (5)	0.2290 (2)	0.040
C22	0.4728 (5)	0.1126 (6)	0.2409 (3)	0.051
C23	0.5295 (6)	0.0967 (7)	0.2993 (4)	0.065
C24	0.5263 (6)	0.1731 (7)	0.3452 (4)	0.065
C25	0.4671 (5)	0.2655 (9)	0.3336 (3)	0.061
C26	0.4087 (5)	0.2843 (5)	0.2750 (3)	0.050
C31	0.2211 (6)	0.0857 (5)	-0.0282 (3)	0.045
C32	0.1240 (7)	0.0962 (6)	-0.0668 (4)	0.063
C33	0.1193 (10)	0.0594 (7)	-0.1275 (4)	0.085
C34	0.2093 (10)	0.0125 (7)	-0.1503 (4)	0.085
C35	0.3070 (10)	0.0010 (6)	-0.1128 (4)	0.075
C36	0.3129 (7)	0.0382 (5)	-0.0510 (4)	0.057
C41	0.2031 (4)	-0.0343 (4)	0.1142 (3)	0.039
C42	0.1496 (5)	-0.1138 (6)	0.0768 (3)	0.047
C43	0.1428 (5)	-0.2203 (5)	0.0971 (4)	0.056
C44	0.1895 (5)	-0.2485 (5)	0.1549 (3)	0.062
C45	0.2429 (6)	-0.1713 (7)	0.1928 (4)	0.065
C46	0.2498 (5)	-0.0642 (6)	0.1725 (3)	0.051

Table 2. Bond lengths (\AA) for the title compounds

[WCl₂(PhC≡CPh)(CH₂=CH₂)(PMe₃)₂]			
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)
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)
C11''—W''	2.443 (2)	C12''—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)

[WCl₂(PhC≡CPh)₂(PMe₃)₂]

C11—W	2.504 (2)	C12—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.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles, for both structures, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71363 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1028]

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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 [Pt₂(μ -Cl)₂Cl₂-(PPh₃)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 PR₃ and H₂O ligands in mutually *trans* positions (Fallis *et al.*, 1991). During a study of the reactions of [Pt₂(μ -Cl)₂Cl₂(PPh₃)₂] with organolithium and Grignard reagents we isolated *trans*-[PtCl₂(H₂O)(PPh₃)] (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 PPh₃ groups