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PREPARATION AND STRUCTURE OF *trans*-(η^1-ALLYL)CHLOROBIS(TRIPHENYLPHOSPHINE)PLATINUM(II), Pt(η^1-C_3H_5)Cl[P(C_6H_5)$_3$]$_2$

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Summary

The structure of *trans*-(η^1-allyl)chlorobis(triphenylphosphine)platinum(II), Pt(η^1-C_3H_5)Cl(PPh_3)$_2$, has been determined from three-dimensional X-ray data. The compound was isolated while attempting to grow crystals of [Pt(η^3-C_3H_5)(PPh_3)$_2$]Cl. The complex crystallizes in the space group C_{2h}^5—$P2_1/n$ with four molecules in a unit cell of dimensions a = 12.580(3), b = 23.067(7), c = 12.316(4) Å and β = 112.30(1)°. Least-squares refinement of the 136 variables has led to a value of the conventional R index (on F) of 0.048 for the 6289 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The complex is a typical square-planar Pt(II) complex; structural parameters: Pt—P 2.304(2) and 2.302(2), Pt—Cl 2.425(2), Pt—C(1) 2.090(4), C(1)—C(2) 1.464(7), C(2)—C(3) 1.311(9) Å, Pt—C(1)—C(2) 112.6(3)°, C(1)—C(2)—C(3) 125.7(6)°. The angle between the plane of the allyl group and the mean coordination plane is 66°; the torsion angle Pt—C(1)—C(2)—C(3) is —119°. The structure is compared with other Pt(II) σ-complexes, and production of the complex rationalized. The isolation of the complex supports suggestions that the fluxionality of [Pt(η^3-C_3H_5)(PPh_3)$_2$]Cl in solution involves a short-lived σ-allyl intermediate.

Introduction

Our general interest in η^3-C_3H_5 complexes [1] has led us to a more particular interest in Pt(II)—(η^3-C_3H_5) complexes. From our previous observations we conclude that M→π^* charge transfer is of some importance in metal—(η^3-allyl) bonding. The observed trends suggest that, when compared with other d^8-allyl complexes, a Pt(II)—(η^3-C_3H_5) complex should have a longer M—C_3H_5 bond and shorter C—C bonds. As [Pt(η^3-C_3H_5)(PPh_3)$_2$]Cl is known [2], and of interest in its own right [2,3], we felt that a structural study of it would be worthwhile. Accordingly, the complex was synthesized and was identified spectroscopically. Single crystals were grown, and the structure determination reported here was accomplished. The data crystal, grown from an authentic sample of [Pt(η^3-C_3H_5)-

$(PPh_3)_2]Cl$, is shown to be *trans*-$Pt(\eta^1$-$C_3H_5)Cl(PPh_3)_2$. Although apparently a minor product of the reaction, its isolation sheds light on the mechanism of the interchange of the allyl protons in the η^3-allyl complex [2]. In view of the recent interest in the chemistry of Pt—(σ-allyl) complexes [4,5], we report the structure of *trans*-$Pt(\eta^1$-$C_3H_5)Cl(PPh_3)_2$ here.

Experimental

The complex $[Pt(\eta^3$-$C_3H_5)(PPh_3)_2]Cl$ was prepared by the method of Volger and Vrieze [2]. The infrared (Nujol mull) and PMR ($CDCl_3$ solution, room temperature and —20°C) spectra of the bulk material, and the melting point (210°C), agree with those reported by Volger and Vrieze [2]. Crystals were grown by layering a benzene solution of the complex with pentane. Among the mass of white microcrystalline needles produced there were a few larger colorless needles. One of these, of approximate dimensions 0.13 × 0.15 × 0.80 mm, was selected for study. On the basis of optical goniometry and X-ray measurements, we established that the crystal belongs to the monoclinic system, and that the principal faces belong to the forms $\{120\}$, $\{11\bar{1}\}$, and $\{\bar{1}12\}$. From Weissenberg photography taken with Mo-K_α radiation, the space group was unambiguously determined to be C_{2h}^5—$P2_1/n$. The lattice constants at 22°C, determined [6] from the setting angles of 12 strong reflections which had been centered manually on a Picker FACS-I diffractometer using Cu-K_α radiation (λ 1.540562 Å), are a 12.580(3), b 23.067(7), c 12.316(4) Å, and β 112.30(1)°, With four formula weights per unit cell, the calculated density is 1.60 g cm^{-3}, in excellent agreement with the measured density, 1.61(1) g cm^{-3}, obtained by flotation of the crystals in a mixture of dibromomethane and hexane.

For data collection Cu-K_α radiation was used. The intensities were measured by the θ — 2θ technique at a takeoff angle of 3.0°. At this angle the intensity of a reflection was about 90% of its maximum value. A receiving counter aperture 4 mm high and 4 mm wide was positioned 35 cm from the crystal. Symmetric scans in 2θ, 0.8° below the $K_{\alpha 1}$ peak to 0.8° above the $K_{\alpha 2}$ peak, were used. Stationary-counter, stationary-crystal background counts of 10 sec were measured at the beginning and end of each scan. For reflections having $I < 3\sigma(I)$, the scan was repeated once with background counting times of 20 sec, and added to the results of the first scan. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts sec^{-1}.

The accessible data set for which $k \leqslant 0$, $l \leqslant 0$, and having $2\theta \leqslant 160°$ was gathered; the intensities of 7628 reflections were recorded. The intensities of the standard reflections (six in the bisecting mode, three in the parallel mode) remained constant within counting statistics.

All data processing was carried out as previously described [6]. The value of p was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. The 6289 unique reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. The linear absorption coefficient, μ, for this compound using Cu-K_α radiation is 99.0 cm^{-1}. An absorption correction was made *, and transmission coefficients ranged from 0.163 to 0.476.

The position of the Pt atom was unambiguously revealed by a Patterson synthesis. A consistent set of P positions (Pt—P 2.3 Å, P—Pt—P 115°) was chosen, and a least-squares refinement on F computed. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, in which $w = 4F_o^2/\sigma^2(F_o^2)$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. Values of the atomic scattering factors and anomalous terms were taken from the usual source [8]. Only the overall scale factor and the positional parameters of the Pt and P atoms were varied. This refinement led to the agreement indices $R = 0.29$ and $R_w = 0.41$, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2)^{1/2}$. At this point, one of the Pt—P distances had increased to about 2.4 Å. On an ensuing difference Fourier map we found a peak of 13 e Å^{-3} *trans* to the other P position, and 2.3 Å away from the Pt atom. Five of the six final phenyl rings were also found. Clearly, instead of the desired *cis* geometry, the triphenylphosphine ligands are *trans* to each other and the chlorine atom is coordinated to the platinum atom. Hence the compound that had crystallized is a σ-allyl complex. The σ-allyl group and the remaining phenyl ring were found on a subsequent difference Fourier map. The Pt, P, Cl, and allyl C atoms were refined anisotropically; the phenyl rings were treated as rigid groups [9] and restricted to their known geometry (6/*mmm* symmetry, d(C—C) 1.392 Å). Each ring carbon atom was assigned an individual isotropic thermal parameter. Hydrogen atoms were included in later structure factor calculations in calculated idealized positions (d(C—H) 0.95 Å) which were not refined.

The final refinement of 136 variables using 6289 observations resulted in the values $R = 0.048$ and $R_w = 0.064$. A structure factor calculation for the 660 reflections omitted from the refinements because $F_o^2 < 3\sigma(F_o^2)$ revealed that in no case was $|F_o^2 - F_c^2| > 5\sigma(F_o^2)$. There are no significant trends in $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, or Miller indices. No extinction correction was thought necessary. The largest peak in the final difference Fourier map is 1.0 e Å^{-3} and is near the Pt atom. The error in an observation of unit weight is 2.41 electrons.

The positional, thermal, and group parameters derived from the last cycle of least-squares refinement are given in Table 1, along with the standard deviations as estimated from the inverse matrix. The positional parameters of the ring carbon atoms which may be derived from the data in Table 1 are presented in Table 2, together with their thermal parameters. The final values of 10 $|F_o|$ and 10 $|F_c|$ in electrons are given in the table of structure amplitudes. This table and that of the root-mean-square amplitudes of vibration have been deposited **.

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* In addition to various local programs for the CDC 6400 computer, programs used in this work include local versions of Zalkin's FORDAP Fourier program, the AGNOST absorption program, and Busing's and Levy's ORFFE function and error program. Our least-squares program NUCLS, in its non-group form, closely resembles the Busing—Levy ORFLS program. The diffractometer was run under the disk-oriented Vanderbilt system [7].

** The Table of structure amplitudes, and the table of the root-mean-square amplitudes have been deposited as NAPS Document No. 03043 (45 pages). Order from ASIS/NAPS, c/o Microfiche Publications, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 11.25 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outisde of the United States and Canada postage is $ 3.00 for a photocopy or $ 1.00 for a fiche.

TABLE I. POSITIONAL AND THERMAL PARAMETERS FOR THE NON-GROUP ATOMS OF

TRANS-PT(N3-C3H5)CL(P(C6H5)3)2

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
PT	0.17093(2)	0.158881(9)	0.00420(2)	53.2(2)	13.50(5)	49.2(3)	-0.60(6)	21.4(1)	-1.83(7)
P(1)	0.1684(1)	0.12623(6)	-0.1781(1)	57.9(9)	14.3(2)	50.(1)	1.0(4)	24.4(8)	-0.8(4)
P(2)	0.1786(1)	0.16847(6)	0.1910(1)	56.9(9)	14.0(2)	48.(1)	-0.8(4)	20.5(8)	-2.2(4)
CL	0.2133(1)	0.04978(6)	0.4577(1)	97.(1)	15.6(2)	67.(1)	3.9(4)	35.(1)	2.2(4)
C(1)	0.1279(4)	0.2369(2)	-0.0464(5)	64.(4)	9.5(7)	57.(5)	6.(1)	17.(4)	3.(2)
C(2)	0.2281(5)	0.2722(2)	-0.0359(6)	74.(4)	14.0(10)	83.(6)	-2.(2)	36.(4)	3.(2)
C(3)	0.2644(6)	0.3174(3)	0.0315(7)	86.(6)	21.(2)	102.(7)	-6.(2)	34.(5)	0.(3)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2 + B22K^2 + B33L^2 + 2B12HK + 2B13HL + 2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

TABLE II. DERIVED PARAMETERS FOR THE RIGID GROUP ATOMS OF

TRANS-PT(N3-C3H5)CL(P(C6H5)3)2

ATOM	X	Y	Z	B.A^2	ATOM	X	Y	Z	B.A^2
C(111)	0.2957(3)	0.0848(2)	-0.1660(4)	3.29(9)	C(211)	0.0514(3)	0.1428(2)	0.2141(4)	3.34(10)
C(112)	0.3994(4)	0.0992(2)	-0.0764(4)	4.6(1)	C(212)	-0.0186(4)	0.1017(2)	0.1373(3)	3.7(1)
C(113)	0.4999(3)	0.0786(2)	-0.0671(4)	5.3(1)	C(213)	-0.1182(3)	0.0828(2)	0.1503(4)	4.3(1)
C(114)	0.4967(3)	0.0275(2)	-0.1474(5)	5.6(2)	C(214)	-0.1478(3)	0.1050(2)	0.2402(4)	4.9(1)
C(115)	0.3930(4)	0.0131(2)	-0.2370(4)	6.2(2)	C(215)	-0.0778(4)	0.1461(2)	0.3169(4)	5.2(2)
C(116)	0.2925(3)	0.0417(2)	-0.2463(4)	5.0(1)	C(216)	0.0218(4)	0.1650(2)	0.3039(4)	4.3(1)
C(121)	0.1648(3)	0.1841(2)	-0.2816(4)	3.38(9)	C(221)	0.1952(3)	0.2437(1)	0.2463(4)	3.23(9)
C(122)	0.2806(3)	0.1988(2)	-0.3064(4)	4.6(1)	C(222)	0.1000(2)	0.2801(2)	0.2152(4)	3.8(1)
C(123)	0.2536(4)	0.2438(2)	-0.3845(5)	5.4(2)	C(223)	0.1131(3)	0.3373(2)	0.2542(5)	4.5(1)
C(124)	0.1518(4)	0.2737(2)	-0.4378(4)	5.4(2)	C(224)	0.2213(4)	0.3580(1)	0.3243(5)	4.9(2)
C(125)	0.0552(3)	0.2596(2)	-0.4138(4)	5.0(2)	C(225)	0.3165(3)	0.3216(2)	0.3554(4)	4.4(1)
C(126)	0.0621(3)	0.2142(2)	-0.3349(4)	4.1(1)	C(226)	0.3034(3)	0.2645(2)	0.3164(4)	3.9(1)
C(131)	0.0435(3)	0.0825(2)	-0.2671(3)	3.13(9)	C(231)	0.3025(3)	0.1341(2)	0.3018(4)	3.8(1)
C(132)	0.0146(3)	0.0746(2)	-0.3874(3)	3.7(1)	C(232)	0.3611(4)	0.1130(2)	0.4603(5)	5.0(2)
C(133)	-0.0827(4)	0.0453(2)	-0.4548(3)	4.4(1)	C(233)	0.4018(5)	0.0906(3)	0.4908(4)	7.1(2)
C(134)	-0.1512(3)	0.0199(2)	-0.4019(4)	4.6(1)	C(234)	0.5023(4)	0.0893(3)	0.4701(5)	6.7(2)
C(135)	-0.1223(3)	0.0257(2)	-0.2810(4)	4.7(1)	C(235)	0.5037(3)	0.1105(3)	0.3448(5)	6.1(2)
C(136)	-0.0258(4)	0.0576(2)	-0.2142(3)	3.8(1)	C(236)	0.4039(4)	0.1329(2)	0.2803(4)	5.0(1)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
R(11)	0.3962(3)	0.0561(1)	-0.1567(3)	1.057(3)	-2.876(3)	0.748(3)
R(12)	0.1579(3)	0.2289(1)	-0.3597(3)	-3.064(3)	-2.411(3)	-2.884(4)
R(13)	-0.0538(2)	0.0512(1)	-0.3345(3)	-1.003(3)	-2.876(2)	-1.627(3)
R(21)	-0.0482(2)	0.1239(1)	0.2271(3)	-1.211(3)	2.667(2)	-1.049(3)
R(22)	0.2683(2)	0.3889(1)	0.2853(3)	3.027(2)	2.837(3)	-0.128(3)
R(23)	0.4024(3)	0.1117(2)	0.3855(3)	1.152(4)	2.724(3)	1.956(4)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

Description of the structure

The data crystal, taken from an authentic sample of $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]Cl$, consists of discrete, neutral molecules of *trans*-$Pt(\eta^1\text{-}C_3H_5)Cl(PPh_3)_2$, occupying general positions in the space group $P2_1/n$. The inner coordination geometry is shown in Fig. 1, a stereo view of the molecule is presented in Fig. 2, and a packing diagram is presented in Fig. 3. A selection of distances and angles is given in Table 3.

The molecules are generally separated by van der Waals' contacts. The closest nonbonded interactions involve the hydrogen atoms of the allyl group. The triphenylphosphine ligands form a pocket into which the allyl group fits, minimizing intermolecular repulsions.

The complex clearly is a typical square-planar Pt(II) complex; the least-squares plane determined by the five atoms of the coordination sphere is given by the equation $11.71x + 4.52y - 0.84z - 2.68 = 0$. The carbon atom is 0.07(1) Å out of this plane, while the displacements of the other atoms are 0.01 Å or less. Although occupying a general position, the complex has approximate C_s site symmetry. The pseudo mirror plane is given by the equation $-4.43x + 4.54y + 12.07z - 0.02 = 0$ and passes through the Pt and Cl atoms and is perpendicular to the P—P vector. The deviations of the angles in the coordination sphere from those of the ideal square planar geometry are small and unimportant.

The two Pt—P bonds are equal within experimental error (mean Pt—P distance 2.303(3) Å), and are typical of values in complexes of this sort. The Pt—Cl distance of 2.425(2) Å is among the longest known, and presumably reflects the large *trans*-influence of the σ-allyl ligand. The Pt—P and Pt—Cl bond distances of several *trans*-$PtXClP_2$ complexes are presented in Table 4. McWeeney et al. [10] have noted a good correlation between the electronegativity of atom X and the Pt—Cl distance in such complexes; the Pt—Cl bond is lengthened as the electronegativity of atom X decreases. When the data presented in Table 4 are added to those compiled earlier [10], the same general trend is observed, but

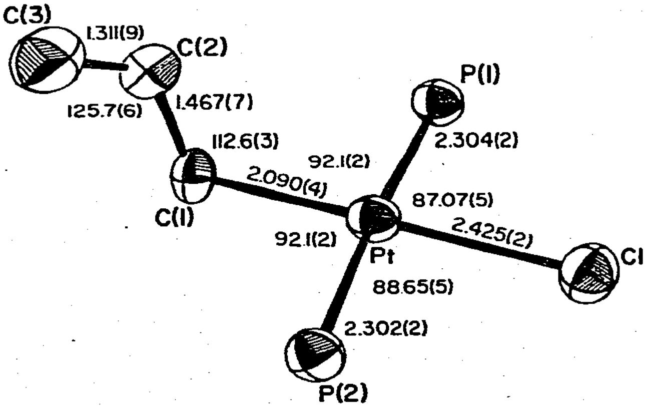

Fig. 1. A perspective view of the coordination sphere of *trans*-$Pt(\eta^1\text{-}C_3H_5)Cl(PPh_3)_2$. The shapes of the atoms in this and the following drawings represent 50% probability contours of thermal motion.

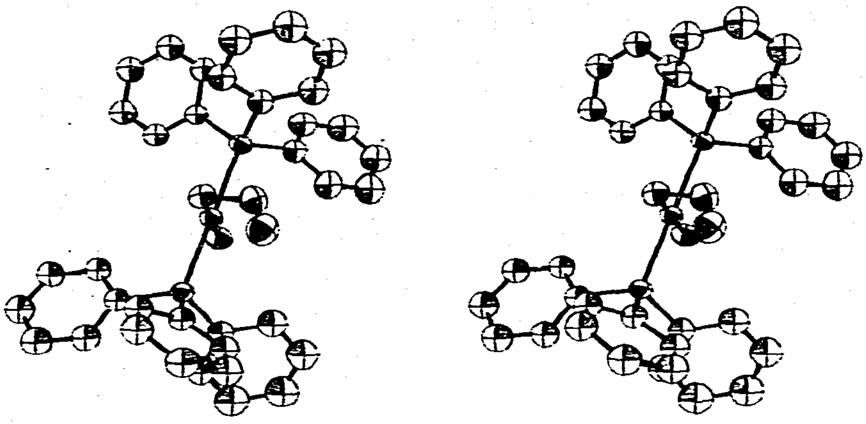

Fig. 2. A stereo view of the complete molecule. The view is down the y-axis, with the x-axis horizontal and to the right. Hydrogen atoms are omitted for clarity.

not as clearly. The rationalization of the *trans*-influence in Pt(II) complexes solely on the basis of electronegativity is probably an oversimplification. We conclude from these data that the *trans*-influence of a σ-allyl group is about equal to that of a trimethylsilylmethyl group or a hydrido ligand.

The Pt—C(1) distance of 2.090(4) Å is typical of Pt(II)—C(sp^3) bonds (cf. the values of 2.079(14) Å in *trans*-Pt(CH_2SiMe_3)Cl(PMe_2Ph)$_2$ [11], and 2.07(1) Å in *trans*-PtMeCl($PMePh_2$)$_2$ [12]), and approximately the value expected from the sum of covalent radii. That the C(1)—C(2) bond length is 1.464(7) Å and that the C(2)—C(3) distance is 1.311(9) Å suggest to us that there is no need to resort to resonance structures to describe the Pt—allyl linkage in this complex. The values of 125.7(6)° for the C(1)—C(2)—C(3) angle and of 112.6(3)° for Pt—C(1)—C(2) angle reinforce this conclusion. The orientation of the allyl group may be described by two parameters: the angle between the plane of

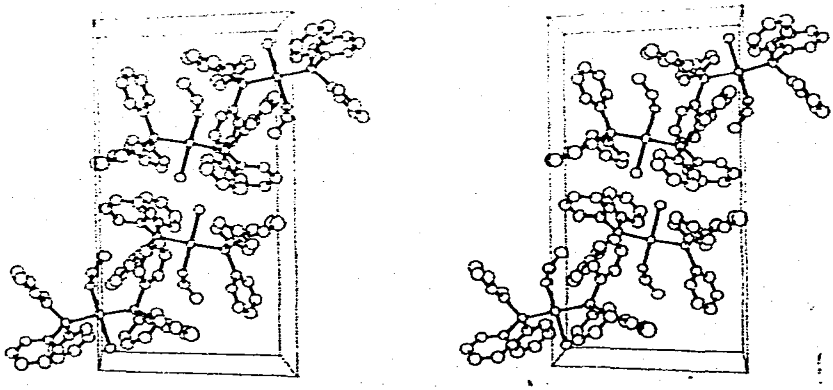

Fig. 3. A stereo drawing illustrating the packing in *trans*-Pt(η^1-C_3H_5)Cl(PPh_3)$_2$. The view is down the x-direction, with the y-axis vertical. Hydrogen atoms are omitted.

TABLE 3

DISTANCES AND ANGLES IN $Pt(\eta^1\text{-}C_3H_5)Cl[P(C_6H_5)_3]_2$

Intramolecular distances (Å)

Pt—P(1)	2.304(2)	Pt—C(3)	4.004(8)	P(1)—C(131)	1.839(3)
Pt—P(2)	2.302(2)	C(1)—C(2)	1.464(7)	P(2)—C(211)	1.827(5)
Pt—Cl	2.425(2)	C(2)—C(3)	1.311(9)	P(2)—C(221)	1.846(4)
Pt—C(1)	2.090(4)	P(1)—C(111) [a]	1.822(4)	P(2)—C(231)	1.814(4)
Pt—C(2)	2.978(5)	P(1)—C(121)	1.834(4)	P—C(avg.)	1.830(12)

Angles (deg)

P(1)—Pt—P(2)	175.70(5)	Pt—P(1)—C(131)	114.1(1)
P(1)—Pt—Cl	87.07(5)	Pt—P(2)—C(211)	113.0(1)
P(2)—Pt—Cl	88.68(5)	Pt—P(2)—C(221)	119.4(2)
P(1)—Pt—C(1)	92.1(2)	Pt—P(2)—C(231)	111.5(2)
P(2)—Pt—C(1)	92.1(2)	C(111)—P(1)—C(121)	103.2(2)
Cl—Pt—C(1)	177.7(1)	C(111)—P(1)—C(131)	106.6(2)
Pt—C(1)—C(2)	112.6(3)	C(121)—P(1)—C(131)	101.3(2)
C(1)—C(2)—C(3)	125.7(6)	C(211)—P(2)—C(221)	103.3(2)
Pt—P(1)—C(111)	111.2(1)	C(211)—P(2)—C(231)	107.3(2)
Pt—P(1)—C(211)	119.1(1)	C(221)—P(2)—C(231)	100.9(2)

Intramolecular nonbonded contacts (Å) [b]

Pt—H(1)C(1)	2.64	Pt—H(136)	2.97
Pt—H(2)C(1)	2.64	Cl—H(136)	2.78
Pt—H(122)	2.93	Cl—H(212)	2.79

Intermolecular nonbonded contacts (Å) [b]

Cl—H(114)	2.78	C(233)—H(134)	2.86
Cl—H(135)	2.79	C(235)—H(115)	2.75
Cl—H(213)	2.89	H(112)—H(125)	2.17
C(3)—H(126)	2.77	H(115)—H(235)	2.21
C(115)—H(233)	2.76	H(116)—H(133)	2.37
C(124)—H(126)	2.89	H(123)—H(222)	2.24
C(214)—H(133)	2.87	H(215)—H(2)C(3)	1.91
C(232)—H(134)	2.81	H(226)—H(2)C(1)	2.39

[a] The labels C(1), C(2), and C(3) denote the carbon atoms of the allyl group. In the labels C(xyz) of the phenyl carbon atoms, x denotes the phosphorus atom to which the ring is attached, y specifies the number of the phenyl ring, and z indicates the position of the particular carbon atom in the ring. [b] In the calculation of these distances, the hydrogen atoms were placed in calculated idealized positions with d(C—H) 1.08 Å.

TABLE 4

STRUCTURAL PARAMETERS OF SOME *trans*-$PtXClP_2$ COMPLEXES

X	P	Pt—Cl (Å)	Pt—P_{av} (Å)	Ref.
p-$HNNC_6H_4F$	PEt_3	2.291(2)	2.320(3)	15
p-$H_2NNHC_6H_4F$	PEt_3	2.303(2)	2.328(2)	16
o-$Ph_2PC_6H_4\overset{|}{C}{=}CHC_6H_4PPh_2$-$o$		2.371(3)	2.268(4)	17
$CH{=}CH_2$	PEt_2Ph	2.398(4)	2.295(4)	18
$C{\equiv}CPh$	PEt_2Ph	2.407(6)	2.304(7)	18
p-NNC_6H_4F	PEt_3	2.413(6)	2.302(4)	19
CH_2SiMe_3	PMe_2Ph	2.415(5)	2.293(7)	11
H	$PEtPh_2$	2.422(9)	2.268(9)	9
σ-C_3H_5	PPh_3	2.425(2)	2.303(3)	This work
$SiMePh_2$	PMe_2Ph	2.45(1)	—	10
$SiMe(1\text{-}C_{10}H_7)Ph$	PMe_2Ph	2.454(4)	2.296(6)	20
CH_3	PMe_2Ph	—	—	12

the allyl group and the mean coordination plane (66°), and the torsion angle Pt—C(1)—C(2)—C(3) (—119°). The closest nonbonded contacts involving the Pt atom are those with the methylene hydrogen atoms of the allyl group, 2.64 Å away. This suggests that there is little Pt—H interaction. Similarly, there is no tendency toward coordination of the C=C double bond to the platinum atom.

The present structure may be compared with three other reported structures containing an allyl group σ-bonded to a Pt(II) ion. The uncertainties in the parameters of $[Pt(\mu\text{-}C_3H_5)(acac)]_2$ and $[Pt(\mu\text{-}C_3H_5)(\mu\text{-}Cl)]_4$ [13] are too large to enable useful comparisons; in addition, these complexes contain bridging allyl groups, σ-bonded to one Pt atom and π-bonded to another. The recent communication of the crystal structure of $Pt(\eta^1\text{-}C_3H_5)Cl(CH_3NC)(PPh_3)$ [14] is of more interest. The bonding parameters are in general similar to those observed here (Pt—C(1) 2.14(2), C(1)—C(2) 1.32(5), C(2)—C(3) 1.24(6) Å, Pt—C(1)—C(2) 110(2)°, C(1)—C(2)—C(3) 144(3)°, Pt—C(1)—C(2)—C(3) 131°, angle between allyl and coordination planes 67°), though the errors are too large to permit detailed comparisons to be made. The orientations of the allyl groups in these two complexes seem to differ. In the isocyanide complex the allyl group seems to extend farther from the metal atom than in the present complex. The isocyanide complex is certainly a less crowded structure than the bis(triphenylphosphine) complex, and it is likely that any differences in the orientation of the allyl group are a result of differences in nonbonded interactions.

It is clearly important to rationalize the production of the present σ-allyl complex. The bulk material prepared by the method of Volger and Vrieze [2] has infrared (Nujol mull) and PMR ($CDCl_3$ solution, —20°C) spectra, and a melting point (210°C, with decomposition) that agree with those given for $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]Cl$ [2]. The "room temperature" (~40°C) PMR spectrum of the bulk material in $CDCl_3$ solutions exhibits, in addition to the phenyl proton resonances, a quartet centered at δ 3.47 ppm (with respect to a TMS internal standard) attributed to four equivalent terminal allyl protons coupled with both the Pt atom and the single central allyl proton. The resonance of this central proton is very faint and occurs at about δ 5.7 ppm. Several crystals which resembled the data crystal morphologically were separated by hand from the bulk material. The PMR spectrum at 10°C in C_6D_6 solution displays a pattern typical of a σ-bonded allyl group, in agreement with the X-ray results.

Formation of the σ-complex can be rationalized in the following way. The cationic π-allyl complex is prepared in benzene, and it is easy to imagine that in such a nonpolar solvent a chloride ion could displace one end of the π-allyl group to form a neutral σ-allyl complex. This is consistent with the known chemistry of the π-allyl complex [4,5]. Once formed, the neutral σ-complex should be more soluble in benzene than the cationic π-complex. The crystals were grown by layering a solution of the bulk material with pentane. Most of the crystals formed were very small — too small to be used for data collection. These are crystals of the rapidly precipitated π-allyl complex. The few larger crystals are those of the σ-allyl complex. These crystals formed more slowly because of their increased solubility over the π-allyl crystals.

The PMR spectrum of $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]Cl$ in $CDCl_3$ solution shows that the molecule is fluxional even at —50°C. Volger and Vrieze [2] proposed, and other authors [4] have concurred, that this dynamic behavior can be explained by the presence of a short-lived σ-allyl intermediate. This proposal seems eminently reasonable, as this work conclusively demonstrates that the proposed σ-allyl complex is present under the same conditions as the π-complex.

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