

metal-organic compounds

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cis-Diphenylbis(1,3,5-triaza-7-phosphaadamantane- κP)-platinum(II)

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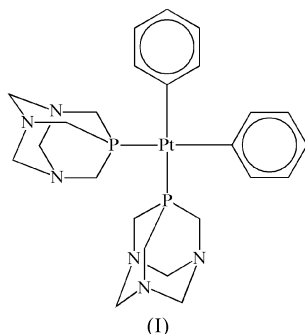
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The structure of the title compound, $[\text{Pt}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_{12}\text{N}_3\text{P})_2]$ or $[\text{Pt}(\text{Ph})_2(\text{PTA})_2]$ (where Ph is phenyl and PTA is 1,3,5-triaza-7-phosphaadamantane), is discussed. Selected geometric parameters are: Pt–P = 2.2888 (16) and 2.2944 (17) Å, Pt–C = 2.052 (5) and 2.064 (6) Å, C–Pt–C = 84.6 (2)° and P–Pt–P = 99.28 (6)°. The effective cone angle for the PTA ligands was calculated as 113°.

Comment

The 1,3,5-triaza-7-phosphaadamantane ligand (PTA) has attracted much attention due to its unique characteristic of enabling the preparation of water-soluble complexes without the complication of introducing a charged species into the complex. Numerous PTA complexes exhibiting catalytic activity have been reported (Darensbourg *et al.*, 1997, 1999; Alyea *et al.*, 1993; Joó *et al.*, 1996).



We report here the structure of the title *cis*-diphenylbis(PTA)platinum(II) complex, (I), as part of our systematic investigation into the basic coordination modes and solution properties of these complexes. Compound (I) is the first example of a Pt^{II} square-planar diphenyl complex with a *cis* geometry containing non-bridged phosphine ligands (Cambridge Structural Database, Version 5.25; Allen, 2002). Similar diphenylplatinum complexes with a *trans* conformation are known (Incarvito *et al.*, 1999; Ertl *et al.*, 1982). The formation of the *cis* complex may be ascribed either to

different synthetic routes or to the small steric demand of the PTA ligand (Daigle *et al.*, 1998; Otto & Roodt, 2001), which enables the more sterically demanding *cis* conformation typically found for two strong *cis* ligands.

The Pt atom of (I) lies on a general position in the asymmetric unit and the coordination polyhedron shows a slightly distorted square-planar arrangement (Table 1). The phenyl rings are almost perpendicular to the coordination plane of the Pt atom [dihedral angle = 85.2 (2)° for the C41-phenyl and 86.1 (2)° for the C31-phenyl]. This perpendicular conformation allows more space for the PTA ligands, resulting in quite a small bite angle of 84.6 (2)° for C41–Pt–C31, compared with 99.28 (6)° for P1–Pt–P2.

The orientation of the PTA ligands is best described by the torsion angles, which were calculated using the methylene substituent on the phosphine closest to the metal coordination plane. Two significantly different values [28.8 (3)° for C41–Pt–P1–C12 and 15.5 (3)° for C31–Pt–P2–C22], were obtained, and may possibly be the result of steric and packing effects.

The most widely used method for determining ligand steric behaviour at a metal centre utilizes the Tolman cone angle (Tolman, 1977), using an *M*–P bond distance of 2.28 Å, a C–H bond distance of 0.97 Å and 1.2 Å as the van der Waals radius of hydrogen. For the calculation of effective cone angles, the Pt–P bond distances determined from the crystallographic data were used (Otto *et al.*, 2000). The value of 113° obtained from effective cone-angle calculations for (I) is in agreement with the previous values, again illustrating the rigidity of PTA (Meij *et al.*, 2002).

High $U_{\text{eq}}(\text{max})/U_{\text{eq}}(\text{min})$ values are observed for atoms lying on the periphery of the molecule in both the phenyl and

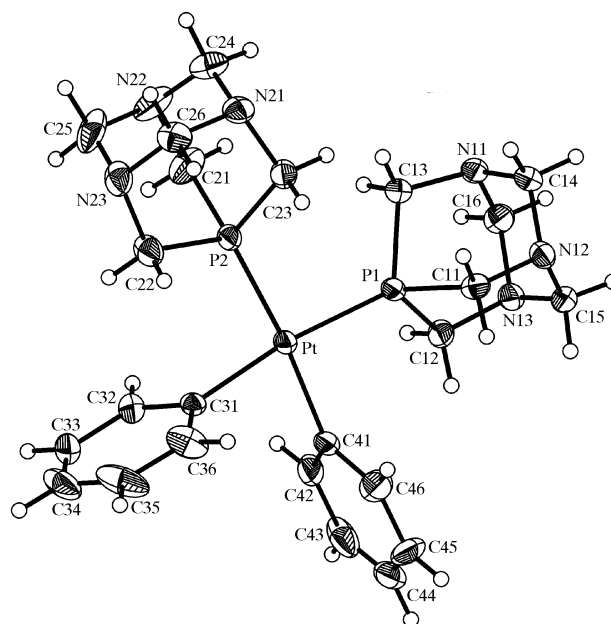


Figure 1

The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

the phosphine parts, indicating some freedom of packing in these regions. This may also explain some observed short C—C distances (Albertsson *et al.*, 1980).

Relatively few structures of the form *cis*-[*M*(*X*)₂(PTA)₂] (where *M* is Pd or Pt and *X* is an anionic substituent) are known. These are compared with (I) in Table 2, clearly showing the higher steric demand of Cl[−] compared with the C₆H₅[−] ligand, with *ca* 5° differences for both the P—*M*—P and *X*—*M*—*X* angles. Larger effective cone angles (Θ_{*E*}) are noted for the chloro complexes, indicating the weaker *trans* influence of Cl[−] compared with PTA. This can also be correlated with the respective *M*—*X* and *M*—P bond distances.

It is interesting to note that, in a comparison with other substituted aryl ligands (Table 3), the C—*M*—C angles do not differ significantly, even though phosphines with various steric demands were used. The exception is the case of the strongly electron-withdrawing (and bulky) C₆F₅[−] group, where differences of *ca* 5° for both the P—*M*—P and *X*—*M*—*X* angles were again noted.

Experimental

[Pt(Ph)₂(cod)] (cod is η⁴-1,5-cyclooctadiene) was prepared according to the literature procedure of Clark & Manzer (1973). To a solution of [Pt(Ph)₂(cod)] (50 mg, 0.11 mmol) in dichloromethane (10 ml) was added PTA (34 mg, 0.22 mmol) dissolved in methanol (10 ml). Crystals of (I) suitable for X-ray analysis separated from the solution over a period of a few hours in quantitative yield. Spectroscopic data: ³¹P{H} NMR (CDCl₃): −77.2 p.p.m. (¹J_{Pt—P} = 1560 Hz).

Crystal data

[Pt(C ₆ H ₅) ₂ (C ₆ H ₁₂ N ₃ P) ₂]	<i>Z</i> = 2
<i>M_r</i> = 663.6	<i>D_x</i> = 1.782 Mg m ^{−3}
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 9.616 (5) Å	Cell parameters from 3164 reflections
<i>b</i> = 10.395 (5) Å	<i>θ</i> = 2–24°
<i>c</i> = 12.477 (5) Å	<i>μ</i> = 5.83 mm ^{−1}
<i>α</i> = 86.112 (5)°	<i>T</i> = 293 (2) K
<i>β</i> = 83.778 (5)°	Needle, colourless
<i>γ</i> = 88.080 (5)°	0.22 × 0.06 × 0.04 mm
<i>V</i> = 1236.5 (10) Å ³	

Data collection

Bruker SMART CCD 1K area-detector diffractometer	7326 independent reflections
<i>ω</i> scans	4483 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 1998)	<i>R</i> _{int} = 0.048
<i>T</i> _{min} = 0.69, <i>T</i> _{max} = 0.77	<i>θ</i> _{max} = 31.6°
12 595 measured reflections	<i>h</i> = −14 → 14
	<i>k</i> = −12 → 15
	<i>l</i> = −17 → 18

Table 1

Selected geometric parameters (Å, °).

Pt—C31	2.052 (5)	Pt—P1	2.2888 (16)
Pt—C41	2.064 (6)	Pt—P2	2.2944 (17)
C31—Pt—C41	84.6 (2)	C12—P1—C11	97.1 (3)
C31—Pt—P1	171.24 (15)	C12—P1—C13	97.2 (3)
C41—Pt—P1	86.71 (15)	C11—P1—C13	97.9 (3)
C31—Pt—P2	89.40 (15)	C21—P2—C23	98.4 (3)
C41—Pt—P2	173.77 (15)	C21—P2—C22	97.8 (3)
P1—Pt—P2	99.28 (6)	C23—P2—C22	96.7 (3)

Table 2

Comparative geometrical data for *cis*-[*M*(*X*)₂(PTA)₂] complexes (Å, °).

<i>M</i> (<i>X</i>)	<i>M</i> —P	<i>M</i> — <i>X</i>	P— <i>M</i> —P	<i>X</i> — <i>M</i> — <i>X</i>	Θ _{<i>E</i>}
Pt(Ph) ^a	2.2888 (16)	2.052 (5)	99.28 (6)	84.6 (2)	113
	2.2944 (17)	2.064 (6)			113
Pt(Cl) ^b	2.2240 (12)	2.3490 (13)	94.26 (4)	87.24 (5)	116
	2.2284 (12)	2.3712 (13)			117
	2.2229 (13)	2.3473 (12)	94.68 (5)	87.06 (5)	116
	2.2300 (12)	2.3663 (13)			116
Pt(Cl) ^{c†}	2.218 (5)	2.358 (5)	94.3	86.2 (2)	117
Pd(Cl) ^d	2.242	2.373	93.58 (5)	88.95	116
	2.255	2.347			115
	2.251	2.347	93.25 (5)	89.15	117
	2.239	2.378			116
Pd(Cl) ^c	2.226 (5)	2.363 (5)	94.4 (2)	90.2 (2)	117
	2.264 (6)	2.360 (5)			117

Notes: (a) this work; (b) Otto *et al.* (1998); (c) Darensbourg *et al.* (1997); (d) Alyea *et al.* (1998). † Protonated form of PTA.

Table 3

Comparative geometrical data for *cis*-[Pt(*X*)₂(PR₃)₂] complexes (Å, °).

2-TolPh = *o*-tolylphenyl; DP(2-PE) = diphenyl(2-phenylethynyl); DP(3,3-DMB) = diphenyl(3,3-dimethylbutynyl); DP(2pTet) = diphenyl(2-*p*-tolyl)-ethynyl; 2-NPh = 2-nitrophenyl; 7-MeNap = 7-methyl-1-naphthyl; 2-OMePh = 2-methoxyphenyl; 3,5-DAMPh = 3,5-bis(diethylaminomethyl)phenyl.

Pt(<i>X</i>)(PR ₃)	<i>M</i> —P	<i>M</i> — <i>X</i>	P— <i>M</i> —P	C— <i>M</i> —C	Θ _{<i>E</i>}
(Ph)(PTA) ^a	2.2888 (16)	2.052 (5)	99.28 (6)	84.6 (2)	113
	2.2944 (17)	2.064 (6)			113
(2-TolPh)(PEt ₃) ^{b†}	2.317 (2)	2.058 (10)	100.0 (1)	83.9 (3)	145
	2.330 (2)	2.091 (6)			140
(C ₆ F ₅)[DP(2-PEPh)] ^c	2.310	2.070	92.86	85.83	148
(C ₆ F ₅)[DP(3,3-DMBPh)] ^c	2.294	2.050	95.02	84.24	151
	2.297	2.059			149
(C ₆ F ₅)[DP(2pTet)] ^c	2.315	2.068	93.28	85.78	151
	2.285	2.109			149
(2-NPh)(PPh ₃) ^d	2.332	2.061	100.37	82.88	‡
	2.313	2.061			
(7-MeNap)(PPh ₃) ^e	2.34 (1)	2.08 (2)	99.8 (2)	85.2 (7)	‡
	2.32 (1)	2.08 (2)			
(2-OMePh)(PPh ₃) ^e	2.309	2.033	100.87	81.56	‡
	2.313	2.033			
(3,5-DAMPh)(PEt ₃) ^f	2.305	2.071	100.17	82.55	150
	2.317	2.058			144

Notes: (a) this work; (b) Rieger *et al.* (1993); (c) Ara *et al.* (2002); (d) Brune *et al.* (1984); (e) Debaerdemaeker *et al.* (1987); (f) James *et al.* (1996). † *Anti* isomer. ‡ H atoms not included in the structure extracted from the CSD (Allen, 2002).

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> (<i>F</i>) = 0.045	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0291 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.083	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 0.88	(Δ/σ) _{max} = 0.001
7326 reflections	Δρ _{max} = 0.99 e Å ^{−3}
298 parameters	Δρ _{min} = −0.72 e Å ^{−3}

The aromatic and methylene H atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: SMART-NT (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus and XPREP (Bruker, 1999); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Berndt, 2001); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1089). Services for accessing these data are described at the back of the journal.

References

- Albertsson, J., Oskarsson, Å., Ståhl, K., Svensson, C. & Ymén, I. (1980). *Acta Cryst.* **B36**, 3072–3078.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Alyea, E. C., Ferguson, G. & Kannan, S. (1998). *Chem. Commun.* pp. 345–346.
- Alyea, E. C., Fisher, K. J., Foo, S. & Philip, B. (1993). *Polyhedron*, **12**, 489–492.
- Ara, I., Fornies, J., Garcia, A., Gomez, J., Lalinde, E. & Moreno, M. T. (2002). *Chem. Eur. J.* **16**, 3698–3716.
- Brandenburg, K. & Berndt, M. (2001). *DIAMOND*. Release 2.1e. Crystal Impact, Postfach 1251, D-53002, Bonn, Germany.
- Bruker (1998). *SADABS* and *SMART-NT* (Version 5.050). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINTE-Plus* (including *XPREP*). Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
- Brune, H.-A., Wiege, M. & Debaerdemaeker, T. (1984). *Z. Naturforsch. Teil B*, **39**, 359–368.
- Clark, H. C. & Manzer, L. E. (1973). *J. Organomet. Chem.* **59**, 411–428.
- Daigle, D. J., Decuir, T., Robertson, J. & Darensbourg, D. J. (1998). *Inorg. Synth.* **32**, 40–45.
- Darensbourg, D. J., Decuir, T., Stafford, N., Robertson, J., Draper, J. & Reibenspies, J. (1997). *Inorg. Chem.* **36**, 4218–4226.
- Darensbourg, D. J., Robertson, J. B., Larkins, D. L. & Reibenspies, J. H. (1999). *Inorg. Chem.* **38**, 2473–2481.
- Debaerdemaeker, T., Berhalter, K., Weisemann, C. & Brune, H. A. (1987). *Acta Cryst.* **C43**, 1253–1255.
- Debaerdemaeker, T., Klein, H.-P., Wiege, M. & Brune, H. A. (1981). *Z. Naturforsch. Teil B*, **36**, 958–966.
- Ertl, J., Debaerdemaeker, T. & Brune, H. A. (1982). *Chem. Ber.* **115**, 3860–3874.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Incarvito, C. D., Mirkin, C. A. & Rheingold, A. L. (1999). Private communication.
- James, S. L., Veldman, N., Spek, A. L. & van Koten, G. (1996). *J. Chem. Soc. Chem. Commun.* pp. 253–256.
- Joó, F., Nadasdi, L., Benyei, A. C. & Darensbourg, D. J. (1996). *J. Organomet. Chem.* **512**, 45–50.
- Meij, A. M. M., Otto, S. & Roodt, A. (2002). *Acta Cryst.* **E58**, m644–m646.
- Otto, S. & Roodt, A. (2001). *Inorg. Chem. Commun.* **4**, 49–52.
- Otto, S., Roodt, A. & Purcell, W. (1998). *Inorg. Chem. Commun.* **1**, 415–417.
- Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
- Rieger, A. L., Carpenter, G. B. & Rieger, P. H. (1993). *Organometallics*, **12**, 842–847.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.