

**SYNTHESIS AND STRUCTURE OF *cis*-PtX<sub>2</sub>(P(t-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>3</sub>)  
 (X = Cl, Br), A PLATINUM  $\pi$ -OLEFIN COMPLEX FORMED BY  
 THE INTRAMOLECULAR ACTIVATION OF A CYCLOPROPYLPHOSPHINE**

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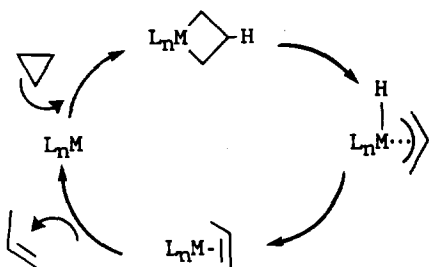
**Summary**

The mixed chloro/bromo  $\pi$ -olefin complexes *cis*-PtX<sub>2</sub>(P(t-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>3</sub>) (**2**) have been prepared by the reaction of Zeise's salt (K[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]) with P(t-Bu)<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>) · HBr in boiling ethanol. The dimer complexes [PtX(P(t-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>)]<sub>2</sub>( $\mu$ -X)( $\mu$ -Y) (**1**) (X, Y = Cl or Br) form first with subsequent activation of cyclopropane to give the monomeric  $\pi$ -olefin complexes (**2**). The mixed  $\pi$ -olefin complexes **2** co-crystallize. The average structure of **2** has been determined by X-ray methods. The relative occupancies in bromine for halogen sites *cis*- and *trans*- to coordinated olefin are 0.464(6) and 0.256(6), respectively. The olefin is symmetrically bound to the Pt atom (Pt–C 2.17(1) Å). The olefinic C–C bond length is 1.38(1) Å.

**Introduction**

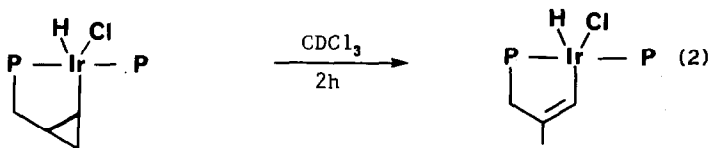
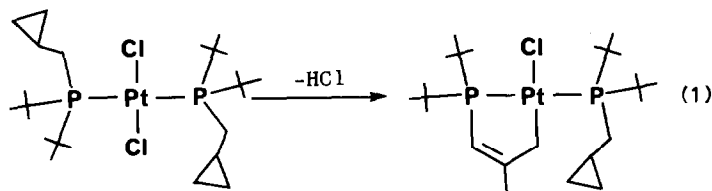
The transition-metal mediated conversion of cyclopropane to olefin has been extensively studied as a prototype for more general intermolecular C–C bond activation [1]. Organometallic species isolated from intermolecular reactions of transition-metal complexes with cyclopropanes are usually metallacyclobutanes [1a,c],  $\eta^3$ -allyl hydride complexes [1b], or  $\pi$ -olefin complexes [1c]. These species comprise a catalytic cycle for the conversion of cyclopropanes to olefins (Scheme 1).

We have been investigating the intramolecular reactions of cyclopropane in transition-metal complexes where the cyclopropane is part of a bulky phosphine ligand [2]. In these ligands the cyclopropane ring may be appended to phosphorus by no, one, or two CH<sub>2</sub> groups. The conversion of *trans*-PtCl<sub>2</sub>(P(t-Bu)<sub>2</sub>CH<sub>2</sub>CH-CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> in 2-methoxyethanol to the  $\sigma$ -allyl complex PtCl(P(t-Bu)CH=



SCHEME 1

$\overline{C(CH_3)CH_2}(P(t-Bu)_2CH_2\overline{CHCH_2}CH_2)$  (eq. 1) [2a] and the synthesis of  $\overline{IrHCl}(P(t-Bu)_2CH_2\overline{CHCH_2}CH_2)(P(t-Bu)_2CH_2\overline{CHCH_2}CH_2)$ , a  $\sigma$ -cyclopropyl complex that rearranges to a  $\sigma$ -vinyl complex  $\overline{IrHCl}(P(t-Bu)_2\overline{CHC(CH_3)=CH})(P(t-Bu)_2CH_2\overline{CHCH_2}CH_2)$  (eq. 2) [2c], have been previously reported.

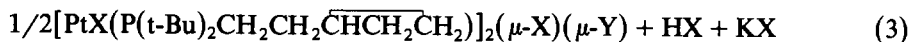
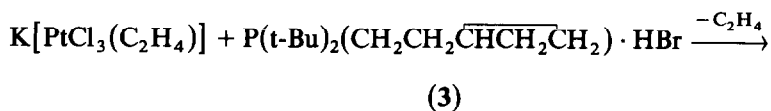


In these reactions, the range of products observed may be influenced by steric factors, especially a bias towards formation of five-membered chelate rings [3]. Thus the phosphine  $P(t-Bu)_2(CH_2\overline{CHCH_2}CH_2)$  reacts with Pt, Pd, and Ir compounds to form complexes with metal-carbon  $\sigma$ -bonds rather than metal-carbon  $\pi$ -bonds probably because a  $\sigma$ -interaction results in an optimally-sized five-membered chelate ring. The short phosphorus-alkyl chain of this cyclopropyl phosphine may hinder formation of stable chelate complexes containing species such as those shown in Scheme 1. In this case the slightly longer alkyl chain of  $P(t-Bu)_2(CH_2CH_2\overline{CHCH_2}CH_2)$  should allow greater flexibility for the formation of such complexes. We now report the intramolecular reaction of  $P(t-Bu)_2(CH_2CH_2\overline{CHCH_2}CH_2)$  with  $Pt^{II}$  to form  $cis-PtX_2(P(t-Bu)_2(CH_2CH_2\overline{CH=CH}CH_3))$  in which coordinated olefin serves as one member of a five-member chelate ring.

## Results and discussion

When one equivalent each of Zeise's salt ( $K[PtCl_3(C_2H_4)]$ ) and  $P(t-Bu)_2(CH_2CH_2\overline{CHCH_2}CH_2) \cdot HBr$  are combined in anhydrous ethanol at room temperature,

ethylene gas evolves and the orange mixed chloro/bromo dimer complexes  $[\text{PtX}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-X})(\mu\text{-Y})$  (**1**) form (eq. 3).



(X, Y = Cl or Br)

Chemical analysis shows a ratio of chlorine to bromine of 3.6/1 in these products. The dimeric nature of **1** was deduced from characteristic doublet patterns in the  $^1\text{H}$  NMR spectrum [3] (Table 1). From the normal cyclopropyl stretching frequency at  $3060\text{ cm}^{-1}$  [2] and the absence of bands from olefin in the IR spectrum we concluded that the cyclopropyl ring of the phosphine ligand is uncoordinated and intact.

The  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra (Table 1) suggest that one species dominates the range of dimers obtained and confirm that the cyclopropyl ring remains intact in this product. The  $^{31}\text{P}$  NMR spectrum of **1** contains two singlet resonances at  $\delta$  35.9 ppm ( $J(\text{P-Pt})$  3872 Hz) and at  $\delta$  34.7 ppm ( $J(\text{P-Pt})$  3964 Hz) with relative peak height ratios 4/1. In the  $^{13}\text{C}$  NMR spectrum of **1**, only the t-Bu methyl region contains well-resolved resonances from isomers of **1** other than the major product. The remaining resonances belong to the major product. A DEPT [4] pulse sequence experiment showed that these result from a quaternary carbon atom, a methine carbon atom, and three kinds of methylene carbon atoms, as expected for the ligand  $\text{P}(\text{t-Bu})_2(\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})$ . The methylene and methine carbon atoms of the cyclopropane group display high field chemical shifts that are nearly identical to those of the free ligand (Table 1).

The analytical data for **1** together with mass spectral data are consistent with the structures  $[\text{PtCl}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-Br})(\mu\text{-Cl})$  and  $[\text{PtCl}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-Cl})_2$  as the major products. The mass spectral data indicate the presence of other products as well. Thus peaks around  $m/e$  933, 488, and 443 appear corresponding to molecular fragments  $[\text{Pt}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-Br})(\mu\text{-Cl})$ ,  $[\text{PtBr}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]$ , and  $[\text{PtCl}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]$ , respectively. Peaks around  $m/e$  976 and 888 for the fragments  $[\text{Pt}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-Br})_2$  and  $[\text{Pt}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-Cl})_2$  also appear. No parent peaks are observed since the limit of detection of the mass spectrometer used is 1000 amu.

If the products from eq. 1 are stirred under mild reflux in ethanol for 14 h a color change from orange to pale yellow occurs in the mixture. The hydrogen halide acid must be present for this reaction to proceed. The reaction products are isolated as very pale yellow crystals that form as the reaction mixture cools. NMR and mass spectral data for the crystals show that they contain more than one complex. Some structural information about the products can be gained from these data. The most prominent resonances in the  $^{31}\text{P}$  NMR spectrum occur as singlets at 63.3 ( $J(\text{P-Pt})$  3258 Hz) and 62.9 ( $J(\text{P-Pt})$  3172 Hz) ppm compared to 35.9 ppm for the non-chelating ligand in **1**. The downfield shift of the phosphorus resonances together with a stretching frequency [6] of  $1525\text{ cm}^{-1}$  (and the absence of cyclopropyl

TABLE 1

SPECTROSCOPIC DATA FOR  $P(t\text{-Bu})_2(\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})$ ,  $[\text{PtX}(\text{P}(t\text{-Bu})_2\text{CH}_2\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2})_2(\mu\text{-X})(\mu\text{-Y})]^a$  (1) AND  $\text{cis-PtX}_2(\text{P}(t\text{-Bu})_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3)^a$  (2) (IR ( $\text{cm}^{-1}$ ); NMR;  $\delta$  (ppm);  $J$  (Hz))

Compound	IR	$^1\text{H}$ NMR	$^{13}\text{C}$ NMR	$^{31}\text{P}$ NMR <sup>c</sup>
$\text{PR}_3^b$	3080 (c-Pro)	$\delta$ 2.16 (m, $\text{PCH}_2$ ), 1.47(t, $\text{CCH}_3$ , $^3J$ 6.5), 0.77(m, $\text{PCH}_2\text{CH}_2$ ), 0.047–0.44(complex c-Pro region)	$\delta$ 36.02 ( $\text{CMe}_3$ , t, $J$ 10.4) 30.85 (s, $\text{PCH}_2\text{CH}_2$ ), 17.19 (br, $\text{PCH}_2$ ) 12.91 (t, $\text{CHCH}_2\text{CH}_2$ $^3J$ 8.0) 4.36 (s, c-Pro methylene)	$\delta$ 26.55
1	3061(c-Pro) 292, 302, 331 (Pt–X)	$\delta$ 1.70(br, $\text{CH}_2$ ), 1.45 (d, $\text{CCH}_3$ , $^3J$ 14.1), 1.22 (br, $\text{CH}_2$ ), 0.425 + 0.168(m, c-Pro)	$\delta$ 36.38 (d, $\text{CMe}_3$ , $J$ 29.2) 30.83, 30.68, 30.18, 30.01 (s, $\text{CCH}_3$ ), 19.15 (d, $\text{PCH}_2$ , $J$ 29.2), 12.59 (d, $\text{CHCH}_2\text{CH}_2$ , $J$ 18.3), 4.51 (s, c-Pro methylene)	$\delta$ 35.9 ( $J(\text{P-Pt})$ 3872) [39.7 ( $J(\text{P-Pt})$ 3964)]
2	1525 (coord. $\text{C}=\text{C}$ ) 273, 312 (Pt–X)	$\delta$ 4.86 (br m, $\text{CH}=\text{CH}$ ), 2.31 (br, $\text{PCH}_2\text{CH}_2$ ) 1.83 (t of d, $^3J$ 23.1, $^2J(\text{P-H})$ 5.9. Complex t-Bu methyl region including 1.515 (d, $J$ 14.9) 1.46 (d, $J$ 14.9), 1.44 (d, $J$ 14.0)	$\delta$ 91.1 + 91.0, 87.7 + 85.9 (s, olefin), 37.58 + 37.16 (d, $\text{CMe}_3$ , $J$ 23.4) 31.43 + 28.95 (s, $\text{CH}_2$ ), 31.47 + 29.19 (s, $\text{CCH}_3$ ) 29.79 (d, $\text{PCH}_2$ , $J$ 35.2) 29.49 (d, $\text{PCH}_2$ , $J$ 34.2)	$\delta$ 63.3 ( $J(\text{P-Pt})$ 3258) 62.9 ( $J$ 3172)

<sup>a</sup> X, Y = Cl or Br. <sup>b</sup>  $\text{PR}_3 = \text{P}(t\text{-Bu})_2(\text{CH}_2\text{CHCHCH}_2\text{CH}_2)$ . <sup>c</sup> The  $^{31}\text{P}$  chemical shifts are downfield from  $\text{H}_3\text{PO}_4$ .

infrared absorptions) in the IR spectrum indicate the presence of coordinated olefin in a five-member chelate ring [6]. The  $^1\text{H}$  NMR spectrum, which contains a broad multiplet at 4.86 ppm typical for coordinated olefin, provides further evidence for this conclusion. For comparison, the infrared absorption for coordinated olefin in *trans*- $\text{Pt}(\text{py})\text{Cl}_2(\text{CH}_2=\text{CMeCMe}_2)$  occurs at  $1515\text{ cm}^{-1}$  and the olefinic protons in this complex exhibit a  $^1\text{H}$  NMR resonance at 4.87 ppm [1c]. The mass spectral data on the present compounds show two parent peaks around  $m/e$  524 and 569 with decay patterns consistent for the  $\pi$ -olefin complexes *cis*- $\text{PtBrCl}(\text{P}(t\text{-Bu})_2\text{CH}_2\text{CH}_2-$

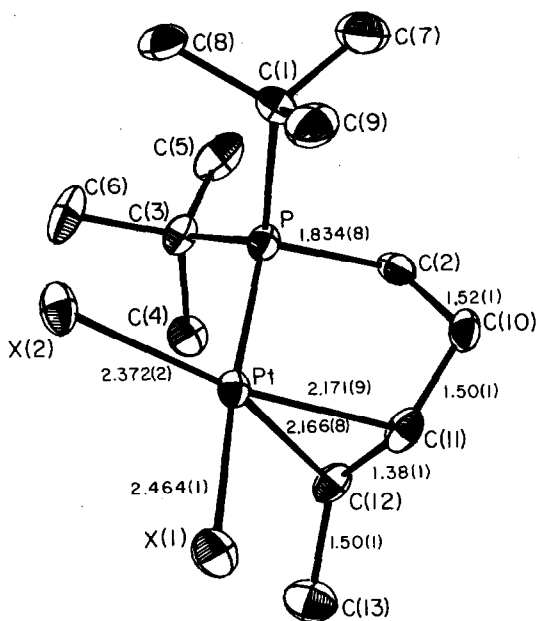


Fig. 1. Structure and numbering scheme for *cis*-PtX<sub>2</sub>(P(*t*-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>) (X = Cl or Br) including bond distances within the metallacycle. Thermal ellipsoids are drawn at the 50% probability level.

CH=CHCH<sub>3</sub>) and *cis*-PtBr<sub>2</sub>(P(*t*-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>3</sub>). An X-ray diffraction study of the crystals showed that they contain a mixture of  $\pi$ -olefin complexes *cis*-PtX(1)X(2)(P(*t*-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>3</sub>) (X = Cl, Br) (2).

Figure 1 shows the average molecular structure and the labeling scheme for 2. Table 2 lists bond distances and angles. The positional parameters (Table 3) reported for X(1) and X(2) represent a weighted average of the actual positional coordinates of the chlorine and bromine atoms in the various isomers that cocrystallize as 2; we were not able to resolve separate sites for chlorine and bromine atoms. The relative occupancies in bromine for sites represented by X(1) and X(2) are 0.464(6) and 0.256(6), respectively.

The square-planar geometry of ligands around Pt is distorted. The Pt, X(1), and X(2) atoms lie approximately in the plane; the P atom is 0.240(2) Å above the plane and the midpoint of the olefin is 0.21 Å below it. The bond angles between ligands coordinated to the Pt atom are also slightly distorted (Table 2). The P-Pt-X(1) bond angle is 171.5(1)°. The distortions from exact square-planar geometry in 2 can be attributed to the steric requirements of the chelate ring. The related chelate complex *cis*-PtCl<sub>2</sub>(AsPh<sub>2</sub>(C(CH)<sub>4</sub>CCH=CH<sub>2</sub>)) exhibits similar distortions [7]. In this complex the As-Pt-Cl(1) bond angle is 175.4(2)° and the midpoint of the olefin is 0.205 Å from the coordination plane defined by the Pt, Cl, and As atoms [7].

The coordinated olefin of 2 is symmetrically bound to Pt (C(11)-Pt = C(12)-Pt = 2.17(1) Å) and makes an angle of 88.4° with the PtX<sub>2</sub>P plane. Although the olefin in *cis*-PtCl<sub>2</sub>(AsPh<sub>2</sub>(C(CH)<sub>4</sub>CCH=CH<sub>2</sub>)) is symmetrically bound to Pt, it defines a more acute angle with the PtCl<sub>2</sub>As plane of 83.6° [7]. The greater

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) IN *cis*-PtX<sub>2</sub>(P(*t*-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>3</sub>), (X = Cl, Br)

Pt-P	2.253(2)	C(1)-C(9)	1.523(13)
Pt-X(1)	2.464(1)	C(2)-C(10)	1.521(11)
Pt-X(2)	2.372(2)	C(3)-C(4)	1.541(11)
Pt-C(11)	2.171(9)	C(3)-C(5)	1.524(12)
Pt-C(12)	2.166(8)	C(3)-C(6)	1.532(12)
P-C(1)	1.903(8)	C(10)-C(11)	1.501(13)
P-C(2)	1.834(9)	C(11)-C(12)	1.382(11)
P-C(3)	1.876(9)	C(12)-C(13)	1.501(11)
C(1)-C(7)	1.533(13)		
C(1)-C(8)	1.547(12)	X(1)···C(13)	3.262(9)
P-Pt-X(1)	171.5(1)	C(7)-C(1)-C(8)	109.4(7)
P-Pt-X(2)	91.49(7)	C(7)-C(1)-C(9)	109.4(8)
X(1)-Pt-X(2)	89.06(6)	C(8)-C(1)-C(9)	107.3(8)
P-Pt-C(11)	84.7(2)	P-C(2)-C(10)	108.5(6)
P-Pt-C(12)	90.0(2)	P-C(3)-C(4)	107.0(5)
X(1)-Pt-C(11)	92.8(2)	P-C(3)-C(5)	110.7(6)
X(1)-Pt-C(12)	93.0(2)	P-C(3)-C(6)	113.0(6)
X(2)-Pt-C(11)	166.7(2)	C(4)-C(3)-C(5)	108.8(7)
X(2)-Pt-C(12)	155.8(2)	C(4)-C(3)-C(6)	107.4(7)
C(11)-Pt-C(12)	37.2(3)	C(5)-C(3)-C(6)	109.8(7)
Pt-P-C(1)	111.6(3)	C(2)-C(10)-C(11)	111.0(7)
Pt-P-C(2)	102.7(3)	Pt-C(11)-C(10)	111.4(5)
Pt-P-C(3)	116.3(3)	Pt-C(11)-C(12)	71.2(5)
C(1)-P-C(2)	105.3(4)	C(10)-C(11)-C(12)	122.4(7)
C(1)-P-C(3)	113.6(4)	Pt-C(12)-C(11)	71.6(5)
C(2)-P-C(3)	105.9(4)	Pt-C(12)-C(13)	114.8(6)
P-C(1)-C(7)	111.0(6)	C(11)-C(12)-C(13)	125.0(7)
P-C(1)-C(8)	111.3(6)		
P-C(1)-C(9)	108.3(6)		

flexibility of the alkyl chain in **2** evidently allows for more normal bonding between the Pt atom and olefin. (Coordinated ethylene in Zeise's salt is oriented at a 90° angle to the PtCl<sub>3</sub> plane [8].) The olefinic C-C bond length in **2** is 1.38(1) Å, the same as that for coordinated olefin in *cis*-PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)(CH<sub>2</sub>=CHOCOCH<sub>3</sub>) [9].

The distance from the best least-squares plane defined for the puckered five-member chelate ring PtPC(2)C(10)C(11) are Pt -0.0001(3), P -0.005(2), C(2) 0.28(1), C(10) -0.32(1), C(11) 0.16(1) Å. Atom C(12) of the olefin sits below this plane. The angle between the best plane through the PtPC<sub>3</sub> ring and the PtPX(1)X(2) plane is 17.8°.

The Pt-X bond lengths differ by 0.092(2) Å. The Pt-X bond lengths *cis*- and *trans*- to the olefin are 2.464(1) and 2.372(2) Å, respectively. This difference in bond lengths (0.092(2) Å) is expected owing to the differing *trans*-influences of phosphine and olefin. In *cis*-PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)(CH<sub>2</sub>=CHOCH<sub>3</sub>) the analogous bond lengths (2.367(3) and 2.314(3) Å) differ by 0.053(4) Å [9]. In **2** the difference in bond distance is probably exaggerated by the presence of more Br atoms in sites defined by X(1) vs. X(2). The Pt-X bond lengths are intermediate between those expected for Pt-Cl and Pt-Br bonds in this environment. Pt-Br bonds where the Br atom is

TABLE 3

DATA COLLECTION AND REFINEMENT DETAILS FOR *cis*-PtX<sub>2</sub>(P(*t*-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH-CH<sub>3</sub>) (X = Cl or Br)

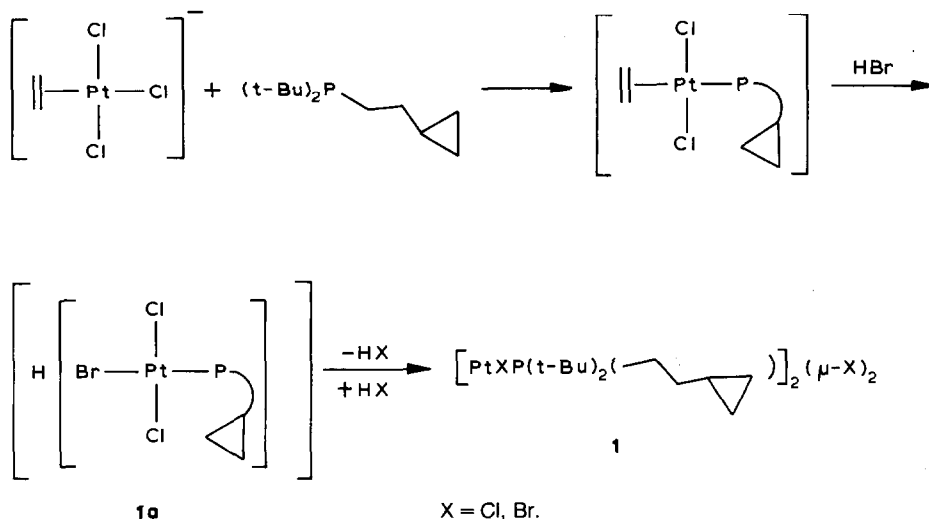
Molecular formula	C <sub>13</sub> H <sub>27</sub> Br <sub>0.72</sub> Cl <sub>1.28</sub> PPt
Mol. wt. (amu)	512.33
Space group	<i>D</i> <sub>2h</sub> <sup>5</sup> - <i>Pbca</i>
<i>a</i> (Å)	11.667(4)
<i>b</i> (Å)	19.557(7)
<i>c</i> (Å)	14.734(6)
<i>V</i> (Å <sup>3</sup> )	3361.9
<i>t</i> of data collection	-152 °C <sup>a</sup>
Crystal dim. (mm)	0.193 × 0.191 × 0.193
Bounding planes	{001} {111} {010}
Crystal vol. (mm <sup>3</sup> )	0.0138
$\rho$ , calculated (g/cm <sup>3</sup> )	2.024
Radiation	graphite-monochromatized Mo-K $\alpha$ ( $\lambda(K_{\alpha 1})$ 0.7093 Å)
Linear absorption coefficient (cm <sup>-1</sup> )	99.3 <sup>b</sup>
Transmission factors	0.171 to 0.231
Take-off angle (°)	2.5
Receiving aperture (mm)	horizontal 2.5 vertical 3.0 17.3 cm from crystal
Scan type	$\omega$ -2 $\theta$
Scan range (°)	0.5 below $K_{\alpha 1}$ to 0.5 above $K_{\alpha 2}$
Scan speed, °/min	2.00
Background counts	extension of 1/4 scan range on each side
Rescan condition	reflections having $I < 3\sigma(I)$ were rescanned for a maximum of 100 s
2 $\theta$ limits (°)	4.0 ≤ 2 $\theta$ ≤ 51.0
Unique data	3652
Unique data ( $F_o^2 > 3\sigma(F_o^2)$ )	2369
<i>p</i> factor	0.050
Final no. of variables	156
<i>R</i> ( $F^2$ )	0.0514
<i>R</i> <sub>w</sub> ( $F^2$ )	0.102
<i>R</i> ( <i>F</i> ) for $F^2 > 3\sigma(F_o^2)$	0.033
Error in observation of unit $e^2$	1.07

<sup>a</sup> 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 Soterm, Z.T. de Vic, 31320 Castanet-Tolosan, France. <sup>b</sup> 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).

*trans* to a ligand of high *trans*-influence are long. Examples are 2.502(1) Å in *trans*-PtBr( $\eta^1$ -styryl)(PPh<sub>3</sub>)<sub>2</sub> [10] and 2.543(1) Å in *trans*-PtBr( $\eta^1$ -allyl)(PEt<sub>3</sub>)<sub>2</sub> [11].

#### Possible reaction pathways

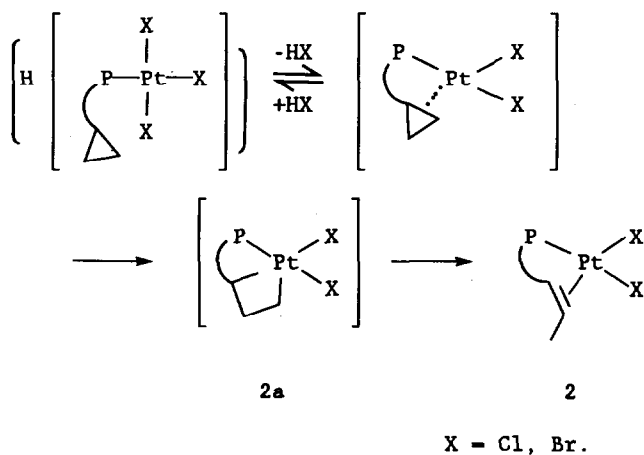
Early work by Chatt [12] showed that [PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]<sup>-</sup> reacts with P(*n*-Pr)<sub>3</sub> at low temperature to form *trans*-PtCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)P(*n*-Pr)<sub>3</sub>; this complex loses olefin readily at room temperature to form [PtCl(P(*n*-Pr)<sub>3</sub>)<sub>2</sub>( $\mu$ -Cl)]<sub>2</sub> [12]. A similar reaction sequence could occur to produce **1** from K[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)] and P(*t*-Bu)<sub>2</sub>(CH<sub>2</sub>-



SCHEME 2

$\text{CH}_2\overline{\text{CHCH}_2\text{CH}_2} \cdot \text{HBr}$ . Since bromide ions are present as HBr, bromide could replace the olefin prior to dimer formation. This would explain the presence of bromine in the dimer products, **1** (Scheme 2). Alternatively, simple halide exchange reactions could be involved [13].

A platonic acid complex **1a** could be important to the formation of **2**. This hypothesis is supported by the observation that HBr must be present as a catalyst for activation of cyclopropane to occur. An acid catalyst is necessary for the formation of  $\text{PtCl}(\text{AsMe}_2\text{C}_5\text{H}_9)$  from  $\text{Na}_2\text{PtCl}_4$  and  $\text{AsMe}_2((\text{CH}_2)_3\text{CH}=\text{CH}_2)$  [14] ( $\text{C}_5\text{H}_9 = (\text{CH}_2)_3\text{CH}=\text{CH}_2$  or  $(\text{CH}_2)_2\text{CH}=\text{CHCH}_3$ ). The acid presumably suppresses formation of bis-phosphine or  $\text{Pt}_2\text{P}_2\text{Cl}_4$  dimer complexes and encourages



SCHEME 3



the olefin to coordinate to platinum. Similarly, the presence of HX in solutions of **1** could encourage coordination of cyclopropane to platinum (Scheme 3).

The platinacyclobutane complex proposed in Scheme 3, **2a**, resembles the 5-coordinate platinacyclobutane complex  $\text{PtCl}_2(\text{py})(\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)_2)$  that decomposes to the  $\pi$ -olefin complex *trans*- $\text{PtCl}_2(\text{py})(\text{CH}_2=\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)_2)$  [1c,15].

## Experimental

### General remarks

All reactions were carried out under an atmosphere of prepurified dinitrogen with the use of standard Schlenk-line techniques.  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$  was used as received from Aldrich Chemical Company. (Di-*t*-butyl)chlorophosphine was used as obtained from Alfa Products. Solvents were purified by standard methods.

Elemental analysis of  $\text{P}(\text{t-Bu})_2(\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2) \cdot \text{HBr}$  was performed by Galbraith Laboratories, Inc., Knoxville, TN; analysis of  $[\text{PtX}(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2)]_2(\mu\text{-X})(\mu\text{-Y})$  (**1**) and of *cis*- $\text{PtX}_2(\text{P}(\text{t-Bu})_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3)$  (**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 (complexes **1** and **2**) or as neat liquids ( $\text{Br}(\text{CH}_2)_2\text{CHCH}_2\text{CH}_2$  and  $\text{P}(\text{t-Bu})_2(\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2)$ ). Mass spectral data were collected with a Hewlett Packard 5985 spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were recorded on a JEOL-FX90 or JNM-FX270 FT-NMR spectrometer.  $^{31}\text{P}$  positive chemical shifts are downfield from 85%  $\text{H}_3\text{PO}_4$ .

X-ray data were collected with the use of  $\text{Mo-K}\alpha_1$  radiation on an Enraf-Nonius CAD4 diffractometer and all the calculations were performed on a Harris 1000 computer by methods and programs standard in this laboratory [16].

### Synthesis of 2-bromoethylcyclopropane

A mixture of 2-cyclopropylethanol [17] (9.117 g, 0.106 mol) and pyridine (2.33 g, 0.029 mol) was added dropwise with magnetic stirring over 3 h to 11.46 g (0.092 mol)  $\text{PBr}_3$  at  $0^\circ\text{C}$ . Volatiles were then distilled from the reaction flask under vacuum. The residue left in the reaction flask was extracted with  $\text{Et}_2\text{O}$ , and the  $\text{Et}_2\text{O}$  extract was combined with the distillate. This mixture was washed twice with saturated aqueous  $\text{NaHCO}_3$  and 5% aqueous  $\text{NaCl}$ , then dried over  $\text{MgSO}_4$  (anhydrous). Fractional distillation of the dried ether solution at reduced pressure gave 2-bromoethylcyclopropane (9.49 g, 60%). IR (neat)  $3017\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.60 (t,  $\text{BrCH}_2$ ,  $J$  6.6 Hz), 1.33 (m,  $\text{BrCH}_2\text{CH}_2$ ), 0.84 (m, cyclopropyl methine), 0.49 + 0.10 (m, cyclopropyl methylene)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  38.11 (s,  $\text{CH}_2\text{Br}$ ); 33.16 (s,  $\text{CH}_2\text{CH}_2\text{Br}$ ); 10.03 (s, cyclopropylmethine); 4.16 (s, cyclopropylmethylene). Anal. Found: C, 39.89; H, 6.26; Br, 53.01.  $\text{C}_5\text{H}_9\text{Br}$  calc: C, 40.30; H, 6.09, Br, 53.60%.

### Syntheses of di-*t*-butyl(ethylcyclopropyl)phosphine hydrobromide ( $\text{P}(\text{t-Bu})_2(\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2) \cdot \text{HBr}$ ) and di-*t*-butyl(ethylcyclopropyl)phosphine ( $\text{P}(\text{t-Bu})_2(\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2)$ )

To a mixture of 3.4 ml (5.1 g, 0.034 mol)  $\text{BrCH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2$  in 20 ml isobutylmethylketone was added dropwise 5.0 ml (5.0 g, 0.03 mol) di-*t*-butylphosphine [18]. The reaction mixture was heated at reflux for 6 h during which

the white phosphine hydrobromide precipitated from solution. After the solvent had been distilled from the reaction flask under reduced pressure, the phosphine hydrobromide was washed with hexane three times and was then dried under vacuum, isolated yield 90% (9.0 g). Analytical data yield C/H/P = 13/28.9/0.97 for the compound of formula  $C_{13}H_{28}BrP$ . Treatment of the phosphine hydrobromide with base gave the free phosphine. Spectroscopic data for  $Pt(t-Bu)_2(CH_2CH_2\overline{CH}CH_2CH_2)$  are given in Table 1.

*Preparation of  $[PtX(P(t-Bu)_2CH_2CH_2\overline{CH}CH_2CH_2)]_2(\mu-X)_2$  (1)*

The complex  $[PtX(P(t-Bu)_2CH_2CH_2\overline{CH}CH_2CH_2)]_2(\mu-X)(\mu-Y)$  (1) (X, Y = Cl or Br) precipitated from a stirred mixture of  $K[PtCl_3(C_2H_4)]$  (0.50 g, 1.3 mmol) and  $P(t-Bu)_2(CH_2CH_2\overline{CH}CH_2CH_2) \cdot HBr$  (0.40 g, 1.3 mmol) in 20 ml anhydrous ethanol. The total reaction time allowed was 1 h. The isolated crude yield of orange product 1 was 0.58 g. Anal. Found: C, 32.65; H, 5.59; Br, 6.87; Cl, 10.91; P, 5.34; for the representative formula  $C_{26}H_{54}BrCl_3P_2Pt_2$  calc: C, 31.06; H, 5.42; Br, 7.95; Cl, 10.58; P, 6.16%. Spectral data for 1 are given in Table 1. The mass spectral data for 1 include peaks at  $m/e$  976, 933, 888, 488, and 443.

*Preparation of  $cis-PtX_2(P(t-Bu)_2CH_2CH_2CH=CHCH_3)$  (2)*

The procedure reported for the preparation of 1 was followed, except the reagents were heated at reflux for a total of 14 h. During this time the color of the reaction mixture gradually changed from orange to pale yellow. Very pale yellow crystals of  $cis-PtX_2(P(t-Bu)_2CH_2CH_2CH=CHCH_3)$  formed in the reaction flask as the mixture cooled; KBr and KCl also precipitated from the mixture. Complex 2 was recrystallized from boiling ethanol, isolated yield 0.43 g. Anal. Found: C, 30.47; H, 5.32; Cl, 9.25; P, 5.57.  $C_{13}H_{27}Br_{0.72}Cl_{1.28}P_2Pt$  (derived from the X-ray data) calc: C, 30.40; H, 5.30; Cl, 8.84; P, 6.04%. Table 1 gives the spectral data for 2. Mass spectral data for 2 indicate the presence of at least two species. Identifiable parent peaks occur at  $m/e$  524 and 569.

*X-Ray study of  $cis-PtX_2(P(t-Bu)_2CH_2CH_2CH=CHCH_3)$  (2)*

Crystals of 2 suitable for X-ray analysis formed as bi-capped parallelepipeds from a cooled solution of 2 in anhydrous ethanol. 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 ( $h0l$ ,  $l \neq 2n$ ;  $hk0$ ,  $h \neq 2n$ ;  $0kl$ ,  $k \neq 2n$ ) together with the presence of orthorhombic symmetry are strongly indicative of the space group  $D_{2h}^{15}-Pbca$ . Six standard reflections monitored during data collection showed no significant decomposition. Details of the 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 atoms were obtained from difference electron density maps. The positions of methylene and methine hydrogen atoms were calculated; these positions and those found for the methyl hydrogen atoms were idealized assuming a C-H bond length of 0.95 Å. A given H atom was assigned an isotropic thermal parameter 1 Å<sup>2</sup> greater than the equivalent isotropic thermal parameter of the carbon atom to which it is attached. Parameters for the hydrogen atoms were not varied in the least-squares refinements. The variables for a given halogen site, in addition to the positional parameters and isotropic thermal parameter of the site,

TABLE 4

POSITIONAL PARAMETERS AND  $B_{eq}$  ( $\text{\AA}^2$ ) FOR *cis*-PtX<sub>2</sub>(P(*t*-Bu)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>3</sub>)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Pt	0.143064(26)	0.256292(14)	0.110631(20)	1.408(8)
P	0.24178(19)	0.35072(10)	0.07126(14)	1.59(5)
Br(1)	0.04463(11)	0.156570(65)	0.176778(89)	2.32(3)
Cl(1)	0.045	0.157	0.177	2.3
Br(2)	-0.02870(14)	0.320073(85)	0.12642(10)	2.22(4)
Cl(2)	-0.029	0.320	0.126	2.2
C(1)	0.23721(77)	0.41806(41)	0.16441(59)	2.1(2)
C(2)	0.39041(71)	0.32018(41)	0.06924(59)	1.9(2)
C(3)	0.21296(72)	0.38582(41)	-0.04503(57)	1.9(2)
C(4)	0.22783(82)	0.32628(44)	-0.11248(55)	2.3(2)
C(5)	0.29874(94)	0.44182(46)	-0.06861(68)	3.2(3)
C(6)	0.09055(87)	0.41297(50)	-0.05599(62)	3.1(3)
C(7)	0.35207(92)	0.45579(45)	0.17160(75)	3.2(3)
C(8)	0.14016(85)	0.47047(43)	0.14763(61)	2.5(2)
C(9)	0.21140(87)	0.38245(43)	0.25401(65)	2.8(2)
C(10)	0.40256(75)	0.26274(41)	0.13817(55)	1.9(2)
C(11)	0.31100(76)	0.20972(42)	0.12518(57)	1.9(2)
C(12)	0.26762(72)	0.19339(39)	0.04061(54)	1.8(2)
C(13)	0.22482(83)	0.12405(46)	0.01308(63)	2.7(2)

included  $\alpha$ , the fractional amount of Br at that site (with Cl at that site being  $1-\alpha$ ). The values of  $\alpha$  for each site were determined in the least-squares refinement, due cognizance being taken of constraints on the derivatives. Table 4 presents the final positional parameters. Table 5 through 7 [19], respectively, give the anisotropic thermal parameters, the hydrogen atom positions, and a listing of  $10|F_o|$  vs.  $10|F_c|$ .

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- 19 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. 04481 for 20 pages of supplementary material. Order from NAPS c/o microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only \$7.75 for photocopies or \$4.00 for microfilm. Outside the U.S. and Canada add postage of \$4.50 for the first 20 pages and \$1.00 for each 10 pages of material thereafter. \$1.50 for microfiche postage.