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THE SPECTROSCOPIC AND STRUCTURAL CHARACTERIZATION OF *trans*-HYDRIDO(1,1-DIMETHYLALLENE)BIS-(TRICYCLOHEXYLPHOSPHINE)PLATINUM(II) HEXAFLUOROPHOSPHATE

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Summary

The platinum hydride cation, *trans*-$[PtH(CH_3OH)(P(C_6H_{11})_3)_2]^+$ reacts with 1,1-dimethylallene at room temperature in dichloromethane to lose methanol and form an allene complex which has been characterised by ^1H NMR spectroscopy and X-ray diffraction. Crystals grown from a mixture of hexane and *o*-dichlorobenzene are monoclinic, space group $P2_1/n$, with cell dimensions a 14.807(2), b 29.404(7), c 11.621(2) Å and β 90.75(1)°. There are four units of *trans*-$[PtH(C_5H_8)(P(C_6H_{11})_3)_2]PF_6$, $C_6H_4Cl_2$ in the cell. Three dimensional X-ray data collected by diffractometer techniques have permitted full matrix least-squares refinement to a conventional agreement factor $R = 0.052$. The platinum atom has a square planar coordination geometry, with the planar allene ligand bonded at an angle of 89.2(6)° to the coordination plane, and Pt—C distances of 2.305(10) and 2.233(10) Å.

Introduction

Recent studies [1—4] have shown that insertion of an unsaturated species such as an olefin or diene into a transition metal—hydride bond occurs by a prior coordination of the unsaturated species to the transition metal in a site *trans* to the hydride ligand. Although spectroscopic evidence for such hydrido-olefin complexes with *trans* geometry is available, structural elucidations of the isolated species are few in number [5,6]. Our investigations [7] of the reaction between the solvated cation *trans*-$[PtH(CH_3OH)(PCy_3)_2]^+$ (PCy_3 = tricyclohexylphosphine) and a number of methyl-substituted cumulated dienes (allenes) have

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led to the isolation of crystalline samples of some of the *trans*-[PtH(1,2-diene)-$(PCy_3)_2]^+$ cationic species. In this paper we describe the spectroscopic and structural characterization of the *trans*-[PtH(1,1-dimethylallene)$(PCy_3)_2]^+$ cation, suitable crystals of which were obtained as the hexafluorophosphate salt, with the inclusion of a molecule of *o*-dichlorobenzene solvent. The spectroscopic evidence for two additional allene products is also presented.

Experimental

Preparation and spectroscopy

The complex *trans*-[PtH(1,1-dimethylallene)$(PCy_3)_2]PF_6$ (I) was formed from the reaction of equimolar amounts of [*trans*-PtH$(CH_3OH)(PCy_3)_2]PF_6$ [8] and 1,1-dimethylallene in dichloromethane at 25°C. Treatment of the solution with n-pentane precipitated white crystals. Similar reactions with 1,2-pentadiene or 2,3-pentadiene in place of 1,1-dimethylallene gave the analogous products.

The ^1H NMR spectrum of I showed that bonding of the substituted allene to the platinum atom occurs through the less sterically-hindered end. This was evident from the resonance of the olefinic protons at δ —4.54 ppm, a broad singlet shifted upfield from the free allene value ($\Delta\delta$ 0.52 ppm). Platinum satellites of one-fourth intensity flanked this peak, J(Pt—H) 40 Hz. The resonances of the methyl protons of the allene ligand were overlapped by the cyclohexyl protons at δ —1.0 to —2.0 ppm and were not observed. The high field hydride resonance at δ 3.13 ppm was a 1/2/1 triplet, indicative of the trans arrangement of the phosphine ligands, J(P—H) 12 Hz [9]. This resonance is shifted downfield from the position in the complex *trans*-[PtH$(CH_3OH)(PCy_3)_2]PF_6$, where the ligand is *trans* to a weakly coordinated solvent molecule [8]. The downfield shift ($\Delta\delta$ 14.7 ppm) of the hydride resonance is indicative of the substantial *trans* influence of the allene ligand. Platinum complexes with coordinated 1,2-pentadiene and 2,3-pentadiene ligands were also characterized spectroscopically and the results are presented in Table 1.

The IR spectrum showed evidence of the hydride ligand from the Pt—H stretching mode ν(Pt—H) 2175 ± 5 cm^{-1}. However the characteristic ν_{asym}-(C=C=C) of the coordinated allene was not observed in the 1680—1760 cm^{-1} region as expected for square-planar complexes [10].

X-ray crystallography

Colourless crystals of *trans*-[PtH(1,1-dimethylallene)$(PCy_3)_2]PF_6$ were

TABLE 1

^1H NMR DATA [a] FOR [*trans*-PtH(allene)$(PCy_3)_2]PF_6$ COMPLEXES

Allene	Hydride resonance		Allene protons	
	δ (ppm)	J(P—H) (Hz)	δ (ppm)	J(Pt—H) (Hz)
1,1-Dimethylallene	+3.13	12	—4.59(m)	40
1,2-Pentadiene	+5.08	12	—4.26(m)	38
2,3-Pentadiene	+5.04	12	—4.01(m)	38

[a] Spectra run in $CDCl_3$ at 25°C with TMS reference.

TABLE 2

CRYSTAL DATA

$C_{45}H_{76}Cl_2F_6P_3Pt$	F.w. 1115.05
Analysis [a] Found (Calc.)	C, 50.62 (50.63); H, 7.23 (6.96)
a 14.807(2) Å	β 90.75(1)°
b 29.404(7) Å	V 5059.2 Å^3
c 11.621(2) Å	$Z = 4$
Density (obsvd) 1.48 g cm^{-3}	(calcd.) 1.47 g cm^{-3}

[a] Chemalytics, Inc., Tempe, Arizona.

obtained by recrystallization from an *o*-dichlorobenzene/hexane mixture, and contained a solvent molecule of *o*-dichlorobenzene per formula unit. Preliminary Weissenberg and precession photographs showed monoclinic symmetry and systematic absences of $k = 2n + 1$ for $0k0$ and $h + l = 2n + 1$ for $h0l$. This is only consistent with the monoclinic space group $P2_1/n$, a nonstandard setting of space group $P2_1/c$ [11].

A suitable crystal (0.302 mm × 0.139 mm × 0.127 mm) was mounted so that its longest dimension [100] was slightly offset from colinearity with the diffractometer spindle axis. The 12 faces of the crystal were identified by optical goniometry as forms {100}, {010}, and {001}, and faces (110), (011), $(\bar{1}\bar{1}0)$, $(\bar{1}10)$, $(0\bar{1}\bar{1})$, and $(\bar{1}11)$.

Lattice constants were determined at 25°C from a least-squares refinement [*] using the setting angles of 30 high-intensity reflections in the range $60° > 2\theta > 45°$. These reflections were carefully centered using prefiltered Cu radiation (λ 1.54056 Å) on a Picker FACS-1 diffractometer. The density of the crystals was determined by flotation in a mixture of CCl_4 and n-pentane. Crystal data are given in Table 2.

Intensity data were measured in the $\theta - 2\theta$ scan mode at a takeoff angle of 1.8°. The counter was positioned 34 cm from the crystal with an aperture size of 5 × 5 mm^2. The reflections were scanned at 2° min^{-1} from 0.75° below the K_{α_1} peak to 0.75° above the K_{α_2} peak. Backgrounds were counted for 10 s at each end of the scan. Copper foil attenuators were automatically inserted for intense reflections. Intensity data with $h \leqslant 0$, $k \geqslant 0$, $\pm l$ were collected in three shells out to a 2θ maximum of 130°. During data collection five standard reflections were measured after every 250 observations. Their intensities decreased by less than 6% throughout data collection. No corrections were made for this decrease.

The intensities of 7123 reflections were recorded in all. After correction for background, Lorentz and polarization effects, 5103 independent reflections were found with significant intensities $I > 3\sigma(I)$, where $\sigma(I) = [Tc + 0.25(tc/tb)^2(B_1 + B_2) + (pI)^2]^{1/2}$, and Tc = total counts, $tc/2tb$ is the ratio of time spent counting peak intensities to that time spent counting backgrounds, B_1 and B_2

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[*] Computing was performed on the DEC PDP-10 and the CDC Cyber 73/14 at the University of Western Ontario. Local versions of the following programs were used: cell refinement and orientation matrix, PICKTT; Fourier syntheses, FORDAP, by A. Zalkin; full-matrix least-squares refinement, WOCLS, a version of J.A. Ibers' NUCLS; function and errors, ORFFE, by W.R. Busing, H.A. Levy and K.O. Martin; and ORTEP for molecular illustrations, by C.K. Johnson.

are the background counts, p is the ignorance factor [12] which was 0.04. An absorption correction was applied to the intensity data [13]. The transmission factors ranged from 0.328 to 0.536 (μ 70.25 cm^{-1} for Cu-K_α radiation).

Structure solution and refinement

The positional parameters for the platinum atom and the two phosphine phosphorus atoms were located from a three dimensional Patterson synthesis. A series of least-squares refinements and difference Fourier synthesis calculations located the remaining 56 non-H atoms. Refinement was carried out by full matrix least-squares techniques. The function minimized is $\Sigma w(|F_0| - |F_c|)^2$, where $|F_0|$ and $|F_c|$ are the observed and calculated structure amplitudes, and $w = 4F_0^2/\sigma^2(F_0^2)$. Scattering factors for neutral Pt, P, F, Cl and C atoms were those of Cromer and Waber [14]. The scattering factors for H were those of Stewart et al. [15]. Anomalous dispersion contributions were included in the calculations of F_c; the values for $\Delta f'$ and $\Delta f''$ for Pt, P, and Cl were those of Cromer and Liberman [16].

At first the cyclohexyl rings (C—C 1.54 Å), the C atoms of the *o*-dichlorobenzene solvate (C—C 1.392 Å) and the F atoms of the hexaflorophosphate anion (P—F 1.58 Å) were refined as rigid groups with overall isotropic thermal parameters [17]. With all of the non-H atoms included with isotropic thermal parameters the structure refined to $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.12$ and $R_2 = (\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2)^{1/2} = 0.15$.

Some disorder was noted in the region of the PF_6 anion. Attempts to refine a disorder model employing two rigid groups were not successful. The best agreement was obtained refining the seven atoms of the anion as individual atoms, with anisotropic thermal parameters.

In a subsequent difference Fourier synthesis, all the cyclohexyl, benzene and methyl H atoms were located at peak heights varying from 0.96(17) to 0.47(17) eÅ^{-3}. Idealized positions for these atoms were determined assuming sp^3 and sp^2 hybridisation for cyclohexyl and benzene C atoms respectively, and a C—H distance of 0.95 Å. Of the two olefinic H atoms attached to C(1), one was readily located, 0.8(1) eÅ^{-3} at (0.231, 0.050, —0.057), while the other was less evident at 0.4(1) eÅ^{-3} at (0.112, 0.038, —0.057). Since the calculation of ideal geometries for these two atoms required arbitrary assumptions, they were not included in the model. In order to define the coordination plane of the Pt atom, a careful search was made for the hydride atom. Two peaks were present in the expected region, each of 0.7(1) eÅ^{-3}, one 1.87 Å and the other 1.53 Å distant from the Pt atom. The closest non-bonding approach to the former was 5 ClHl, at 2.30 Å, whereas the latter was 2.29 Å from P(1), a distance less than the sum of the Van der Waals radii, 3.1 Å. We therefore tentatively assigned the peak at fractional coordinates (0.150, 0.182, 0.090) to the hydride ligand, though we do not place much confidence in these coordinates. This atom was not included in the model, nor were any attempts made to refine H atom parameters.

The final cycles employed 4871 unique observations and 238 variables, and resulted in values of $R_1 = 0.052$ and $R_2 = 0.057$. In a total difference Fourier synthesis the highest peak of 0.9(1) eÅ^{-3} at (0.1655, 0.3333, —0.1988) was associated with the *o*-dichlorobenzene solvent molecule. Other peaks greater

TABLE 3

ATOMIC POSITIONAL AND THERMAL PARAMETERS [a]

Atom	x	y	z	U_{11} [b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	1628.7(3)	1289.9(1)	30.2(3)	385(2)	437(2)	438(2)	7(3)	22(1)	−7(3)
P(1)	3186(2)	1357(1)	299(2)	442(15)	412(15)	424(13)	−5(12)	15(10)	−27(11)
P(2)	70(2)	1326(1)	263(2)	408(13)	444(14)	443(13)	16(13)	21(10)	7(13)
P(3)	1640(2)	2791(1)	2973(3)	510(20)	917(26)	869(24)	−13(18)	17(17)	−82(21)
Cl(1)	1746(4)	4634(2)	−3331(5)	1578(46)	1495(45)	1765(50)	159(36)	209(37)	658(38)
Cl(2)	1652(7)	4608(3)	−667(6)	4547(139)	2029(74)	1659(62)	54(78)	−13(71)	−872(56)
C(1)	1662(7)	578(3)	−800(8)	500(65)	508(62)	505(60)	24(50)	28(49)	−65(51)
C(2)	1634(7)	908(4)	−1630(10)	437(66)	623(71)	603(71)	−11(52)	38(52)	−111(60)
C(3)	1632(7)	1091(4)	−2639(11)	454(67)	781(80)	628(79)	−39(59)	25(56)	−40(68)
C(4)	1595(8)	1601(5)	−2910(11)	678(87)	937(103)	810(89)	−98(75)	51(67)	196(76)
C(5)	1660(10)	792(5)	−3700(11)	1020(112)	1240(123)	622(83)	−180(92)	115(75)	−93(82)
F(1)	2697(5)	2766(4)	2964(8)	543(48)	2074(103)	1237(70)	−47(56)	−26(45)	8(68)
F(2)	1635(7)	2482(5)	4022(12)	1009(78)	2833(157)	2565(148)	140(84)	224(82)	1887(133)
F(3)	1707(8)	3203(4)	3818(10)	1757(105)	2041(123)	1600(100)	62(87)	−209(79)	−1046(94)
F(4)	1659(7)	3126(4)	1946(8)	1294(82)	2112(115)	1215(77)	105(75)	103(62)	650(78)
F(5)	1600(7)	2412(4)	2046(13)	1154(84)	1801(107)	3330(180)	236(74)	−274(95)	−1740(119)
F(6)	590(5)	2821(3)	2971(7)	534(47)	1968(96)	1187(67)	202(54)	100(43)	34(64)

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[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. The positional and thermal parameters have been multiplied by 10^4. [b] $U_{ij} = \beta_{ij}/(2\pi^2 a_i^{\star} a_j^{\star})$ Å^2. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE 4

GROUP PARAMETERS

Group	x_g [a]	y_g	z_g	δ	ϵ	η
Cy 1	0.3375(3)	0.0843(2)	0.2763(4)	0.088(5)	−2.645(3)	1.234(5)
Cy 2	0.3998(3)	0.2387(2)	0.0298(4)	−1.949(4)	−2.524(4)	2.818(5)
Cy 3	0.4571(3)	0.0950(2)	−0.1642(4)	0.859(6)	2.370(3)	−1.796(6)
Cy 4	−0.1311(3)	0.0930(2)	−0.1736(4)	2.394(6)	−2.392(3)	−1.717(6)
Cy 5	−0.0791(3)	0.2350(2)	0.0406(4)	−1.131(4)	2.506(4)	2.723(5)
Cy 6	−0.0097(3)	0.0764(2)	0.2667(4)	−3.210(5)	2.595(3)	1.230(5)
Ph	0.1606(5)	0.3723(3)	−0.2054(7)	−3.207(8)	−2.674(9)	1.532(8)

[a] x_g, y_g and z_g are the fractional coordinates of the group origin; δ, ϵ and η (radians) are the group orientation angles. See ref. 17.

than 0.5 e Å^{-3} corresponded to the hydride ligand, and the two olefinic H atoms, or were of no chemical significance. A listing of atomic positional and thermal parameters is given in Table 3. Group parameters are listed in Table 4, and derived group atom parameters are presented in Table 5. H atom parameters are given in Table 6, and observed and calculated structure amplitudes, as $10F_0$ vs. $10F_c$ in electrons can be obtained *. The error in an observation of unit weight was 1.81 electrons.

Description of the structure

The crystals contain discrete ions and molecules of solvent. Atom F(5) of the PF_6 anion is in the vicinity of the probable location of the hydride H atom, as is shown in the stereoview (Fig. 1). The shortest cation—anion distance is 2.53 Å, between F(1) and 5C4H1 **.

For the solvent molecule, the closest approach to the cation is 2.44 Å between 7C5H1 and 5C3H1. The inner coordination sphere of the cation is shown in Fig. 2, and selected intraionic bond distances and angles are given in Table 7.

The cation has a distorted square planar geometry, with *trans*-phosphine ligands. The dimethylallene ligand is coordinated to the metal primarily through the $H_2C{=}C$ double bond, with the bulky $C(CH_3)_2$ substituent bent back away from the metal atom. The solution ^{1}H NMR spectrum is consistent with this geometry. The Pt—C(1) and Pt—C(2) distances are 2.305(10) and 2.233(10) Å, significantly different by 5.1 σ. These values are longer than those observed in another Pt complex in which the allene ligand is perpendicular to the coordination plane, for in the dimer $[Cl_2Pt((CH_3)_2C{=}C{=}C(CH_3)_2)]_2$ distances of 2.25(2) and 2.07(2) Å were found [18,19]. Shorter distances of 2.107(8) and 2.049(7) Å were observed in $(P(C_6H_5)_3)_2Pt(CH_2{=}C{=}C(CH_3)_2)$,

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* The table of observed and calculated structure factors has been deposited as NAPS document. Please contact ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

** All non bonding distances have been calculated assuming C—H 1.05 Å for sp^3 hybridization, and 1.00 Å for sp^2 hybridization at C.

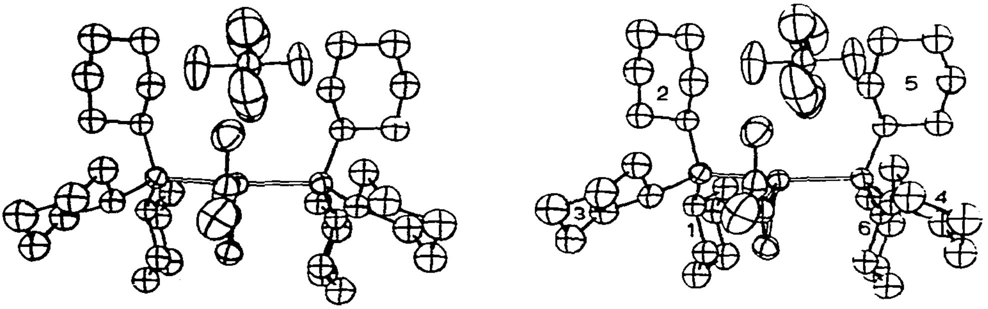

Fig. 1. Stereoview showing the cation and the anion.

in which the allene ligand lies in the plane of the Pt and P atoms [20]. Internuclear distances for allene complexes of Rh and Pd have been tabulated by other authors [10,21].

Two least-squares planes have been calculated, and the results are given in Table 8. The five C atoms of the allene ligand are coplanar within experimental error. The plane of the allene ligand is at an angle of 89.2(6)° to the Pt, P, P plane.

The distances C(1)—C(2) and C(2)—C(3) within the allene ligand are 1.367(14) and 1.290(15) Å, respectively, consistent with values found for other allene ligands [10,21]. The deviation from linearity upon coordination is 20(1)°, and is slightly less than the values ranging from 25 to 40° observed elsewhere [10,21]. The C(4) methyl group in the 1,2-diene ligand is bent away from the bulky phosphine ligands. The bond angles C(2)—C(3)—C(4) and C(4)—C(3)—C(5) are 127(1) and 114(1)°, respectively, and are significantly different from the value expected for sp^2 hybridization at C(3). The C(2)—C(3)—C(5) angle however is 120(1)°. The shortest non-bonding distances between H atoms on C(4) and C(5) with the cyclohexyl H atoms are 2.17 Å with 4C2H2 and 2.33 Å with 3C6H2, respectively. The angles observed and the environments of the methyl groups are very similar to those found in the platinum(0) complex of the same ligand by Yasuoka et al. [20]. In that case the shortest approach was phenyl H atom H(36) to a methyl H atom at 2.50 Å, and steric repulsions were thought to be responsible for the distortions observed.

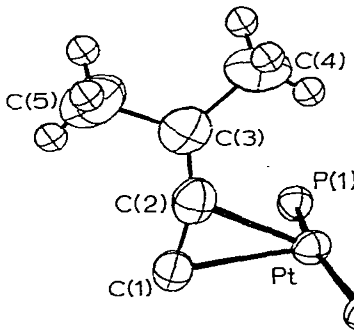

Fig. 2. Inner coordination sphere of the cation. Atoms are drawn with 50% probability thermal ellipsoids.

(continued on p. 127)

TABLE 5

DERIVED GROUP ATOM PARAMETERS

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
Cyclohexyl (1)					*Cyclohexyl (5)*				
1C(1)	3509(5)	1085(2)	1667(4)	3.5(2)	5C(1)	−317(4)	1910(2)	511(6)	3.9(2)
1C(2)	3248(5)	578(2)	1695(5)	4.5(2)	5C(2)	−1320(4)	1960(2)	823(6)	5.0(2)
1C(3)	3632(5)	358(2)	2802(6)	5.7(3)	5C(3)	−1498(4)	2447(2)	1253(6)	5.3(3)
1C(4)	3240(6)	601(2)	3859(5)	6.2(3)	5C(4)	−1265(5)	2789(2)	300(7)	5.9(3)
1C(5)	3501(5)	1108(2)	3830(4)	5.9(3)	5C(5)	−262(5)	2740(2)	−11(7)	5.6(3)
1C(6)	3117(5)	1327(2)	2724(5)	4.9(2)	5C(6)	−84(4)	2253(2)	−442(5)	4.2(2)
Cyclohexyl (2)					*Cyclohexyl (6)*				
2C(1)	3535(4)	1950(2)	487(6)	3.6(2)	6C(1)	−234(5)	1026(2)	1597(4)	3.5(2)
2C(2)	3261(4)	2268(2)	−512(5)	5.0(2)	6C(2)	143(5)	1251(2)	2700(6)	4.9(2)
2C(3)	3447(5)	2765(2)	−165(7)	5.5(2)	6C(3)	−238(6)	1007(2)	3761(4)	6.4(3)
2C(4)	4460(5)	2825(2)	109(7)	6.5(3)	6C(4)	41(6)	503(2)	3737(5)	6.4(3)
2C(5)	4734(5)	2507(2)	1108(6)	6.1(3)	6C(5)	−337(5)	278(2)	2635(6)	6.0(3)
2C(6)	4548(4)	2010(2)	761(6)	4.8(2)	6C(6)	45(5)	522(2)	1574(5)	4.2(2)
Cyclohexyl (3)					*o-Dichlorobenzene*				
3C(1)	3881(4)	1060(2)	−782(5)	3.7(2)	7C(1)	1661(7)	4145(3)	−2593(11)	7.3(3)
3C(2)	4840(5)	910(2)	−420(4)	4.9(2)	7C(2)	1626(8)	4119(4)	−1398(10)	10.7(5)
3C(3)	5224(4)	589(2)	−1340(6)	5.2(2)	7C(3)	1571(9)	3698(5)	−859(7)	12.7(6)
3C(4)	5260(4)	839(3)	−2503(5)	6.2(3)	7C(4)	1551(8)	3301(4)	−1515(13)	11.0(5)
3C(5)	4301(5)	990(3)	−2864(4)	5.8(3)	7C(5)	1586(8)	3327(3)	−2710(12)	10.8(5)
3C(6)	3918(4)	1311(2)	−1944(5)	4.7(2)	7C(6)	1641(7)	3748(5)	−3249(7)	9.3(4)
Cyclohexyl (4)									
4C(1)	−618(4)	1041(2)	−858(5)	3.6(2)					
4C(2)	−706(4)	1315(2)	−1984(5)	4.5(2)					
4C(3)	−1072(5)	1004(3)	−2949(4)	5.3(2)					
4C(4)	−2005(4)	820(3)	−2614(5)	5.8(3)					
4C(5)	−1917(5)	546(2)	−1488(6)	5.5(3)					
4C(6)	−1551(5)	856(2)	−523(4)	4.8(2)					

TABLE 6. HYDROGEN ATOM POSITIONAL ($\times 10^4$) AND THERMAL PARAMETERS

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
C4H1 [a]	1625	1766	−2204	7.06	3C6H2	3325	1402	−2173	5.16
C4H2	2091	1680	−3374	7.06	4C1H1	−277	779	−1057	3.87
C4H3	1045	1668	−3300	7.06	4C2H1	−1108	1562	−1876	4.94
C5H1	1094	803	−4097	8.24	4C2H2	−129	1429	−2190	4.94
C5H2	2122	895	−4202	8.24	4C3H1	−1123	1172	−3643	5.77
C5H3	1784	485	−3482	8.24	4C3H2	−665	757	−3056	5.77
1C1H1	4152	1100	1738	3.95	4C4H1	−2408	1065	−2505	6.54
1C2H1	2612	549	1682	4.90	4C4H2	−2229	627	−3207	6.54
1C2H2	3493	428	1045	4.90	4C5H1	−2490	431	−1278	6.08
1C3H1	3472	44	2819	6.07	4C5H2	−1511	298	−1592	6.08
1C3H2	4272	384	2817	6.07	4C6H1	−1954	1103	−412	5.46
1C4H1	2600	570	3847	6.73	4C6H2	−1496	688	175	5.46
1C4H2	3474	462	4543	6.73	5C1H1	10	2010	1171	4.30
1C5H1	3259	1254	4487	6.32	5C2H1	−1688	1900	170	5.29
1C5H2	4140	1133	3850	6.32	5C2H2	−1464	1748	1417	5.29
1C6H1	2480	1298	2715	5.21	5C3H1	−2112	2477	1456	5.77
1C6H2	3280	1638	2713	5.21	5C3H2	−1128	2504	1920	5.77
2C1H1	3219	2059	1145	3.79	5C4H1	−1631	2730	−355	6.56
2C2H1	3601	2189	−1173	5.38	5C4H2	−1371	3089	569	6.56
2C2H2	2635	2228	−685	5.38	5C5H1	−118	2949	−501	6.20
2C3H1	3278	2957	−795	6.01	5C5H2	106	2796	646	6.20
2C3H2	3104	2839	483	6.01	5C6H1	−454	2192	−1104	4.56
2C4H1	4802	2748	−558	7.26	5C6H2	530	2219	−640	4.56
2C4H2	4575	3130	309	7.26	6C1H1	−880	1033	1651	3.63
2C5H1	5356	2546	1277	6.96	6C2H1	778	1229	2715	5.12
2C5H2	4390	2584	1765	6.96	6C2H2	−34	1561	2721	5.12
2C6H1	4887	1934	109	5.12	6C3H1	−8	1144	4447	7.22
2C6H2	4713	1816	1386	5.12	6C3H2	−881	1027	3759	7.22
3C1H1	3566	786	−940	3.87	6C4H1	681	479	3753	6.74
3C2H1	5216	1173	−347	5.47	6C4H2	−192	350	4398	6.74
3C2H2	4816	760	301	5.47	6C5H1	−166	−35	2626	6.30
3C3H1	5814	498	−1108	5.68	6C5H2	−978	297	2632	6.30
3C3H2	4847	330	−1403	5.68	6C6H1	681	499	1588	4.62
3C4H1	5637	1098	−2430	6.73	6C6H2	−192	382	900	4.62
3C4H2	5498	639	−3064	6.73	7C3H1	1548	3665	−46	13.75
3C5H1	4323	1139	−3583	6.29	7C4H1	1512	3005	−1176	12.30
3C5H2	3924	726	−2934	6.29	7C5H1	1570	3061	−3184	11.55
3C6H1	4292	1570	−1879	5.16	7C6H1	1665	3776	−4062	9.96

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[a] C4H1, C4H2 and C4H3 are bonded to C(4), etc. All atoms have thermal parameters 10% greater than that of the atom to which they are bonded.

TABLE 7

SELECTED INTERATOMIC DIMENSIONS

Atoms	Distance (Å)	Atoms	Angle (deg)
Pt—P(1)	2.332(2)	P(1)—Pt—P(2)	163.79(8)
Pt—P(2)	2.329(2)	P(1)—Pt—C(1)	96.1(3)
Pt—C(1)	2.305(10)	P(1)—Pt—C(2)	98.3(3)
Pt—C(2)	2.233(10)	P(2)—Pt—C(1)	96.7(3)
		P(2)—Pt—C(2)	97.9(3)
C(1)—C(2)	1.367(14)		
C(2)—C(3)	1.290(15)	C(1)—Pt—C(2)	35.0(4)
C(3)—C(4)	1.533(17)	C(1)—C(2)—Pt	75.3(6)
C(3)—C(5)	1.516(17)	C(1)—C(2)—C(3)	160(1)
		C(2)—C(1)—Pt	69.6(6)
		C(2)—C(3)—C(4)	127(1)
P(1)—1C(1)	1.838(6)	C(2)—C(3)—C(5)	120(1)
P(1)—2C(1)	1.831(7)	C(3)—C(2)—Pt	125.1(9)
P(1)—3C(1)	1.852(7)	C(4)—C(3)—C(5)	114(1)
P(2)—4C(1)	1.845(6)		
P(2)—5C(1)	1.835(7)	Pt—P(1)—1C(1)	108.9(2)
P(2)—6C(1)	1.845(6)	Pt—P(1)—2C(1)	111.9(2)
		Pt—P(1)—3C(1)	115.3(2)
		1C(1)—P(1)—2C(1)	104.0(3)
		1C(1)—P(1)—3C(1)	103.9(3)
		2C(1)—P(1)—3C(1)	111.8(3)
		Pt—P(2)—4C(1)	115.9(2)
		Pt—P(2)—5C(1)	111.9(2)
		Pt—P(2)—6C(1)	109.2(2)
		4C(1)—P(2)—5C(1)	111.4(3)
		4C(1)—P(2)—6C(1)	103.8(3)
		5C(1)—P(2)—6C(1)	103.6(3)

TABLE 8

SELECTED LEAST-SQUARES PLANES

Coefficients of the plane equation, $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	14.80	0.802	−0.051	2.514
2	0.105	−21.73	7.829	−2.756

Deviations of atoms from the planes (Å).

Atom	Plane 1	Plane 2
Pt	0.0000(4)	−0.0056(4)
P(1)		0.075(2)
P(2)		0.081(3)
C(1)	−0.004(10)	0.89(1)
C(2)	−0.014(10)	−0.48(1)
C(3)	0.002(11)	
C(4)	−0.010(12)	
C(5)	0.025(14)	

The phosphine ligands are bent towards the probable location of the hydride ligand with a P—Pt—P angle of 163.79(8)°. All cyclohexyl rings are in the chair conformation, with a mean P—C(1) distance of 1.841(7) Å. Dimensions within the PF_6 anion show small deviations from O_h symmetry, with P—F distances ranging from 1.52(1) to 1.566(8) Å, mean 1.55(2) Å, and angle means of 90(3) and 177(2)°. The solvent molecule is planar within experimental error, with a mean C—Cl distance of 1.676(6) Å.

It has been noted previously [21] that, in other square planar complexes in which the allene ligand is perpendicular to the coordination plane, the midpoint of the coordinated C=C bond does not lie on the plane. A similar geometry is adopted in this study, Table 8. However, the uncertainty in the position of the hydride ligand precludes detailed comparisons of the present geometry with other studies.

Discussion

The cation is believed to be representative of the intermediate in the insertion of an allene into a metal—H bond. However, unlike the reaction with allene itself [22], formation of the η^3-allyl product was not observed in this case. This failure of insertion to occur is believed to be due to steric constraints resulting from the methyl substituents on the allene and the bulky phosphine ligands. It has been shown that the *cis* coordination of two PCy_3 ligands involves considerable "intermeshing" of the cyclohexyl rings. For example, the P—Pt—P angle of 100.17(4)° in $Pt(PPh_3)_2(F_3CC{\equiv}CCF_3)$ [23] increases to 110.28(6)° in $Pt(PCy_3)_2(F_3CC{\equiv}CCF_3)$, and a different conformation is observed for the phosphine substituents [24]. In $Pt(PCy_3)_2(\eta^3\text{-}C_3H_5)$ [25] preliminary indications are that the P—Pt—P angle is 111°. Thus the η^3-allyl product from the insertion of 3-methyl-1,2-butadiene may be too large to be coordinated along with the PCy_3 ligands.

The metal—allene bonding is thought to be similar to metal—olefin bonding, and may be discussed in terms of the Dewar—Chatt—Duncanson [26—28] bonding model with the incorporation of an additional π-back-bonding overlap between the filled metal d_{xy} orbital and the empty π^* orbital of the uncoordinated double bond [10,21].

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