

***cis*-Dichlorobis(triethylarsine)-  
platinum(II) and *cis*-dichlorobis-  
(triethylphosphine)platinum(II)**Stefanus Otto<sup>a\*</sup> and Alfred Johannes Muller<sup>b</sup><sup>a</sup>Inorganic Chemistry 1, Centre for Chemistry and Chemical Engineering, University of Lund, PO Box 124, SE-221 00 Lund, Sweden, and <sup>b</sup>Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa  
Correspondence e-mail: stefanus.otto@inorg.lu.se

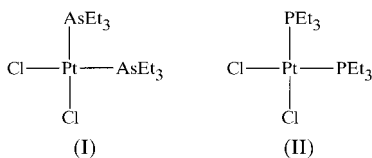
Received 3 September 2001

Accepted 28 September 2001

The crystal structure of *cis*-[PtCl<sub>2</sub>(C<sub>6</sub>H<sub>15</sub>As)<sub>2</sub>], (I), is isostructural with a previously reported structure of *cis*-[PtCl<sub>2</sub>(C<sub>6</sub>H<sub>15</sub>P)<sub>2</sub>], (II). A new polymorph of (II) is also reported here. Selected geometrical parameters in the arsine complex are Pt—Cl 2.3412 (12) and 2.3498 (13), Pt—As 2.3563 (6) and 2.3630 (6) Å, Cl—Pt—Cl 88.74 (5), As—Pt—As 97.85 (2), and Cl—Pt—As 171.37 (4) and 177.45 (4)°. Corresponding parameters in the phosphine complex are Pt—Cl 2.364 (2) and 2.374 (2), Pt—P 2.264 (2) and 2.262 (2) Å, Cl—Pt—Cl 85.66 (9), P—Pt—P 98.39 (7), and Cl—Pt—P 170.26 (7) and 176.82 (8)°.

**Comment**

Although dihalo-bisphosphine complexes of platinum(II) are well documented in the literature, very few crystallographic studies are reported for the analogous arsine complexes. Some complexes with a *trans* geometry have been documented (Otto & Roodt, 1997; Johansson *et al.*, 2000), but only one complex of this nature, with a *cis* geometry, *viz.* *cis*-[PtCl<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>] (Otto & Johansson, 2001), has appeared in the literature. Crystallographic studies on these complexes are important for understanding the coordination mode of the ligands involved, especially to establish their respective *trans* influences.



As part of our systematic investigation of these systems, crystals of *cis*-dichlorobis(triethylarsine)platinum(II), (I), were obtained and the structure solved. We have also redetermined the structure of the analogous *cis*-dichlorobis(triethylphosphine)platinum(II) complex, (II), for which only a preliminary report was found (Caldwell *et al.*, 1977) and for

which no geometrical parameters were available. Compound (I) is isostructural with the polymorph reported by Caldwell *et al.* (1977), while (II) was found to be a new polymorph of the previously reported complex.

Both complexes have a distorted square-planar geometry, with the neutral ligands in a *cis* configuration, see Figs. 1 and 2. They crystallize on general positions in the monoclinic space groups *P2<sub>1</sub>/n* and *Cc* for (I) and (II), respectively, resulting in the chemically equivalent ligands being crystallographically different.

In (I), the Pt—As1 and Pt—As2 bond distances are significantly different (see Table 1), while Pt—Cl1 and Pt—Cl2 are more similar. The As1—Pt—Cl1 angle differs by 6.08 (4)° from the As2—Pt—Cl2 angle, while the As2—Pt—Cl1 and Cl1—Pt—Cl2 angles are close to 90°. The As1—Pt—As2 and As1—Pt—Cl2 angles of 97.85 (2) and 83.18 (4)° suggest that As1 is sterically repelled from As2 to compensate for the crowding between these two large ligands. These angles can be understood by studying the Cl—Pt—As—C torsion angles describing the orientation of the arsine ligands around the Pt—As bonds. Each As ligand has one substituent, C111 and C211, almost in the coordination plane, with Cl2—Pt—As1—C111 and Cl1—Pt—As2—C211 torsion angles of 177.4 (2) and -7.68 (19)°, respectively. In the case of As2, C211 points towards Cl1, while on As1, C111 points towards As2. The compression in the As1—Pt—Cl1 angle is thus facilitated by the resulting staggered conformation of As1 with respect to Cl2, as illustrated by the Cl2—Pt—As—C121 and Cl2—Pt—As—C131 torsion angles of -60.69 (17) and 52.0 (2)°, respectively. A consequence of this effect is that As2 is orientated with its remaining two substituents in a staggered conformation with respect to As1, as indicated by the As1—Pt—As2—C221 and As1—Pt—As2—C231 torsion angles of -68.20 (17) and 53.83 (16)°, respectively.

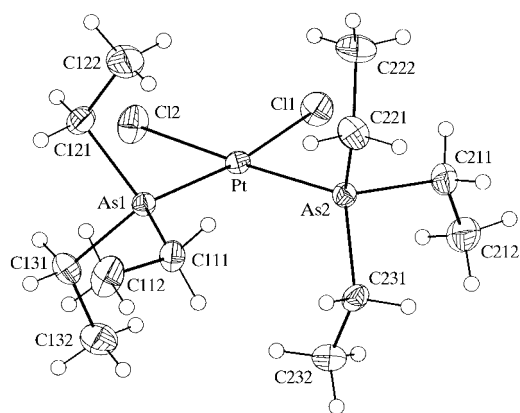
In (II), both the Pt—Cl1 and Pt—Cl2 distances, and the Pt—P1 and Pt—P2 distances (see Table 2) are quite similar for the respective ligands. Due to the shorter Pt—P bond distance, compared with Pt—As, a larger repulsion between the PEt<sub>3</sub> ligands results in a P1—Pt—P2 angle of 98.39 (7)°. The P2—Pt—Cl1 angle is close to that obtained for (I), while the Cl1—Pt—Cl2 and Cl2—Pt—P1 angles are compressed to 85.66 (9) and 84.63 (9)°, respectively. The orientation of P1 was very similar to that found for As1 in (I), with a Cl2—Pt—P1—C111 torsion angle of 176.7 (4)°, while the Cl1—Pt—P2—C211 torsion angle differed by more than 7° from the corresponding angle in (I) with a value of -0.1 (4)°. A staggered conformation was observed for P1 with respect to Cl2 [similar to As1 in (I)], as shown by the Cl2—Pt—P1—C121 and Cl2—Pt—P1—C131 torsion angles of -60.5 (4) and 53.8 (3)°, respectively. A similar behaviour was exhibited by P2 with respect to P1, with P1—Pt—P2—C221 and P1—Pt—P2—C232 torsion angles of -61.8 (4) and 61.5 (4)°, respectively.

The expected elongation of *ca* 0.1 Å is observed for the As—C bond distances [average 1.949 (5) Å] compared with the P—C distances [average 1.827 (9) Å], in correspondence with the increase in the atomic radii. Furthermore, the average C—As—C angle of 102.6 (2)° is slightly smaller than the

average C—P—C angle of 104.0 (5)°, in accordance with the normal geometry for these ligands.

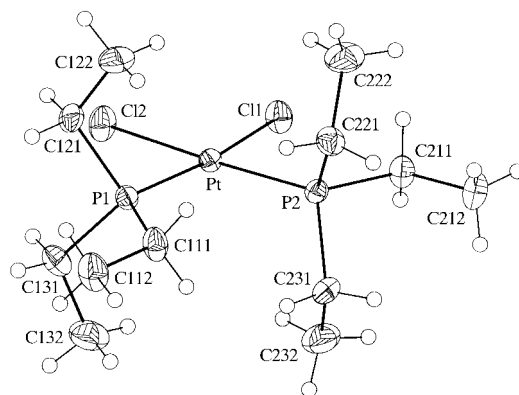
The ethyl substituents have different orientations in the solid state (see Figs. 1 and 2), resulting in different effective steric demands. A modified calculation of the Tolman cone angles (Tolman, 1977) was used to calculate the effective cone angles for the ligands (Otto *et al.*, 2000). The effective cone angle is based on Tolman's model but the crystallographically obtained geometry is used without any modifications. A van der Waals radius of 1.2 Å for hydrogen and calculated C—H bond distances of 0.97 Å for CH<sub>2</sub> and 0.96 Å for CH<sub>3</sub> were used. In (I), the effective cone angles for As1 and As2 were calculated as 144 and 155°, while in (II), values of 146 and 147° were obtained for P1 and P2, respectively. Values for the effective cone angles, obtained in this way, can thus give a qualitative indication of the similarity/difference between the packing modes of ligands in different crystallographic environments. The larger value for As2, compared with the other three ligands, can be attributed to the orientation of C211 and C212, which are almost perpendicular to the coordination plane. In the other ligands, this group is bent to point away from the coordination plane, resulting in the smaller and comparable cone-angle values. The accepted value for the Tolman cone angle for PEt<sub>3</sub> is 132°, but this value was calculated using models in which the steric demand for all the substituents was minimized according to the original definition (Tolman, 1977). This, however, is not the case when calculating the effective cone angle, resulting in the larger values obtained for the latter.

In Table 3, the title compounds are compared with related complexes, illustrating the effect of phosphine, arsine and stibine ligands on the geometrical parameters. The increase observed in the Pt—L bond distances when going from P to As to Sb donor ligands is consistent with the increase in the atomic radii of these elements. In the PEt<sub>3</sub> and AsEt<sub>3</sub> structures, an elongation is observed in the Pt—Cl bond distances *trans* to the phosphine ligand compared with those *trans* to the arsine. This is in agreement with the established *trans* influence series for these ligands (Otto & Johansson, 2001). In the Pt—Cl bond distances *trans* to the triphenyl-substituted



**Figure 1**  
The structure of *cis*-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. The H atoms are of arbitrary size.

ligands, a clear tendency is, however, not observed, with the bond distances affected to the same extent by packing forces (within the same molecule) and by the *trans* influences of the respective L ligands.



**Figure 2**  
The structure of *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. The H atoms are of arbitrary size.

## Experimental

For the preparation of *cis*-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>], (I), AsEt<sub>3</sub> (0.043 ml, 0.30 mmol) was added to a nitrogen-flushed solution of *cis/trans*-[PtCl<sub>2</sub>(SMEt<sub>2</sub>)<sub>2</sub>] (50 mg, 0.13 mmol) in dry dichloromethane. After 1 h, the solvent was removed while maintaining a positive nitrogen pressure. The crude product was washed with ether and was recrystallized from dichloromethane. *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>], (II), was prepared according to the literature procedure of Parshall (1970) and was recrystallized from a mixture of acetone and dichloromethane.

## Compound (I)

### Crystal data

[PtCl<sub>2</sub>(C<sub>6</sub>H<sub>15</sub>As)<sub>2</sub>]  
M<sub>r</sub> = 590.19  
Monoclinic, P2<sub>1</sub>/n  
a = 8.0566 (16) Å  
b = 17.754 (4) Å  
c = 13.083 (3) Å  
β = 94.20 (3)°  
V = 1866.4 (6) Å<sup>3</sup>  
Z = 4

D<sub>x</sub> = 2.100 Mg m<sup>-3</sup>  
Mo Kα radiation  
Cell parameters from 6559 reflections  
θ = 2.3–30.9°  
μ = 11.31 mm<sup>-1</sup>  
T = 293 (2) K  
Rectangular, colourless  
0.12 × 0.11 × 0.04 mm

### Data collection

Siemens SMART CCD diffractometer  
ω scans  
Absorption correction: empirical (SADABS; Sheldrick, 1996)  
T<sub>min</sub> = 0.328, T<sub>max</sub> = 0.651  
19 330 measured reflections  
5905 independent reflections  
4285 reflections with I > 2σ(I)

R<sub>int</sub> = 0.071  
θ<sub>max</sub> = 31.9°  
h = -11 → 11  
k = -25 → 24  
l = -19 → 17  
First 50 frames repeated after data collection  
intensity decay: none

### Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.034  
wR(F<sup>2</sup>) = 0.072  
S = 0.93  
5905 reflections  
162 parameters

H-atom parameters constrained  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0281P)<sup>2</sup>]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> = 0.002  
Δρ<sub>max</sub> = 1.14 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -2.05 e Å<sup>-3</sup>

**Table 1**  
Selected geometric parameters (Å, °) for (I).

Pt—Cl1	2.3412 (12)	As1—C131	1.946 (4)
Pt—Cl2	2.3498 (13)	As1—C121	1.952 (5)
Pt—As1	2.3563 (6)	As2—C221	1.949 (5)
Pt—As2	2.3630 (6)	As2—C231	1.950 (5)
As1—C111	1.942 (5)	As2—C211	1.957 (5)
Cl1—Pt—Cl2	88.74 (5)	C111—As1—C131	104.6 (2)
As1—Pt—As2	97.85 (2)	C111—As1—C121	104.3 (2)
As1—Pt—Cl1	171.37 (4)	C131—As1—C121	100.5 (2)
As2—Pt—Cl2	177.45 (4)	C221—As2—C231	103.9 (2)
As1—Pt—Cl2	83.18 (4)	C221—As2—C211	101.2 (2)
As2—Pt—Cl1	90.11 (4)	C231—As2—C211	100.8 (2)
Cl2—Pt—As1—C111	177.4 (2)	As1—Pt—As2—C211	175.68 (19)
Cl2—Pt—As1—C121	−60.69 (17)	As1—Pt—As2—C221	−68.20 (17)
Cl2—Pt—As1—C131	52.0 (2)	As1—Pt—As2—C231	53.83 (16)
Cl1—Pt—As2—C211	−7.68 (19)	As2—Pt—As1—C111	−4.96 (19)
Cl1—Pt—As2—C221	108.44 (17)	As2—Pt—As1—C121	116.96 (17)
Cl1—Pt—As2—C231	−129.54 (17)	As2—Pt—As1—C131	−130.3 (2)

## Compound (II)

### Crystal data

[PtCl<sub>2</sub>(C<sub>6</sub>H<sub>15</sub>P)<sub>2</sub>]  
*M<sub>r</sub>* = 502.29  
 Monoclinic, *Cc*  
*a* = 19.773 (4) Å  
*b* = 7.5310 (15) Å  
*c* = 13.726 (3) Å  
 $\beta$  = 117.31 (3)°  
*V* = 1816.1 (6) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.837 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6951 reflections  
 $\theta$  = 2.3–31.7°  
 $\mu$  = 8.18 mm<sup>−1</sup>  
*T* = 293 (2) K  
 Rectangular, colourless  
 0.35 × 0.30 × 0.18 mm

### Data collection

Siemens SMART CCD diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.092, *T<sub>max</sub>* = 0.229  
 9281 measured reflections  
 4284 independent reflections  
 4059 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.053  
 $\theta_{\text{max}}$  = 32.0°  
*h* = −28 → 22  
*k* = −10 → 11  
*l* = −19 → 17  
 First 50 frames repeated after data collection  
 intensity decay: none

**Table 2**  
Selected geometric parameters (Å, °) for (II).

Pt—P1	2.264 (2)	P1—C131	1.827 (9)
Pt—P2	2.262 (2)	P1—C121	1.827 (7)
Pt—Cl1	2.364 (2)	P2—C211	1.821 (9)
Pt—Cl2	2.374 (2)	P2—C231	1.829 (9)
P1—C111	1.824 (8)	P2—C221	1.831 (9)
Cl1—Pt—Cl2	85.66 (9)	C111—P1—C131	103.7 (4)
P1—Pt—P2	98.39 (7)	C111—P1—C121	104.0 (5)
P1—Pt—Cl1	170.26 (7)	C131—P1—C121	103.7 (5)
P2—Pt—Cl2	176.82 (8)	C211—P2—C231	102.3 (4)
P1—Pt—Cl2	84.63 (9)	C211—P2—C221	103.6 (5)
P2—Pt—Cl1	91.33 (7)	C231—P2—C221	106.5 (5)
Cl2—Pt—P1—C111	176.7 (4)	P1—Pt—P2—C211	179.3 (3)
Cl2—Pt—P1—C121	−60.5 (4)	P1—Pt—P2—C221	−61.8 (4)
Cl2—Pt—P1—C131	53.8 (3)	P1—Pt—P2—C231	61.5 (4)
Cl1—Pt—P2—C211	−0.1 (4)	P2—Pt—P1—C111	−4.3 (4)
Cl1—Pt—P2—C221	118.8 (4)	P2—Pt—P1—C121	118.5 (4)
Cl1—Pt—P2—C231	−117.9 (4)	P2—Pt—P1—C131	−127.2 (3)

**Table 3**  
Comparative bond distances (Å) for *cis*-[PtCl<sub>2</sub>(*L*)<sub>2</sub>] complexes.

<i>L</i>	Pt— <i>L</i> 1	Pt— <i>L</i> 2	Pt—Cl1	Pt—Cl2	Note
PEt <sub>3</sub>	2.264 (2)	2.262 (2)	2.364 (2)	2.374 (2)	(i)
AsEt <sub>3</sub>	2.3563 (6)	2.3630 (6)	2.3412 (12)	2.3498 (13)	(ii)
PPh <sub>3</sub>	2.267 (3)	2.244 (3)	2.329 (3)	2.360 (3)	(iii)
AsPh <sub>3</sub>	2.3599 (9)	2.3770 (9)	2.3515 (18)	2.3251 (18)	(iv)
SbPh <sub>3</sub>	2.491 (1)	2.510 (1)	2.354 (3)	2.326 (4)	(v)

Notes: (i) this work; (ii) this work; (iii) Anderson *et al.* (1982); (iv) Otto & Johansson (2001); (v) Wendt *et al.* (1998).

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.034  
*wR*(*F*<sup>2</sup>) = 0.092  
*S* = 1.02  
 4284 reflections  
 162 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0648P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.98 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -2.06 \text{ e \AA}^{-3}$   
 Absolute structure: Flack (1983)  
 Flack parameter = 0.035 (10), 1109 Friedel pairs

For both complexes, the H atoms were refined as riding, with C—H distances of 0.96 or 0.97 Å. Both the minimum and maximum residual electron densities for both structures are located within 1.5 Å of the Pt atom.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999).

Financial assistance from the South African NRF, the Research Fund of the University of the Free State and the Swedish International Development Cooperation Agency is gratefully acknowledged. The Chemical Centre of the University of Lund, Sweden, is thanked for the use of their diffractometer for the data collection. Professors A. Roodt and Å. Oskarsson are thanked for useful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1505). Services for accessing these data are described at the back of the journal.

## References

- Anderson, G. K., Clark, H. C., Davies, J. A., Ferguson, G. & Parvez, M. (1982). *J. Crystallogr. Spectrosc. Res.* **12**, 449–458.  
 Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.  
 Caldwell, A. N., Manojlovic-Muir, L., Muir, K. W. & Solomun, T. (1977). *Eur. Crystallogr. Meet.*, Abstract PL.57, p. 210.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Johansson, M. H., Otto, S., Roodt, A. & Oskarsson, Å. (2000). *Acta Cryst.* **B56**, 226–233.  
 Otto, S. & Johansson, M. H. (2001). *Inorg. Chim. Acta*. Accepted.  
 Otto, S. & Roodt, A. (1997). *Acta Cryst.* **C53**, 280–282.  
 Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.  
 Parshall, G. W. (1970). *Inorg. Synth.* **12**, 26–28.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.  
 Wendt, O. F., Scodinu, A. & Elding, L. I. (1998). *Inorg. Chim. Acta*, **277**, 237–241.