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Crystal and Molecular Structure of Trans-(Methyl)chlorobis(triphenylphosphine)platinum(II)

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The crystal and molecular structure of trans-$Pt(CH_3)Cl(PPh_3)_2$ *has been determined. Crystals are monoclinic, space group* $P2_1/n$, $a = 11.813(7)$, $b = 23.523(9)$, $c = 12.306(7)$ Å, $\beta = 111.7(1)^\circ$, $Z = 4$. *2676 observed reflections were measured with a diffractometer; the structure was solved by Patterson-Fourier methods and refined by full-matrix least-squares to a final conventional* R *of 0.049* ($R_w = 0.041$). *The crystal contains discrete neutral* trans-$Pt(CH_3)Cl(PPh_3)_2$ *molecules, separated by normal van der Waals contacts. The complex is a typical square-planar Pt(II) species. Structural parameters:* Pt–Cl = 2.431(3), Pt–C = 2.08(1), Pt–P = 2.295(3) *and* 2.298(3) Å; P(1)–Pt–Cl = 88.1(1), P(1)–Pt–C(1) = 92.3(4), P(2)–Pt–Cl = 88.1(1) *and* P(2)–Pt–C(1) = 91.6(4)°.

Introduction

We are studying a number of palladium(II) and platinum(II) complexes in an attempt to find correlations between molecular structure and chemical behaviour [1–6]. In the course of this research we had the opportunity of obtaining good crystals of *trans*-(methyl)chlorobis(triphenylphosphine)platinum(II), suitable for crystal structure studies.

Structural and spectroscopic features together with reactivity evidence indicate that the σ M–C (alkyl) bonds of organo-transition metal complexes increase in strength with increasing electronegativity of the alkyl chain (R_X), as dictated by alkyl substituents, such as X = F, CN, NO_2, *etc.* [7–9]. In view of the recent interest concerning the unusual stability of Pt-(σ-R_X) complexes [8–19] and mainly to compare bonding parameters and ligand–ligand steric interactions of the unsubstituted alkyl complexes (Pt–R_H) with those of the electronegatively substituted alkyl analogs (Pt–R_X), we report here on the crystal and molecular structure of *trans*-$PtCl(CH_3)(PPh_3)_2$. Moreover the present X-ray structure analysis was thought to provide an ideal basis for a study of structural features with their possible implications in the more general subject of *cis*- and *trans*-influence.

Experimental

Single crystals of *trans*-$PtCl(CH_3)(PPh_3)_2$, suitable for X-ray structural analysis, were obtained by evaporation of the solvent from ethanolic solutions. Precession photographs and single-crystal diffractometry showed that the crystals belong to the monoclinic system, space group $P2_1/n$, with $a = 11.813(7)$, $b = 23.523(9)$, $c = 12.306(7)$ Å, $\beta = 111.7(1)^\circ$, $V = 3177.3$ Å^3, $D_o = 1.61$, $D_c = 1.616$ g cm^{-3} for $Z = 4$; λ (MoK$\bar{\alpha}$) = 0.7107 Å, μ (MoK$\bar{\alpha}$) = 48.59 cm^{-1}.

Intensity data were collected from a crystal of approximate dimensions 0.2 × 0.3 × 0.2 mm, on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.3°, scan speed = 0.04° s^{-1}). 4992 independent reflections up to $\theta = 24^\circ$ were measured, of which 2676 had $I \geqslant 3\sigma(I)$, $\sigma(I)$ being calculated from counting statistics. During the data collection two standard reflections were measured every 180 min to check the stability of the crystals and electronics. Intensities were corrected for Lorentz and polarisation effects and were converted to an absolute scale by Wilson's method. An experimental absorption correction was applied [20].

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed the position of the Pt atom. The positions of the remaining non-hydrogen atoms were derived from subsequent difference Fourier maps. The structure was refined by full-matrix least-squares procedure. The function minimized was $\Sigma w[|F_o|-|F_c|]^2$ in which $w = [\sigma^2(F_o) + 0.01\ F_o^2]^{-1}$. The scattering factors were those of the International Tables for X-ray Crystallography [21]. The correction for the real and imaginary parts of the anomalous dispersion was applied to Pt, Cl and P [22].

The refinement was carried out with the phenyl rings treated as rigid groups and restricted to their

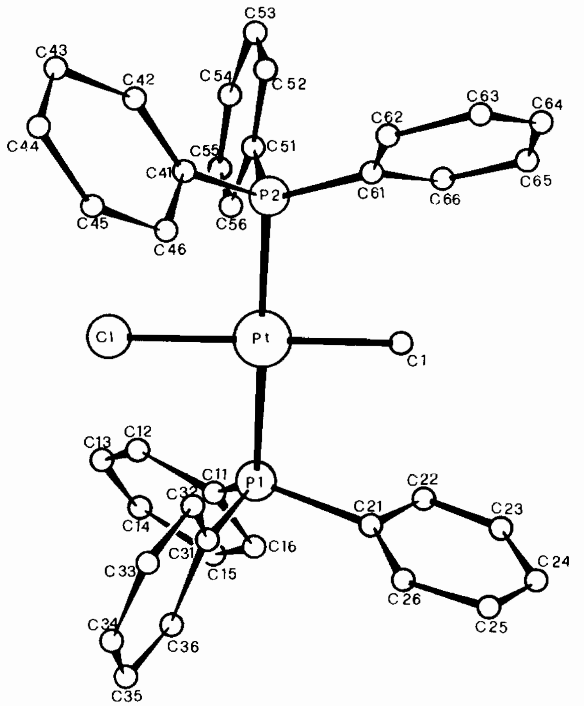

Fig. 1. A perspective view of the neutral molecule of *trans*-$PtCl(CH_3)(PPh_3)_2$, with the atomic numbering system used in the analysis. Hydrogen atoms are omitted for clarity.

normal geometry (D_{6h} symmetry, C–C = 1.395 Å) using the group-refinement procedure [23]. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. The remaining non-hydrogen atoms were allowed to vibrate anisotropically. The conventional R value fell to 0.050. At this stage a difference Fourier map yielded the coordinates of the H atoms of the phenyl rings. The refinement was carried on with the H atoms of the phenyl rings constrained to their normal geometry (C–H = 0.95 Å) using the group-refinement procedure. The final R value for the 2676 observed reflections with $I \geqslant 3\sigma(I)$ was 0.049 ($R_w = 0.041$).

The calculations were carried out the CYBER 76 computer of the C.I.N.E.C.A. with the SHELX-76 program for crystal structure determination [24].

TABLE I. Atomic Positional (Fractional Coordinates) Parameters with Estimated Standard Deviations in Parentheses for the Complex.

Atom	X	Y	Z
Pt	0.1745(1)	0.1525(0)	0.9967(0)
Cl	0.2042(3)	0.0522(2)	1.0472(3)
C(1)	0.1652(16)	0.2391(6)	0.9592(14)
	Triphenylphosphine group 1		
P(1)	0.1629(3)	0.1287(2)	0.8117(3)
C(11)	0.0313(8)	0.0856(4)	0.7260(6)
C(12)	−0.0343(8)	0.0555(4)	0.7809(6)
C(13)	−0.1334(8)	0.0221(4)	0.7147(6)
C(14)	−0.1668(8)	0.0188(4)	0.5937(6)
C(15)	−0.1012(8)	0.0490(4)	0.5388(6)
C(16)	−0.0021(8)	0.0824(4)	0.6050(6)
C(21)	0.1512(8)	0.1864(4)	0.7083(9)
C(22)	0.0401(8)	0.2148(4)	0.6584(9)
C(23)	0.0284(8)	0.2593(4)	0.5801(9)
C(24)	0.1277(8)	0.2755(4)	0.5517(9)
C(25)	0.2387(8)	0.2471(4)	0.6016(9)
C(26)	0.2504(8)	0.2026(4)	0.6799(9)
C(31)	0.2967(9)	0.0876(4)	0.8185(8)
C(32)	0.4051(9)	0.0956(4)	0.9141(8)
C(33)	0.5086(9)	0.0644(4)	0.9232(8)
C(34)	0.5037(9)	0.0251(4)	0.8367(8)
C(35)	0.3953(9)	0.0170(4)	0.7411(8)
C(36)	0.2818(9)	0.0483(4)	0.7320(8)
	Triphenylphosphine group 2		
P(2)	0.1809(3)	0.1696(2)	1.1824(3)
C(41)	0.3134(8)	0.1358(4)	1.2918(9)
C(42)	0.3115(8)	0.1151(4)	1.3973(9)
C(43)	0.4187(8)	0.0954(4)	1.4833(9)
C(44)	0.5277(8)	0.0964(4)	1.4637(9)
C(45)	0.5296(8)	0.1171(4)	1.3582(9)
C(46)	0.4224(8)	0.1368(4)	1.2722(9)
C(51)	0.0456(8)	0.1442(3)	1.2066(7)
C(52)	0.0132(8)	0.1665(3)	1.2960(7)
C(53)	−0.0910(8)	0.1468(3)	1.3120(7)
C(54)	−0.1626(8)	0.1048(3)	1.2387(7)
C(55)	−0.1302(8)	0.0824(3)	1.1493(7)
C(56)	−0.0260(8)	0.1021(3)	1.1333(7)
C(61)	0.1981(7)	0.2439(4)	1.2356(8)
C(62)	0.3106(7)	0.2634(4)	1.3127(8)
C(63)	0.3223(7)	0.3192(4)	1.3542(8)
C(64)	0.2215(7)	0.3553(4)	1.3186(8)
C(65)	0.1090(7)	0.3357(4)	1.2415(8)
C(66)	0.0973(7)	0.2800(4)	1.2000(8)

Description of the Structure

A perspective view of the molecule showing its conformation and the atomic numbering system used in the analysis is presented in Fig. 1. The final structural parameters with their e.s.d.s of the non-hydrogen atoms are reported in Table I; in Table II bond lengths and valence angles for all non-hydrogen atoms, uncorrected for changes due to thermal vibrations, are given. Some least-sqares planes and dihedral angles are shown in Table III. The structure, described by the cell constants, the symmetry operations of the space group and the atomic parameters, consists of the packing of discrete neutral molecules of *trans*-$PtCl(CH_3)(PPh_3)_2$ separated by van der Waals contacts. The closest Pt······Pt approach is 8.18 Å and all remaining intermolecular contacts agree with those predicted from radii-sum rules.

TABLE II. Bond Lengths (A) and Angles (°) for the Complex.

Distances

Triphenylphosphine group 1

		C(23)–C(24)	1.395
P(1)–C(11)	1.827(9)	C(24)–C(25)	1.395
C(11)–C(12)	1.395	C(25)–C(26)	1.395
C(12)–C(13)	1.395	C(26)–C(21)	1.395
C(13)–C(14)	1.395	P(1)–C(31)	1.828(9)
C(14)–C(15)	1.395	C(31)–C(32)	1.395
C(15)–C(16)	1.395	C(32)–C(33)	1.395
C(16)–C(11)	1.395	C(33)–C(34)	1.395
P(1)–C(21)	1.832(10)	C(34)–C(35)	1.395
C(21)–C(22)	1.395	C(35)–C(36)	1.395
C(22)–C(23)	1.395	C(36)–C(31)	1.395

Triphenylphosphine group 2

		C(53)–C(54)	1.395
P(2)–C(41)	1.827(10)	C(54)–C(55)	1.395
C(41)–C(42)	1.395	C(55)–C(56)	1.395
C(42)–C(43)	1.395	C(56)–C(51)	1.395
C(43)–C(44)	1.395	P(2)–C(61)	1.849(9)
C(44)–C(45)	1.395	C(61)–C(62)	1.395
C(45)–C(46)	1.395	C(62)–C(63)	1.395
C(46)–C(41)	1.395	C(63)–C(64)	1.395
P(2)–C(51)	1.831(9)	C(64)–C(65)	1.395
C(51)–C(52)	1.395	C(65)–C(66)	1.395
C(52)–C(53)	1.395	C(66)–C(61)	1.395

Coordination plane

Pt–Cl	2.431(3)	Pt–P(1)	2.298(3)
Pt–C(1)	2.08(1)	Pt–P(2)	2.295(3)

Angles

Triphenylphosphine group 1

Pt–P(1)–C(11)	115.7(3)	P(1)–C(21)–C(26)	121.5(3)
Pt–P(1)–C(21)	117.9(3)	C(21)–C(22)–C(23)	120.0
Pt–P(1)–C(31)	110.4(3)	C(22)–C(23)–C(24)	120.0
C(11)–P(1)–C(21)	100.4(4)	C(23)–C(24)–C(25)	120.0
C(21)–P(1)–C(31)	105.4(4)	C(24)–C(25)–C(26)	120.0
C(31)–P(1)–C(11)	105.7(4)	C(25)–C(26)–C(21)	120.0
P(1)–C(11)–C(12)	120.5(2)	C(26)–C(21)–C(22)	120.0
P(1)–C(11)–C(16)	119.5(2)	P(1)–C(31)–C(32)	118.4(3)
C(11)–C(12)–C(13)	120.0	P(1)–C(31)–C(36)	121.6(3)
C(12)–C(13)–C(14)	120.0	C(31)–C(32)–C(33)	120.0
C(13)–C(14)–C(15)	120.0	C(32)–C(33)–C(34)	120.0
C(14)–C(15)–C(16)	120.0	C(33)–C(34)–C(35)	120.0
C(15)–C(16)–C(11)	120.0	C(34)–C(35)–C(36)	120.0
C(16)–C(11)–C(12)	120.0	C(35)–C(36)–C(31)	120.0
P(1)–C(21)–C(22)	118.5(3)	C(36)–C(31)–C(32)	120.0

Triphenylphosphine group 2

Pt–P(2)–C(41)	111.1(3)	P(2)–C(51)–C(56)	119.0(2)
Pt–P(2)–C(51)	113.3(3)	C(51)–C(52)–C(53)	120.0

(continued overleaf)

TABLE II. *(continued)*

Pt–P(2)–C(61)	118.5(3)	C(52)–C(53)–C(54)	120.0
C(41)–P(2)–C(51)	107.4(4)	C(53)–C(54)–C(55)	120.0
C(51)–P(2)–C(61)	103.9(4)	C(54)–C(55)–C(56)	120.0
C(61)–P(2)–C(41)	101.4(4)	C(55)–C(56)–C(51)	120.0
P(2)–C(41)–C(42)	122.2(3)	C(56)–C(51)–C(52)	120.0
P(2)–C(41)–C(46)	117.4(3)	P(2)–C(61)–C(62)	120.3(2)
C(41)–C(42)–C(43)	120.0	P(2)–C(61)–C(66)	119.6(2)
C(42)–C(43)–C(44)	120.0	C(61)–C(62)–C(63)	120.0
C(43)–C(44)–C(45)	120.0	C(62)–C(63)–C(64)	120.0
C(44)–C(45)–C(46)	120.0	C(63)–C(64)–C(65)	120.0
C(45)–C(46)–C(41)	120.0	C(64)–C(65)–C(66)	120.0
C(46)–C(41)–C(42)	120.0	C(65)–C(66)–C(61)	120.0
P(2)–C(51)–C(52)	121.0(2)	C(66)–C(61)–C(62)	120.0
		Coordination plane	
P(1)–Pt–P(2)	175.7(1)	P(2)–Pt–C(1)	91.6(4)
P(1)–Pt–C(1)	92.3(4)	P(2)–Pt–Cl	88.1(1)
P(1)–Pt–Cl	88.1(1)	C(1)–Pt–Cl	175.1(5)

TABLE III. Some Least-Squares Planes and Distances (A) of Atoms to the Plane. The equation of the plane is in the form $AX + BY + CZ = D$, where, X, Y, Z are coordinates referred to orthogonal A space.

Plane 1: $0.9470\,X + 0.0858\,Y + 0.3096\,Z = 1.5178$

Pt	−0.024	Cl(1)	0.068
P(1)	−0.060	C(1)	0.075
P(2)	−0.060		

Plane 2: $-0.4185\,X + 0.8335\,Y - 0.3609\,Z = -0.0883$
Pt, P(1), C(11)

Plane 3: $0.9509\,X + 0.0351\,Y + 0.0374\,Z = 1.2778$
Pt, P(1), C(21)

Plane 4: $0.5295\,X + 0.8469\,Y - 0.0487\,Z = 1.1735$
Pt, P(1), C(31)

Plane 5: $0.5609\,X + 0.8265\,Y + 0.0466\,Z = 2.1093$
Pt, P(2), C(41)

Plane 6: $-0.3578\,X + 0.8852\,Y - 0.2973\,Z = 0.6720$
Pt, P(2), C(51)

Plane 7: $0.9287\,X - 0.1034\,Y + 0.3560\,Z = 1.3899$
Pt, P(2), C(61)

Twist Angle (°)[a] between the Least-Squares Plane of the Phenyl Ring and corresponding Pt–P–C plane

Pt–P(1)–C(11) and C(11)–C(16)	18.3
Pt–P(1)–C(21) and C(21)–C(26)	75.2
Pt–P(1)–C(31) and C(31)–C(36)	27.4
Pt–P(2)–C(41) and C(41)–C(46)	25.9
Pt–P(2)–C(51) and C(51)–C(56)	21.5
Pt–P(2)–C(61) and C(61)–C(66)	77.9

TABLE III. *(continued)*

Dihedral Angles (°) between the Phenyl Rings	
C(11)–C(16) and C(21)–C(26)	65.0
C(11)–C(16) and C(31)–C(36)	71.5
C(21)–C(26) and C(31)–C(36)	85.3
C(41)–C(46) and C(51)–C(56)	72.1
C(41)–C(46) and C(61)–C(66)	82.8
C(51)–C(56) and C(61)–C(66)	59.5

[a] The twist angle is here taken to be the acute dihedral angle between the Pt–P–C and C_6 planes.

The P atoms are *trans* to one another and together with the Cl atom lie at three of the four corners of a distorted square. The fourth corner is occupied by the methyl carbon atom. The Pt atom is at the centre of the square. The least-squares plane (Table III) through the five atoms of the coordination sphere indicates that this portion of the molecule is significantly non-planar, nor are the four ligand atoms surrounding the platinum atom planar. Moreover there are slight but significant deviations of angles between the platinum atom and its nearest neighbors from the idealized values of 90 and 180°. These facts suggest, as is verified by some of the shortest intramolecular non-bonded distances listed in Table IV, that there is considerable steric crowding in the vicinity of the platinum atom. As was expected from the cell constants and the space group, the complex is isostructural with *trans*-$\mathrm{PtCl(CH_2CN)(PPh_3)_2}$, [25] and with *trans*-PtCl $(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{PPh_3})_2$, [26].

TABLE IV. Shorter Intramolecular Non-bonded Distances (Å).

Cl······C(31)	3.47
Cl······P(1)	3.29
Cl······P(2)	3.29
C(1)······C(21)	3.28
C(1)······C(61)	3.27
C(1)······P(1)	3.17
C(1)······P(2)	3.14

Discussion

It has been suggested [27, 28] that in platinum complexes the Pt–P bond length will depend on the π-acceptor properties of the other ligands; they will reduce the amount of dπ–dπ bonding possible between the platinum and phosphorus atoms and hence the Pt–P distance should be increased. Therefore the longest Pt–P bonds (2.34 and 2.35 Å) are found in $Pt(CO)Cl(PEt_3)_2^+$, [29], where the coordinated carbon monoxide is believed to possess appreciable π-acceptor properties [28]. The mutually *trans* Pt–P bonds in the present compound are equal in length, 2.295(3) and 2.298(3) Å, and very close to those observed in the analogous compounds *trans*-$PtCl(CH_3)(PMePh_2)_2$, 2.291(2) and 2.292(2) Å, [30] and *trans*-$PtCl(CH_3)(PEt_3)_2$, 2.296(3) Å [31].

Moreover they fall within the range found recently for Pt–P distances in several square-planar Pt(II) complexes [26, 32, 33].

In addition the Pt–P distances in the present complex are slightly shorter than those found in the analogous compounds *trans*-$PtCl(CH_2CN)(PPh_3)_2$, 2.308(3) and 2.310(3) Å, [25] and *trans*-$PtCl(\eta^1$-$C_3H_5)(PPh_3)_2$, 2.302(2) and 2.304(2) Å, [26]. Therefore dπ–dπ interaction between Pt and P atoms in these complexes would increase along the series $CH_2CN < \eta^1$-$C_3H_5 < CH_3$.

The Pt–C(1) bond length, 2.08(1) Å, agrees well with the sum of appropriate covalent radii (2.08 Å) and with the Pt–C σ-bonds in some platinum alkyl complexes, *e.g.*, 2.08(1) Å in *trans*-$PtCl(CH_2CN)(PPh_3)_2$, [25], 2.081(6) Å in *trans*-$PtCl(CH_3)(PMePh_2)_2$, [30], and 2.090(4) Å in *trans*-$PtCl(\eta^1$-$C_3H_5)(PPh_3)_2$ [26]. It is interesting to note that the methyl group in the present complex also seems to be ineffective in shortening the Pt–C bond. On the contrary the Pt–C bond in the perfluoroethyl derivative *trans*-$PtCl(CF_2CF_3)(PMePh_2)_2$, 2.002(9) Å, [30] is significantly shorter, indicating the effectiveness of the fluorine groups.

The Pt–Cl distance of 2.431(3) Å, which is longer than predicted from radii-sum rules (2.30 Å), is close to the values found in *trans*-$PtCl(Me_3$–Si–$CH_2)(PMe_2Ph)_2$, 2.415(5) Å, [34], in *trans*-$PtCl(\eta^1$-$C_3H_5)(PPh_3)_2$, 2.425(2) Å, [26], and in *cis*-$[PtCl_2$-$CH(CH_2NH_2CHMePhe)CH_2)_2$ $CH{:}CH_2]$, 2.430 Å, [35].

The Pt–P and Pt–Cl bond distances of several *trans*-$PtXClP_2$ complexes have been reported recently by Ibers [26]. McWeeney *et al.* [36] have noted a good correlation between the electronegativity of the atom X (*trans* to Cl) and the Pt–Cl distances in such complexes; the Pt–Cl bond is lengthened as the electronegativity of atom X decreases. Although the rationalization of the *trans*-influence in Pt(II) complexes solely on the basis of electronegativity is probably an oversimplification, as has been emphasized by Ibers [26], we conclude from the above data [25, 26, 30, 34, 36] that the *trans*-influence of the methyl group is very close to those of the σ-C_3H_5, trimethylsilylmethyl group, hydrido ligand and slightly greater than that of a cyanoalkyl group.

The triphenylphosphine geometry in this compound, as judged by P–C distances and C–P–C angles, is nearly identical with the geometry of the

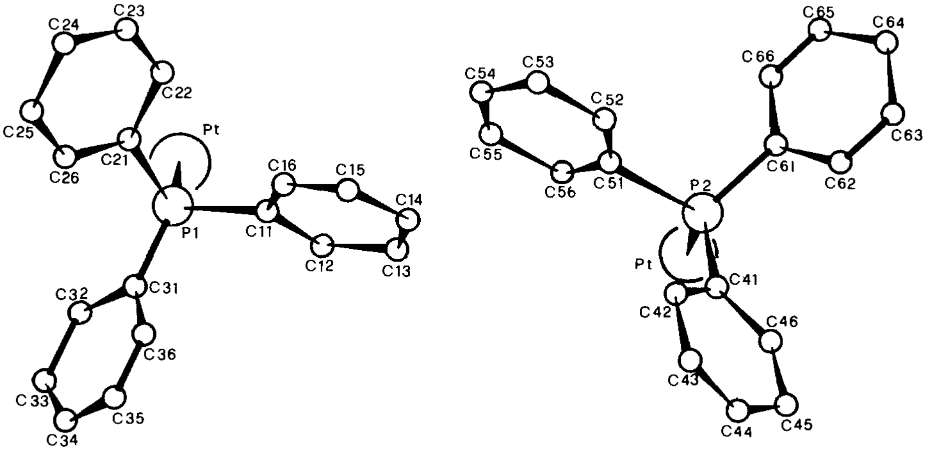

Fig. 2. Conformations of the two triphenylphosphine ligands viewed along the P–Pt bonds.

triphenylphosphine ligand and its derivatives in other transition metal complexes, [23, 25, 26, 36, 38]. In particular the P–C distances range from 1.827 to 1.849 Å and average 1.832(9) Å; The C–P–C angles range from 100.4 to 107.4° and average 104.2(4)°.

In many compounds containing coordinated PPh_3 groups [39] it was found that the plane of one of the phenyl rings essentially contains the metal-phosphorus vector, another phenyl ring is twisted *ca.* 90° about its P–C bond with respect to the first ring, while the third phenyl ring assumes an intermediate orientation. The examined complex does not conform to this stereochemistry (Fig. 2). Of the phenyl groups attached to P(2), the ring C(61)–C(66) lies roughly at right angles to the plane Pt, P(2), C(61) while the other two rings C(41)–C(46) and C(51)–C(56) are both at angles of *ca.* 23° with respect to their corresponding Pt–P–C planes. For P(1), however, while the ring C(11)–C(16) is only slightly twisted from the plane Pt, P(1), C(11), the ring C(21)–C(26) lies roughly at right angles to the plane Pt, P(1), C(21). The third ring C(31)–C(36) is in an intermediate position with respect to the plane Pt, P(1), C(31) (Tably III).

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