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METALS IN ORGANIC SYNTHESES

IX [*]. THE ISOLATION AND MOLECULAR STRUCTURE OF *trans*-$[PtCl(COC_6H_{13}\text{-n})(PPh_3)_2]$, AN INTERMEDIATE PRECURSOR IN THE CATALYTIC HYDROFORMYLATION OF 1-HEXENE

R. BARDI, A.M. PIAZZESI,

Biopolymer Research Centre, CNR, University of Padova, Via Marzolo 1, 35100 Padova (Italy)

A. DEL PRA,

Istituto Chimico Farmaceutico e Tossicologico, Università di Milano, Viale Abruzzi 42, 20131 Milano (Italy)

G. CAVINATO and L. TONIOLO [*]

Istituto di Chimica Generale ed Inorganica e di Chimica Inorganica Industriale, University of Padova, Via Loredan 4, 35100 Padova (Italy)

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Summary

The complex *trans*-$[PtCl(COC_6H_{13}\text{-n})(PPh_3)_2]$ (I) has been synthesized by treating *cis*-$[PtCl_2(PPh_3)_2]$ and 1-hexene with carbon monoxide under pressure in EtOH at 100°C. When in combination with $SnCl_2 \cdot 2H_2O$, complex I is an intermediate precursor in the highly regioselective catalytic hydroformylation of 1-hexene, which readily occurs in a solvent such as a ketone.

The crystal and molecular structure of complex I has been determined from three dimensional X-ray diffractometer data. The complex crystallizes in the triclinic space group $P\bar{1}$. Cell parameters are as follows: a 15.869(8), b 12.306(8), c 11.437(7) Å, α 109.8(1), β 76.6(1), γ 112.9(1)°, $Z = 2$. Full-matrix least-squares refinement converged at $R = 0.058$ ($R_w = 0.064$). The structure has approximately square planar geometry, and shows no unusual dimensions.

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Introduction

The current interest in homogeneous olefin hydroformylation catalyzed by ligand stabilized platinum(II)—Group IVB metal halide complexes is mainly associated with the fact that the catalytic system is highly active and regioselective towards the desired straight-chain aldehydes [2,3]. Recently, the isolation and molecular structure of *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ were reported; this complex separated in 75% yield from an alcoholic solution in the course of the attempted hydroformylation and hydrocarboalkoxylation of propene using a $[PtCl_2(PPh_3)_2]/SnCl_2$ precursor [4]. In contrast this system is very active in catalytic hydroformylation in a non-polar solvent, such as benzene [2], or a moderately polar one, such as a ketone [3]. From the latter solvent the catalyst was recovered as *trans*-$[Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2]$ in the course of propene hydroformylation; it is believed that the presence of a Pt—Sn bond, in a complex such as that just mentioned, plays a key role in promoting the catalytic formation of the aldehyde from the acyl derivative, even though it is not crucial for the formation of the acyl ligand since *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ can be isolated even in the absence of $SnCl_2$ [4].

Here we report the catalytic properties and the molecular structure of *trans*-$[PtCl(COC_6H_{13}\text{-}n)(PPh_3)_2]$ (I) which was synthesized as described below.

Experimental

Materials

Carbon monoxide and hydrogen were purchased from the S.I.O. Company. Alcohols and $SnCl_2 \cdot 2H_2O$ were commercial grade. 1-Hexene was passed through a column of neutral Al_2O_3 and distilled before use. The catalyst precursor *cis*-$[PtCl_2(PPh_3)_2]$ was prepared from $[H_2PtCl_6] \cdot 6H_2O$ and PPh_3 [5].

General procedure

The yields and the isomeric composition of the reaction products were determined by GLC, using a Hewlett—Packard gas chromatograph Model 5830 A equipped with a Hewlett—Packard GC terminal Model 18850. Analyses were carried out using a 6 ft long column of SE 30 25% on Chrom. P at 120°C. Infrared spectra were taken in Nujol mull using a spectrophotometer Perkin—Elmer Mod. 683.

Carbonylations were carried out in a stainless steel stirred autoclave of about 75 ml capacity, which was placed in a thermostatted oil bath. The catalyst and reagents were placed in a Pyrex glass bottle inside the autoclave in order to avoid contamination from other metallic species and to avoid effects from the metal surface of the autoclave.

Synthesis of trans-$[PtCl(COC_6H_{13}\text{-}n)(PPh_3)_2]$ (I)

A mixture of 118 mg of *cis*-$[PtCl_2(PPh_3)_2]$ (0.15 mmol), 113 mg of $SnCl_2 \cdot 2H_2O$ (0.5 mmol), 10 mmol of 1-hexene and 10 ml of EtOH was placed in the bottle which was introduced into the autoclave. The autoclave was cooled in an ice bath purged with carbon monoxide, and then pressurized with 100 atm of CO at room temperature. The autoclave was then placed in a thermostatted oil bath, its temperature was raised to 100°C in ca. 10 min. After 4 h the autoclave was cooled in an ice bath, then after ca. 1 day at room temperature it was depressurized. White crystals of complex I were filtered off, washed with EtOH and dried under vacuum. Yield 75%. Found: C, 59.15; H, 4.86; Cl, 4.00. $C_{43}H_{43}ClOP_2Pt$ calcd.: C, 59.47; H, 4.99; Cl, 4.08%. No significant hydrocarboalkoxylation was observed.

Practically the same results were obtained using 0.1 mmol of PPh_3 in place of $SnCl_2 \cdot 2H_2O$.

1-Hexene hydroformylation

In a typical experiment, 0.05 mmol of *cis*-$[PtCl_2(PPh_3)_2]$, 0.25 mmol of $SnCl_2 \cdot 2H_2O$, 10 mmol of 1-hexene, and 9.4 ml of methyl ethyl ketone (MEK) were introduced into the bottle contained in the autoclave (whose free volume was reduced to ca. 50 ml). After purging with CO, molecular hydrogen (50 atm) and carbon monoxide (50 atm) were introduced in the autoclave at room temperature and the autoclave was then placed in a thermostatted oil bath at 70°C. After 4 h the autoclave was cooled in an ice bath and slowly depressurized. The contents of the bottle were analyzed by GLC after the usual work up. The linear/branched isomer ratio was 93/7.

When *trans*-$[PtCl(COC_6H_{13}\text{-n})(PPh_3)_2]$ or *trans*-$[PtHCl(PPh_3)_2]$ was used in place of *cis*-$[PtCl_2(PPh_3)_2]$, the linear/branched isomer ratio was 95/5.

Collection and reduction of X-ray intensity data

Suitable crystals for X-ray analysis of complex were separated directly from the reaction medium (in EtOH).

Approximate unit cell dimensions were obtained from preliminary Weissenberg and precession photographs. Structure analysis defined the centro-symmetric triclinic space group $P\bar{1}$. For $Z = 2$ neither molecule has any imposed crystal symmetry. Full details of the crystal data are listed in Table 1.

Intensity data were collected on a Philips PW 1100 four-circle diffractometer. Accurate unit cell dimensions and crystal orientation matrices, together with

TABLE 1

CRYSTAL DATA

a	15.869(8) Å
b	12.306(8) Å
c	11.437(7) Å
α	109.8(1)°
β	76.6(1)°
γ	112.9(1)°
formula wt	868.42
$\rho_{obsd.}$	1.50 g cm^{-3}
$\rho_{calcd.}$	1.499 g cm^{-3}
Z	2
Unit cell volume	1922.9 $Å^3$
Space group	$P\bar{1}$ (after structure analysis)
Crystal dimensions	0.3 × 0.3 × 0.5 mm
Absorption coeff.	40.3 (Mo-K_α) cm^{-1}

TABLE 2

DETAILS OF DATA COLLECTION

Radiation	Mo-K_α, λ 0.7107 Å
Monochromator	graphite crystal
Scan method	θ—2θ
Scan speed	0.03 deg s^{-1}
Scan width	1.20°
"Standard" reflections	2 every 180 min
"Standard" indices	$(3\bar{3}\bar{1})$, $(\bar{3}31)$
2θ scan limit	44°
Number of data	4698
Number of data with $I > 3\sigma(I)$	4230

their estimated standard errors, were obtained from least-squares refinement of the 2ϑ, ω, χ and φ values of 25 carefully centered high-angle reflections. Full details of the experimental conditions and data collection method used are given in Table 2.

TABLE 3

FRACTIONAL ATOMIC POSITIONAL PARAMETERS [$\times 10^4$ or $\times 10^3$ for C(1) to C(7)] WITH THE e.s.d.'s IN PARENTHESES

Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$
Pt	2481(1)	1322(1)	2943(1)	C(2)	443(1)	262(1)	209(1)
Cl	898(2)	—20(2)	2688(3)	C(3)	546(2)	305(2)	204(2)
P(1)	2059(2)	2950(2)	3062(2)	C(4)	583(2)	440(2)	232(2)
P(2)	2797(2)	—382(3)	2844(2)	C(5)	666(2)	547(2)	233(2)
O	4021(6)	2829(9)	4266(9)	C(6)	671(2)	664(2)	231(2)
C(1)	379(1)	239(1)	321(1)	C(7)	765(2)	730(3)	251(3)
Phenyl ring 1.				*Phenyl ring 4.*			
C(11)	1357(5)	3403(5)	4530(7)	C(41)	4011(5)	—241(7)	2686(5)
C(12)	885	2562	5227	C(42)	4464	—751	1558
C(13)	334	2886	6336	C(43)	5391	—601	1478
C(14)	256	4051	6748	C(44)	5867	60	2525
C(15)	728	4892	6050	C(45)	5414	570	3653
C(16)	1279	4568	4942	C(46)	4487	420	3733
Phenyl ring 2.				*Phenyl ring 5.*			
C(21)	1379(6)	2647(7)	1841(8)	C(51)	2295(5)	—918(6)	4243(7)
C(22)	1421	1702	753	C(52)	1617	—496	5065
C(23)	898	1430	—199	C(53)	1241	—882	6146
C(24)	332	2103	—65	C(54)	1543	—1691	6405
C(25)	289	3049	1023	C(55)	2221	—2114	5584
C(26)	813	3321	1975	C(56)	2597	—1727	4503
Phenyl ring 3.				*Phenyl ring 6.*			
C(31)	2975(5)	4402(6)	2990(5)	C(61)	2374(5)	—1650(5)	1500(7)
C(32)	3160	4868	1968	C(62)	2451	—1364	390
C(33)	3852	5995	1963	C(63)	2196	—2302	—700
C(34)	4359	6655	2980	C(64)	1864	—3526	—681
C(35)	4174	6188	4002	C(65)	1787	—3812	428
C(36)	3482	5062	4007	C(66)	2043	—2874	1519

Solution and refinement of the structure

The structure was solved by conventional Patterson and Fourier syntheses. The refinement of the structural model, which was by the method of full-matrix least-squares, 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. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual thermal parameter [6]. The Pt, Cl and P atoms were allowed to vibrate anisotropically while the oxygen and carbon atoms of the acyl ligand were assigned isotropic thermal parameters. Hydrogen atoms could not be located from electron density difference maps and therefore were included in the scattering models in calculated idealized position (C—H 0.95 Å) but not varied.

The function minimized was $\Sigma w\Delta^2$, ($\Delta = |F_o| - |F_c|$) and w was $[\sigma^2(F_o) + 0.00618\ F_o{}^2]^{-1}$. Weighting-scheme analysis showed no serious dependence of the mean $w\Delta^2$ on either $|F_o|$ and λ^{-1} sen ϑ. Atomic scattering factors were taken from ref. 7. Allowance was made for the anomalous scattering of platinum, chlorine and phosphorus atoms, using values of $\Delta f'$ and $\Delta f''$ from reference 8. The final conventional R value for the 4230 observed reflections with $I \geqslant 3\sigma(I)$ were 0.058 ($R_w = 0.064$).

Final atomic positional parameters are in Table 3 and a selection of functions derived from them are presented in Tables 4—6. Final atomic thermal param-

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) WITH THE e.s.d.'s IN PARENTHESES

Distance		Distance	
PtCl	2.431(3)	P(2)—C(61)	1.813(2)
Pt—P(1)	2.302(3)	C(1)—O	1.22(1)
Pt—P(2)	2.301(3)	C(1)—C(2)	1.47(2)
Pt—C(1)	2.02(1)	C(2)—C(3)	1.50(3)
P(1)—C(11)	1.831(2)	C(3)—C(4)	1.47(3)
P(1)—C(21)	1.813(3)	C(4)—C(5)	1.46(3)
P(1)—C(31)	1.826(2)	C(5)—C(6)	1.43(3)
P(2)—C(41)	1.837(3)	C(6)—C(7)	1.43(3)
P(2)—C(51)	1.829(3)		
Angle		**Angle**	
P(1)—Pt—P(2)	176.0(1)	C(11)—P(1)—C(31)	102.4(1)
P(1)—Pt—Cl	88.9(1)	C(21)—P(1)—C(31)	103.5(1)
P(1)—Pt—C(1)	93.0(3)	C(41)—P(2)—C(51)	103.4(2)
P(2)—Pt—C(1)	90.8(3)	C(41)—P(2)—C(61)	102.8(1)
P(2)—Pt—Cl	87.2(1)	C(51)—P(2)—C(61)	107.8(1)
Cl—Pt—C(1)	177.3(3)	Pt—C(1)—O	119.8(8)
Pt—P(1)—C(11)	113.0(1)	Pt—C(1)—C(2)	116.8(8)
Pt—P(1)—C(21)	113.7(1)	C(2)—C(1)—O	123(1)
Pt—P(1)—C(31)	117.8(1)	C(1)—C(2)—C(3)	124(1)
Pt—P(2)—C(41)	117.7(1)	C(2)—C(3)—C(4)	109(2)
Pt—P(2)—C(51)	112.3(1)	C(3)—C(4)—C(5)	145(2)
Pt—P(2)—C(61)	111.8(2)	C(4)—C(5)—C(6)	125(2)
C(11)—P(1)—C(21)	105.1(2)	C(5)—C(6)—C(7)	98(2)

TABLE 5

SOME MEAN PLANES WITH THE DISTANCES (Å) OF THE ATOMS TO THE PLANE

Plane 1:	$-0.0717X + 0.1648Y + 0.9837Z = 2.7786$				
	Pt	−0.022	Cl	0.012	
	P(1)	−0.002	C(1)	0.014	
	P(2)	−0.002			
Plane 2:	$0.7885X - 0.3119Y + 0.5301Z = 5.1331$				
	Pt, C(1), C(2), C(3), C(4), C(5), C(6), C(7), O				
Plane 3:	$0.7294X + 0.6367Y + 0.2501Z = 4.6107$				
	Pt, P(1), C(11)				
Plane 4:	$0.6190X + 0.3438Y - 0.7061Z = 1.0047$				
	Pt, P(1), C(21)				
Plane 5:	$0.0945X + 0.2800Y + 0.9553Z = 3.5201$				
	Pt, P(1), C(31)				
Plane 6:	$0.0918X + 0.2828Y + 0.9548Z = 3.5113$				
	Pt, P(2), C(41)				
Plane 7:	$0.7587X + 0.5908Y + 0.2744Z = 4.7337$				
	Pt, P(2), C(51)				
Plane 8:	$0.6777X + 0.3196Y - 0.6622Z = 1.3350$				
	Pt, P(2), C(61)				

TABLE 6

SOME TWIST, DIHEDRAL AND TORSION ANGLES (°)

(a) *Twist Angle (°) between the phenyl ring and corresponding Pt—P—C plane*

Pt—P(1)—C(11)	and	C(11)—C(16)	20.7
Pt—P(1)—C(21)	and	C(21)—C(26)	21.1
Pt—P(1)—C(31)	and	C(31)—C(36)	69.3
Pt—P(2)—C(41)	and	C(41)—C(46)	74.2
Pt—P(2)—C(51)	and	C(51)—C(56)	15.8
Pt—P(2)—C(61)	and	C(61)—C(66)	36.3

(b) *Dihedral angles (°) between the phenyl rings*

C(11)—C(16)	and	C(21)—C(26)	71.6
C(11)—C(16)	and	C(31)—C(36)	67.0
C(21)—C(26)	and	C(31)—C(36)	75.4
C(41)—C(46)	and	C(51)—C(56)	65.6
C(41)—C(46)	and	C(61)—C(66)	87.3
C(51)—C(56)	and	C(61)—C(66)	63.0

(c) *Torsion angles (°)*

Pt—C(1)—C(2)—C(3)	−160
C(1)—C(2)—C(3)—C(4)	−94
C(2)—C(3)—C(4)—C(5)	−169
C(3)—C(4)—C(5)—C(6)	158
C(4)—C(5)—C(6)—C(7)	172

eters and tables of structure factors are available as supplementary material. All calculations were carried out with SHELX-76 program for crystal structure determination [9].

Results and discussion

After reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with 1-hexene and carbon monoxide (100 atm, 100° C) in EtOH, either in the presence of $SnCl_2$ or in its absence, I separates out as white crystals in 75—80% yield. Its IR spectrum shows $\nu(C{=}O)$ at 1656 cm^{-1}, close to the value found for the butanoyl analog [4] and for other alkanoyl complexes of platinum(II) [10].

Complex I is also obtained when from *trans*-$[PtHCl(PPh_3)_2]$, and so it is likely that it is produced by the scheme proposed for the formation of *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ [4]:

$$[PtCl_2(PPh_3)_2] \xrightarrow{CH_3CH_2OH} [PtHCl(PPh_3)_2] \xrightarrow{\text{1-hexene}}$$

$$[PtCl(C_6H_7\text{-}n)(PPh_3)_2] \xrightarrow{CO} [PtCl(COC_6H_7\text{-}n)(PPh_3)_2] \xrightarrow{EtOH}$$

$$[PtHCl(PPh_3)_2] + n\text{-}C_6H_7COOEt$$

There is no significant catalysis of the formation of the ester, as was found when propene was used [4].

In MEK, complex I is highly active in hydroformylation, when in combination with $SnCl_2$.

Practically the same regioselectivity is obtained with complex I (95%) as from *cis*-$[PtCl_2(PPh_3)_2]$ (93%). It is noteworthy that a significantly higher regioselectivity is reached when *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ is used in place of *cis*-$[PtCl_2(PPh_3)_2]$ (93 vs. 83%) for the hydroformylation of propene. In this case the different regioselectivity is believed to be due to the effect of HCl on the regioselective steps of the catalysis; $[PtCl_2(PPh_3)_2]$ and $[PtCl(COPr\text{-}n)(PPh_3)_2]$ are equivalent during the catalysis except that they differ by a molecule of HCl [4]. It is likely that the larger steric hindrance caused by the 1-hexene and of the $(COC_6H_{13}\text{-}n)$ ligands compared to that of the propene and (COPr-n) ligands, modifies the equilibria between several catalytic intermediates to such an extent as to reduce the effect of HCl on the regioselectivity in the hydroformylation of 1-hexene when *cis*-$[PtCl_2(PPh_3)_2]$ is used.

Structure of complex I

The stereochemical arrangement of the complex, with the atom numbering used, is shown in Fig. 1.

The structure described by the cell constants, the symmetry operations of the space group and the atomic parameters consists of the packing of discrete neutral molecules of *trans*-$[PtCl(COC_6H_{13}\text{-}n)(PPh_3)_2]$, separated by Van der Waals contacts. The closest Pt····Pt approach is 8.24 Å, and all other intermolecular contacts agree with those predicted from radii-sum rules.

In the complex a square plane about the metal atom is defined by the phosphorus atoms of two triphenylphosphine ligands, one chlorine atom and the donor $C(sp^2)$ atom of the acyl ligand. In addition individual atoms are displaced by <0.02 Å from the coordination plane of the Pt atom (Table 5).

In the phosphine ligands, corresponding bond lengths and valency angles,

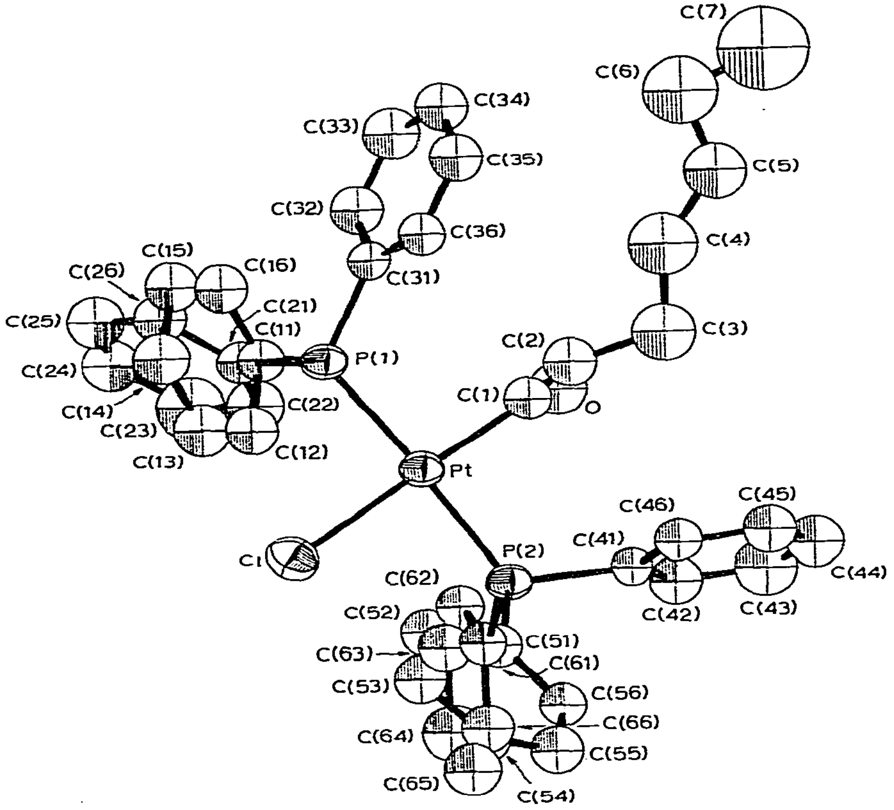

Fig. 1. Molecular structure of *trans*-[PtCl(COC$_6$H$_{13}$-n)(PPh$_3$)$_2$].

as well as orientations and conformations, agree well. The interbond angles at the phosphorus atoms show the usual departures from the tetrahedral value. In many compounds containing coordinated PPh$_3$ groups [11] it was found that the plane of one of the phenyl rings essentially contains the metal—phosphorus vector, another phenyl ring is twisted ca. 90° about its P—C bond, with respect to the first ring, while the third phenyl ring assumes an intermediate orientation. The present complex does not conform to this stereochemistry. Of the phenyl groups attached to P(1), the ring C(31)—C(36) lies roughly at right angles to the plane Pt, P(1), C(31), while the other two rings C(11)—C(16) and C(21)—C(26) are both at angles of ca. 21° with respect to their corresponding Pt—P—C planes. For P(2), while the ring C(41)—C(46) lies approximately at right angles to the Pt—P(2)—C(41) plane, the rings C(51)—C(56) and C(61)—C(66) are tilted with respect the corresponding Pt—P—C planes by 16 and 36° respectively. The mutually *trans*- Pt—P bonds are equal in length, 2.301(3) and 2.302(3) Å, and agree well with the weighted average, 2.302(1) Å, for Pt^{II}—P bond lengths in 22 complexes containing mutually *trans* tertiary phosphines of the type PR$_n$Ph$_{3-n}$ (R = alkyl; n = 0—3) (12). The metal—acyl linkage, 2.01(1) Å, is slightly shorter than the value of 2.05 Å predicted for these bond lengths from the sum of the σ covalent radii (the covalent radius of platinum(II) in its planar derivatives is 1.31 Å while that of C(sp^2) is 0.74 Å [13]). This would indicate the formation of a strong bond between the platinum(II) ion and the acyl carbon. The large *trans* influence of σ-bonded carbon is well established [14]. The consequence of this in the present structure is that the Pt—Cl bond *trans* to Pt—C(acyl) is among the longest Pt—Cl bonds known [4], with observed bond length of 2.431(3) Å.

Within the acyl ligand an approximately *T,G,T,T,T* conformation (*T*, *trans*; *G*, *gauche*) of the carbon atoms chain is observed (Table 6), with mean C_{sp^3} — C_{sp^3} bond distance of 1.46(2) Å, which is significantly shorter than that predicted from available covalent radii (1.54 Å) [13]. This difference may be attributed to the error introduced by the large thermal motions of these carbon atoms.

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