

*Journal of Organometallic Chemistry*, 118 (1976) 355–362  
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**THE MOLECULAR AND CRYSTAL STRUCTURE OF *trans*-HYDRIDOBIS-(TRIPHENYLPHOSPHINE)(1,3-DI-*p*-TOLYLTRIAZENIDO)PLATINUM(II) [PtH(PPh<sub>3</sub>)<sub>2</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NNNC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*)]**

A. IMMIRZI

*Istituto di Chimica delle Macromolecole del C.N.R., Milano (Italy)*

G. BOMBIERI \*

*Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova (Italy)*

and L. TONIOLO

*Istituto di Chimica Generale, Università di Padova (Italy)*

(Received April 2nd, 1976)

### Summary

The structure of the title compound has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The material crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in a cell of dimensions  $a$  14.649(2),  $b$  15.082(2),  $c$  10.929(1) Å,  $\alpha$  110.99(5)°,  $\beta$  102.40(5)°,  $\gamma$  84.54(5)°. Full-matrix least-squares treatment of 4673 observed intensities gave an unweighted  $R$  value of 0.069. The platinum atom has square-planar coordination with Pt–P(1) 2.268(5), Pt–P(2) 2.267(5), Pt–N(1) 2.09(2) Å. The presence of the hydrogen atom is inferred from IR and <sup>1</sup>H NMR data. The triazenido ligand,  $\sigma$  bonded to the metal through N(1), lies perpendicular to the coordination plane.

---

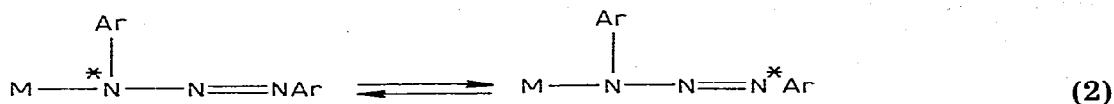
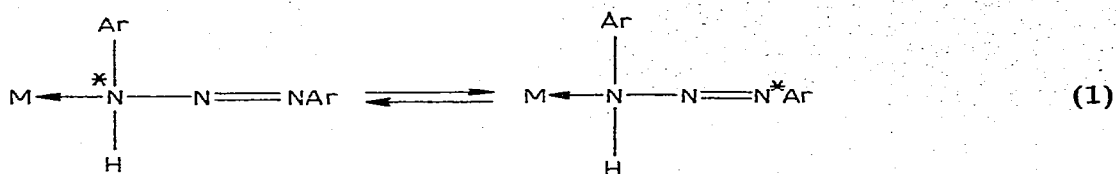
### Introduction

There is increasing interest in the variety of coordination modes in the chemistry of 1,3-diaryltriazene transition metal complexes [1–3].

In solution, when acting as monodentate, the triazene ligand or its deprotonated form can show fluxional behaviour according to eq. 1 and 2.

---

\* To whom correspondence should be addressed.



Variable  $^1\text{H}$  NMR spectra of palladium(II) and platinum(II) triazenido complexes have shown a fluxional process which has been interpreted as involving an intermediate having the triazenido ligand,  $\sigma, \sigma'$ -facing the metal [4]. This interpretation agrees with the X-ray results [4,5] which show that the triazenido ligand (eq. 2) is  $\sigma$ -bonded through one terminal nitrogen atom, while a second nitrogen atom shows a short  $\text{M} \cdots \text{N}$  contact which would favour the intermediate described above.

As part of a study of the coordination of triazenes to platinum(II) and palladium(II) the structure of  $\text{PtH}(\text{PPh}_3)_2(\text{dtt})$  was considered to be of interest ( $\text{dtt} = p\text{-CH}_3\text{C}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{CH}_3\text{-}p$ ).

## Experimental

Pale yellow prismatic crystals were obtained by recrystallization from a benzene/ethanol mixture.

The crystal data are summarized in Table 1. All the X-ray experiments were performed using a single crystal PW-1100 Philips diffractometer with graphite monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda$  0.71069 Å). The unit cell and space group were determined from 25 strong reflections collected with a randomly oriented crystal in a reciprocal space position defined by  $7^\circ < \theta < 12^\circ$ ,  $-5^\circ < \chi < 60^\circ$  and  $0^\circ < \varphi < 90^\circ$ . The unit cell was found to be triclinic and the experimental

TABLE 1  
CRYSTAL DATA FOR  $(\text{PPh}_3)_2\text{PtH}(\text{MePhN}_3\text{PhMe})$

$\text{PtP}_2\text{HN}_3\text{C}_{50}\text{H}_{44}$ :	f.w. 945
Crystal description:	pale yellow prisms
Systematic absence:	none
Space group:	$P\bar{1}$
Cell constants:	$a$ 14.649(2), $b$ 15.082(2), $c$ 10.929(1) Å $\alpha$ 116.99(5)°, $\beta$ 102.40(5)°, $\gamma$ 84.54(5)°
Volume:	2201 Å <sup>3</sup>
Density:	obs. 1.39 g cm <sup>-3</sup> ; calcd. 1.43 g cm <sup>-3</sup> for $Z = 2$
$\mu(\text{Mo-K}\alpha)$ :	34.53 cm <sup>-1</sup>

density of  $1.39 \text{ g cm}^{-3}$  (flotation) is in agreement with the calculated value of  $1.43 \text{ g cm}^{-3}$  for  $Z = 2$ .

For accurate lattice parameter determination precise values of Bragg angles for 57 strong reflections with  $8^\circ < \theta < 16^\circ$  were measured by determining the centres of gravity of the peak profile  $I = f(\theta)$  and averaging for positive and negative  $\theta$  angles. The lattice parameters and their standard deviations were determined by means of a least-squares calculation minimizing  $\sum(\sin \theta_{\text{obs}} - \sin \theta_{\text{cacld}})^2$ .

The diffracted intensities were measured by the  $\omega$ -scan method with a scan speed of  $1.2 \text{ deg min}^{-1}$  and a scan width of  $0.8^\circ$ . Two background counts of 20 sec each were done at each end of the scan.

Of the 5720 reflections examined 4673 having a net intensity greater than  $3\sigma$  ( $\sigma$ , standard error based on count statistics) were measured in the structure determination and refinement. Every hour three standard reflections were monitored to check the crystal stability; only statistical variations were observed.

### Structure determination and refinement

The structure was determined by the heavy atom method. Pt and P atoms positions were obtained from the Patterson function which indicated a centrosymmetric heavy-atom distribution. The subsequent Fourier synthesis with structure factors phased by Pt and P contributions confirmed the full  $P\bar{1}$  symmetry and gave the positions of remaining 50 carbon and 3 nitrogen atoms.

Atomic positions and thermal parameters were refined by the full-matrix least-squares method using first isotropic thermal vibration parameters and finally allowing to the platinum and two phosphorous atoms to vibrate anisotropically. Owing to the limited capacity of the memory, blocks of 200 variables were used. The function minimized was  $\sum w(|F_{\text{obs}}| - |F_{\text{calcd}}|)^2$  and unit weight factors were assigned to all the observed reflections. All attempts to locate the hydrogen atoms by a difference Fourier map were unsuccessful. In particular we failed to locate the hydrido hydrogen, although some positive electron density was found in the region in which this atom would be present.

Computations were carried out on a CDC 6600 computer using the X-ray 70 program package [6]. The scattering factors were those given by Cromer and Waber [7], using the anomalous dispersion corrections for Pt [8]. In the final cycles the positions of the 38 aromatic hydrogen atoms were calculated by assuming C—H 1.08 Å and the contributions of these atoms were included in  $F_{\text{calcd}}$  with scattering factor taken from ref. 9 and isotropic temperature factors equal to that of the atoms to which they are bonded.

The final  $R = \sum(\Delta F)/\sum(F_{\text{obs}})$  based on the 4673 observed reflections was 0.069. The ratios of the parameter shifts to standard deviations in the last cycle were less than  $0.1 \sigma$ .

Final positional and thermal parameters obtained from the least-squares refinement are given in Table 2 and bond lengths and angles in Table 3. Table 4 shows selected torsional angles of the dtt ligand. A list of observed and calculated structure factors ( $\times 10$ ) can be obtained from the authors.

TABLE 2

FINAL COORDINATES ( $\times 10^4$ ) AND THERMAL PARAMETERS ( $\times 10^3$ ) FOR THE ATOMS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	U
Pt	2972.5(6)	1900.8(6)	4331.0(9)	a
P(1)	1699(4)	1156(4)	2859(6)	a
P(2)	4394(4)	2462(4)	5531(6)	a
N(1)	2259(12)	3174(12)	5165(16)	53(4)
N(2)	2145(12)	3841(12)	4632(17)	54(4)
N(3)	2529(12)	3595(13)	3610(18)	61(5)
C(1)	1368(17)	137(17)	3134(24)	65(6)
C(2)	371(23)	-192(24)	2572(33)	105(10)
C(3)	68(27)	-1018(27)	2763(38)	121(12)
C(4)	741(29)	-1448(28)	3419(40)	126(12)
C(5)	1763(33)	-1149(33)	4076(46)	152(15)
C(6)	1976(22)	-340(23)	3777(32)	97(9)
C(7)	646(16)	1884(16)	2780(23)	62(6)
C(8)	243(19)	2197(19)	3917(28)	81(8)
C(9)	-594(21)	2803(21)	3875(30)	90(8)
C(10)	-984(24)	3070(24)	2762(35)	105(10)
C(11)	-608(28)	2732(28)	1586(40)	125(12)
C(12)	242(22)	2135(22)	1650(32)	98(9)
C(13)	1961(16)	748(16)	1192(23)	62(6)
C(14)	2534(19)	1334(20)	929(28)	82(8)
C(15)	2799(19)	1031(20)	-374(28)	81(8)
C(16)	2541(22)	220(22)	-1254(31)	94(9)
C(17)	1883(22)	-419(22)	-1087(32)	98(9)
C(18)	1641(20)	-157(21)	249(30)	88(8)
C(19)	4931(16)	1825(17)	6650(24)	66(6)
C(20)	4522(20)	1039(21)	6557(29)	88(8)
C(21)	4930(25)	523(25)	7460(36)	112(11)
C(22)	5787(22)	868(23)	8386(32)	96(9)
C(23)	6213(26)	1641(27)	8545(37)	120(11)
C(24)	5807(26)	2224(26)	7656(37)	119(11)
C(25)	5193(16)	2370(16)	4436(23)	60(6)
C(26)	6154(22)	2772(22)	5027(31)	96(9)
C(27)	6809(32)	2877(32)	4086(47)	154(16)
C(28)	6412(24)	2238(24)	2756(35)	106(10)
C(29)	5539(25)	1922(24)	2180(34)	107(10)
C(30)	4937(21)	1995(21)	3107(30)	89(8)
C(31)	4385(17)	3708(17)	6549(24)	65(6)
C(32)	4148(28)	3980(29)	7791(41)	129(3)
C(33)	4250(30)	4985(32)	8706(44)	140(14)
C(34)	4284(24)	5631(25)	8182(36)	109(10)
C(35)	4444(28)	5362(29)	6923(42)	130(13)
C(36)	4471(21)	4377(22)	6089(30)	90(8)
C(37)	1839(15)	3388(15)	6277(21)	55(5)
C(38)	2027(16)	2720(17)	6957(24)	65(6)
C(39)	1606(17)	2844(17)	8066(24)	70(6)
C(40)	993(16)	3600(17)	8482(24)	69(6)
C(41)	804(18)	4230(18)	7809(26)	77(7)
C(42)	1236(15)	4155(15)	6760(21)	55(5)
C(43)	2430(16)	4337(16)	3057(22)	61(6)
C(44)	2996(18)	4249(18)	2139(26)	75(7)
C(45)	2883(26)	4758(27)	1385(37)	119(11)
C(46)	2295(20)	5592(20)	1650(28)	84(8)
C(47)	1770(21)	5706(22)	2602(31)	95(9)
C(48)	1814(18)	5080(19)	3290(26)	77(7)
C(49)	2154(28)	6259(28)	787(40)	130(13)
C(50)	531(22)	3726(23)	9620(32)	101(9)

(continued)

TABLE 2 (continued)

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Pt	468(5)	484(5)	552(6)	42(4)	138(4)	146(4)
P(1)	474(33)	478(33)	586(36)	-10(26)	64(27)	155(28)
P(2)	484(33)	556(35)	540(34)	23(24)	143(27)	166(28)

<sup>a</sup> Anisotropic thermal parameters ( $\times 10^4$ ) in the form:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

## Description of the structure

The structure consists of the packing of discrete molecules of  $\text{PtH}(\text{dtt})(\text{PPh}_3)_2$ .

Fig. 1 is a perspective view of the molecule showing the labelling of the atoms while in Fig. 2 the projection of the cell content along  $[010]$  is shown. The position of the hydrido hydrogen is missing because it was not determined by X-ray analysis but the presence of this hydrogen has been unambiguously established by IR ( $\nu(\text{Pt}-\text{H})$   $2143\text{ cm}^{-1}$ ) and  $^1\text{H}$  NMR (triplet centered at  $\tau$  24.2 ppm) data [10].

Besides the hydrido hydrogen the other atoms bonded to the Pt atom indicate a distorted square coordination geometry with *trans*-P(1) and -P(2) atoms from the two triphenylphosphines and the N(1) from the triazenido ligand. The Pt atom deviates from the plane constituted by the three above-mentioned atoms by 0.08 Å. The other N atom, labelled N(3), is in close contact with the metal

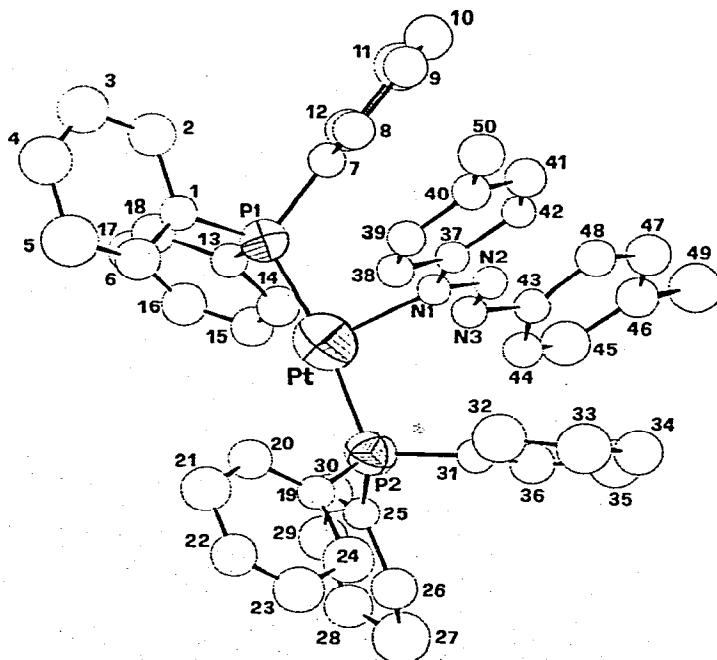


Fig. 1. Perspective view of the molecule.

TABLE 3

SOME IMPORTANT INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) IN THE COMPLEX WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

## (a) Bond distances

Pt—P(1)	2.268(5)	C(38)—C(39)	1.42(4)
Pt—P(2)	2.267(5)	C(39)—C(40)	1.38(3)
Pt—N(1)	2.09(2)	C(40)—C(41)	1.36(4)
P(1)—C(1)	1.80(3)	C(41)—C(42)	1.39(4)
P(1)—C(7)	1.81(2)	C(42)—C(37)	1.40(3)
P(1)—C(13)	1.82(3)	C(40)—C(50)	1.51(5)
P(2)—C(19)	1.82(3)	C(43)—C(44)	1.40(4)
P(2)—C(25)	1.81(3)	C(44)—C(45)	1.29(6)
P(2)—C(31)	1.81(2)	C(45)—C(46)	1.43(5)
N(1)—N(2)	1.31(3)	C(46)—C(47)	1.38(5)
N(1)—C(37)	1.40(3)	C(47)—C(48)	1.39(5)
N(2)—N(3)	1.28(3)	C(48)—C(43)	1.36(3)
N(3)—C(43)	1.43(4)	C(46)—C(49)	1.58(6)
C(37)—C(38)	1.43(4)		

## (b) Non-bonded contacts

Pt...N(3)	2.91	C(32)...C(37)	3.48
Pt...N(2)	2.99	C(7)...N(1)	3.28
Pt...C(38)	3.24	C(32)...N(1)	3.48
Pt...C(14)	3.43	C(31)...N(2)	3.52
Pt...C(20)	3.48	N(1)...C(8)	3.23
Pt...C(30)	3.46	N(1)...P(1)	3.22
Pt...H(14)	2.90	N(1)...P(2)	3.20
Pt...H(20)	2.81	C(37)...C(8)	3.20
Pt...H(30)	2.77	C(31)...N(1)	3.20
Pt...H(38)	2.64	C(36)...N(2)	3.47
		C(36)...N(3)	3.44

## (c) Bond angles

P(1)—Pt—N(1)	95.1(4)	N(3)—C(43)—C(48)	126(2)
P(2)—Pt—N(1)	94.2(4)	C(44)—C(43)—C(48)	118(3)
N(1)—Pt—N(3)	47.1(7)	C(43)—C(44)—C(45)	124(3)
Pt—P(1)—Cl	114.1(8)	C(44)—C(45)—C(46)	120(4)
Pt—P(1)—C(7)	115.7(7)	C(45)—C(46)—C(47)	115(3)
Pt—P(1)—C(13)	108.2(8)	N(1)—C(37)—C(38)	115(2)
C(1)—P(1)—C(7)	105.4(12)	N(1)—C(37)—C(42)	128(2)
C(1)—P(1)—C(13)	107.2(11)	C(38)—C(37)—C(42)	117(2)
C(7)—P(1)—C(13)	105.5(11)	C(37)—C(38)—C(39)	120(2)
Pt—P(2)—C(19)	113.0(8)	C(38)—C(39)—C(40)	120(3)
Pt—P(2)—C(25)	110.7(7)	C(39)—C(40)—C(41)	120(3)
Pt—P(2)—C(31)	114.2(8)	C(40)—C(41)—C(42)	122(2)
C(19)—P(2)—C(25)	107.3(12)	C(41)—C(42)—C(37)	121(2)
C(19)—P(2)—C(31)	106.6(11)	C(39)—C(40)—C(50)	120(3)
C(25)—P(2)—C(31)	104.4(12)	C(41)—C(40)—C(50)	120(2)
Pt—N(1)—C(37)	125(2)	N(3)—C(43)—C(44)	116(2)
P(1)—Pt—P(2)	169.6(2)	C(46)—C(47)—C(48)	123(3)
Pt—N(1)—N(2)	121(1)	C(47)—C(48)—C(43)	119(3)
N(2)—N(1)—C(37)	114(2)	C(45)—C(46)—C(49)	123(3)
N(1)—N(2)—N(3)	111(2)	C(47)—C(46)—C(49)	122(3)
N(2)—N(3)—C(43)	111(2)		

(2.81 Å); if we consider the N(3) atom as “coordinated” we can describe the coordination mode as a distorted trigonal bipyramid: the equatorial substituents being N(1), N(3) and the hydrido hydrogen, and the apical ligands being the two phosphines. Such a structure might be postulated as the intermediate which accounts for the fluxional behaviour of the compound [4].

TABLE 4  
TORSION ANGLES ( $^{\circ}$ ) (average e.s.d.  $2^{\circ}$ )

Pt—P(1)—C(1)—C(6)	-24
Pt—P(1)—C(7)—C(8)	-67
Pt—P(1)—C(13)—C(14)	-35
Pt—P(2)—C(19)—C(20)	8
Pt—P(2)—C(25)—C(30)	-1
Pt—P(2)—C(31)—C(32)	85
N(1)—Pt—P(1)—C(1)	243
N(1)—Pt—P(1)—C(7)	6
N(1)—Pt—P(1)—C(13)	124
N(1)—Pt—P(2)—C(19)	117
N(1)—Pt—P(2)—C(25)	238
N(1)—Pt—P(2)—C(31)	-5
N(2)—N(1)—C(37)—C(42)	8
N(2)—N(3)—C(43)—C(48)	-18

The angles A—B—C—D are defined as 0 when the bonds A—B and C—D are *cis* planar. They are counted positive when looking along the central B—C bond, the far bond is rotated clockwise with respect to the near bond.

The Pt—P distances (2.268(5) and 2.267(5) Å) are virtually identical with those (*viz.* 2.267(8) and 2.269(8) Å) in the compound *trans*-Pt(PPh<sub>2</sub>Et)<sub>2</sub>HCl [11], and are among the shortest distances found between P and second or third row transition elements. The Pt—N(1) bond distance of 2.09(2) Å is longer than that found in *trans*-PdCl(PPh<sub>3</sub>)<sub>2</sub>(dtf), 2.033(4) Å [5], probably because of the higher *trans* influence of the hydrogen; moreover in the latter compound the M—P distances (*viz.* 2.329(3) and 2.320(3) Å) are significantly longer when one considers that palladium(II) and platinum(II) have essentially the same radii. This might be an indication of a stronger M—P  $\pi$ -bonding contribution in our case (see the Owston et al. discussion [12]).

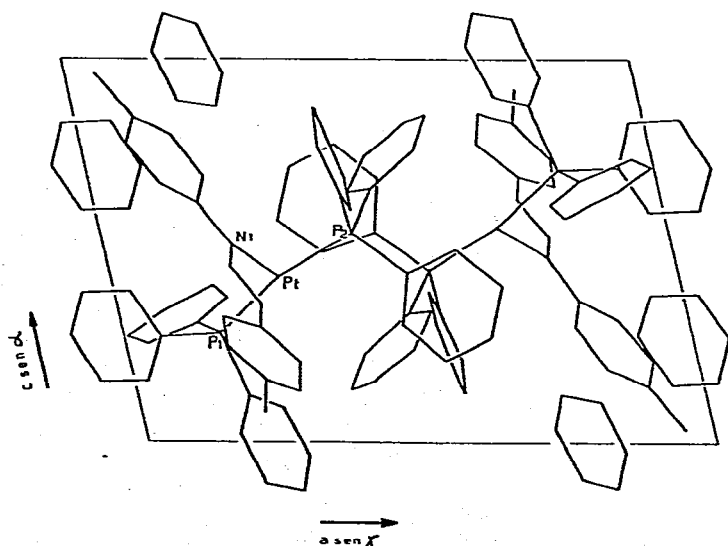


Fig. 2. Unit cell content viewed down the *b* axis.

In addition to the interactions Pt...N(2) (2.99 Å) and Pt...N(3) (2.91 Å) the Pt atom is involved in a short intramolecular contact of 2.64 Å to an *ortho* hydrogen atom of a tolyl ring. (The Pt...C(38) distance associated with this contact Pt...H is 3.24 Å).

The P(1)—Pt—P(2) angle of 169.6(2)° deviates from the ideal value of 180° as in the other hydrido compound [11] and is smaller than that in *trans*-PdCl(dtt)(PPh<sub>3</sub>)<sub>2</sub> (178.0(1)°) [5]. This is probably due to steric interactions between the dtt ligand and the triphenylphosphine groups and to the smaller Van der Waals radius of hydrogen with respect to the chlorine atom; this allows, a greater approach between the two *trans*-PPh<sub>3</sub> groups in our case. Some relevant contacts in the molecule are shown in Table 3.

The dtt ligand maintains the conformation previously seen in PdCl(PPh<sub>3</sub>)<sub>2</sub>(dtt) with the sequence C(37)—N(1)—N(2)—N(3)—C(43) almost zig-zag planar. With respect to this plane the tolyl groups are slightly twisted, 9.6 and 13.3°, respectively, (cf. in the Pd compound, 4.4 and 15.2°). The C(37)—N(1)—N(2)—N(3)—C(43) plane makes an angle of 89.9° with the coordination plane and the metal atom is coplanar to it ( $\Delta$  0.004 Å).

The bond distances and angles in the dtt ligand are comparable to those of the Pd complex. The triphenylphosphine groups have the expected values for bond lengths and angles within the limits of their e.s.d.'s.

The conformation of the two phosphine ligands are rather different as already observed in the PdCl(PPh<sub>3</sub>)<sub>2</sub>(dtt) compound. The conformation of P(1)Ph<sub>3</sub> resembles that of one phosphine in the above mentioned compound, and is roughly similar to that obtained by conformational analysis [13]. That of P(2)Ph<sub>3</sub> on the contrary is completely different with two torsion angles near 0 (see Table 4).

The presence of numerous C...C and C...N intramolecular contacts among dtt and phenyls (see Table 3) accounts for the deviations from the usual conformation.

## References

- 1 K.R. Laing, S.D. Robinson and M.F. Uttley, *J. Chem. Soc. Dalton Trans.*, (1974) 1205.
- 2 J. Kuyper, P.I. van Vliet and K. Vrieze, *J. Organometal. Chem.*, 96 (1975) 289.
- 3 S. Candeloro De Sanctis, N.V. Pavel and L. Toniolo, *J. Organometal. Chem.*, 108 (1976) 409.
- 4 L. Toniolo, U. Croatto, A. Immirzi and G. Bombieri, *Inorg. Chim. Acta.*, in press.
- 5 G. Bombieri, A. Immirzi and L. Toniolo, *Inorg. Chem.*, in press.
- 6 J.M. Stewart, F.A. Kundell and J.C. Baldwin, *X-ray '70 System of Crystallographic Programs*, version of July 1970, Univ. Maryland.
- 7 D.T. Cromer and J.T. Waber, *Acta Cryst.*, 18 (1976) 104.
- 8 D.T. Cromer, *Acta Cryst.*, 18 (1976) 17.
- 9 *International Tables for X-ray Crystallography*, Vol. 111 1962, Kynoch Press, Birmingham.
- 10 L. Toniolo, G. De Luca and C. Panattoni, *Synth. Inorg. Metalorg. Chem.*, 3 (1973) 221.
- 11 R. Eisenberg and J.A. Ibers, *Inorg. Chem.*, 4 (1965) 773 and refs. cited therein.
- 12 P.G. Owston, J.M. Partridge and J.M. Rowe, *Acta Cryst.*, 13 (1960) 246.
- 13 C.P. Brock and J.A. Ibers, *Acta Cryst.*, B, 29 (1973) 2426.