

(Di-*tert*-butylmethylphosphane)(η^2 -di-*tert*-butylphosphanylphosphinidene)-(triphenylphosphane)platinum(0)Antoni Konitz,^a Harald Krautscheid^b and Jerzy Pikies^{a*}^aDepartment of Inorganic Chemistry, Gdańsk University of Technology, 11/12 G. Narutowicz Street, 80952 PL Gdańsk, Poland, and ^bInstitut für Anorganische Chemie, Universität Leipzig, D-04103 Leipzig, Germany
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The crystal structure of the title compound, [Pt(C₈H₁₈P₂)(C₉H₂₁P)(C₁₈H₁₅P)] or [(Ph₃P)(^tBu₂PMe)Pt(η^2 -^tBu₂PP)], contains four molecules in the asymmetric unit with slightly different conformations. The P–P distances in the ^tBu₂PP ligands are similar for all four molecules [2.0661 (13)–2.0678 (13) Å] and indicate a multiple character of the P–P bond in the ^tBu₂PP ligand. Molecules of the asymmetric unit can be assembled into a tetrahedron that fulfils the requirements for a rhombic disphenoid. The coordination of the Pt atom in all four molecules is square planar, with r.m.s. deviations from the PtP₄ planes in the range 0.03–0.05 Å. All planes of the PtP₄ groups are approximately parallel to the *ab* plane of the unit cell. The structure represents an unusual unsymmetrical platinum phosphinidene derivative.

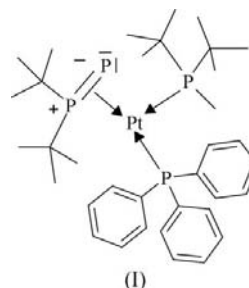
Comment

In the course of our studies on the reactivity of phosphanylphosphinidenophosphorane, ^tBu₂P–P=P^tBu₂(Me), towards platinum(0) complexes, the formation of side-on bonded complexes with the di-*tert*-butylphosphanylphosphinidene ligand (^tBu₂P=P) has been established (Krautscheid *et al.*, 1997). The reaction of an excess of ^tBu₂PMe with [(Ph₃P)₂Pt(η^2 -^tBu₂P=P)] yields the title compound, (I), via a ligand-exchange process (Matern *et al.*, 2000) (Fig. 1).

Only one isomer of (I) was found in the reaction mixture on the basis of the ³¹P{¹H} NMR spectrum. This regioselectivity is probably caused by two factors, firstly the steric hindrance of the bulky ^tBu₂P group and the planarity of the P₄Pt systems in (I), and secondly [using molecule (Ia) as an example] the difference in the *trans* effects of ^tBu₂P11 and atom P12. Thus, the observed Pt–P13 distance in (I) is longer than Pt–P14 and ^tBu₂PMe is more weakly bonded to the Pt atom than PPh₃. The same phenomenon is observed in [(EtPh₂P)₂Pt(η^2 -^tBu₂P=P)] (Krautscheid *et al.*, 1997).

To date, only three Pt⁰ complexes of this type have been structurally characterized, namely [(EtPh₂P)₂Pt(η^2 -^tBu₂-

P=P)], with a P–P distance of 2.071 (1) Å (Krautscheid *et al.*, 1997), [(dippe)Pt(η^2 -^tBu₂P=P)], with a P–P distance of 2.072 (3) Å (dippe is Ph₂PCH₂CH₂PPh₂; Krautscheid *et al.*, 1998), and [(Ph₃P)(^tBu₂PH)Pt(η^2 -^tBu₂P=P)], with a P–P distance of 2.067 (3) Å (Krautscheid *et al.*, 2000). Three other complexes with phosphanylphosphinidene ligands, but with different side-on bonded metal centres, have been reported by Cummins and co-workers: [(ArNⁱPr)₃W(η^2 -Ph₂P=P)] (Ar is 3,5-Me₂C₆H₃), with a P–P distance of 2.097 (2) Å (Fox *et al.*, 2007), [(ArNNp)₃Nb(η^2 -Ph₂P=P)], with a P–P distance of 2.073 (4) Å, and [(ArNNp)₃Nb(η^2 -^tBu₂P=P)], with a P–P distance of 2.089 (2) Å (Ar is 3,5-Me₂C₆H₃ and Np is neopentyl; Figueroa & Cummins, 2004).



The molecular structure of (I) is shown in Fig. 2. The geometry around the Pt atom in (I) is square planar, with a small mean deviation from the PtP₄ plane. The P–P distance in the ^tBu₂P=P ligand in all four molecules of (I) is significantly shorter than the P–P distances in side-on bonded diphosphenes, e.g. 2.121 (2) Å in [(Ph₃P)₂Pt(η^2 -PhP=P)]. In the free molecule of Mes*P=PMe*, the P=P double bond is 2.034 (2) Å (Mes* is 2,4,6-^tBu₃C₆H₂; Chatt *et al.*, 1982). This distance suggests a multiple P–P bond character in (I) with a multiplicity slightly greater than two. The short P–P distance in the ^tBu₂PP group can most probably be explained by a zwitterionic formula (see scheme). The Pt–PPh₃ (mean 2.302 Å), Pt–P^tBu₂Me (mean 2.323 Å) and Pt–P^tBu₂ distances (mean 2.329 Å; all s.u. values for the Pt–P bonds are close to 0.001 Å) are in good agreement with the typical value for *trans*-(R₃P)₂PtCl₂ [2.319 (1) Å; Johansson & Otto, 2000]. The Pt–P(unsubstituted) distance is significantly longer [mean 2.410 (2) Å].

Molecules of (I) display slightly different conformations (Table 1). The Pt1–P14–C118–C123 torsion angle and analogous angles in the other three molecules are different, at –6.9 (3), –3.0 (3), 7.5 (3) and 3.4 (3)°, respectively, while the P14–Pt1–P13–C117 torsion angle and analogous angles in the other three molecules are 11.87 (14), 11.41 (15), –12.12 (15) and –11.70 (14)°, respectively.

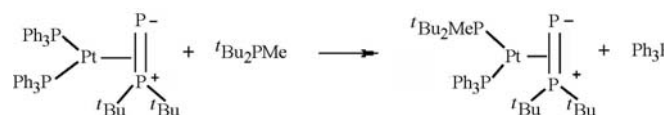
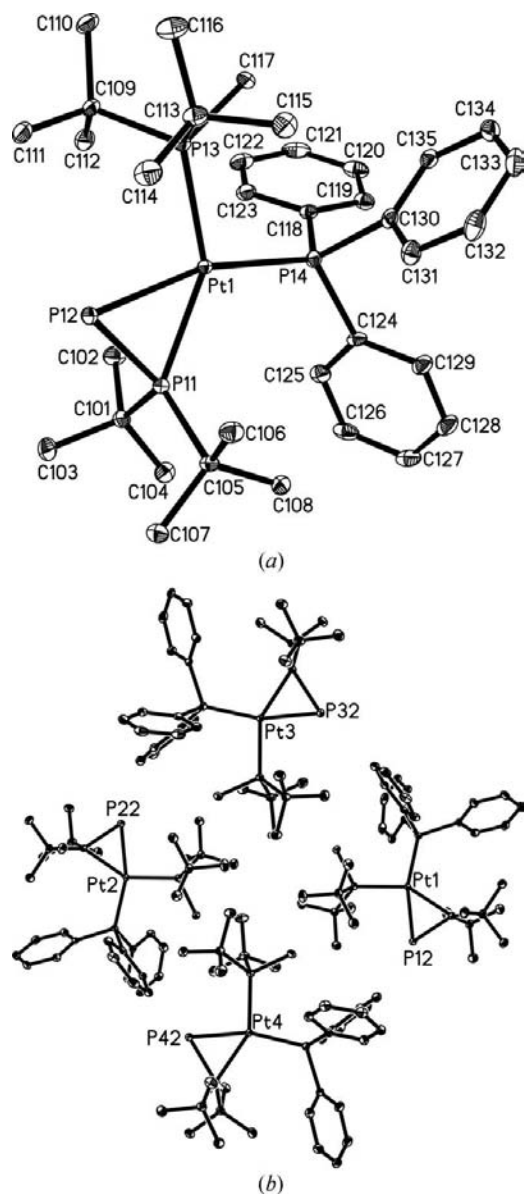
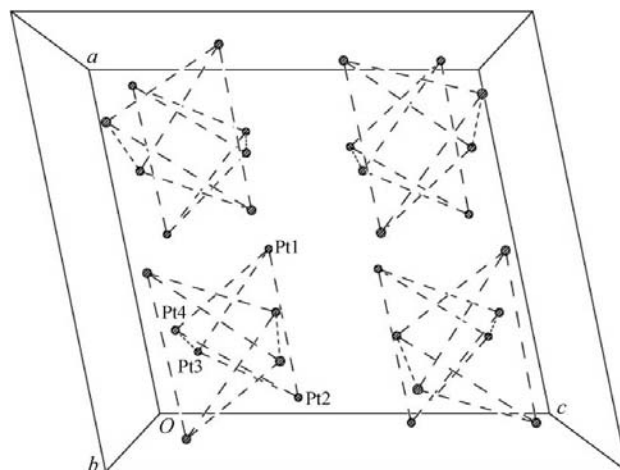


Figure 1
Reaction scheme for the synthesis of (I).


Figure 2

A view of molecule (Ia), showing (a) the atom-labelling scheme and (b) the tetrahedral assembly of the four molecules. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

The only significant nonbonding interactions in (I) are a single weak intramolecular C—H...P interaction in each molecule (Table 2). The molecules of (I) can be assembled into a tetrahedron that nearly fulfils the requirements for a rhombic disphenoid, with two almost perpendicular longer edges [angle 89.95 (1)°] having Pt1—Pt2 = 12.4255 (8) Å and Pt3—Pt4 = 12.4293 (8) Å, and four shorter edges with distances in the range 11.7803 (11)–11.9164 (9) Å. Molecules in each tetrahedron interact through dispersion forces of the *tert*-butyl groups. The closest contacts between tetrahedra come from dispersion forces of the phenyl rings, but without stacking interactions. Fig. 3 shows the packing of Pt tetrahedra and molecules along the *b* axis.


Figure 3

View of the packing of (I) along the *b* axis, showing tetrahedra based on Pt atoms.

Experimental

Compound (I) was obtained by a ligand-exchange method from di-*tert*-butylmethylphosphane and bis(η^2 -di-*tert*-butylphosphanylphosphinidene)(triphenylphosphane)platinum(0) according to the method of Matern *et al.* (2000). Single crystals of (I) were obtained by recrystallization from hexane at 195 K. ^{31}P NMR (85% H_3PO_4 as an external reference standard): δ 50.60 (P1), -54.98 (P2), 38.48 (P3), 20.34 (P4), $^1J(\text{Pt}-\text{P1}) = 1819.8$ Hz, $^1J(\text{Pt}-\text{P2}) = -71.7$ Hz, $^1J(\text{Pt}-\text{P3}) = 3445.4$ Hz, $^1J(\text{Pt}-\text{P4}) = 3264.2$ Hz, $^1J(\text{P1}-\text{P2}) = -605.5$ Hz, $^2J(\text{P1}-\text{P3}) = 205.1$ Hz, $^2J(\text{P2}-\text{P3}) = -17.8$ Hz, $^2J(\text{P2}-\text{P4}) = 13.6$ Hz, $^2J(\text{P3}-\text{P4}) = -1.1$ Hz.

Crystal data

[Pt(C₈H₁₈P₂)(C₉H₂₁P)(C₁₈H₁₅P)]
 $M_r = 793.74$
 Monoclinic, $C2/c$
 $a = 29.924$ (2) Å
 $b = 29.928$ (2) Å
 $c = 33.233$ (3) Å
 $\beta = 101.646$ (9)°

$V = 29150$ (4) Å³
 $Z = 32$
 Mo $K\alpha$ radiation
 $\mu = 4.05$ mm⁻¹
 $T = 120$ K
 $0.15 \times 0.09 \times 0.05$ mm

Data collection

Kuma KM-4 four-axis diffractometer with Sapphire2 CCD detector
 Absorption correction: analytical [CrysAlis RED (Oxford Diffraction, 2006); analytical numeric absorption correction using a multifaceted

crystal model based on expressions derived by Clark & Reid (1995)]
 $T_{\min} = 0.414$, $T_{\max} = 0.672$
 74063 measured reflections
 25787 independent reflections
 20921 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.068$
 $S = 1.09$
 25787 reflections

1493 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 2.08$ e Å⁻³
 $\Delta\rho_{\min} = -0.71$ e Å⁻³

All H atoms were positioned geometrically and refined using a riding model, with C—H distances fixed according to temperature and type (methyl C—H = 0.98 Å and aromatic C—H = 0.95 Å), with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2$ (or 1.5 for CH₃ groups) times $U_{\text{eq}}(\text{C})$.

Table 1

Selected geometric parameters (Å, °).

Pt1—P11	2.3255 (10)	Pt3—P33	2.3333 (9)
Pt1—P12	2.4125 (9)	Pt3—P34	2.3021 (10)
Pt1—P13	2.3316 (10)	Pt4—P41	2.3308 (9)
Pt1—P14	2.3041 (9)	Pt4—P42	2.4091 (10)
Pt2—P21	2.3309 (9)	Pt4—P43	2.3330 (9)
Pt2—P22	2.4099 (9)	Pt4—P44	2.3006 (10)
Pt2—P23	2.3324 (10)	P11—P12	2.0665 (13)
Pt2—P24	2.3024 (9)	P21—P22	2.0678 (13)
Pt3—P31	2.3288 (9)	P31—P32	2.0661 (13)
Pt3—P32	2.4087 (10)	P41—P42	2.0676 (13)
Pt1—P14—C118	114.36 (12)	P31—Pt3—P33	147.17 (3)
Pt2—P24—C218	116.73 (11)	P41—Pt4—P43	146.67 (3)
Pt3—P34—C318	114.86 (12)	P13—Pt1—P14	102.00 (3)
Pt4—P44—C418	116.67 (12)	P23—Pt2—P24	102.42 (3)
P11—Pt1—P13	147.08 (3)	P33—Pt3—P34	101.84 (3)
P21—Pt2—P23	146.73 (3)	P43—Pt4—P44	102.50 (3)
P14—Pt1—P13—C117	11.87 (14)	Pt1—P14—C118—C123	−6.9 (3)
P24—Pt2—P23—C217	11.40 (15)	Pt2—P24—C218—C223	−3.0 (3)
P34—Pt3—P33—C317	−12.09 (15)	Pt3—P34—C318—C323	7.5 (3)
P44—Pt4—P43—C417	−11.70 (14)	Pt4—P44—C418—C423	3.3 (3)

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C111—H11E···P12	0.98	2.56	3.470 (5)	155
C211—H21D···P22	0.98	2.60	3.510 (4)	154
C311—H31F···P32	0.98	2.55	3.468 (4)	155
C411—H41D···P42	0.98	2.60	3.505 (4)	154

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3157). Services for accessing these data are described at the back of the journal.

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