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SYNTHESIS AND STRUCTURE OF *trans*-$\text{PtCl}_2(\text{P(t-Bu)}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2\text{C}}\text{H}_2)_2$, A PLATINUM(II) COMPLEX CONTAINING THE NEW LIGAND (DI-t-BUTYL)CYCLOBUTYLMETHYLPHOSPHINE

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Summary

The synthesis and spectral properties of *trans*-dichlorobis((di-t-butyl)cyclobutylmethylphosphine)platinum(II), *trans*-$\text{PtCl}_2(\text{P(t-Bu)}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2\text{C}}\text{H}_2)_2$, and of the new phosphine (di-t-butyl)cyclobutylmethylphosphine, $\text{P(t-Bu)}_2(\text{CH}_2\text{-}\overline{\text{CHCH}_2\text{CH}_2\text{C}}\text{H}_2)$, are described. The crystal structure of the Pt complex has been determined. The material crystallizes in the monoclinic system, space group C_{2h}^5-$P2_1/c$, with two formula units in a cell of dimensions a 8.521(2), b 12.774(1), c 14.374(2) Å, β 104.71(2)°. A total of 5667 unique reflections were measured on a CAD4 diffractometer at 113 K. The final value of $R(F)$ is 0.028 for those 4223 reflections having $F_o^2 > 3\sigma(F^2)$. The crystal structure consists of the packing of discrete neutral molecules of *trans*-$\text{PtCl}_2(\text{P(t-Bu)}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2\text{C}}\text{H}_2)_2$. A crystallographic center of symmetry is imposed on each molecule. Important intramolecular distances include Pt–P, 2.353(1) and Pt–Cl, 2.306(1) Å. The shortest non-bonding distance between the Cl atom and a carbon atom of a t-Bu group is Cl $\cdots$ C(4), 3.387(3) Å. No interaction between the Pt atom and the cyclobutane ring is observed. The absence of extreme steric congestion in the complex may explain the lack of such an interaction.

Introduction

Certain transition metals, particularly the Pt group metals, catalyze the rearrangement of small strained-ring molecules to olefins [1.2]. Such C–C bond activation proceeds fairly readily compared with C–C and C–H bond activation in less strained rings or in simple, non-cyclic aliphatic hydrocarbons. However, in the presence of transition metals intramolecular bond activation is common in non-cyclic hydrocarbons that are part of a bulky phosphine or other donor ligand [3]. Usually a metal–carbon bond and thus a chelate ring results from the activation. These orthometallation reactions are extremely sensitive to steric factors, such as conges-

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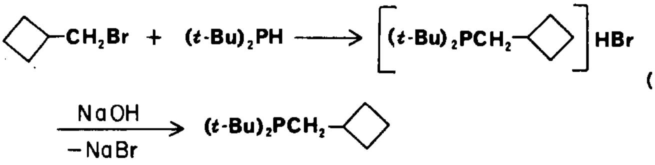
tion in the starting complex and size of the chelate ring in the orthometallated product [3b]. Generally, ease of orthometallation increases with increasing relief of ligand crowding by ring formation. Five-atom metallacycles form most readily [3a,4]. The importance of electronic factors is illustrated by the greater reactivity of aromatic C–H bonds relative to weaker aliphatic C–H bonds in orthometallation reactions [4].

The phosphine $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2C}H_2)$ undergoes facile intramolecular activation of cyclopropane in its monomeric chloro complexes of Ir^{I}, Pt^{II}, and Pd^{II} to form five-atom metallacycles that contain metal–carbon σ-bonds [2]. In contrast, in analogous complexes the related cyclobutylmethyl phosphine $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2CH_2C}H_2)$ discussed here is not activated [5]. In an attempt to understand this lack of reactivity we have performed a single-crystal X-ray structure analysis of *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2$.

Results and discussion

Synthesis of (di-t-butyl)cyclobutylmethylphosphine

To prepare the phosphine we followed a method used to prepare $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2C}H_2)$ (eq. 1) [2b]. Traditional routes to $(t\text{-}Bu)_2PR$ species, namely



(1)

reaction of alkyllithium reagents with $P(t\text{-}Bu)_2Cl$ [6], were not available owing to the ease with which $LiCH_2\overline{CH(CH_2)_2C}H_2$ rearranges to $Li\overline{CH(CH_2)_3C}H_2$ [7].

The $^{31}P\{^1H\}$ NMR spectrum of $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2CH_2C}H_2)$ consists of a singlet resonance at δ 21.47 ppm. This is upfield of the resonance (δ 28.5 ppm) reported for $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2C}H_2)$ [2b]. Since the phosphorus cone angle is generally proportional to the ^{31}P chemical shift [8] $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2C}H_2)$ may be more sterically demanding in its coordination complexes than is $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2CH_2C}H_2)$.

The ^{13}C NMR spectrum shows the expected doublet resonances for C nuclei coupled to P. The large coupling constant (20.8 Hz) observed for the equivalent cyclobutylmethylene C atoms results from multiple coupling pathways between these C atoms and the P atom ($^3J + ^5J$).

Synthesis of trans-dichlorobis(di-t-butyl)cyclobutylmethylphosphine)platinum(II), trans-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2$

K_2PtCl_4 reacts with $P(t\text{-}Bu)_2(CH_2\overline{CHCH_2CH_2C}H_2)$ in aqueous acetone to give exclusively *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2$. The *trans* configuration of the phosphine ligands is inferred from the characteristic appearance in the ^1H NMR spectrum of a pseudo-triplet resonance from the t-Bu methyl groups on phosphorus [3a]. The ^{31}P NMR spectrum contains a single resonance for the two equivalent phosphine ligands at δ 32.37 ppm with Pt–P satellite peaks having J(Pt–P) 2453.6 Hz. For comparison, the P–Pt coupling constant in *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2C}H_2)_2$ [2b] is 2470.7 Hz while the ^{31}P NMR chemical shift is 30.8 ppm.

Structure of trans-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2CH_2})_2$

The crystal structure consists of neutral, centrosymmetric molecules of *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2CH_2})_2$ separated by normal Van der Waals' contacts. The closest intermolecular distance between non-hydrogen atoms occurs between atoms Cl and C(3) (3.642(4) Å). The molecular structure and labeling scheme for the complex are shown in Fig. 1. Bond distances and angles are given in Table 1. Because of the crystallographically imposed symmetry, the $PtCl_2P_2$ portion of the structure is planar. The P–Pt–Cl angle is 89.07(3)°.

Bond distances and angles within the cyclobutane ring are normal [9]. The average bond length in the ring is 1.541(3) Å and the average C–C–C angle is 88.5(2)°. The ring adopts a butterfly conformation. The deviations from the least-squares plane calculated for atoms C(10) to C(13) are −0.078(3), 0.111(4), −0.147(4), and 0.159(4) Å, respectively. The dihedral angle between the cyclobutyl ring plane and the $PtCl_2P_2$ plane is 55.2°.

The t-Bu groups of the symmetry-related phosphorus ligands are staggered about the Pt–Cl bond axis (Fig. 2); this is the same conformation as that adopted by the phosphorus ligands in *trans*-$PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ [10]. The Pt–P bond length of 2.353(1) Å is slightly longer than the non-ring Pt–P bond lengths of 2.342(4) and 2.333(2) Å in $\overline{PtCl(P(t\text{-}Bu)C(CH_3)_2CH_2}(\overline{CHCH_2CH_2}))(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})$ [10] and $\overline{PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$ [2b], respectively. Some Pt–P bond lengths for *trans*-$PtClXP_2$ complexes [11,12] appear in Table 2. The Pt–P bond lengths provide a measure of steric congestion in these similar molecules. For instance, in going from X = Cl to X = I, the Pt–P bond lengths in the complexes *trans*-$PtX_2(PCy_3)_2$ increase from 2.337(2) to 2.371(2) Å [12]. This difference has been attributed to the greater steric requirements of the

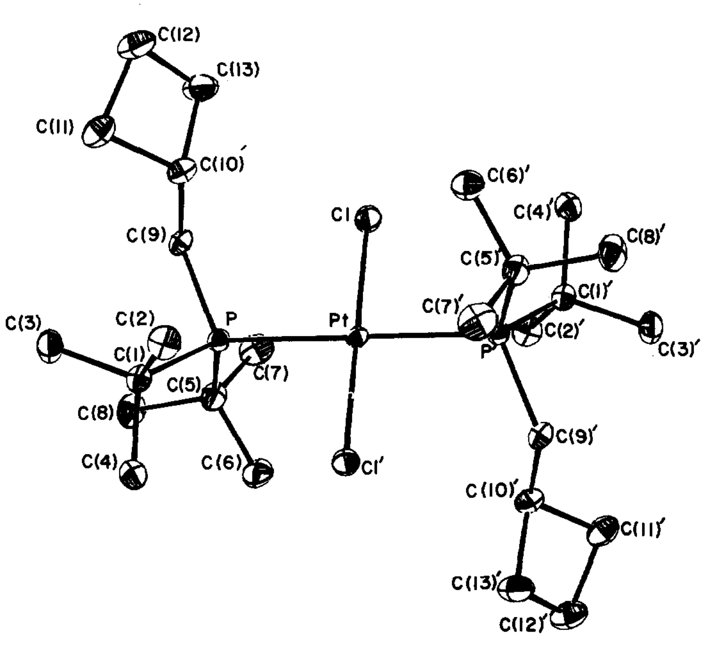


Fig. 1. The structure and atomic numbering scheme of *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2CH_2})_2$.

TABLE 1

DISTANCES (Å) AND ANGLES (°) FOR *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2$

Pt–Cl	2.306(1)	Cl–Pt–P	89.07(3)
Pt–P	2.353(1)	Pt–P–C(1)	117.1(1)
P–C(1)	1.890(3)	Pt–P–C(5)	107.6(1)
P–C(5)	1.887(3)	Pt–P–C(9)	112.6(1)
P–C(9)	1.839(3)	C(1)–P–C(5)	112.0(1)
C(1)–C(2)	1.549(4)	C(1)–P–C(9)	104.0(1)
C(1)–C(3)	1.544(4)	C(5)–P–C(9)	102.7(1)
C(1)–C(4)	1.537(5)	P–C(1)–C(2)	106.3(2)
C(5)–C(6)	1.539(5)	P–C(1)–C(3)	112.1(2)
C(5)–C(7)	1.534(5)	P–C(1)–C(4)	114.6(2)
C(5)–C(8)	1.530(5)	P–C(5)–C(6)	109.2(2)
C(9)–C(10)	1.531(4)	P–C(5)–C(7)	108.5(2)
C(10)–C(11)	1.556(5)	P–C(5)–C(8)	113.0(2)
C(10)–C(13)	1.542(5)	C(2)–C(1)–C(3)	107.8(3)
C(11)–C(12)	1.538(5)	C(2)–C(1)–C(4)	108.4(3)
C(12)–C(13)	1.528(5)	C(3)–C(1)–C(4)	107.3(3)
Cl···C(9)	3.160(3)	C(6)–C(5)–C(7)	107.6(3)
Cl···P	3.268(1)	C(7)–C(5)–C(8)	108.5(3)
Cl···C(10)	3.319(3)	P–C(9)–C(10)	118.1(2)
Pt···C(5)	3.431(3)	C(9)–C(10)–C(11)	120.5(3)
		C(9)–C(10)–C(13)	116.8(3)
		C(11)–C(10)–C(13)	87.2(3)
		C(10)–C(11)–C(12)	88.8(3)
		C(11)–C(12)–C(13)	88.4(3)
		C(10)–C(13)–C(12)	89.6(3)

iodo ligand rather than to an electronic *cis*-effect [12a]. The more congested diiodo complex readily eliminates phosphine to form the iodo-bridged dimer $[PtI(PCy_3)]_2(\mu\text{-}I)_2$ [12b].

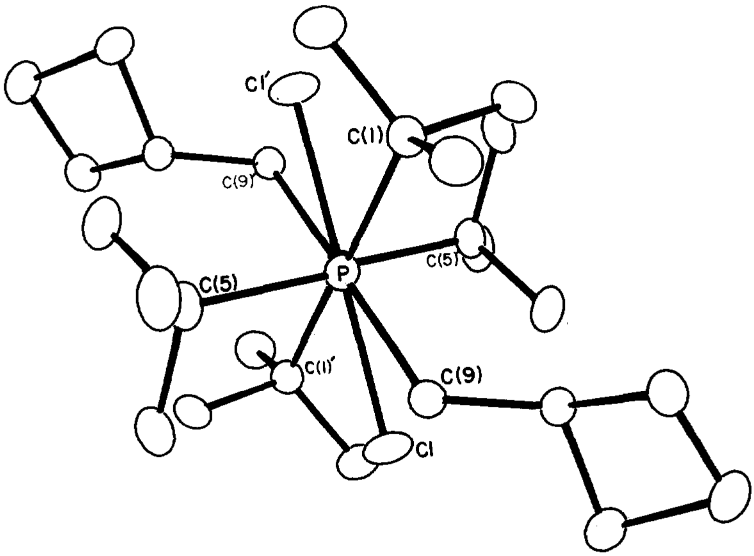


Fig. 2. A view down the P–Pt–P bond axis of *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2$.

TABLE 2

Pt–P BOND LENGTHS (Å) FOR *trans*-$\mathrm{PtClXP_2}$ COMPLEXES (X = Cl, alkyl)

Complex	Pt–P(1)	Pt–P(2) [a]	Ref.
$\mathrm{PtCl(CH_3)(PMePh_2)_2}$	2.291(2)	2.292(2)	11a
$\mathrm{PtCl(C(SiMe_3)_3)(PMePh_2)_2}$	2.294(5)	2.295(5)	11b
$\mathrm{PtCl(vinyl)(PEt_2Ph)_2}$	2.295(3)	[2.295(3)]	11c
$\mathrm{PtCl(acetyl)(PMePh_2)_2}$	2.297(2)	2.301(2)	11d
$\mathrm{PtCl_2(PEt_3)_2}$	2.298(18)	[2.298(18)]	11e
$\mathrm{PtCl(C_6H_5)(PPh_3)_2}$	2.297(6)	2.303(6)	11f
$\mathrm{PtCl(hexylcarbonyl)(PPh_3)_2}$	2.301(3)	2.302(3)	11g
$\mathrm{PtCl(\sigma\text{-}allyl)PPh_3)_2}$	2.302(2)	2.304(2)	11h
$\mathrm{PtCl_2(PCy_3)_2}$	2.337(2)	[2.337(2)]	12a
$\mathrm{PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2}$	2.353(1)	[2.353(1)]	this work
$\mathrm{PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2C}H_2)_2}$	2.373(1)	[2.373(1)]	10

[a] [ ] indicates the *trans*-phosphorus atoms are crystallographically equivalent.

Though steric congestion in *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2}$ is pronounced, the ligand crowding does not lead to strong non-bonding interactions between the Cl atom and t-Bu carbon atoms: the shortest such interaction is Cl ··· C(4) 3.387(3) Å. Atom C(9), the non-ring methylene carbon atom of the methylcyclobutyl group, is only 3.160(3) Å from the Cl atom; its H atoms point away from the Pt–Cl bond axis. As judged from the C–P–C angles, the steric requirements of the t-Bu groups exceed those of the methylcyclobutyl group: the (t-Bu)–P–($\mathrm{CH_2\overline{CHCH_2CH_2C}H_2}$) angles are 104.0(1) and 106.3(2)° while the (t-Bu)–P–(t-Bu) bond angle is 112.0(1)°. This angle is 112.2(2)° in *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2C}H_2)_2}$ [10].

If we compare the molecular structures it appears that *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2}$ is less sterically congested than is *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2C}H_2)_2}$ [10]. This cyclopropyl complex on silica forms the platinacyclobutane complex $\mathrm{\overline{PtCl(P(t\text{-}Bu)C(CH_3)_2C}H_2(\overline{CHCH_2C}H_2))(P(t\text{-}Bu)_2\overline{CHCH_2C}H_2)}$ [10]. The non-ring Pt–P bond distance in this orthometallated complex is 0.031(2) Å shorter than the Pt–P bond distance in the parent, a reflection of the extent to which steric congestion is relieved upon orthometallation [10]. A similar bond contraction probably occurs for *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2C}H_2)_2}$ upon orthometallation. Thus we can estimate a Pt–P bond distance in this cyclopropylmethyl complex of 2.364 Å by adding 0.031 Å to the non-ring Pt–P bond distance in $\mathrm{\overline{PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)C}H_2)(P(t\text{-}Bu)_2CH_2\overline{CHCH_2C}H_2)}$ [2b]. This estimated bond distance is very slightly longer than the Pt–P bond distance in the present complex *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2}$, 2.353(1) Å. It is interesting that the ^{31}P NMR chemical shifts are consistent with a smaller cone angle in the present phosphine.

The delicate balance of steric forces in *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2)_2}$ is striking. Ligand crowding is minimized by slight distortions of tetrahedral angles between phosphorus substituents and of right angles in the platinum coordination sphere. Planarity of the $\mathrm{PtP_2Cl_2}$ unit is not disrupted. Perhaps in this way non-bonded repulsions are satisfied and a spontaneous orthometallation reaction, like those observed for *trans*-$\mathrm{PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2C}H_2)_2}$ [2b] and $\mathrm{[PtBrP(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2C}H_2]_2(\mu\text{-}Br)_2}$ [5], does not occur.

Experimental

General remarks

All reactions were carried out under an atmosphere of pre-purified dinitrogen with the use of standard Schlenk-line techniques. K_2PtCl_4 was used as received from Johnson-Matthey, Inc. (Di-t-butyl)chlorophosphine and cyclobutylmethanol were used as received from Alfa Products and Aldrich Chemical Company, respectively. Solvents were purified by standard methods.

Elemental analysis of $P(t\text{-}Bu)_2(CH_2CHCH_2CH_2CH_2) \cdot HBr$ was performed by Galbraith Laboratories, Inc., Knoxville, TN; analysis of *trans*-$PtCl_2(P(t\text{-}Bu)_2\text{-}CH_2CHCH_2CH_2CH_2)_2$ was performed by Micro-Tech Laboratories, Skokie, IL. Infrared spectra were obtained with the use of a Perkin–Elmer 283 spectrometer from samples prepared as KBr pellets. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL-FX90 or JNM-FX270 FT-NMR spectrometer. ^{31}P positive chemical shifts are downfield from 85% H_3PO_4.

X-ray data were collected with the use of Mo-K_{α_1} radiation on an Enraf–Nonius CAD4 diffractometer and all calculations were performed on a Harris 1000 computer by methods and programs standard in this laboratory [13].

Synthesis of (di-t-butyl)cyclobutylmethylphosphine, $P(t\text{-}Bu)_2(CH_2CHCH_2CH_2CH_2)$

The synthesis is analogous to that reported for (di-t-butyl)cyclopropylmethylphosphine [2b]. One equivalent of (di-t-butyl)phosphine [14] was added to a solution of 0.56 g (0.038 mol) of cyclobutylmethyl bromide (synthesized by bromination of cyclobutylmethanol by the method of Ingold et al. [15]) in 20 ml isobutyl methyl ketone. The mixture was heated at mild reflux for 6 h; the white hydrobromide adduct of $P(t\text{-}Bu)_2(CH_2CHCH_2CH_2CH_2)$ precipitated as the reaction mixture cooled. Solvent was removed under vacuum and the hydrobromide salt was washed with hexane. Anal. Found: C, 51.47; H, 9.22; P, 10.25. $C_{13}H_{28}BrP$ calc.: C 52.80; H, 9.56; P, 10.49%. The phosphine was isolated in approximately 40% yield by treatment of the hydrobromide salt with base. ^1H NMR ($CDCl_3$) δ 2.39 (d, $PCH_2CH(CH_2)_2CH_2$, J 10.5 Hz), 1.60–2.29 (complex cyclobutyl region), 1.38 (d, $PC(CH_3)_3$, ^3J(P–H) 16.6 Hz); ^{13}C NMR ($CDCl_3$) δ 35.98 (d, CH_2-P, ^1J(P–C) 22.0 Hz), 30.80 (d, $C(CH_3)_3$, ^1J(P–C) 19.5 Hz), 29.91(d, $CH(CH_2)_2CH_2$, ^2J(P–C) 11.0 Hz), 29.60 (d, $C(CH_3)_3$, ^2J(P–C) 13.4 Hz), 29.10 (d, $CHCH_2CH_2CH_2$, $(^3J+{}^5J)$(P–C) 20.8 Hz), 17.99 (s, $CHCH_2CH_2CH_2$); ^{31}P NMR ($CDCl_3$) δ 21.47.

Synthesis of trans-dichlorobis(di-t-butyl)cyclobutylmethylphosphineplatinum(II), trans-$PtCl_2(P(t\text{-}Bu)_2CH_2CHCH_2CH_2CH_2)_2$

(Di-t-butyl)cyclobutylmethylphosphine (0.50 g, 2.3 mmol) and K_2PtCl_4 (0.355 g, 0.855 mmol) were combined in 10 ml aqueous acetone and stirred together for 12 h. The yellow precipitate was filtered and recrystallized from CH_2Cl_2/hexane in 94% yield. Anal. Found: C, 44.96; H, 7.85; P, 8.98. $C_{26}H_{54}Cl_2P_2Pt$ calc.: C, 44.96; H, 7.84; P, 8.92%. ^1H NMR ($CDCl_3$) δ 2.77 (br m, $CH(CH_2)_2CH_2$), 1.81–2.30 (complex cyclobutyl methylene region), 1.74 (m, CH_2, P), 1.46 (t, $C(CH_3)_3$, ^3J(P–H) apparent) 6.5 Hz). ^{13}C NMR ($CDCl_3$) δ 36.00 (t, $C(CH_3)_3$, ^1J(P–C) (apparent) 10.4 Hz), 33.46 (s, $CH(CH_2)_2CH_2$), 32.29 (s, $CHCH_2CH_2CH_2$), 30.62 (s, $C(CH_3)_3$), 23.44 (br, CH_2P), 18.34 (s, $CHCH_2CH_2CH_2$), ^{31}P NMR δ 32.37 (s, J(Pt–P) 2453.6 Hz); IR ν(Pt–Cl) 330 cm^{-1}.

X-Ray study of trans-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2CH_2})_2$

Crystals suitable for X-ray diffraction study were obtained as parallelepipeds by slow evaporation of a CH_2Cl_2/hexane solution of *trans*-$\text{PtCl}_2(\text{P(t-Bu)}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2\text{CH}_2})_2$. Lattice constants were obtained from least-squares analysis of 25 reflections that had been centered on a Nonius CAD4 diffractometer. Systematic absences in the data ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) together with the presence of monoclinic symmetry are strongly indicative of the centrosymmetric space group C_{2h}^5-$P2_1/c$. Six standard reflections monitored every 3 h during data collection

TABLE 3

CRYSTAL AND REFINEMENT DATA FOR *trans*-$\text{PtCl}_2(\text{P(t-Bu)}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2\text{CH}_2})_2$

Molecular formula	$C_{26}H_{54}Cl_2P_2Pt$
Formula wt., amu	694.66
Space group	C_{2h}^5-$P2_1/c$
a (Å)	8.521(2)
b (Å)	12.774(1)
c (Å)	14.374(2)
β (°)	104.71(2)
V (Å^3)	1513.3
Z	2
T of data collection	113 K [a]
Crystal dim., (mm)	0.12×0.21×0.73
Crystal vol. (mm^3)	0.020
ρ, calculated (113 K) (g/cm^3)	1.524
Radiation	graphite-monochromatized Mo-K_α ($\lambda(K_{\alpha_1})$ 0.7093 Å)
Linear absorption coefficient (cm^{-1})	49.77
Transmission factors	0.332 to 0.557 [b]
Take-off angle (°)	2.25
Scan mode	$\omega - 2\theta$
Scan speed (° min^{-1})	4.00
Scan range (°)	0.5 below K_{α_1} to 0.5 above K_{α_2}
Background counts	extension of 1/4 scan range on each side
Rescan condition	$I \leq 3\sigma(I)$ rescanned for a maximum time of 100 s
Data collected	$\pm h,k,l$
2θ limits (°)	2.4–66.0
Unique data	5667
Unique data ($F_o^2 > 3\sigma(F_o^2)$)	4223
p factor	0.04
Final no. of variables	140
$R(F^2)$ (including $F_o^2 < 0$)	0.042
$R_w(F^2)$ (including $F_o^2 < 0$)	0.088
$R(F)$ for $F^2 > 3\sigma(F_o^2)$	0.028
Error in observation of unit weight (e^2)	1.11

[a] The low-temperature system for the Nonius CAD4 diffractometer is based on a design by Prof. J.J. Bonnet and S. Askenazy and is commercially available from Soterem, Z.T. de Vic, 31320 Castanet-Tolosan, France. [b] The analytical method as employed in the Northwestern absorption program AGNOST was used for the absorption correction (J. de Meulenaer and H. Tompa, Acta Crystallogr., 19 (1965) 1014).

TABLE 4

POSITIONAL PARAMETERS AND B_{eq} (Å^2) FOR *trans*-$\text{PtCl}_2(\text{P(t-Bu)}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2\text{C}}\text{H}_2)_2$

Atom	x	y	z	B
Pt	0	1/2	1/2	1.168(3)
P	0.037495(90)	0.355233(59)	0.406688(53)	1.24(1)
Cl	−0.06954(11)	0.599399(61)	0.361697(53)	2.03(2)
C(1)	−0.03450(37)	0.22378(23)	0.43982(22)	1.52(6)
C(2)	−0.19666(42)	0.24411(28)	0.46677(24)	2.01(8)
C(3)	−0.06873(45)	0.14646(25)	0.35449(25)	2.10(8)
C(4)	0.08266(45)	0.16939(25)	0.52514(25)	2.05(8)
C(5)	0.25822(37)	0.35232(26)	0.40505(23)	1.77(7)
C(6)	0.36435(41)	0.36029(30)	0.50883(27)	2.27(8)
C(7)	0.29361(42)	0.44872(32)	0.35001(28)	2.44(9)
C(8)	0.30393(42)	0.25422(32)	0.35672(28)	2.39(9)
C(9)	−0.06684(36)	0.37057(23)	0.27870(20)	1.46(6)
C(10)	−0.25086(37)	0.38684(25)	0.25175(22)	1.64(6)
C(11)	−0.36634(42)	0.30065(29)	0.19609(25)	2.13(8)
C(12)	−0.46690(44)	0.38698(33)	0.13372(27)	2.60(9)
C(13)	−0.32140(45)	0.46013(33)	0.16612(27)	2.39(8)

showed no significant decomposition. Details of data collection and refinement are summarized in Table 3.

The position of the Pt atom was determined from a Patterson map. The positions of the remaining non-hydrogen atoms were obtained from a series of electron density syntheses. Approximate positional parameters for methyl hydrogen atoms were obtained from difference electron density maps calculated immediately prior to the final cycle of least-squares refinement on F_o^2. These parameters along with the positional parameters for methylene and methine hydrogen atoms were then idealized. In these calculations a C–H bond length of 0.95 Å was assumed and a given H atom was assigned an isotropic thermal parameter 1 Å^2 greater than the equivalent isotropic thermal parameter of the C atom to which it is attached. Parameters for the hydrogen atoms were held fixed during the final cycle. Table 4 presents the final positional parameters, Table 5 the anisotropic thermal parameters [16], Table 6 the hydrogen-atom positions [16], and Table 7 a listing of $10|F_o|$ vs. $10|F_c|$ [16].

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16 Supplementary material includes anisotropic thermal parameters (ORTEP-II-Type 8) (Table 5), hydrogen-atom positions (Table 6), and structure amplitudes (Table 7). See NAPS document no. 04480 for 26 pages of supplementary material. Order from NAPS c/o Microfiche Publicatios, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in US funds only \$ 8.55 for photocopies or \$ 4.00 for microfilm. Outside the US and Canada add postage of \$ 1.50 for the first 20 pages and \$ 1.00 for each 10 pages of material thereafter. \$ 1.50 for microfiche postage.