Inorganica Chimica Acta, 36 (1979) 121–125
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Crystal and Molecular Structure of *trans*-$PtCl(CH_2CN)(PPh_3)_2$

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Received January 26, 1979

The structure of trans-$PtCl(CH_2CN)(PPh_3)_2$ *has been determined from three-dimensional X-ray data. The complex crystallizes in the monoclinic system, space group* C_{2h}^5*-P2₁/n with four molecules in a unit cell of dimensions,* a = *12.366(5),* b = *23.019(8),* c = *12.303(4) Å,* β = *110.7(1)°. Least-squares refinement of 137 variables has led to a value of the conventional R index (on F) of 0.038 for the 4313 independent reflections having* $I \geqslant 3\sigma(I)$*. The complex is a typical square-planar Pt(II) complex; structural parameters: Pt–P, 2.308(3) and 2.310(3), Pt–Cl, 2.390(3), Pt–C(1), 2.08(1), C(1)–C(2), 1.44(2), C(2)–N(1), 1.15(2) Å; Pt–C(1)–C(2), 111.1(8)° and C(1)–C(2)–N(1), 180.0(8)°. The crystal packing is determined only by van der Waals interactions and all intermolecular contacts agree with those predicted from radii-sum rules.*

Introduction

Recently there has been several features of interest in the preparation and reactivity of cyanoalkyl complexes of transition metals in low oxidation states. In particular, insertion reactions should give organic moieties with two functional groups, coordination of the cyano group could lead to *cis–trans* isomerization reactions, and σ- or π-bonded CN should be prone to addition reactions of alcohols, thiols, amines and water by nucleophilic attack [1–5].

Besides in organometallic chemistry some evidence indicates that the σM–C bonds increase in strength on passing from alkyls ($M\text{-}R_H$) to more electronegative cyanolakyl or fluoroalkyl derivatives ($M\text{-}R_X$, X = one or more CN or F groups) [6–9]. This bond strength seems more enhanced when the electronegative substituents are in α position of the alkyl chain. Hitherto only some complexes of this type have been synthesized. Among these the more extensively investigated are the cyanomethyl derivatives of d^8 metals Pd(II) and Pt(II) [$M\text{-}R_X$:R_X = CH_2CN [7–15], $CH(CN)_2$ [15] and $C(CN)_3$ [16–17]. The first cyanomethyl of Pt(II), *trans*-$PtCl(CH_2CN)(PPh_3)_2$, *1*, was prepared by Kemmit *et al.* [18] in 1972 by oxidative addition of $ClCH_2CN$ to $Pt(PPh_3)_4$; more recently its preparation was reinvestigated and its spectroscopic properties were reported [9]. Treatment of *1* with $NaBH_4$ in alcohol yields *trans*-$PtH(CH_2CN)(PPh_3)_2$, *2* [8], a rare example of stable platinum(II) complex with a hydride ligand *trans* to an sp^3 carbon.

The crystal structure analysis of the above *1* and *2* complexes has been carried out because a detailed knowledge of the stereochemistry of the ligands about platinum is of interest in complementing conclusions drawn from NMR and other studies of *trans*-influence. A preliminary account of this work has been given elsewhere [19].

We present here the detailed crystal and molecular structure of *1* while the crystallographic results obtained on *2* are in press [20].

Experimental

Single crystals of *trans*-$PtCl(CH_2CN)(PPh_3)_2$, suitable for X-ray structural analysis, were obtained by slow evaporation of the solvent from acetone solutions. Precession photographs and single-crystal diffractometry showed that the crystals belong to the monoclinic system, space group $P2_1/n$ with a = 12.366(5), b = 23.019(8), c = 12.303(4) Å, β = 110.7(1)°, V = 3276.0 Å³; D_o = 1.60, D_c = 1.61 g cm^{-3} for Z = 4; $\mu(MoK\alpha)$ = 47.08 cm^{-1}.

Intensity data were collected from a crystal of approximate dimensions 0.25 × 0.30 × 0.35 mm, on a Philips PW1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.2°, scan speed = 0.04° s^{-1}). 4884 independent reflections up to θ = 25° were measured, of which 4313 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 crystal and the electronics. Intensities were corrected for Lorentz and polarisation effects and were converted to an absolute scale by Wilson's method. Experimental absorption correction was applied following the method proposed by North, Phillips and Mathews [21].

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed the position of the Pt atom; the conventional R value was 0.20. 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

$$\Sigma w[|F_o|-|F_c|]^2, \text{ in which } w = \frac{1.8}{\sigma^2(F_o) + 0.007\,F_o^2}$$

The scattering factors were those of the International Tables for X-ray Crystallography [22]. The correction for the real and imaginary parts of the anomalous dispersion was applied to Pt, Cl and P [23].

The refinement was carried out with the phenyl rings treated as rigid groups and restricted to their normal geometry (D_{6h} symmetry, C–C = 1.395 Å), using the group-refinement procedure [24]. 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 R value fell to 0.045. 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 4313 observed reflections with $I \geqslant 3\sigma(I)$ was 0.038 (R_w = 0.039).

The calculations were carried out on the CYBER 76 computer of the "Centro di Calcolo Interuniversitario Italia Nord Orientale" with the SHELX-76 system of crystallographic programs [25].

Description of the Structure

A perspective view of the molecule showing its conformation 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, not corrected for changes due to thermal vibrations, are given. Some least-squares planes and dihedral angles are shown in Table III.

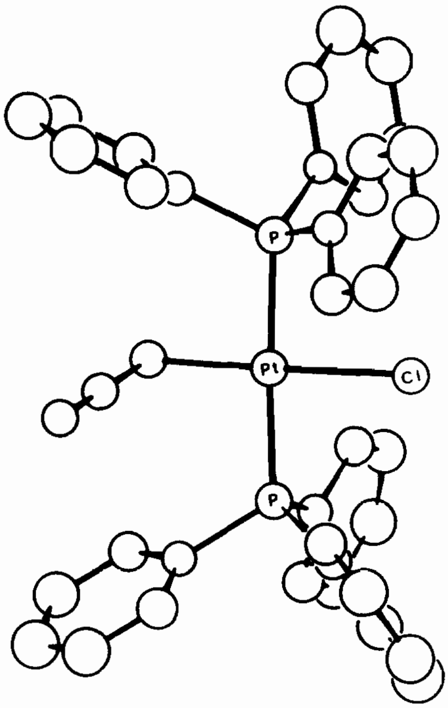

Fig. 1. A perspective view of the neutral molecule of $PtCl(CH_2CN)(PPh_3)_2$.

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 $PtCl(CH_2CN)(PPh_3)_2$ separated by van der Waals contacts. The closest Pt....Pt approach is 7.75 Å and all remaining intermolecular contacts agree with those predicted from radii-sum rules. 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 C(sp^3) atom of the CH_2CN group. 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 their idealized values of 90 and 180°. These fact suggest, as is verified by some of the short intramolecular non-bonded distances listed in Table IV, that there is considerable steric crowding in the vicinity of the platinum atom.

Discussion

Several workers [26–27] have suggested that the Pt–P bond length will depend on the π-acceptor properties of the other ligands; the presence of a

TABLE I. Fractional Coordinates and Temperature Factors[a] ($\times 10^3$) with Their e.s.d.'s in Parentheses, for the Non-hydrogen Atoms.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	0.16457(3)	0.15060(1)	0.99150(3)	32.1(3)	30.5(2)	28.8(2)	−0.7(2)	11.3(1)	1.7(2)
Cl	0.2144(2)	0.0521(1)	1.0490(2)	59(1)	36(1)	42(1)	4(1)	24(1)	6(1)
P(1)	0.1624(2)	0.1263(1)	0.8086(2)	33(1)	34(1)	29(1)	−2(1)	12(1)	1(1)
P(2)	0.1741(2)	0.1697(1)	1.1788(2)	32(1)	35(1)	29(1)	−3(1)	12(1)	0(1)
C(1)	0.1091(7)	0.2346(4)	0.9387(8)	32(5)	35(5)	39(5)	1(4)	10(4)	6(4)
C(2)	0.2052(8)	0.2742(4)	0.9682(8)	38(5)	44(6)	49(5)	11(4)	20(4)	5(4)
N	0.2823(10)	0.3060(5)	0.9919(9)	56(7)	78(8)	104(8)	23(6)	24(6)	−17(7)
Phenyl ring A									
C(1)	0.0031(5)	0.0778(3)	0.6054(5)	47(2)					
C(2)	−0.0943(5)	0.0452(3)	0.5434(5)	64(2)					
C(3)	−0.1565(5)	0.0165(3)	0.6021(5)	61(2)					
C(4)	−0.1215(5)	0.0203(3)	0.7228(5)	50(2)					
C(5)	−0.0241(5)	0.0530(3)	0.7848(5)	42(2)					
C(6)	0.0382(5)	0.0817(3)	0.7261(5)	30(2)					
Phenyl ring B									
C(1)	0.3947(5)	0.0943(2)	0.9090(5)	50(2)					
C(2)	0.4934(5)	0.0630(2)	0.9154(5)	59(2)					
C(3)	0.4890(5)	0.0231(2)	0.8287(5)	61(2)					
C(4)	0.3858(5)	0.0143(2)	0.7356(5)	67(2)					
C(5)	0.2871(5)	0.0456(2)	0.7292(5)	57(2)					
C(6)	0.2916(5)	0.0856(2)	0.8159(5)	34(2)					
Phenyl ring C									
C(1)	0.0503(4)	0.2106(3)	0.6454(5)	47(2)					
C(2)	0.0441(4)	0.2568(3)	0.5698(5)	52(2)					
C(3)	0.1446(4)	0.2780(3)	0.5571(5)	59(2)					
C(4)	0.2513(4)	0.2531(3)	0.6199(5)	62(2)					
C(5)	0.2576(4)	0.2070(3)	0.6955(5)	52(2)					
C(6)	0.1571(4)	0.1858(3)	0.7082(5)	31(2)					
Phenyl ring D									
C(1)	0.4046(5)	0.1400(3)	1.2567(4)	48(2)					
C(2)	0.5093(5)	0.1213(3)	1.3380(4)	61(2)					
C(3)	0.5133(5)	0.1002(3)	1.4456(4)	65(2)					
C(4)	0.4125(5)	0.0978(3)	1.4720(4)	74(2)					
C(5)	0.3078(5)	0.1165(3)	1.3907(4)	57(2)					
C(6)	0.3039(5)	0.1376(3)	1.2831(4)	36(2)					
Phenyl ring E									
C(1)	−0.0240(5)	0.1034(3)	1.1292(4)	42(2)					
C(2)	−0.1233(5)	0.0834(3)	1.1463(4)	55(2)					
C(3)	−0.1495(5)	0.1026(3)	1.2416(4)	58(2)					
C(4)	−0.0764(5)	0.1418(3)	1.3200(4)	54(2)					
C(5)	0.0229(5)	0.1618(3)	1.3029(4)	46(2)					
C(6)	0.0491(5)	0.1426(3)	1.2076(4)	32(2)					
Phenyl ring F									
C(1)	0.0865(4)	0.2802(2)	1.2016(5)	43(2)					
C(2)	0.0959(4)	0.3379(2)	1.2380(5)	56(2)					
C(3)	0.2041(4)	0.3612(2)	1.3011(5)	60(2)					
C(4)	0.3029(4)	0.3268(2)	2.3278(5)	63(2)					
C(5)	0.2935(4)	0.2690(2)	1.2914(5)	48(2)					
C(6)	0.1853(4)	0.2457(2)	1.2283(5)	34(2)					

[a] Anisotropic temperature factors are in the form: $\exp[-2\pi^2(\Sigma_{ij}U_{ij}a_i^*a_j^*h_ih_j)]$; isotropic temperature factors are listed as U_{11}.

TABLE II. Intramolecular Bond Distances and Angles with e.s.d.'s in Parentheses.

Pt–P(1)	2.310(3)	P(1)–Pt–P(2)	176.3(1)
Pt–P(2)	2.308(3)	P(1)–Pt–Cl	88.4(1)
Pt–C(1)	2.08(1)	P(2)–Pt–Cl	88.2(1)
Pt–Cl	2.390(3)	Cl–Pt–C(1)	175.9(3)
C(1)–C(2)	1.44(2)	P(1)–Pt–C(1)	91.8(2)
C(2)–(N)	1.15(2)	P(2)–Pt–C(1)	91.7(2)
P(1)–C(16)	1.828(7)	Pt–C(1)–C(2)	111.0(8)
P(1)–C(26)	1.827(7)	C(1)–C(2)–N	180.0(8)
P(1)–C(36)	1.830(7)	Pt–P(1)–C(16)	113.3(3)
P(2)–C(46)	1.820(7)	Pt–P(1)–C(26)	111.6(3)
P(2)–C(56)	1.814(7)	Pt–P(1)–C(36)	117.5(3)
P(2)–C(66)	1.842(7)	Pt–P(2)–C(46)	110.3(3)
		Pt–P(2)–C(56)	112.5(3)
		Pt–P(2)–C(66)	118.9(3)
		C(16)–P(1)–C(26)	106.7(5)
		C(16)–P(1)–C(36)	102.9(5)
		C(26)–P(1)–C(36)	103.8(5)
		C(46)–P(2)–C(56)	108.8(5)
		C(46)–P(2)–C(66)	102.0(5)
		C(56)–P(2)–C(66)	103.4(5)

TABLE III. Least-Squares Plane through the Square-planar Coordination Sites and Distances (Å) of Atoms to the Plane. Dihedral Angles (°) Involving the Coordination Plane and Those of the Phenyl Rings. The equation of the plane is in the form AX + BY + CZ = D, where X, Y, Z are coordinates referred to orthogonal Å space.

Plane 1	0.9304X + 0.2593Y + 0.2592Z = 1.717			
	Pt	0.022	Cl	−0.054
	P(1)	0.046	C(1)	−0.059
	P(2)	0.046	C(2)*	1.25
Dihedral angles (°)				
Plane 1	-phenyl	A	69.2	
"	"	B	60.8	
"	"	C	77.4	
"	"	D	67.6	
"	"	E	74.3	
"	"	F	74.8	
Phenyl	A - phenyl	B	69.0	
"	A "	C	56.8	
"	B "	C	89.2	
"	D "	E	61.1	
"	D "	F	87.7	
"	E "	F	58.4	

*Atom not used in the plane calculation.

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

Cl. . .P(2)	3.27
Cl. . .P(1)	3.28
P(2). .C(1)	3.15
P(2). .C(2)	3.65
P(1). .C(1)	3.16
P(1). .C(2)	3.87
Pt. . .C(2)	2.92

ligand with such a property will reduce the amount of dπ–dπ bonding possible between the platinum and phosphorus atoms and hence the Pt–P distance should be increased. Thus is not surprising to find the longest Pt–P bonds (2.34 and 2.35 Å) in Pt(CO)Cl$(PEt_3)_2^+$ [28], since CO has strong π-acceptor properties. In the present compound the mutually *trans* Pt–P bonds are equal in length, 2.308(3) and 2.310(3) Å, and fall within the range found recently for Pt–P distances in several square-planar Pt(II) complexes [29–31]. This argument suggests that there is small, if any, d → p back-donation in the platinum(II)–cyanomethyl linkage. In addition the Pt–P distances in the present compound are significantly longer than those found in the parent compound *trans*-$[PtH(CH_2CN)(PPh_3)_2]$, *2*, 2.272(4) and 2.276(4) Å [19]. This implies a stronger dπ–dπ interaction between Pt and P in the hydrido complex.

The Pt–C(1) bond length, 2.08(1) Å, agrees well with the sum of the appropriate covalent radii (2.08 Å) and with the Pt–C σ-bonds in platinum alkyl complexes, *e.g.*, 2.081(6) Å in *trans*-$[PtCl(CH_3)(PMePh_2)_2]$ [32], 2.120(7) Å in *trans*-$[Pt(I\text{-}SO_2)(CH_3)(PPh_3)_2]$ [30] and 2.090(4) Å in *trans*-$[PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2]$ [29]. It is interesting to note that the electronegative cyano group, in the present complex, seems to be ineffective in shortening the Pt–C bond as one can see by comparing its value with those found in the above quoted complexes. On the contrary the Pt–C bond in the perfluoroethylderivative *trans*-$[PtCl(CF_2CF_3)(PMePh_2)_2]$, 2.014(11) Å [32], is significantly shorter, indicating the effectiveness of the fluorine groups.

The Pt–Cl distance of 2.390(3) Å, which is longer than predicted from radii-sum rules (2.30 Å), is slightly shorter than the values found in *trans*-$[PtCl(Me_3\text{-}Si\text{-}CH_2)(PMe_2PH)_2]$, 2.415(5) Å [33], in *trans*-$[Pt(\eta^1\text{-}C_3H_5)Cl(PPh_3)_2]$, 2.425(2) Å [29] and in *cis*-$[PtCl_2CH(CH_2NH_2CHMePhe)\{CH_2\}_2CH{:}CH_2]$, 2.430 Å [34].

The Pt–P and Pt–Cl bond distances of several *trans*-$PtXClP_2$ complexes have been presented in a recent paper of Ibers [29]. McWeeney *et al.* [35] have noted a good correlation between the electronegativity of 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 [29], we conclude from the above data [29–35] that the *trans*-influence of the cyanoalkyl group is slightly smaller than that of a trimethylsilyl methyl group or a hydrido ligand.

The cyanoalkyl moiety undergoes a large thermal motion, which affects the accuracy of its geometry. Its configuration is linear within the experimental error and the C(1)–C(2)–N(1) line is tilted of 111.1° with respect to the Pt–C(1) bond. For the C(2)–N(1) distance the value 1.15(2) Å has been found and it is essentially the same in methyl cyanide and other similar molecules [36]. This value is that expected for a triple bond with a small amount of double bond character.

The C(1)–C(2) distance (1.44(2) Å) is slightly shorter than the corresponding value in methyl cyanide and other related compounds and corresponds to about 25% double-bond character [36].

The triphenylphosphine geometry in this compound, as judged by P–C distances and C–P–C and P–C–C angles, is nearly identical with the geometry of the triphenylphosphine ligand and its derivatives in other transition metal complexes [20, 24, 29, 37]. In particular the P–C distances range from 1.812 to 1.842 Å and average 1.827(4) Å; the C–P–C angles range from 102.0 to 108.8° and average 104.6(5)°; the P–C–C angles range from 117.2 to 122.4° and average 119.9°.

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