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Ligand Profiles of Tricyclohexylphosphine. Structure of (π-Allyl)bis(tricyclohexylphosphine)platinum Hexafluorophosphate

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Received March 21, 1978

The crystal structure of $[Pt(C_3H_5)(PCy_3)_2]^+PF_6^-\cdot C_7H_8$ has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 19.362$ (1) Å, $b = 11.964$ (1) Å, $c = 21.718$ (1) Å, and $\beta = 109.61$ (1)°. A calculated density of 1.45 g cm^{-3} for four formula weights per unit cell agrees with the observed value of 1.45 g cm^{-3}. The coordination about the platinum atom is essentially square planar with the PCy_3 ligands cis to each other. Pertinent metrical details are Pt–P (av) 2.330 (3) Å, Pt–C(terminal) 2.24 (2) Å, Pt–C(central) 2.17 (4) Å, $\angle$P–Pt–P 111.2 (1)°, $\angle$C–Pt–C 68.3 (6)°, and $\angle$P–Pt–C (av) 90.3 (7)°. The observed lengthening of the Pt–P and Pt–C bond lengths is discussed in terms of both steric and electronic effects. The "ligand profiles" of the PCy_3 ligands are computed and compared with "profiles" of other PCy_3 ligands. This work reveals the first case of the π-allyl group occupying two discrete orientations within the coordination sphere of an organometallic compound in the solid state. This phenomenon may partially explain the temperature-dependent features of the NMR spectra of the compound. Full-matrix least-squares refinement has yielded a conventional R of 0.047 (0.072 for weighted R) based on the 3495 reflections whose intensities are significantly above background ($I_{net} > 7$ counts s^{-1}).

Introduction

The utilization of metal–phosphine complexes as catalysts has stimulated a great deal of research in the past 2 decades.[1] Both electronic and steric effects have been shown to contribute to the structure of these compounds. In 1970, Tolman[2] defined a steric parameter, the cone angle θ, which describes the bulkiness of PR_3 ligands. More recently, Ferguson et al.[3] and Payne et al.,[4] using crystallographic structural data, have expanded Tolman's concept by calculating a series of $\theta/2$ values as a function of the angle of rotation about the metal to phosphorus bond to generate a resultant "ligand profile". The low-temperature ^{1}H NMR spectra of $[Pt(C_3H_5)(PCy_3)_2]^+PF_6^-$ revealed a fluctionality that was interpreted as a nonequivalence of the syn protons of the π-allyl group.[5] The authors attributed this phenomenon to an intermeshing of the PCy_3 ligands to the extent that rotation of these ligands about the Pt–P bonds is restricted. Since this compound is expected to possess structural features related to steric bulk as well as electronic influences, an X-ray study was initiated.

Experimental Section

A sample for the diffraction study was kindly supplied by Attig and Clark and was recrystallized from methylene chloride and toluene. The data crystal (clear) was mounted with b^* parallel to the ϕ axis of the goniometer. All X-ray measurements were made on a Diano XRD-700 diffractometer equipped with a single-crystal orienter, with Cu Kα radiation, and at ambient room temperature (~21 °C).

Intensity weighted plots of the reciprocal lattice revealed systematic absences consistent with the space group $P2_1/n$. Cell parameters listed in Table I were obtained by least-squares refinement of 36 independent 2θ measurements with Kα_1 and Kα_2 well resolved. Measurements of ω scans for several reflections showed the peaks to be single, narrow, and symmetrical indicating suitable quality for the stationary-crystal, stationary-counter technique of data collection (5° takeoff angle, 1° receiving slit) using a balanced nickel-cobalt filter pair.

At frequent intervals throughout the data collection, the crystal was aligned (1° takeoff angle, 0.05° receiving slit) and the intensities of six check reflections were monitored. Examination of the net intensities of these check reflections revealed a linear isotropic decay (9% by the end of data collection). The intensity data were broken into five blocks of approximately equal size and the appropriate decay correction factor was applied to each block.

Additional corrections for absorption as a function of crystal shape[6] (correction factors ranging from 1.54 to 2.17), for Lorentz and polarization effects and for α_1–α_2 splitting,[7] were applied. The method used to calculate standard deviations in the observed structure factor amplitudes has been described elsewhere.[8]

Solution and Refinement of the Structure

The coordinates of the platinum and the three phosphorus atoms were determined from a sharpened three-dimensional Patterson map. A subsequent electron density map revealed the positions of the six fluorine atoms and the eighteen carbon atoms associated with P(2). Two cycles of full-matrix least-squares refinement of this model yielded $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.203$ and $R_2 = [\sum(w||F_o| - |F_c||^2)/\sum w|F_o|^2]^{1/2} = 0.328$, where $w = 1/\sigma^2(|F_o|)$. A difference electron density map then revealed the positions of the remaining carbon atoms of the cation and a toluene molecule of solvation. The toluene molecule showed no signs of disorder and was treated as a planar rigid body (no methyl hydrogens were included). Additional refinement of this model employing anisotropic temperature factors for the Pt and the three P atoms yielded $R_1 = 0.060$ and $R_2 = 0.089$.

A difference electron density map calculated at this time revealed a second orientation for the central atom of the π-allyl group, several peaks of 0.25 to 0.80 e Å^{-3} in reasonable positions for hydrogen atoms of the cyclohexyl rings, and several peaks between 1 and −1 e Å^{-3} in the vicinity of the Pt atom and the PF_6^- group. A difference map computed after a structure factor calculation excluding atom C(2) from the structure showed two distinct positions for the central carbon atom of the π-allyl group with occupancy factors of 0.6 and 0.4. These peaks were labeled C(2A) and C(2B), respectively. The cyclohexyl hydrogen atoms were idealized[9] and given thermal parameters of $B = 5.5$ Å^2. Two additional cycles of least-squares refinement (hydrogen atoms were not allowed to vary and were reidealized before the final cycle) yielded a final $R_1 = 0.047$ and $R_2 = 0.072$. A final difference map showed peaks ranging between 0.9 and −0.9 e Å^{-3} near the Pt atom and the PF_6^- group, as well as a randomly fluctuating background below 0.5 eÅ^{-3}. Atomic scattering factors for the Pt, P, F, and C atoms were taken from Cromer and Waber.[10] The anomalous dispersion corrections for the platinum and phosphorus atoms were taken from Cromer and Liberman.[11] Scattering factors for the hydrogen atoms were those of Stewart, Davidson, and Simpson.[12] Final atomic parameters are listed in Tables II and III.

Table I

Crystal Data for $PtP_3F_6C_{39}H_{71}\cdot C_7H_8$

formula wt 1034.1
$a = 19.362$ (1) A
$b = 11.964$ (1) A
$c = 21.718$ (1) A
$\beta = 109.61$ (1)°
$V = 4738.7$ A^3
$d_{calcd} = 1.45$ g cm^{-3}
$d_{measd} = 1.45$ g cm^{-3} (flotation in $AgNO_3$)

monoclinic
systematic absences
$0k0$ for k odd
$h0l$ for $h + l$ odd
equiv positions
$\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z)$
space group $P2_1/n$
$Z = 4$
$F(000) = 2120$ e

Data Collection

crystal dimensions: 0.07 × 0.10 × 0.20 mm
μ(Cu K$\bar{\alpha}$) = 70.15 cm^{-1}
4360 symmetry-independent reflections for $5 < 2\theta < 95°$

Discussion

The structure of $[Pt(C_3H_5)(PCy_3)_2]^+PF_6^-\cdot C_7H_8$ exists as discrete cations, anions, and solvate molecules. The smallest

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Table II. Fractional Coordinates $\times 10^4$ and Temperature Factors[a] $\times 10^3$ of the Anisotropic Atoms

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt[b]	49144 (2)	8717 (5)	29822 (3)	368 (4)	279 (4)	372 (4)	−8 (3)	152 (3)	−8 (3)
P(1)	4488 (2)	2592 (3)	3214 (2)	31 (2)	33 (2)	37 (2)	−1 (2)	11 (2)	−2 (2)
P(2)	5436 (2)	1044 (3)	2166 (3)	32 (2)	34 (2)	39 (2)	−1 (2)	12 (2)	−3 (2)
P(3)	2794 (3)	541 (4)	4889 (3)	87 (4)	61 (3)	96 (4)	1 (3)	42 (3)	0 (2)

[a] Numbers in parentheses are the estimated standard deviations in the units of the least significant digits. The temperature factor expression for the anisotropic atoms is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] Positional parameters are presented $\times 10^5$ and thermal parameters are presented $\times 10^4$ for this atom.

Table III. Fractional Coordinates $\times$ 10^4 and Thermal Parameters[a] $\times$ 10^3

Isotropic Atoms

atom	x	y	z	U_{iso}, Å^2
C(1)	4473 (9)	45 (13)	3700 (7)	64 (4)
C(2A)	5074 (21)	−516 (26)	3675 (18)	101 (18)
C(2B)	4523 (30)	−704 (38)	3227 (26)	90 (25)
C(3)	5176 (8)	−959 (12)	3080 (7)	57 (4)
Cy(1)				
C(4)	4709 (6)	2667 (10)	4110 (6)	37 (3)
C(5)	5499 (7)	2361 (11)	4500 (6)	46 (4)
C(6)	5569 (8)	2117 (12)	5208 (7)	58 (4)
C(7)	5308 (8)	3078 (13)	5511 (7)	61 (4)
C(8)	4535 (8)	3416 (12)	5119 (7)	55 (4)
C(9)	4465 (7)	3677 (12)	4393 (6)	49 (4)
Cy(2)				
C(10)	3483 (7)	2788 (10)	2898 (6)	39 (3)
C(11)	3053 (8)	1854 (12)	3111 (7)	57 (4)
C(12)	2235 (9)	2140 (13)	2878 (8)	72 (5)
C(13)	1950 (9)	2248 (15)	2144 (8)	84 (5)
C(14)	2360 (9)	3144 (14)	1933 (7)	71 (5)
C(15)	3174 (7)	2867 (11)	2150 (6)	50 (4)
Cy(3)				
C(16)	4831 (7)	3887 (10)	2931 (6)	38 (4)
C(17)	4430 (7)	4980 (11)	2951 (6)	47 (4)
C(18)	4715 (8)	5896 (11)	2596 (7)	53 (4)
C(19)	5548 (9)	6031 (13)	2907 (8)	68 (5)
C(20)	5938 (8)	4928 (12)	2919 (7)	55 (4)
C(21)	5650 (7)	4032 (11)	3268 (6)	46 (4)
Cy(4)				
C(22)	6462 (6)	951 (10)	2472 (6)	35 (3)
C(23)	6816 (7)	1958 (11)	2861 (6)	49 (4)
C(24)	7657 (8)	1939 (14)	3004 (6)	70 (5)
C(25)	7977 (9)	888 (14)	3375 (8)	75 (5)
C(26)	7596 (9)	−141 (14)	3004 (7)	69 (5)
C(27)	6765 (8)	−96 (12)	2851 (7)	54 (4)
Cy(5)				
C(28)	5154 (7)	−199 (11)	1631 (6)	47 (4)
C(29)	4345 (7)	−469 (12)	1409 (6)	50 (4)
C(30)	4185 (8)	−1653 (13)	1130 (7)	65 (5)
C(31)	4504 (10)	−1787 (16)	596 (9)	92 (6)
C(32)	5297 (9)	−1499 (14)	776 (8)	73 (5)
C(33)	5429 (8)	−296 (13)	1038 (7)	59 (4)
Cy(6)				
C(34)	5233 (6)	2312 (10)	1645 (6)	39 (3)
C(35)	4430 (7)	2375 (12)	1250 (6)	49 (4)
C(36)	4233 (8)	3539 (13)	926 (7)	60 (4)
C(37)	4720 (8)	3858 (12)	530 (7)	58 (4)
C(38)	5533 (8)	3720 (12)	917 (7)	58 (4)
C(39)	5700 (7)	2572 (12)	1220 (6)	51 (4)
F(1)	3166 (7)	1139 (10)	5572 (6)	140 (5)
F(2)	2685 (6)	1729 (11)	4544 (6)	136 (4)
F(3)	2436 (8)	−47 (14)	4217 (8)	178 (6)
F(4)	2932 (9)	−607 (15)	5221 (8)	199 (7)
F(5)	2059 (8)	640 (11)	5022 (7)	162 (5)
F(6)	3559 (7)	474 (11)	4778 (6)	148 (5)

Group C_7H_8:[b] $x_0 = 0.7515$ (3), $y_0 = 0.4413$ (7), $z_0 = 0.4922$ (4); $\phi = -2.687$ (10), $\theta = 2.233$ (5), $\rho = -1.996$ (10); $U = 0.0098$ (2)

Derived Toluene Group Atoms

atom	x	y	z
TC(1)	7557	5378	4575
TC(2)	7715	4337	4363
TC(3)	7673	3372	4711
TC(4)	7472	3449	5270
TC(5)	7314	4491	5482
TC(6)	7357	5455	5134
TC(7)	7603	6428	4196
TH(2)	7851	4284	3982
TH(3)	7780	2664	4567
TH(4)	7443	2793	5507
TH(5)	7178	4543	5862
TH(6)	7249	6163	5278

[a] The temperature factor expression for the isotropic atoms is $\exp[-8\pi^2 U_{\text{iso}}(\sin^2\theta)/\lambda^2]$. [b] A description of the group parameters is provided elsewhere.[13] Angular coordinates are in radians. The internal coordinates of the toluene molecule were defined as follows: the molecule was defined to lie in the xy plane with the center of the six-membered ring at the origin, the vector from the origin to TC(1) was coincident with the positive x axis, and the vector from the origin to the midpoint of TC(5)-TC(6) was coincident with the positive y axis. The standard geometry of toluene was assumed.[14]

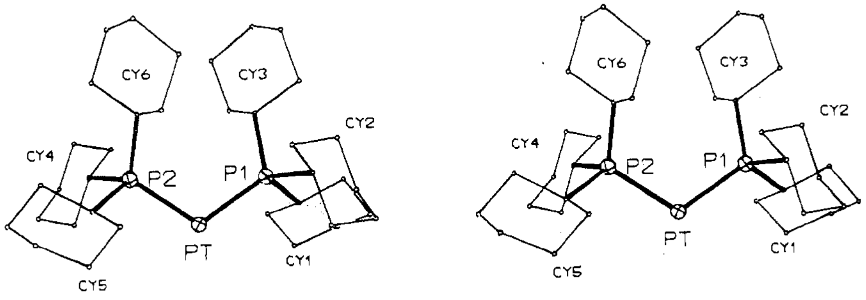

Figure 1. Stereoview of the $Pt(PCy_3)_2$ moiety illustrating the meshing of the bulky ligands.

intermolecular nonbonded contact distance is 2.42 Å (H(13A)···H(18A)) and the smallest intermolecular distance between nonhydrogen atoms is 3.33 Å (F(1)···C(2A)). Bond distances and bond angles are given in Tables V and VI, respectively. Figures 1 and 2 depict the stereochemistry of the cation.

Table V. Selected Bond Distances (Å) for $[Pt(C_3H_5)(PCy_3)_2]^+PF_6^-\cdot C_7H_8$

Pt–P(1)	2.335 (3)	C(10)–C(11)	1.56 (2)
Pt–P(2)	2.327 (4)	C(10)–C(15)	1.54 (2)
Pt–C(1)	2.24 (2)	C(11)–C(12)	1.53 (2)
Pt–C(2A)	2.19 (3)	C(12)–C(13)	1.51 (2)
Pt–C(2B)	2.16 (5)	C(13)–C(14)	1.50 (2)
Pt–C(3)	2.24 (2)	C(14)–C(15)	1.52 (2)
P(1)–C(4)	1.85 (1)	C(16)–C(17)	1.53 (2)
P(1)–C(10)	1.85 (1)	C(16)–C(21)	1.52 (2)
P(1)–C(16)	1.87 (1)	C(17)–C(18)	1.55 (2)
P(2)–C(22)	1.88 (1)	C(18)–C(19)	1.53 (2)
P(2)–C(28)	1.85 (1)	C(19)–C(20)	1.52 (2)
P(2)–C(34)	1.85 (1)	C(20)–C(21)	1.52 (2)
P(3)–F(1)	1.59 (1)	C(22)–C(23)	1.50 (2)
P(3)–F(2)	1.59 (1)	C(22)–C(27)	1.51 (2)
P(3)–F(3)	1.56 (2)	C(23)–C(24)	1.55 (2)
P(3)–F(4)	1.53 (2)	C(24)–C(25)	1.51 (2)
P(3)–F(5)	1.55 (2)	C(25)–C(26)	1.52 (2)
P(3)–F(6)	1.58 (1)	C(26)–C(27)	1.53 (2)
C(1)–C(2A)	1.36 (4)	C(28)–C(29)	1.51 (2)
C(1)–C(2B)	1.39 (5)	C(28)–C(33)	1.55 (2)
C(2A)–C(3)	1.47 (4)	C(29)–C(30)	1.53 (2)
C(2B)–C(3)	1.44 (6)	C(30)–C(31)	1.49 (2)
C(4)–C(5)	1.52 (2)	C(31)–C(32)	1.49 (3)
C(4)–C(9)	1.50 (2)	C(32)–C(33)	1.54 (2)
C(5)–C(6)	1.52 (2)	C(34)–C(35)	1.50 (2)
C(6)–C(7)	1.49 (2)	C(34)–C(39)	1.53 (2)
C(7)–C(8)	1.51 (2)	C(35)–C(36)	1.55 (2)
C(8)–C(9)	1.57 (2)	C(36)–C(37)	1.52 (2)
		C(37)–C(38)	1.52 (2)
		C(38)–C(39)	1.51 (2)

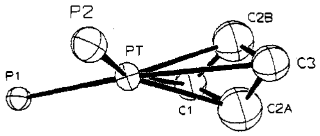

Figure 2. Perspective view of the coordination plane illustrating the two orientations of the π-allyl ligand.

Each cyclohexyl ring is in a chair conformation. The absolute value of the endocyclic torsion angles[15] varies from 50.8 to 60.9° with a mean value of 57.3°. The absolute values of only two such angles are less than 53.3° (ωC(35)–C(36)–C(37)–C(38) = 50.8° and ωC(36)–C(37)–C(38)–C(39) = 51.8°). These values compare favorably with those found in $Ni(C_{14}H_{10})(PCy_3)_2$.[16] The average C–C–C bond angle in the cyclohexyl rings is 110.5°, with only one C–C–C angle deviating more than 2σ from this average. The average C–C bond distance in the cyclohexyl rings is 1.52 Å.

The phosphorus atoms and the atoms C(1) and C(3) of the π-allyl group form a distorted square-planar configuration about the Pt atom with the PCy_3 ligands cis to each other. The planes formed by the two orientations of the π-allyl group form dihedral angles of 66.5 and 70.6° with the plane defined by the atoms P(1), P(2), C(1), and C(3). As seen from Table VII, the Pt–P bond lengths in the title compound are significantly longer than those in $Pt(PCy_3)_2$[21] and *trans*-$PtH(S_2CH)(PCy_3)_2$.[22] Bond lengthening of this type can frequently be rationalized using the electronic concept of the trans influence.[24] Ligands which exhibit a larger trans influence lengthen the bonds which are opposite them in square-planar and octahedral compounds. Clark et al. have found that the trans influences of PR_3 and a σ-bonded carbon atom are approximately equal. Raper and McDonald[25] have shown that the trans influence of a σ-bonded carbon atom is greater than that of a π-bonded carbon atom. One would then expect the π-bonded carbon atoms to produce no lengthening of the Pt–P bonds in the title compound. The lengthening of the Pt–P bonds in this work must be a consequence of the steric bulk of the PCy_3 ligands. In agreement with this conclusion, other compounds[4,20,23] which exhibit high degrees of crowding of the PR_3 ligands reveal bond lengths similar to or even longer than those in this work. In these cases several short intramolecular nonbonded contact distances between ligands occur which also reflect extensive crowding in each compound. The data in

Table VI. Selected Bond Angles (deg) for $[Pt(C_3H_5)(PCy_3)_2]^+PF_6^-\cdot C_7H_8$

P(1)–Pt–P(2)	111.2 (1)	C(16)–C(17)–C(18)	108.8 (11)
P(1)–Pt–C(1)	89.6 (4)	C(17)–C(18)–C(19)	110.7 (12)
P(2)–Pt–C(3)	91.0 (4)	C(18)–C(19)–C(20)	111.1 (12)
C(1)–Pt–C(3)	68.3 (6)	C(19)–C(20)–C(21)	110.9 (12)
Pt–P(1)–C(4)	107.3 (4)	C(20)–C(21)–C(16)	109.9 (11)
Pt–P(1)–C(10)	115.8 (4)	C(21)–C(16)–C(17)	110.3 (11)
Pt–P(1)–C(16)	118.0 (4)	C(22)–C(23)–C(24)	110.6 (11)
Pt–P(2)–C(22)	113.8 (4)	C(23)–C(24)–C(25)	109.4 (13)
Pt–P(2)–C(28)	107.2 (5)	C(24)–C(25)–C(26)	110.7 (14)
Pt–P(2)–C(34)	118.6 (4)	C(25)–C(26)–C(27)	112.0 (13)
C(4)–P(1)–C(10)	103.1 (6)	C(26)–C(27)–C(22)	109.7 (12)
C(4)–P(1)–C(16)	108.9 (6)	C(27)–C(22)–C(23)	109.8 (11)
C(10)–P(1)–C(16)	102.6 (6)	C(28)–C(29)–C(30)	112.0 (12)
C(22)–P(2)–C(28)	103.2 (6)	C(29)–C(30)–C(31)	109.0 (13)
C(22)–P(2)–C(34)	104.3 (6)	C(30)–C(31)–C(32)	115.4 (15)
C(28)–P(2)–C(34)	108.5 (6)	C(31)–C(32)–C(33)	110.0 (14)
P(1)–C(4)–C(5)	114.0 (9)	C(32)–C(33)–C(28)	108.4 (12)
P(1)–C(4)–C(9)	118.4 (9)	C(33)–C(28)–C(29)	109.1 (11)
P(1)–C(10)–C(11)	113.7 (9)	C(34)–C(25)–C(36)	110.7 (11)
P(1)–C(10)–C(15)	112.8 (9)	C(35)–C(36)–C(37)	112.1 (12)
P(1)–C(16)–C(17)	117.4 (9)	C(36)–C(37)–C(38)	112.4 (12)
P(1)–C(16)–C(21)	111.4 (9)	C(37)–C(38)–C(39)	111.7 (12)
P(2)–C(22)–C(23)	112.5 (9)	C(38)–C(39)–C(34)	111.4 (11)
P(2)–C(22)–C(27)	114.5 (9)	C(39)–C(34)–C(35)	110.6 (11)
P(2)–C(28)–C(29)	115.3 (10)	F(1)–P(3)–F(2)	89.1 (7)
P(2)–C(28)–C(33)	118.0 (10)	F(1)–P(3)–F(4)	90.7 (9)
P(2)–C(34)–C(35)	110.9 (9)	F(1)–P(3)–F(5)	87.0 (8)
P(2)–C(34)–C(39)	119.2 (9)	F(1)–P(3)–F(6)	90.7 (8)
C(1)–C(2A)–C(3)	125.7 (29)	F(2)–P(3)–F(3)	90.9 (8)
C(1)–C(2B)–C(3)	125.9 (40)	F(2)–P(3)–F(5)	92.0 (7)
C(4)–C(5)–C(6)	109.8 (11)	F(2)–P(3)–F(6)	87.5 (7)
C(5)–C(6)–C(7)	111.6 (12)	F(3)–P(3)–F(4)	89.3 (9)
C(6)–C(7)–C(8)	112.1 (12)	F(3)–P(3)–F(5)	93.5 (9)
C(7)–C(8)–C(9)	110.9 (12)	F(3)–P(3)–F(6)	88.8 (8)
C(8)–C(9)–C(4)	108.5 (11)	F(4)–P(3)–F(5)	90.4 (9)
C(9)–C(4)–C(5)	112.1 (11)	F(4)–P(3)–F(6)	90.2 (9)
C(10)–C(11)–C(12)	109.9 (12)		
C(11)–C(12)–C(13)	109.8 (13)		
C(12)–C(13)–C(14)	110.1 (14)		
C(13)–C(14)–C(15)	110.5 (13)		
C(14)–C(15)–C(10)	109.6 (12)		
C(15)–C(10)–C(11)	107.6 (11)		

Table VII. A Comparison of Pt–P Bond Lengths (Å) and P–Pt–P Bond Angles (deg) in Compounds Containing the $Pt(PR_3)_2$ Fragment

compound	$Pt-P(PCy_3)$ length	P–Pt–P	ref
	cis-$Pt(PR_3)_2$		
$[Pt(C_3H_5)(PCy_3)_2]^+$-$PF_6^-\cdot C_7H_8$	2.335 (3), 2.327 (4)	111.2 (1)	this work
$Pt(PCy_3)_2(F_3CC{\equiv}CCF_3)$	2.309 (2)	110.2 (1)	4
$Pt(PPh_3)_2(F_3CC{\equiv}CCF_3)$		110.17 (4)	17
$Pt(PPh_3)_2(CO\cdot OCMe_2$-$C{:}CH_2)$		99.8 (1)	18
$Pt(PPh_3)_2(C_8H_{12}O)$		108.6 (1)	19
	trans-$Pt(PR_3)$		
$Pt(PCy_3)_2I_2$	2.371 (2)		20
$Pt(PCy_3)_2$	2.231 (4)		21
$Pt(PCy_3)_2(S_2CH)$	2.274 (5), 2.278 (5)		22
	$Pt(PR_3)_3$		
$[PtH(PCy_3)_2$-$(PPh_3)]^+PF_6^-$	2.346 (3), 2.325 (3)		23

Table VIII. $\theta/2$ Values vs. ϕ in 20° Intervals from "Ligand Profiles" of PCy_3 Ligands

compound	defining atoms[a]	α[b]	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	ref
$[Pt(C_3H_5)L_2]^+$ [c]	Pt, P(1), P(2)	0	58	69	73	72	54	82	88	80	61	58	60	75	79	76	75	68	54	54	58	this work
$[Pt(C_3H_5)L_2]^+$	Pt, P(2), P(1)	0	58	69	73	71	54	81	88	80	61	58	61	76	79	76	75	67	54	54	58	this work
$Ni(C_{14}H_{10})L_2$	Ni, P(1), P(2)	170	63	75	77	74	60	79	86	74	58	58	58	73	70	74	79	68	58	60	63	16
$Ni(C_{14}H_{10})L_2$	Ni, P(2), P(1)	−8	57	67	69	67	58	81	88	77	59	57	57	66	68	81	84	80	57	57	57	16
LS	M,[d] P, C(1)	100	65	78	82	79	57	79	82	78	65	61	58	77	80	82	80	77	58	61	65	27
PtI_2L_2	Pt, P, I	4	59	69	71	69	53	76	81	72	57	53	58	76	75	80	83	74	57	56	59	20
$CuClO_4L_2$	Cu, P, C(11)	−15	61	72	77	74	57	80	88	77	61	57	61	78	79	81	80	74	57	57	61	26
$Pt(F_3CC{\equiv}CCF_3)L_2$	Pt, P(1), P(2)	−15	56	62	66	67	55	82	90	81	63	60	61	79	84	82	78	76	55	55	56	4
$Pt(F_3CC{\equiv}CCF_3)L_2$	Pt, P(2), P(1)	0	57	65	71	71	55	72	85	78	61	60	60	80	87	84	76	77	58	55	57	4
$[Hg(NO_3)_2L]_2$	Hg, P, C(11)	−46	70	81	87	84	53	53	74	87	81	61	58	53	76	79	86	85	84	66	59	3

[a] The three atoms defining the reference ($\phi = 0$) plane are listed in the order P1, P2, and P3. [b] The angular shift in ϕ necessary to obtain the best agreement of $\theta/2$ values vs. ϕ. [c] $L = PCy_3$. [d] A hypothetical metal atom position 2.26 A from the P atom along the P–S bond was used in this calculation.

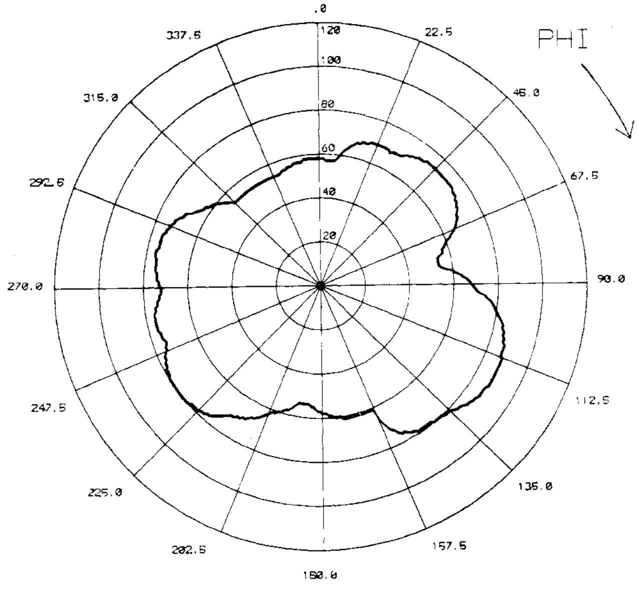

Figure 3. Ligand profile involving P(1).

Table IX. Cone Angles, C–P–C Bond Angles, and Metal–Phosphorus Bond Lengths for Some Compounds Containing PCy_3 Ligands

compound	θ	C–P–C (av), deg	M–P, A	ref
$[Hg(NO_3)_2PCy_3]_2$	175	109.6	2.359	3
$CuClO_4(PCy_3)_2$	165	106.5	2.262	26
PCy_3S	164	105.4	2.26[a]	27
$Ni(C_{14}H_{10})(PCy_3)_2$	161, 162	104.7	2.227, 2.241	16
$[Pt(C_3H_5)(PCy_3)_2]^+ \cdot PF_6^- \cdot C_7H_8$	162, 162	105.1	2.335, 2.327	this work
$Pt(PCy_3)_2I_2$	157	105.2	2.371	20

[a] Refer to footnote *d* in Table VIII.

Table VII also reveal that the P–Pt–P bond angles of the title compound, of $Pt(PCy_3)_2(F_3CC{\equiv}CCF_3)$[4] and of $Pt(PPh_3)_2(C_8H_{12}O)$[18] are considerably larger than those found in other cis $Pt(PR_3)$ compounds due to steric crowding between the PR_3 ligands. A similar trend has been noted in $Cu(PR_3)_2$ compounds.[26]

Figure 1 dramatizes the extent to which the PCy_3 ligands are meshed together with Cy(3) protruding between Cy(4) and Cy(6). This feature illustrates the major limitation of the cone angle concept for quantitative use due to the assumption of spherically symmetrical cone angles. Such an assumption would then disallow the intermeshing of these bulky ligands which is commonly observed. To help relieve this deficiency we have devised a program similar to that of Ferguson et al.[3] whereby a "ligand profile" is generated as an array of angles $\theta/2$ vs. ϕ; where $\theta/2$ is the angle between the metal–phosphorus bond and a vector from the metal atom which touches the van der Waals sphere of the outermost atom of the ligand and ϕ is the angle of clockwise rotation of this vector away from a reference plane. The reference plane is defined by three points, P_1, P_2, and P_3, where $P_1 \rightarrow P_2$ corresponds to the $+z$ axis, $z \times (P_1 \rightarrow P_3)$ defines the $+y$ axis, and $y \times z$ defines the $+x$ direction. Figure 3 shows a polar plot of $\theta/2$ vs. ϕ involving P(1) of the title compound.

"Ligand profiles" were calculated for several compounds containing the PCy_3 ligand. In each case van der Waals radii were set as follows: hydrogen, 1.20 Å; carbon, 1.80 Å; phosphorus, 1.90 Å. In cases where the hydrogen atoms were idealized before calculation of a profile, C–H bond distances were set at 0.95 Å so that the hydrogen atom positions would agree closely with those obtained from difference electron density maps. A distinct similarity of the shapes of these "ligand profiles" can be readily noted by inspection of Table VIII which contains a list of $\theta/2$ values at 20° intervals in ϕ for several compounds.

Since the reference plane used in calculating the "ligand profiles" for the bis(phosphine) complexes corresponds to the principal coordination plane, the values $\phi = 0°$ and $\phi = 180°$ are symmetry equivalent. The data in Table VIII then indicate that the PCy_3 ligands have nearly the same orientation with respect to the principal coordination plane in each of the complexes. For the mono(phosphine) complexes the shape of the profile is virtually identical with those for the bis(phosphine) complexes; however, the maxima no longer occur at the same values for ϕ in the various compounds. It is worth noting that the dimeric mercury compound[3] possesses the ligand profile least similar to the other profiles. These similarities indicate that the cone angle concept may be much more quantitative than previously thought and that it may provide an accurate basis for construction of molecular models of organometallic compounds containing PCy_3 ligands.

The magnitude of the $\theta/2$ values at each value of ϕ in these profiles is affected by both the length of the metal–phosphorus bond and the degree to which the ligand undergoes a "compression"[1] of the C–P–C angles. Using Tolman's equation[1]

$$\theta = \tfrac{2}{3} \sum_{i=1}^{3} \theta_i/2$$

where $\theta_i/2$ corresponds to the maximum $\theta/2$ value for each of the three cyclohexyl rings of the ligand, we can obtain cone angle values for each of the PCy_3 ligands for which profiles were calculated. Table IX contains a list of these cone angles, the average C–P–C bond angles, and the metal–phosphorus bond distances for each compound. The decrease in the cone angle due to a decrease in the average C–P–C bond angle is quite obvious. The decrease in the cone angle due to lengthening of the metal–phosphorus bond is a more subtle feature. The range of the cone angles, 18°, agrees well with Tolman's projected ±10° error in predicting cone angles. The cone angles of $[Hg(NO_3)_2PCy_3]_2$[3] and $Cu(ClO_4)(PCy_3)_2$[26] have previously been reported as 181 and 174°, respectively. The difference between these values and the values reported in this work presumably reflects the difference in the C–H distances used in idealizing the hydrogen atom positions.

The geometry of the π-allyl group appears normal. The absence of other published structures containing the Pt(π-allyl) moiety precludes a direct comparison of Pt–C bond distances; however, an indirect approach can be used to obtain expected values for these distances. Using the Pd–P and Pt–P bond lengths in the isomorphous compounds $Pd(PCy_3)_2$[28] and $Pt(PCy_3)_2$[21] to reflect the difference in the covalent radii, $r_{Pt} - r_{Pd}$, one obtains a value of -0.03 Å. Applying this difference to the Pd–C bond lengths in $PdCl(C_3H_5)_2$,[29] a compound in which the trans influence is expected to be slight, yields the values Pt–C(terminal) of 2.09 Å and Pt–C(central) of 2.08 Å. These expected distances are approximately 0.1 Å shorter than the values observed in each case. These differences are the results of the combined effects of steric crowding and the larger trans influence of PCy_3 compared to Cl^-.

This work reveals the first well-documented case for a π-allyl ligand occupying two discrete orientations within the coordination sphere of an organometallic compound. This highly unusual arrangement of the π-allyl group in the solid state may be a manifestation of the stabilizing effect of the PCy_3 ligand and suggests a possible second interpretation of the NMR spectrum since it has been postulated that exchange between similar orientations of π-allyl groups in other compounds[30-32] causes similar thermally dependent NMR features.

Acknowledgment. The authors gratefully acknowledge the financial support of this work by the Robert A. Welch Foundation (Grant No. AE-544).

Registry No. $[Pt(C_3H_5)(PCy_3)_2]^+PF_6^-\cdot C_7H_8$, 66922-19-8.

Supplementary Material Available: Listing of structure factor amplitudes and Table IV, atomic parameters of the idealized cyclohexyl H atoms (22 pages). Ordering information is given on any current masthead page.

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