folding line was found in (5-CF$_3$-tetrazolate)Co(DH)$_2$-PBu$_3^n$ (Takach, Holt, Alcock, Henry & Nelson, 1980) and was attributed to a positive or non-bonded attraction between the tetrazole N atoms and the C atoms of the five-membered ring of the DH unit. Present results do not give support to this hypothesis, the orientation of the triazole ring being very close to that found in pyridine derivatives (Clearfield *et al.*, 1978). We note that substitution of N$_3$ by the more bulky triazole derivative provokes a decrease of the Co displacement from the coordination plane and of the bending angle α as well as an increase of the P—Co—N (axial) angle (Table 3). Similar variations have already been observed (Bresciani-Pahor *et al.*, 1980) in other cobaloximes, containing PPh$_3$, when the methyl group in the axial position is replaced by the bulky neopentyl group.
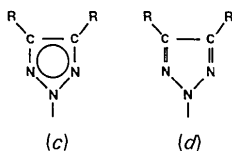
The Co—P bond is significantly lengthened from 2·311 (1) in (I) to 2·333 (1) Å in (II), suggesting that triazole derivatives exert a *trans* influence which is stronger than that of the azide. This parallels the observed tendency for formation of five-coordinate species in triazolate compounds (Beck *et al.*, 1982).

The bond lengths (Table 3) and the planarity of the triazole ring, from which the Co is displaced by only 0·02 (4) Å, suggest a delocalization over the ring atoms (form *c*). However, a contribution from the localized form (*d*) cannot be ruled out.

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Structure of *trans*-Bis(dimethylphenylphosphine)bis(pyrazole)platinum, [Pt(C$_3$H$_4$N$_2$)$_2$-{P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$]

BY J. D. OLIVER,* D. F. MULLICA, DAVID A. GROSSIE, W. O. MILLIGAN AND H. O. PERKINS

Departments of Chemistry and Physics, Baylor University, Waco, Texas 76798, USA

Abstract. $M_r = 607 \cdot 55$, monoclinic, $C2/c$, $a = 21 \cdot 509$ (6), $b = 6 \cdot 290$ (2), $c = 17 \cdot 934$ (4) Å, $\beta = 102 \cdot 54$ (2)°, $V = 2368 \cdot 7$ Å^3, $Z = 4$, $D_m = 1 \cdot 70$, $D_x = 1 \cdot 70$ Mg m^{-3}, λ(Mo K$\bar{\alpha}$) = $0 \cdot 71073$ Å, μ(Mo Kα) = $6 \cdot 13$ mm^{-1}, $F(000) = 1192$, $T = 291$ K. Final $R = 0 \cdot 028$ for 1416 unique observed reflections. The Pt atom lies on a crystallographic inversion center with a *trans* arrangement of the dimethylphenylphosphine and pyrazole ligands. The plane of the pyrazole ring forms an angle of $73 \cdot 8°$ with the square-planar coordination plane defined by the Pt, P and coordinated N atoms of the pyrazole ligand. The coordinated pyrazole ligand is flat and virtually isometric. Selected geometrical details are Pt—P = $2 \cdot 305$ (3), Pt—N = $2 \cdot 027$ (7), average C—C (phenyl) = $1 \cdot 382$ (14) Å, P—Pt—N = $91 \cdot 7$ (2)°.

Introduction. The determination of the crystal structure of the title compound (hereinafter referred to as PTPP) was initiated as part of a continuing study of the steric requirements of coordinated trisubstituted phosphine ligands. Platinum metal and organoplatinum complexes are often used as catalysts for hydrogen-transfer reactions. This reaction generally includes a catalytic

* Present address: The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45247, USA.

Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\times 10^3)$ *with e.s.d.'s in parentheses*

	x	y	z	$U_{eq}*(\text{Å}^2)$
Pt	2500	2500	5000	33 (1)
P	3012 (1)	4626 (4)	4275 (1)	39 (2)
N(1)	1773 (3)	1931 (11)	4094 (4)	39 (4)
N(2)	1837 (4)	542 (15)	3556 (5)	59 (6)
C(1)	1262 (5)	331 (20)	3083 (6)	63 (8)
C(2)	832 (5)	1587 (20)	3334 (7)	67 (8)
C(3)	1168 (4)	2568 (25)	3979 (5)	58 (6)
C(4)	3661 (4)	3216 (16)	3990 (6)	41 (7)
C(5)	3509 (5)	1431 (19)	3525 (6)	53 (7)
C(6)	3976 (6)	313 (19)	3267 (6)	65 (8)
C(7)	4591 (6)	958 (24)	3467 (8)	83 (11)
C(8)	4758 (5)	2720 (31)	3924 (8)	94 (13)
C(9)	4294 (5)	3865 (21)	4179 (7)	74 (10)
C(10)	3366 (5)	7008 (15)	4775 (6)	54 (8)
C(11)	2535 (5)	5571 (17)	3366 (6)	56 (7)

* U_{eq} defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

cycle whose intermediates are metal hydrides. These hydrides and organometallic intermediates are extremely reactive. Decomposition of this complex to the metal could easily occur under reduction situations if some stabilizing ligand were not incorporated into the metal complex. The functions of these stabilizing ligands are numerous. Primarily they bind strongly to the metal so that it may undergo any changes in oxidation state, ligation, coordination number and stereochemistry during the catalytic cycle without precipitation of the metal. These ligands also influence the path of the reaction by their steric interactions with any incoming reactants. The most commonly used ligands for stabilizing the intermediate organometallic species are tertiary phosphines.

Experimental. Crystals of the title compound obtained from Dr H. C. Clark of the University of Guelph; D_m by flotation method in aqueous silver nitrate, yellow, rectangular-shaped crystal, $0.05 \times 0.14 \times 0.32$ mm, glass-fiber mount, Enraf–Nonius CAD-4F four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation and an Si(Li) energy-dispersive detector (Mullica, Beall, Milligan & Oliver, 1979); cell constants from setting angles of 25 reflections; correction for Lorentz, polarization and absorption effects, $t(\text{min.})$–$t(\text{max.}) = 0.426$–0.735; intensity data collected by θ–2θ scan technique, variable scan rate of 0.67 to 4.0° min^{-1}; intensities of two check reflections (111 and 200) measured every 2 h revealed only random deviations ($<2\%$) from mean intensities; 3174 unique reflections ($3 < 2\theta < 52°$, range of hkl: 0→26, 0→7, −22→21), 1416 reflections with $I > 3\sigma(I)$ used in solution and refinement of the structure using previously described programs (Oliver & Rice, 1976); heavy-atom technique; H atoms located in a difference Fourier map and included at fixed positions with

$U = 0.076$ Å^2; full-matrix least-squares refinement on F yielded $R = 0.028$, $R_w = 0.032$, $w = \sigma(F_o)^{-2}$ with $\sigma(F_o) = [Ip + Ib + 0.02(Ip - Ib)^2]^{1/2}$ where Ip and Ib are the peak and background counts respectively, $S = 0.71$, $(\Delta/\sigma)_{max} = 0.01$; max. and min. peaks in final ΔF map 0.58 and -0.24 e Å^{-3}; scattering factors and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are given in Table 1.* A perspective drawing of PTPP is shown in Fig. 1, which also illustrates the atom-labeling scheme used. A stereoscopic view of the molecular packing is shown in Fig. 2. Bond lengths and bond angles are presented in Table 2.

The Pt atom lies on a crystallographic inversion center $(\frac{1}{4},\frac{1}{4},\frac{1}{2})$ and has a square-planar coordination geometry. The phenyl ring and the pyrazole rings are planar with the largest displacement of any non-H atom from its plane being 0.008 and 0.007 Å respectively. The planes of the phenyl ring and the pyrazole ring

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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, and an illustration of the ligand profile about the phosphine P atom have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39099 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
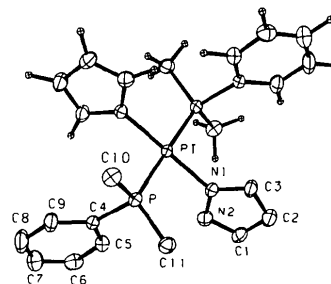

Fig. 1. Perspective drawing of PTPP displaying ellipsoids of 50% probability. The H atoms are drawn artificially small.
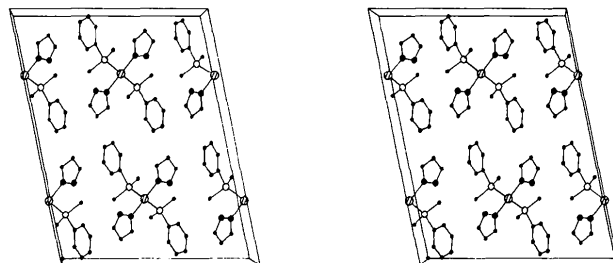

Fig. 2. Stereoscopic packing diagram viewed along the b axis. The cross-hatched circles, open circles and large filled circles represent the Pt, P and N atoms, respectively.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Pt–P	2·305 (3)	C(1)–C(2)	1·365 (16)
Pt–N(1)	2·027 (7)	C(2)–C(3)	1·371 (16)
P–C(4)	1·819 (10)	C(4)–C(5)	1·395 (15)
P–C(10)	1·826 (10)	C(4)–C(9)	1·390 (15)
P–C(11)	1·827 (11)	C(5)–C(6)	1·386 (16)
N(1)–N(2)	1·326 (12)	C(6)–C(7)	1·355 (18)
N(1)–C(3)	1·335 (11)	C(7)–C(8)	1·378 (23)
N(2)–C(1)	1·350 (14)	C(8)–C(9)	1·388 (16)
Pt–P–C(4)	111·4 (3)	N(1)–N(2)–C(1)	107·3 (8)
Pt–P–C(10)	113·4 (3)	N(2)–C(1)–C(2)	109·2 (10)
Pt–P–C(11)	116·6 (3)	C(1)–C(2)–C(3)	105·5 (9)
C(4)–P–C(10)	105·9 (5)	C(2)–C(3)–N(1)	108·3 (9)
C(4)–P–C(11)	103·0 (5)	C(3)–N(1)–N(2)	109·7 (8)
C(10)–P–C(11)	105·4 (5)	C(4)–C(5)–C(6)	121·1 (10)
Pt–N(1)–N(2)	120·8 (6)	C(5)–C(6)–C(7)	119·7 (12)
Pt–N(1)–C(3)	128·9 (7)	C(6)–C(7)–C(8)	120·8 (12)
P–Pt–N(1)	91·7 (2)	C(7)–C(8)–C(9)	120·0 (11)
P–C(4)–C(5)	117·8 (8)	C(8)–C(9)–C(4)	120·2 (11)
P–C(4)–C(9)	124·0 (8)	C(9)–C(4)–C(5)	118·2 (10)

form angles of 104·2 and 73·8° with the coordination plane of the Pt atom. The angle between the plane of the pyrazole ring and the coordination plane is similar to the values found in other related compounds (Atwood, Dixon, Eadie, Stobart & Zaworotko, 1983; Bushnell, Dixon & Khan, 1974, 1978; Bushnell & Dixon, 1978). The angle between the plane of the phenyl ring and the plane of the pyrazole ring is 155·1°.

The orientation of the phenyl ring to the coordination plane can be defined by the torsion angle, Pt–P–C(4)–C(5) (62·6°). In other Pt complexes with *trans*-disposed dimethylphenylphosphine ligands (Hitchcock, 1976; Lin, Chen & Fackler, 1978; O'Flynn & McDonald, 1976; Stepaniak & Payne, 1974*a,b*, 1978), this torsion angle ranges from 78·1 to 101·9° and in one instance was observed to be 11·8°. This torsion angle thus tends to be approximately 90° (to minimize the steric interaction between the *ortho* H atom of the phenyl ring and the Pt atom), but can assume other values to accommodate other non-bonded steric interactions.

The Pt–P bond length, 2·305 (3) Å, of PTPP is very similar to the average Pt–P bond length, 2·30 (1) Å, observed in other structures of Pt complexes containing *trans*-disposed dimethylphenylphosphine ligands. The bond lengths of the pyrazole ligand indicate that the five-membered ring is almost isometric and has a geometry similar to those of coordinated pyrazolyl groups of polypyrazolylborate ligands (*e.g.* Oliver & Rice, 1976) and coordinated pyrazolide ions (*e.g.* Henslee & Oliver, 1977).

The structural analysis of PTPP serves to extend our previous investigations (Smith & Oliver, 1978; Oliver, Mullica & Milligan, 1982) of the steric requirements of coordinated phosphine ligands. To define quantitatively the steric bulk of these ligands, several authors (Alyea, Dias, Ferguson & Restivo, 1977; Richardson & Payne, 1977; Smith & Oliver, 1978)

have expanded Tolman's (1970) concept of a ligand cone angle by using crystallographic coordinates to generate a series of half-cone angles ($\theta/2$) as a function of the angle of rotation about the metal–P bond, which is termed a ligand profile. A plot of the ligand profile for the dimethylphenylphosphine ligand of PTPP has been deposited.* The calculation reveals a maximum $\theta/2$ value of 73° for the phenyl substituent and a maximum $\theta/2$ value of 66° for each of the methyl substituents. The minimum $\theta/2$ value for this conformation of the ligand is 34°.

No intermolecular contacts shorter than the sum of the respective van der Waals radii of the atoms were observed.

* See deposition footnote.

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