The most important feature of this reaction is then that the reductive elimination of the benzyl group in the Pd(IV) intermediate comprises attack of the benzyl carbon atom on the aromatic carbon atom of the dmba and not, as predicted, on the benzylic carbon atom of the dmat-Si. Very likely, the isolation of **9** as an ammonium salt resulted from a subsequent reaction of the initially formed cross-coupled product with an excess of benzyl bromide.

Registry No. **1**, 93184-81-7; **2**, 93184-81-7; **3**, 106799-29-5; **4**, 93184-75-9; **5**, 93184-76-0; **6a**, 106861-78-3; **6b**, 106782-04-1; **7**, 106782-01-8; **8**, 106782-02-9; **9**, 106782-03-0; $Pd(SEt_2)_2Cl_2$, 14873-91-7; $[Pd(dmba)(\mu\text{-}Cl)]_2$, 18987-59-2; $[Pd(8\text{-}mg)(\mu\text{-}Cl)]_2$, 28377-73-3; $[Pd((S)\text{-}dmba)(\mu\text{-}Cl)]_2$, 34424-15-2; benzyl bromide, 100-39-0.

Supplementary Material Available: Listings of positional parameters for hydrogen atoms, thermal parameters, and least-squares planes (Table VI) for **6b** and a table reporting selected structural data in various palladabicyclic compounds (Table VII) (7 pages); a listing of structure factors for **6b** (11 pages). Ordering information is given on any current masthead page.

Preferential Activation of a *tert*-Butyl Group over a Cyclopropyl Group in the Intramolecular Reaction of *trans*-Dichlorobis(di-*tert*-butylcyclopropylphosphine)platinum(II) To Form a Platinaphosphacyclobutane. Synthesis and Structure of $PtCl_2[P(t\text{-}Bu)_2\overline{CHCH_2CH_2}]_2$ and Its Derivatives

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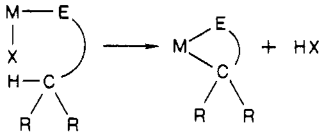
The complex $\overline{PtCl[P(t\text{-}Bu)(CMe_2CH_2})(\overline{CHCH_2CH_2})](P(t\text{-}Bu)_2\overline{CHCH_2CH_2})$ (**2**) has been obtained by the elution of *trans*-$PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (**1**) on silica or Florisil supports and by the reaction of **1** with thallium(I) acetate. The complex *trans*-$PtHCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (**3**) is a byproduct of the Florisil-assisted reaction. Complex **3** has also been synthesized by reduction of **1** with hydrazine hydrate. The dimer $[PtCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})]_2(\mu\text{-}Cl)_2$ (**4**) forms from **1** in dioxane or toluene/acetic acid solvent. Complexes **1**–**3** have been characterized by means of elemental analysis and IR and NMR spectroscopy. The structures of **1**–**4** have been determined by X-ray methods.

Introduction

Sterically assisted intramolecular activation that leads to metallacycles has been observed for numerous transition-metal complexes.[1] A common reaction sequence is shown in Scheme I where E can be almost any donor group and the metallacyclic ring may contain as few as three or as many as six atoms. Systems where $E(CR_2H)$ is a bulky tertiary phosphine ligand have been extensively investigated.[1b–e]

Scheme I



(1)

Although electronic factors become important with ligands of like steric bulk,[1d] certain steric factors, such as large phosphorus cone angle, halide ion (I > Br > Cl), and ring size (5 > 4 > 6), optimize conditions.[1b,d,f] The phosphine $P(t\text{-}Bu)_3$ forms four-membered metallacycles in its complexes with Pt(II) much more easily than does $P(t\text{-}Bu)_2Ph$ because of the larger contribution of *t*-Bu relative to Ph to the phosphorus cone angle.[1f] The less sterically congested complex $PtCl_2(P(t\text{-}Bu)Ph_2)_2$ undergoes very little ortho-metalation after prolonged periods at reflux in 2-methoxyethanol, but with the addition of LiBr to the reaction mixture the internally metalated complex $PtBr(P(t\text{-}Bu)C_6H_4Ph)(P(t\text{-}Bu)Ph_2)$ is formed after 48 h at reflux. The complex *trans*-$PtCl_2(P(t\text{-}Bu)_2(o\text{-}Tol))_2$ (Tol = tolyl) undergoes internal metalation more readily than the corresponding $P(t\text{-}Bu)_2Ph$ complexes since the resulting metallacycle contains five atoms. Still, Pt(II) complexes of the extremely bulky $P(t\text{-}Bu)_3$ ligand are more reactive with respect to internal metalation than are those of $P(t\text{-}Bu)_2(o\text{-}Tol)$.

In complexes exhibiting similar steric congestion, aromatic substituents on phosphorus are metalated more easily than are aliphatic ones despite larger aryl C–H bond energies. The π-electron cloud of the aryl group is more readily attacked by an electrophilic metal atom.[2] Cyclopropane should be similarly more reactive, as electron density located in relatively high s-character orbitals away

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(1) (a) Collman, J. P.; Hegedus, L. J. *Principles and Applications of Organo-transition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Shaw, B. L. *J. Organomet. Chem.* **1980**, *200*, 307 and references therein. (c) Goel, R. G.; Montemayor, R. G. *Inorg. Chem.* **1977**, *16*, 2183. (d) Cheney, A. J.; Mann, B. E; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 3833. (e) Werner, H.; Kraus, H. J. *J. Organomet. Chem.* **1981**, *204*, 415. (f) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(2) A notable exception is $[PdCH_2CMe_2P(t\text{-}Bu)Ph]_2(\mu\text{-}Cl)_2$ prepared by reaction of $PdCl_2P(t\text{-}Bu)_2Ph$ with AgOAc. See ref 1e.

Table I. Spectroscopic Data for Complexes *trans*-$\text{PtCl}_2(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (1), $\overline{\text{PtCl[P(}t\text{-Bu)(CMe}_2\text{CH}_2}\text{)(}\overline{\text{CHCH}_2\text{CH}_2}\text{)](P(}t\text{-Bu)}_2\overline{\text{CHCH}_2\text{CH}_2}$ (2), and *trans*-$\text{PtHCl}(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (3)[a]

		NMR		
complex	IR	^{1}H	^{13}C	^{31}P
1	332 (ν_{Cl})	1.53 (t, CCH_3, J(P–H) = 6.4), 0.72–1.02 (m, CHCH_2CH_2)		12.6 (s, J(Pt–P = 2563.3)
2	230 (ν_{Cl})	1.44 (d of d, t-Bu (18 H), ^3J(P–H) = 12.0, ^5J(P–H) = 1.6), 1.38 (d, t-Bu (9 H), J(P–H) = 13.8), 1.36 (d, Me (3 H), J(P–H) = 13.6), 1.11 (d, Me (3 H), J(P–H) = 13.7), complex cyclopropyl region	−3.82 (d, J(C–P) = 28.9, J(C–Pt) = 81.0), complex cyclopropyl and methyl regions (4.10–6.22; 27.8–31.2), 35.39 (d of d, ^1J(C–P) = 17.4, ^3J(C–P) = 5.8), 37.91 (d, J(C–P) = 18.52), 50.08 (d of d, ^1J(C–P) = 31.3, ^3J(C–P) = 4.6)	−14.08 (d, J(P–P) =402.3, J(Pt–P) = 2212.6), 38.24 (J(P–P) = 402.3, J(Pt–P) = 2816.2)
3	2250 (ν_{H}), 278 (ν_{Cl})	1.43 (t, CCH_3, J(P–H) = 6.6), −19.58 (t, J(P–H) = 10.1, J(Pt–H) = 576.4)		64.96 (J(Pt–P) = 3028.0)

[a] Chemical shifts in ppm. Coupling constants in Hz.

from the internuclear C–C bond axis is more accessible than electron density on acyclic or less strained alicyclic substrates.[3]

We now report, contrary to this expectation, isolation of $\overline{\text{PtCl[P(}t\text{-Bu)(CMe}_2\text{CH}_2}\text{)(}\overline{\text{CHCH}_2\text{CH}_2}\text{)](P(}t\text{-Bu)}_2\overline{\text{CHCH}_2\text{CH}_2}\text{)}$ (2), a platinaphosphacyclobutane formed by the preferential metallation of a *tert*-butyl group over a cyclopropyl group in *trans*-$\text{PtCl}_2(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (1).

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of prepurified dinitrogen with the use of standard Schlenk-line techniques. Chromatographic separations were performed in air. K_2PtCl_4 was used as received from Johnson-Matthey, Inc. Solvents were purified by standard methods.

Elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL. Infrared spectra were obtained with a Perkin-Elmer 283 spectrometer from samples prepared as KBr pellets or as mulls in Nujol pressed between CsBr windows. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL FX90Q or JNM-FX 270 FT-NMR spectrometer or on a Varian FX400 FT-NMR spectrometer. ^{31}P positive chemical shifts are downfield from 85% H_3PO_4. Table I summarizes the spectral data for each complex excluding complex 4.

X-ray data were collected on an Enraf-Nonius CAD4 diffractometer, and all calculations were performed on a Harris 1000 computer by methods and programs standard in this laboratory.[4] Lattice constants were obtained from least-squares analysis of 25 automatically centered reflections. Data reduction and refinement details are summarized in Table II.

Positional parameters for methyl hydrogen atoms were obtained from difference electron density maps, and these parameters were then idealized. Methylene and methyne hydrogen atom positions were 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 H atoms were held fixed during subsequent refinements. Analysis of F_o^2 as a function of F_o^2, $\lambda^{-1}\sin\theta$, and Miller indices for structures of 1–4 showed no unusual trends.

Final atomic coordinates are given in Table III. Table IV[5] presents the anisotropic thermal parameters, Table V[5] the hydrogen atom positions, and Table VI[5] listings of $10|F_o|$ vs. $10|F_c|$.

Preparation of Di-*tert*-butylcyclopropylphosphine. A solution of cyclopropyllithium (prepared from 8.00 g of cyclopropyl bromide and 1.00 g of Li metal in 50 mL of ether) was added over 10 min to 10 g (55.4 mmol) of di-*tert*-butylchlorophosphine[6] in 25 mL of ether. The reaction mixture was stirred at room temperature for 12 h. Phosphine and ether were removed from the reaction flask under vacuum (1 mm). The phosphine was redistilled at reduced pressure: bp 50 °C (15 mm).

Owing to the pyrophoric nature of the phosphine, its hydrogen bromide adduct (prepared by bubbling HBr gas through an ether solution of $\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2}$) is more readily analyzed. Anal. Calcd for $\text{C}_{11}\text{H}_{23}\text{P}\cdot\text{HBr}$: C, 49.95; H, 9.05; P, 11.59; Br, 29.90. Found: C, 48.35; H, 8.83; P, 10.00; Br, 30.15. IR: 3080 cm^{-1}. ^{1}H NMR: δ 1.14 (d, J = 10.5 Hz), 0.49 (m), 0.40 (m). ^{31}P NMR δ 31.5.

Synthesis of *trans*-Dichlorobis(di-*tert*-butylcyclopropylphosphine)platimun(II), *trans*-$\text{PtCl}_2(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (1). K_2PtCl_4 (0.28 g, 0.67 mmol) and di-*tert*-butylcyclopropylphosphine (0.25 g, 1.34 mmol) were stirred in a mixture of 30 mL of acetone or ethanol and 10 mL of distilled water for 24 h. The yellow product (0.41 g, 95%) was recrystallized from hexane. Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{Cl}_2\text{P}_2\text{Pt}$: C, 41.38; H, 7.26; Cl, 11.10; P, 9.70. Found: C, 41.58; H, 7.23; Cl, 11.56; P, 9.87.

Synthesis of the Derivative Compounds. Compound 1 was eluted with toluene on a column of 100–200 mesh Florisil. Typically two bands were eluted that upon removal of solvent yielded yellow and white powders, respectively. Recrystallization of the yellow powder from dioxane or acetic acid/toluene afforded 1 with some crystals of $[\text{PtCl}(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-Cl})_2$ (4). Complex 4 was identified by X-ray diffraction methods. (Quantities obtained were insufficient for characterization by NMR and IR spectroscopic techniques.) Recrystallization of the white powder from toluene yielded $\overline{\text{PtCl[P(}t\text{-Bu)(CMe}_2\text{CH}_2}\text{)(}\overline{\text{CHCH}_2\text{CH}_2}\text{)](P(}t\text{-Bu)}_2\overline{\text{CHCH}_2\text{CH}_2}\text{)}$ (2) and *trans*-$\text{PtHCl}(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})$ (3). No hydride product 3 was isolated if Florisil was heated to 200 °C for 1 h prior to its use as the support. The complexes 1, 2, and 3 were identified by their characteristic NMR and IR spectra (Table I) and by single crystal x-ray diffraction methods.

Alternative Synthesis of $\overline{\text{PtCl[P(}t\text{-Bu)(CMe}_2\text{CH}_2}\text{)(}\overline{\text{CHCH}_2\text{CH}_2}\text{)](P(}t\text{-Bu)}_2\overline{\text{CHCH}_2\text{CH}_2}\text{)}$ (2). When 1 was eluted with toluene on a silica gel (on glass) TLC plate, mean pore diameter 60 Å, 2 was isolated in approximately 60% yield. Complex 2 also formed when 1 was combined with 1 equiv of thallium(I) acetate in anhydrous ethanol and heated at reflux for 2 h. Anal. Calcd for $\text{C}_{22}\text{H}_{45}\text{ClP}_2\text{Pt}$: C, 43.89; H, 7.53; P, 10.29; Cl, 5.89. Obsd: C, 43.14; H, 7.23; P, 10.05; Cl, 6.55.

Alternative Synthesis of *trans*-$\text{PtHCl}(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (3). The hydride was synthesized in nearly quantitative yield by reduction by hydrazine hydrate of the dichloro complex 1 in absolute ethanol. Anal. Calcd for $\text{C}_{22}\text{H}_{47}\text{ClP}_2\text{Pt}$: C, 43.74; H, 7.84; P, 10.25; Cl, 5.88. Obsd: C, 43.24;

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[3] Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461 and references therein.

[4] Waters, J. M. ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273.

[5] Supplementary material.

[6] Di-*tert*-butylchlorophosphine was used as obtained from Alfa Chemicals without further purification.

Table II. Data Collection and Refinement Details

	1	2	3	4
compd	*trans*-PtCl$_2$(P(*t*-Bu)$_2$-CHCH$_2$CH$_2$)$_2$	PtCl[P(*t*-Bu)$_2$(CMe$_2$CH$_2$)-(CHCH$_2$CH$_2$)]-(P(*t*-Bu)$_2$CHCH$_2$CH$_2$)	*trans*-PtHCl(P(*t*-Bu)$_2$-CHCH$_2$CH$_2$)$_2$	[PtCl(P(*t*-Bu)$_2$-CHCH$_2$CH$_2$)]$_2$(μ-Cl)$_2$
formula	$C_{22}H_{46}Cl_2P_2Pt$	$C_{22}H_{45}ClP_2Pt$	$C_{22}H_{47}ClP_2Pt$	$C_{22}H_{46}Cl_4P_2Pt_2$
mol wt, amu	638.56	602.09	604.11	904.55
space group	C_{4h}^4—$P4_2/n$	D_{2h}^{15}—$Pbca$	D_{2h}^{16}—$Pnam$[a]	C_{2h}^5—$P2_1/n$
a, Å	17.770 (10)	12.651 (5)	16.344 (10)	8.099 (11)
b, Å	17.770[b]	14.576 (3)	11.124 (7)	15.221 (21)
c, Å	8.229 (4)	27.552 (15)	14.371 (9)	12.389 (18)
β, deg	90	90	90	106.24 (6)
V, Å^3	2598.6	5080.7	2612.8	1466.3
Z	4	8	4	2
t of data collectn, °C	−160	−160	−160	−108[c]
cryst color	yellow	pale yellow	colorless	orange
cryst dimens, mm	0.20 × 0.16 × 0.43	0.05 × 0.28 × 0.32	0.13 × 0.14 × 0.34	0.10 × 0.11 × 0.36
cryst vol, mm^3	0.0124	0.004 76	0.005 83	0.004 04
ρ_{calcd}, g/cm^3	1.632	1.574	1.536	2.048
radiatn	graphite-monochromated Mo Kα (λ(Kα_1) = 0.7093 Å)			
linear abs coeff, cm^{-1}	57.90	58.15	56.54	101.14
transmissn factors	0.342–0.411[d]	0.223–0.738	0.433–0.582	0.311–0.459
takeoff angle, deg	2.5	3.0	3.0	3.0
receiving aperture, mm (17.3 cm from crystal)	2.0 × 2.0	3.0 × 2.0	3.0 × 2.0	3.0 × 2.0
scan range, deg (in ω)	0.5 below Kα_1 to 0.5 above Kα_2	0.65 below Kα_1 to 0.65 above Kα_2	0.55 below Kα_2 to 0.55 above Kα_2	0.45 below Kα_1 to 0.45 above Kα_2
bkgd counts	extension of $^1/_4$ scan range on each side			
scan speed, deg/min	2.75	2.00 (2° ≤ θ ≤ 20°), 1.65 (θ > 20°)	2.75	2.75 (2° ≤ θ ≤ 20°), 2.00 (θ > 20°)
rescan condition	$I \leq 3\sigma(I)$	$I \leq 4\sigma(I)$	$I \leq 4\sigma(I)$	$I \leq 5\sigma(I)$
2θ limits, deg	4–60	4–50	4–50	4–60
data collected	$+h,+k,+l$	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,\pm l$
unique data	3584	4490	3742	4384
unique data with $F_o^2 > 3\sigma(F_o^2)$	2063	2484	2394	3342
p factor for $\sigma(F_o^2)$	0.04	0.04	0.04	0.04
final no. of variables	125	235	131	137
$R(F^2)$ (including $F_o^2 < 0$)	0.049	0.100	0.068	0.067
$R_w(F^2)$ (including $F_o^2 < 0$)	0.101	0.131	0.107	0.095
R(F) for $F^2 > 3\sigma(F_o^2)$	0.035	0.050	0.042	0.038
error in observn of unit wt, e^2	1.21	1.19	1.20	1.16

[a] Refinement of 3 as an ordered structure in space group $Pna2_1$ was not successful. Moreover, F_o^2 (hkl) and F_o^2 ($hk\bar{l}$), after correction for absorption, agree as expected for space group $Pnam$, which was therefore assumed. [b] Cell parameters were refined under constraints $a = b$ or $\alpha = \gamma = 90°$ or $\alpha = \beta = 90°$ as appropriate. [c] The low-temperature system is based on a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. T. deVic, 31320, Castanet-Tolosan, France. [d] Analytical method (Meulenaer, J. de; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014).

H, 7.89; P, 10.12; Cl, 5.78. When 1 was refluxed for 8 h in acetic acid or in a mixture of 10% acetic acid in dimethylformamide, both the metallated *tert*-butyl complex 2 and the hydride 3 formed. These products were identified by their characteristic ^{31}P chemical shifts.

Results

***trans*-$PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (1).** K_2PtCl_4 reacts with di-*tert*-butylcyclopropylphosphine in aqueous ethanol or acetone to afford 1 as the sole product. The trans configuration, which is expected owing to the extreme bulk of the coordinated phosphine ligands, is confirmed by NMR spectra of the crude product.[1b] A single resonance (J(Pt–P) = 2563 Hz) is observed in the ^{31}P NMR spectrum. The second-order proton spectrum shows a virtual triplet for the *tert*-butyl protons. The resonances from the cyclopropyl groups apparently overlap; only one broad multiplet appears in the cyclopropyl region of the proton spectrum.

Reactions of 1. When 1 is refluxed for 50 h in 2-methoxyethanol, no metalation of the phosphine ligands occurs. Rather, the hydride *trans*-$PtHCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (3) is formed in approximately 65% yield. Complexes of the type *trans*-$PtHCl(PR_3)_2$, such as 3, are generally prepared by reduction of the parent dichloro compound by hydrazine hydrate.[7] Boiling 2-methoxyethanol,[1d] ethyl and isopropyl alcohols (in conjunction with hydroxide ion),[7] and hot formic acid (with some H_2O present)[7] may also act as reducing agents. Indeed, compound 3 may be synthesized by reduction of 1 with hydrazine hydrate in refluxing ethanol. Spectra for complex 3 are typical of *trans*-$PtHCl(PR_3)_2$ complexes (Table I). As for 1, a pseudotriplet pattern in the proton NMR spectrum arises from the *t*-Bu protons on the phosphine ligands. There is the distinctive upfield triplet resonance (−19.58 ppm) in the proton spectrum from the hydride ligand. In the ^{31}P spectrum, the single resonance from the equivalent phosphine ligands appears at 64.96 ppm. These features are characteristic of the trans configuration.[7b]

When 1 is eluted with toluene on a Florisil column or heated at reflux for two hours in acetic acid, a mixture of the metalated complex $\overline{PtCl[P(t\text{-}Bu)(CMe_2CH_2)}(\overline{CHCH_2CH_2}](P(t\text{-}Bu)_2\overline{CHCH_2CH_2})$ (2) and 3 is obtained. A small amount of the dimer $[PtCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2}]_2(\mu\text{-}Cl)_2$ (4) is also obtained when 1 is recrystallized from dioxane or acetic acid/toluene. When 1 is eluted with toluene on silica gel, only the metalated complex 2 is obtained. Similarly, when equimolar quantities of 1 and TlOAc are heated at reflux in anhydrous ethanol, compound 2 is obtained in almost quantitative yield with only minute quantities of 3 being visible in the ^{31}P NMR spectrum. When 1 is eluted on silica gel pretreated with triethylamine, only pure 1 is recovered.

The NMR spectra (Table I) of the metalated complex 2 clearly show that a *t*-Bu methyl group rather than a cyclopropyl group on phosphorus has been activated to form the four-membered metallacycle.[8] The large upfield shift of the resonance of the chelating phosphine in the 12-line ^{31}P spectrum relative to that of the nonchelating phosphine is typical of phosphorus in a four-member ring.[8b] The proton spectrum shows four resonances that correspond to methyl protons with relative integrations 6:3:1:1.

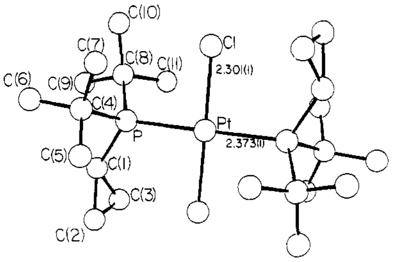

Figure 1. Structure and numbering scheme for *trans*-$PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (1). H atoms have been omitted for the sake of clarity.

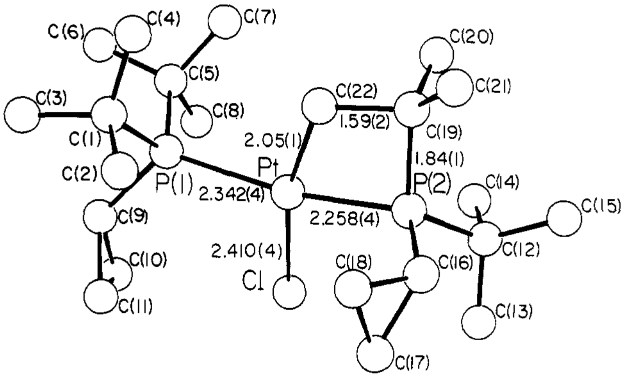

Figure 2. Numbering scheme for atoms of $\overline{PtCl[P(t\text{-}Bu)(CMe_2CH_2)}(\overline{CHCH_2CH_2})](P(t\text{-}Bu)_2\overline{CHCH_2CH_2})$ (2).

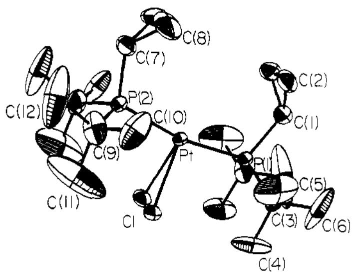

Figure 3. Molecular structure and numbering scheme for *trans*-$PtHCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (3) showing the disorder in the chloro ligand. Here and in subsequent figures thermal ellipsoids at the 50% probability level are given.

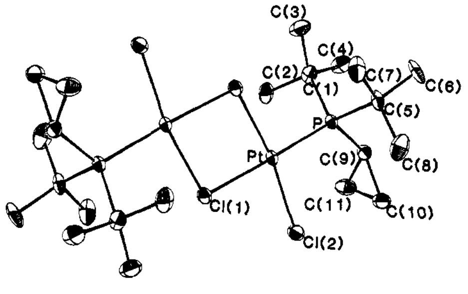

Figure 4. Molecular structure and numbering scheme for $[PtCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})]_2(\mu\text{-}Cl)_2$ (4).

The 3:1:1 pattern of doublets results from substituents on the chelating phosphorus ligand. The large doublet is from the *tert*-butyl ($P–C(CH_3)_3$) protons while the two smaller doublets are from the dimethyl ($\overline{P–C(CH_3)_2CH_2Pt}$) protons. The latter methyl groups are nonequivalent because they reside on a ring that contains a chiral center (on phosphorus).[1e,9] The remaining resonance is from the

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[7] (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075. (b) Chatt, J.; Chini, P. *J. Chem. Soc. A* **1970**, 1538.

[8] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

[9] Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. *Organic Structure Analysis*; Macmillan: New York, 1976; p 56.

Table III. Atomic Coordinates for Structures 1–4

atom	x	y	z	atom	x	y	z
			$\mathit{trans}\text{-PtCl}_2(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (**1**)				
Pt	1/2	1/2	0	C(5)	0.60136 (36)	0.59858 (32)	0.33515 (68)
Cl	0.515094 (74)	0.618107 (74)	−0.10982 (20)	C(6)	0.71387 (33)	0.51676 (39)	0.37602 (75)
P	0.627697 (67)	0.500113 (69)	0.08445 (16)	C(7)	0.58604 (34)	0.46533 (31)	0.40816 (71)
C(1)	0.69482 (31)	0.56895 (29)	0.00716 (63)	C(8)	0.68043 (29)	0.41124 (30)	0.02588 (61)
C(2)	0.68719 (33)	0.65164 (34)	−0.02752 (64)	C(9)	0.76602 (30)	0.42208 (33)	0.01170 (64)
C(3)	0.69886 (33)	0.59855 (31)	−0.16665 (76)	C(10)	0.66757 (31)	0.34490 (20)	0.14082 (76)
C(4)	0.63365 (28)	0.52005 (29)	0.30958 (64)	C(11)	0.65144 (31)	0.39094 (32)	−0.14672 (68)
			$\overline{\text{PtCl[P}(t\text{-Bu})(\text{CMe}_2\text{C}}\text{H}_2)(\overline{\text{CHCH}_2\text{C}})_2](\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})$ (**2**)				
Pt	0.486610 (31)	0.147916 (30)	0.134152 (17)	C(10)	0.1783 (12)	0.2181 (13)	0.10955 (72)
Cl	0.33331 (27)	0.07043 (28)	0.16599 (15)	C(11)	0.2287 (15)	0.2927 (14)	0.14107 (70)
P(1)	0.39960 (26)	0.24318 (24)	0.07855 (13)	C(12)	0.5969 (12)	−0.05007 (94)	0.19859 (53)
P(2)	0.60455 (26)	0.07254 (23)	0.18096 (13)	C(13)	0.5202 (15)	−0.0572 (10)	0.24002 (60)
C(1)	0.4596 (12)	0.36173 (93)	0.07337 (59)	C(14)	0.5568 (12)	−0.10883 (96)	0.15580 (58)
C(2)	0.4844 (15)	0.3965 (10)	0.12378 (68)	C(15)	0.7071 (13)	−0.0850 (11)	0.21424 (75)
C(3)	0.3828 (14)	0.4323 (12)	0.05174 (67)	C(16)	0.6340 (11)	0.12945 (92)	0.23682 (48)
C(4)	0.5612 (11)	0.36486 (96)	0.04569 (58)	C(17)	0.5430 (11)	0.1658 (11)	0.26733 (55)
C(5)	0.3944 (11)	0.1865 (10)	0.01784 (50)	C(18)	0.6161 (12)	0.22999 (98)	0.24204 (56)
C(6)	0.3505 (11)	0.2463 (12)	−0.02313 (51)	C(19)	0.70968 (91)	0.10433 (95)	0.13830 (56)
C(7)	0.5029 (13)	0.1519 (11)	0.00332 (49)	C(20)	0.7237 (11)	0.03270 (95)	0.09796 (52)
C(8)	0.3207 (13)	0.1034 (11)	0.02459 (61)	C(21)	0.81607 (96)	0.1347 (11)	0.15797 (53)
C(9)	0.26467 (95)	0.2782 (10)	0.09009 (51)	C(22)	0.6383 (10)	0.18410 (86)	0.11657 (50)
			$\mathit{trans}\text{-PtHCl}(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (**3**)[a]				
Pt	0.362670 (19)	−0.045887 (30)	1/4	C(6)	0.4987 (12)	0.3130 (10)	0.1352 (13)
P(1)	0.41704 (14)	0.14488 (21)	1/4	C(7)	0.17569 (77)	−0.1876 (11)	1/4
P(2)	0.28317 (15)	−0.21629 (22)	1/4	C(8)	0.13600 (54)	−0.08788 (97)	0.1990 (16)
C(1)	0.33736 (61)	0.25920 (97)	1/4	C(9)	0.29657 (58)	−0.30990 (74)	0.14289 (61)
C(2)	0.26008 (44)	0.24876 (72)	0.19818 (56)	C(10)	0.28757 (64)	−0.22654 (98)	0.06025 (65)
C(3)	0.47580 (47)	0.18259 (65)	0.14125 (62)	C(11)	0.38032 (92)	−0.3666 (18)	0.1393 (10)
C(4)	0.55229 (53)	0.1112 (12)	0.13409 (71)	C(12)	0.2312 (11)	−0.4073 (10)	0.13260 (93)
C(5)	0.42421 (71)	0.1482 (16)	0.05965 (69)	Cl(1)	0.48676 (20)	−0.14845 (31)	0.20196 (28)
			$[\text{PtCl}(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})]_2(\mu\text{-Cl})_2$ (**4**)				
Pt	0.331497 (31)	0.418771 (14)	0.455903 (20)	C(5)	−0.01638 (87)	0.44569 (41)	0.23436 (61)
Cl(1)	0.52082 (22)	0.48250 (10)	0.62608 (13)	C(6)	−0.1307 (11)	0.41693 (47)	0.11710 (68)
Cl(2)	0.21945 (23)	0.33691 (10)	0.57235 (14)	C(7)	0.0535 (10)	0.53912 (45)	0.22547 (80)
P	0.15910 (21)	0.364689 (96)	0.29399 (13)	C(8)	−0.1270 (11)	0.44992 (54)	0.31620 (85)
C(1)	0.28586 (90)	0.33248 (42)	0.19184 (60)	C(9)	0.03943 (87)	0.26393 (39)	0.29361 (56)
C(2)	0.45247 (97)	0.28967 (49)	0.26335 (72)	C(10)	−0.0514 (10)	0.23060 (46)	0.37582 (61)
C(3)	0.3276 (12)	0.41018 (51)	0.12570 (70)	C(11)	0.1064 (12)	0.18476 (45)	0.36650 (68)
C(4)	0.1932 (11)	0.26331 (50)	0.10577 (64)				

[a] The position of the disordered hydride ligand was not determined.

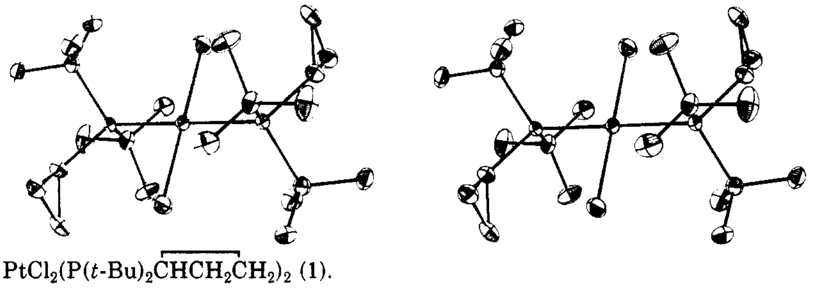

Figure 5. Stereoview of $\text{PtCl}_2(\text{P}(t\text{-Bu})_2\overline{\text{CHCH}_2\text{CH}_2})_2$ (**1**).

methyl protons on the nonchelating phosphine ligand. In the ^{13}C spectrum, resonances corresponding to the three different quaternary carbon centers appear. A DEPT[10] pulse-sequence experiment revealed that the upfield resonance that exhibits platinum sidebands results from a methylene carbon center.

X-ray Crystal Structures of 1–4. Subtle steric and electronic effects appear to dictate the range of products obtained from 1. To gain insight into these effects, we turned to a crystallographic study of the complexes. The molecular structures and labeling schemes for complexes 1, 2, 3, and 4 are illustrated in Figures 1, 2, 3, and 4, respectively. Stereoviews for complexes 1 and 2 are shown in Figures 5 and 6, respectively.

***trans*-$\mathbf{PtCl_2(P(\mathit{t}\text{-}Bu)_2(\overline{CHCH_2CH_2}))_2}$ (1).** The crystal structure of 1 consists of discrete molecules (Figure 5), each with crystallographically imposed symmetry $\bar{1}$ (Figure 1). The shortest intermolecular non-hydrogen separation (3.552 (6)Å) is between atoms Cl and C(6).

Bond distances and angles are in Table VII. Owing to the imposed crystallographic symmetry the PtP_2Cl_2 unit is planar. The two Cl–Pt–P angles are 90.16 (4) and 89.84 (4)°. Each Cl atom leans slightly toward atom C(2) of the cyclopropane ring (Cl–C(2) = 3.188 (6) Å) and relatively away from the terminal methyl groups of the *tert*-butyl carbon atoms (shortest Cl–Me distances Cl–C(10) = 3.322

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(10) (a) Bendall, M. R.; Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc.* **1981**, *103*, 4603. (b) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.

Table VII. Selected Bond Distances (Å) and Angles (deg)

trans-$PtCl_2(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (1)

Bond Distances

Pt–Cl	2.301 (1)	C(2)–C(3)	1.498 (8)	P–C(8)	1.899 (5)	C(8)–C(9)	1.537 (7)
Pt–P	2.373 (1)	C(4)–C(5)	1.524 (7)	C(1)–C(2)	1.503 (8)	C(8)–C(10)	1.529 (7)
P–C(1)	1.823 (5)	C(4)–C(6)	1.528 (7)	C(1)–C(3)	1.526 (7)	C(8)–C(11)	1.553 (7)
P–C(4)	1.889 (6)	C(4)–C(7)	1.523 (7)				

Bond Angles

Cl–Pt–P	90.16 (4)	P–C(4)–C(7)	111.8 (4)	P–C(1)–C(3)	126.1 (4)	C(9)–C(8)–C(11)	106.7 (4)
Pt–P–C(1)	121.6 (2)	C(5)–C(4)–C(6)	109.7 (5)	C(2)–C(1)–C(3)	59.3 (3)	C(10)–C(8)–C(11)	109.7 (4)
Pt–P–C(4)	109.9 (2)	C(5)–C(4)–C(7)	107.6 (4)	C(1)–C(2)–C(3)	61.1 (4)	C(9)–C(8)–C(10)	106.9 (4)
Pt–P–C(8)	113.4 (2)	C(6)–C(4)–C(7)	107.7 (5)	C(1)–C(3)–C(2)	59.6 (4)		
C(1)–P–C(4)	100.3 (2)	P–C(8)–C(9)	113.8 (4)	P–C(4)–C(5)	106.6 (4)		
C(1)–P–C(8)	98.4 (2)	P–C(8)–C(10)	114.2 (4)	P–C(4)–C(6)	113.3 (4)		
C(4)–P–C(8)	112.2 (2)	P–C(8)–C(11)	105.2 (4)				

$\overline{PtCl[P(t\text{-}Bu)(CMe_2}CH_2)(\overline{CHCH_2CH_2})](P(t\text{-}Bu)_2\overline{CHCH_2CH_2})$ (2)

Bond Distances

Pt–Cl	2.410 (4)	C(5)–C(7)	1.516 (18)	P(2)–C(12)	1.855 (14)	C(12)–C(15)	1.546 (20)
Pt–P(1)	2.342 (4)	C(5)–C(8)	1.540 (19)	P(2)–C(16)	1.787 (13)	C(16)–C(17)	1.521 (19)
Pt–P(2)	2.258 (4)	C(9)–C(10)	1.500 (21)	P(2)–C(19)	1.835 (14)	C(16)–C(18)	1.490 (19)
Pt–C(22)	2.048 (13)	C(9)–C(11)	1.491 (22)	C(1)–C(2)	1.511 (21)	C(17)–C(18)	1.488 (19)
P(1)–C(1)	1.893 (14)	C(10)–C(11)	1.531 (27)	C(1)–C(3)	1.535 (20)	C(19)–C(20)	1.535 (19)
P(1)–C(5)	1.867 (14)	C(12)–C(13)	1.502 (21)	C(1)–C(4)	1.496 (20)	C(19)–C(21)	1.517 (17)
P(1)–C(9)	1.810 (12)	C(12)–C(14)	1.543 (20)	C(5)–C(6)	1.530 (19)	C(19)–C(22)	1.589 (18)

Bond Angles

Cl–Pt–P(1)	97.91 (12)	P(1)–C(5)–C(6)	114.9 (10)	Pt–P(2)–C(19)	89.4 (4)	C(13)–C(12)–C(15)	110.4 (13)
Cl–Pt–P(2)	95.50 (13)	P(1)–C(5)–C(7)	110.6 (9)	C(12)–P(2)–C(16)	103.5 (6)	C(14)–C(12)–C(15)	109.0 (13)
Cl–Pt–C(22)	163.9 (4)	P(1)–C(5)–C(8)	105.1 (10)	C(12)–P(2)–C(19)	116.7 (7)	P(2)–C(16)–C(17)	118.7 (10)
P(1)–Pt–P(2)	166.58 (11)	C(6)–C(5)–C(7)	108.9 (12)	C(16)–P(2)–C(19)	106.5 (6)	P(2)–C(16)–C(18)	120.5 (10)
P(1)–Pt–C(22)	97.6 (4)	C(6)–C(5)–C(8)	108.5 (12)			C(17)–C(16)–C(18)	59.2 (10)
P(2)–Pt–C(22)	69.0 (4)	C(7)–C(5)–C(8)	108.5 (13)	P(1)–C(1)–C(2)	108.7 (10)	C(16)–C(17)–C(18)	59.4 (10)
Pt–P(1)–C(1)	113.7 (5)	P(1)–C(9)–C(11)	119.5 (11)	P(1)–C(1)–C(3)	112.8 (11)	C(16)–C(18)–C(17)	61.4 (10)
Pt–P(1)–C(5)	109.9 (5)	P(1)–C(9)–C(10)	125.8 (11)	P(1)–C(1)–C(4)	114.3 (10)	P(2)–C(19)–C(20)	112.1 (10)
Pt–P(1)–C(9)	119.7 (5)	C(10)–C(9)–C(11)	61.6 (11)	C(2)–C(1)–C(3)	105.3 (14)	P(2)–C(19)–C(21)	119.2 (11)
C(1)–P(1)–C(5)	110.5 (7)	C(9)–C(10)–C(11)	59.0 (11)	C(2)–C(1)–C(4)	106.3 (14)	P(2)–C(19)–C(22)	90.8 (8)
C(1)–P(1)–C(9)	97.7 (7)	C(9)–C(11)–C(10)	59.5 (12)	C(3)–C(1)–C(4)	109.0 (13)	C(20)–C(19)–C(21)	110.8 (11)
C(5)–P(1)–C(9)	104.4 (7)			P(2)–C(12)–C(13)	107.4 (10)	C(20)–C(19)–C(22)	106.9 (12)
Pt–P(2)–C(12)	125.7 (5)	P(2)–C(12)–C(15)	110.1 (10)	P(2)–C(12)–C(14)	110.6 (10)	C(21)–C(19)–C(22)	115.2 (11)
Pt–P(2)–C(16)	113.8 (5)	C(13)–C(12)–C(14)	109.3 (13)			Pt–C(22)–C(19)	104.8 (8)

trans-$PtHCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})_2$ (3)

Bond Distances

Pt–Cl	2.427 (3)	C(2)–C(2′)[a]	1.489 (16)	P(1)–C(3)	1.882 (8)	C(7)–C(8)	1.480 (17)
Pt–P(1)	2.301 (2)	C(3)–C(4)	1.484 (11)	P(2)–C(7)	1.785 (13)	C(8)–C(8′)	1.47 (5)
Pt–P(2)	2.298 (2)	C(3)–C(5)	1.494 (14)	P(2)–C(9)	1.871 (9)	C(9)–C(10)	1.514 (12)
P(1)–C(1)	1.820 (11)	C(3)–C(6)	1.501 (12)	C(1)–C(2)	1.471 (11)	C(9)–C(11)	1.508 (14)
						C(9)–C(12)	1.529 (14)

Bond Angles

Cl–Pt–P(1)	96.4 (1)	P(1)–C(3)–C(4)	111.6 (7)	Pt–P(2)–C(7)	114.1 (4)	C(8)–C(7)–C(8′)	59.4 (17)
Cl–Pt–P(2)	94.9 (1)	P(1)–C(3)–C(5)	107.6 (6)	Pt–P(2)–C(9)	113.1 (3)	P(2)–C(9)–C(10)	107.0 (6)
P(1)–Pt–P(2)	168.3 (1)	P(1)–C(3)–C(6)	113.0 (7)	C(7)–P(2)–C(9)	102.4 (4)	P(2)–C(9)–C(11)	111.5 (6)
Pt–P(1)–C(1)	111.6 (3)	C(4)–C(3)–C(5)	106.5 (8)	C(9)–P(2)–C(9′)	110.7 (5)	P(2)–C(9)–C(12)	113.1 (9)
Pt–P(1)–C(3)	113.7 (2)	C(4)–C(3)–C(6)	107.6 (10)	P(1)–C(1)–C(2)	124.0 (7)	C(10)–C(9)–C(11)	108.5 (11)
C(1)–P(1)–C(3)	102.1 (3)	C(5)–C(3)–C(6)	110.1 (12)	C(2)–C(1)–C(2′)	60.8 (8)	C(10)–C(9)–C(12)	106.9 (7)
C(3)–P(1)–C(3′)	112.3 (6)	P(2)–C(7)–C(8)	124.4 (8)	C(1)–C(2)–C(2′)	59.6 (4)	C(11)–C(9)–C(12)	109.6 (11)

$[PtCl(P(t\text{-}Bu)_2\overline{CHCH_2CH_2})]_2(\mu\text{-}Cl)_2$ (4)

Bond Distances

Pt–Cl(1)	2.435 (3)	C(1)–C(3)	1.529 (10)	P–C(1)	1.903 (7)	C(5)–C(8)	1.531 (11)
Pt–Cl(1′)[b]	2.324 (3)	C(1)–C(4)	1.537 (9)	P–C(5)	1.870 (7)	C(9)–C(10)	1.502 (9)
Pt–Cl(2)	2.278 (3)	C(5)–C(6)	1.551 (10)	P–C(9)	1.814 (7)	C(9)–C(11)	1.513 (9)
Pt–P	2.255 (3)	C(5)–C(7)	1.546 (9)	C(1)–C(2)	1.537 (10)	C(10)–C(11)	1.489 (12)

Bond Angles

Cl(1)–Pt–Cl(1)′	81.05 (11)	C(2)–C(1)–C(3)	110.3 (6)	Pt–P–C(9)	120.6 (2)	C(6)–C(5)–C(8)	109.0 (7)
Cl(1)–Pt–Cl(2)	86.30 (12)	C(2)–C(1)–C(4)	106.8 (6)	C(1)–P–C(5)	113.5 (3)	C(7)–C(5)–C(8)	107.6 (6)
Cl(1)–Pt–P	177.49 (5)	C(3)–C(1)–C(4)	107.2 (6)	C(1)–P–C(9)	99.7 (3)	P–C(9)–C(10)	130.3 (5)
Cl(1)′–Pt–P	96.52 (1)	P–C(5)–C(6)	111.9 (5)	C(5)–P–C(9)	102.1 (3)	P–C(9)–C(11)	124.8 (5)
Cl(2)–Pt–P	96.11 (2)	P–C(5)–C(7)	112.4 (5)	P–C(1)–C(2)	106.0 (5)	C(10)–C(9)–C(11)	59.2 (5)
Pt–P–C(1)	111.8 (2)	P–C(5)–C(8)	106.7 (5)	P–C(1)–C(3)	113.5 (5)	C(9)–C(10)–C(11)	60.8 (5)
Pt–P–C(5)	108.9 (2)	C(6)–C(5)–C(7)	109.1 (6)	P–C(1)–C(4)	112.8 (5)	C(9)–C(11)–C(10)	60.0 (5)

[a] Primed atoms are related to corresponding unprimed atoms by a mirror plane at $z = ^1/_4$. [b] Primed atoms are related to corresponding unprimed atoms by a center of symmetry.

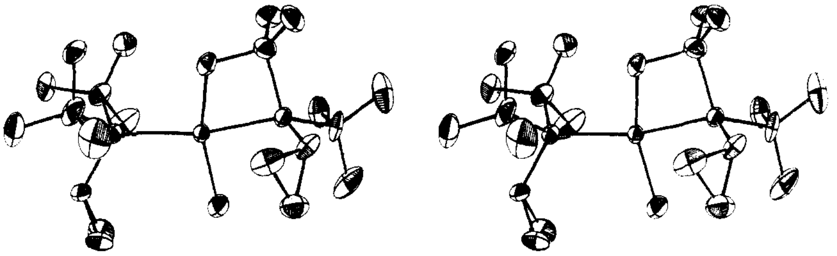

Figure 6. Stereoview of $PtCl[P(t\text{-}Bu)(CMe_2CH_2)(CHCH_2CH_2)](P(t\text{-}Bu)_2CHCH_2CH_2)$ (2).

(6) Å and Cl–C(7) = 3.384 (7) Å).[11] This may reflect the larger contribution of the *tert*-butyl groups to the phosphorus cone angle.[1f,12] The dihedral angle between cyclopropane and the $PtCl_2P_2$ unit is 98.2 (3)°. This arrangement minimizes destabilizing close contacts between the Cl atoms and the methyl hydrogen atoms of the *tert*-butyl groups. Several carbon atoms of the *tert*-butyl groups are closer to the Pt center than are atoms C(2) or C(3) of the cyclopropyl group. Hydrogen atom C(5)H(2) is closest to the Pt center (3.13 vs 3.76 Å for the next closest).

Bond distances in the cyclopropyl ring are normal: C(1)–C(2) = 1.503 (3), C(1)–C(3) = 1.526 (7), and C(2)–C(3) = 1.498 (8) Å. Some typical distances are 1.488 (7)–1.527 (6) Å in *cis*-$Pt(CHCH_2CH_2)_2(PMe_2Ph)_2$[13] and 1.510 (5) Å in cyclopropane.[14]

The Pt–P distance of 2.373 (1) Å is longer than the 2.302 (1) Å distance reported for the weighted average of 22 Pt(II)–P bond lengths in complexes with mutually *trans*-(PR_nPh_{3-n})[15] tertiary phosphines but is the same as that of 2.371 (2) Å in $PtI_2(PCy_3)_2$.[16] As in the diiodo complex, the relatively long Pt–P bond length in 1 can be attributed to steric congestion in the molecule.[17] The Pt–Cl distance, 2.301 (1) Å, is typical for *trans*-$PtCl_2(PR_3)_2$ complexes (for example, $PtCl_2(PCy_3)_2$, 2.317 (2) Å,[18] and $PtCl_2(PEt_3)_2$, 2.294 (9) Å).[15]

The P–C(*t*-Bu) bond distances in 1 (1.889 (6) and 1.899 (5) Å) are the same as those observed for the nonmetalated phosphorus ligand in 2. At 1.823 (5) Å, the P–C(cyclopropyl) distance is significantly shorter.

$PtCl[P(t\text{-}Bu)(CMe_2CH_2)(CHCH_2CH_2)](P(t\text{-}Bu)_2CHCH_2CH_2)$ (2). The structure of 2 is shown in Figure 2 with a stereoview in Figure 6. The geometry is approximately square-planar about the Pt center. The average deviation from the least-squares plane ($PtClCP_2$) is 0.030 Å. The platinaphosphacyclobutane ring is puckered; atom C(19) is below (0.276 Å) while atom C(22) is above (0.220 Å) the best plane defined by the four ring atoms. The dihedral angle between these two planes is 10.6°.

Geometric constraints on the four-atom ring prevent idealized 90° bond angles between ligands on the Pt atom. Thus, the P(2)–Pt–C(22) bond angle is only 69.0 (4)°. The Pt–P(2) bond is much shorter than the Pt–P(1) bond (2.258 (4) vs. 2.342 (4) Å). These two distortions appear to be general for platinaphosphacyclobutanes. In $[Pt(P(t\text{-}Bu)_2CMe_2CH_2]_2(\mu\text{-}NNCMeCHCMe)_2$[19] Pt–P bond lengths are 2.224 (7) and 2.207 (6) Å and the P–Pt–CH_2 bond angles are 69.8 (6) and 69.9 (7)°. In $Pt(\eta^1\text{-}Cp)(P(t\text{-}Bu)_2CMe_2CH_2)(PPh_3)$[20] the analogous bond lengths and bond angles are 2.284 Å (vs. 2.313 Å for Pt–PPh_3) and 68.1°. As noted above 2.302 (1) Å is probably a typical Pt–P bond length in complexes of this type.

The trans influence of atom C(22) on the Cl atom in 2 is not affected by the distortions of the four-atom ring: the Pt–Cl distance of 2.410 (4) Å in 2 is the same as that of 2.401 (2) Å in $PtCl(P(t\text{-}Bu)_2CHCCMeCH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$.[21a]

***trans*-$PtHCl(P(t\text{-}Bu)_2CHCH_2CH_2)_2$ (3).** Each molecule (Figure 3) is situated on a mirror plane that contains the Pt, P(1), P(2), C(1), and C(7) atoms. The disordered Cl atom is 0.67 Å from this mirror plane. The shortest intermolecular distance, 3.652 (13) Å, is between atoms Cl and C(7).

The geometry about the Pt atom is approximately square-planar. The P(1)–Pt–Cl and P(2)–Pt–Cl bond angles are 96.36 (10)° and 96.86 (10)°, respectively. The phosphine ligands fold toward the presumed positions of the disordered hydride ligand. The P(1)–Pt–P(2) bond angle of 166.6 (1)° is equal to 166.50 (5)°, the weighted average of the P–Pt–P bond angles for ten *trans*-$PtHX(PR_3)_2$ complexes containing bulky phosphine ligands.[22] The average weighted Pt–P bond distances for these complexes is 2.277 (1) Å compared with 2.301 (2) and 2.298 (2) Å for the Pt–P bond distances in 3.[22] In the present complex the cyclopropyl groups on the phosphorus atoms enclose the hydride coordination site; the dihedral angle between the cyclopropyl groups is 64.95°. A similar geometry is adopted by cyclohexyl substituents on the phosphorus atoms in *trans*-$PtHX(PCy_3)_2$ complexes.[22d] As in 1, the *t*-Bu groups in 3 are staggered about the Pt–Cl axis. Despite the more acute P(1)–Pt–P(2) bond angle, *t*-Bu methyl groups in 3 remain close to the Cl atom. Thus the shortest C–Cl distance (C(11)···Cl = 3.12 (2) Å) in 3 is comparable to its counterpart (C(20)···Cl = 3.188 (6) Å) in 1. The average of the C(11)···Cl and C(11)′···Cl distances,

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3.38 (2) Å, in **3** is longer. This distance corresponds to the second closest Cl atom to methyl carbon atom distance in **1**, 3.384 (7) Å. The Pt–P–C bond angles in **3** are much less distorted than those in **1**. The largest Pt–P–C bond angles for **1** and **3** are 121.6 (2)° and 113.7 (2)°, respectively.

Bond distances and angles in the cyclopropyl rings are normal. As in **1**, the P–C(*t*-Bu) bond distances are significantly longer than are the P–C(cyclopropyl) bond distances.

$[PtCl(P(t\text{-}Bu)_2CHCH_2CH_2)]_2(\mu\text{-}Cl)_2$ (4). In this structure (Figure 4) the binuclear molecules have crystallographically imposed symmetry $\bar{1}$ and are separated by normal van der Waals' contacts. The closest non-hydrogen intermolecular distances are C(1)···C(8) (3.608 (9) Å) and Cl(2)···C(9) (3.551 (7) Å). The intramolecular Pt–Pt distance is 3.618 (1) Å, which is identical with that observed for the closely related dimer $[Pt(P(t\text{-}Bu)_2CMe_2CH_2)]_2(\mu\text{-}Cl)_2$.[23]

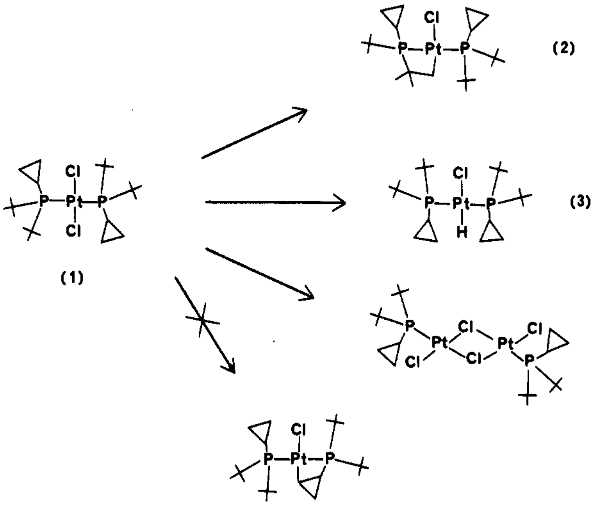
The bridging Cl atoms are asymmetrically bound to the Pt atoms (Pt–Cl(1) = 2.324 (3) and 2.435 (3) Å). This asymmetry results from the different trans influences exerted by the Cl(2) and P atoms. The same difference in Pt–(μ-Cl) bond lengths is found in $[PtCl(PPr_3)]_2(\mu\text{-}Cl)_2$.[24] The Pt–P bond distance in **4** of 2.255 (3) Å is perhaps longer than that of 2.230 (9) Å in the PPr_3 dimer, presumably because of the greater bulk of $P(t\text{-}Bu)_2CHCH_2CH_2$ relative to PPr_3. However, the distance between Pt and the terminal Cl atom (trans to μ-Cl) is the same for both compounds: 2.278 (3) Å for **4** and 2.279 (9) Å for the PPr_3 complex.[24] The P–C distances are normal; as in complexes **1**, **2**, and **3**, the P–C(cyclopropyl) bond is shorter than either P–C(*t*-Bu) bond.

The geometry about Pt is square planar; the average deviation from the best least-squares plane is 0.017 Å for $PtCl_3P$. The P atom is approximately tetrahedral with atoms C(1) and C(5) above and below this plane and atoms Pt and C(9) in it. The cyclopropane ring makes a dihedral angle of 82.2° with the $PtCl_3P$ plane. This arrangement minimizes steric interaction between atom Cl(2) and atoms C(10) and C(11); the closest cyclopropyl C···Cl distance is 3.376 (9) Å compared with 3.188 (6) Å in **1**. Hydrogen atoms H(2)C(3) and H(3)C(3) lie approximately in the $PtPCl_3$ plane while atom H(1)C(3) is 1.61 Å out of the plane. This arrangement decreases steric interaction between Cl(1) and the H atoms on atom C(3) (H(1)C(3)···Cl(1) = 3.79 Å). A similar balancing of steric forces is seen in $[PtCl(PPr_3)]_2(\mu\text{-}Cl)_2$.[24] The remaining bond lengths and angles have typical values.

Discussion

The intramolecular conversion of **1** on silica or Florisil to **2** appears to depend on the Brønsted acid nature of the supports:[25,26] supports pretreated with triethylamine do not catalyze the reaction. Product **3** is formed through an apparent reduction process. Florisil is a mixed oxide whose main constituents are silica and magnesia in a ratio of 5:1.[26a,c,d] MgO surfaces induce reductive processes,[27] and this type of reaction may explain the formation of product **3**. The complexity of surface chemistry coupled with limited experimental data do not allow us to reach further conclusions.

Scheme II



Complexes similar to **1** undergo metalation reactions on alumina. As opposed to Florisil, alumina shows both Lewis acid and Lewis base properties.[25] The complex $PdClCp(P(O\text{-}o\text{-}Tol)_3)$ in CH_2Cl_2/pentane solution reacts with Al_2O_3 (on passage through a chromatographic column) to form the ortho-metalated complex $PdCp(P(O\text{-}o\text{-}Tol)_2(OCC(CH_3)(CH)_3C)$.[28] However, no metalation of $PdClCp(P(t\text{-}Bu)_2Ph)$ occurs on Al_2O_3, although the related complex $PdCl_2P(t\text{-}Bu)_2Ph)_2$ undergoes facile metalation of a *t*-Bu group when combined with AgOAc in chloroform.[1e] This reaction proceeds through an acetate intermediate.[1e]

Similarly, the reaction of **1** in acetic acid to form **2** may proceed via an acetate intermediate in view of the nearly quantitative reaction of **1** with TlOAc in boiling ethanol to give **2**. Formation of the hydride competes with formation of **2** in refluxing acetic acid. However, the hydride is not an intermediate in the reaction: when the hydride **3** is heated at reflux in acetic acid for up to 48 h, it is recovered unchanged.

The complexes $PtHX(P(t\text{-}Bu)_3)_2$ eliminate H_2 to form $PtX(P(t\text{-}Bu)_2CMe_2CH_2)(P(t\text{-}Bu)_3)$.[29b] Steric factors and choice of solvent influence the intramolecular metalation of $P(t\text{-}Bu)_3$ in these complexes. Metalation occurs easily in the order X = I > Br > Cl in benzene solution and is accelerated by trace amounts of acid or alcohol. For X = H or CN metalation does not occur.[29a] Thus **3** differs markedly from $PtHX(P(t\text{-}Bu)_3)_2$ (X = Cl, Br, I). Perhaps **3** fails to undergo metalation because it is a relatively uncongested molecule.

The complexes $PtX(P(t\text{-}Bu)_2CMe_2CH_2)(P(t\text{-}Bu)_3)$ (X = I, Br, Cl) lose coordinated $P(t\text{-}Bu)_3$ to afford the halo-bridged dinuclear complexes $[Pt(P(t\text{-}Bu)_2CMe_2CH_2)]_2(\mu\text{-}X)_2$.[29] Formation of such dimers is dependent on solvent[29a] and halide ion.[29b] As for metalation of $PtHX(P(t\text{-}Bu)_3)_2$

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complexes, the rate of dimer formation increases in going from X = Cl to I, presumably for steric reasons.[29b] The dimers form more quickly in ethanol than in noncoordinating solvents, such as dichloromethane or benzene.[29b] A similar loss of $\mathrm{P}(t\text{-Bu})_2(\overline{\mathrm{CHCH_2CH_2}})$ from 1 in toluene/acetic acid or dioxane must lead to formation of 4. Oxidation of free phosphine to phosphine oxide hinders the reverse reaction.[29a]

Under various conditions complex 1 forms the less sterically congested complexes 2, 3, and 4. However, complex 1 fails to form an internally metalated σ-cyclopropyl complex even though such a complex would be less sterically congested than 1 (Scheme II).

We have previously reported the intramolecular activation of the cyclopropyl ring of the phosphine ligand by the Pt center in *trans*-$\mathrm{PtCl_2(P(}t\text{-Bu)_2CH_2\overline{CHCH_2CH_2})_2}$ to form a σ-allyl complex.[21a] In this complex the cyclopropyl group is accessible to the Pt atom. In the structures of the present complexes 1–4, the cyclopropyl rings are well removed from the Pt center. Thus, geometric constraints may prevent precoordination of the cyclopropane group to the Pt atom that would encourage cleavage of the strong cyclopropyl C–H bond. If no electronic interactions occur between Pt and cyclopropane in 1 in solution, then a *t*-Bu C–H bond (91.0 kcal/mol) should be more reactive than a cyclopropyl C–H bond (~101 kcal/mol),[30] in agreement with the reaction chemistry found here. Whether activation of this type is thermodynamically or kinetically controlled is not known.[1b]

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Registry No. 1, 107202-80-2; 2, 107202-81-3; 3, 107202-82-4; 4, 107202-83-5; K_2PtCl_4, 10025-99-7; di-*tert*-butylcyclopropylphosphine, 107245-36-3; cyclopropyl bromide, 4333-56-6; di-*tert*-butylchlorophosphine, 13716-10-4.

Supplementary Material Available: Anisotropic thermal parameters (Table IV) and hydrogen atom positions (Table V) (10 pages); structure amplitudes (Table VI) (68 pages). Ordering information is given on any current masthead page.

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Photorearrangements of CuCl Complexes of 1,5,9-Cyclododecatrienes: Wavelength Dependence

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Irradiation of the CuCl complexes of the cis–trans isomers of 1,5,9-cyclododecatriene (CDT) in the presence of an excess of these ligands at wavelength >290 nm caused sequential interconversions of all the possible isomers: *ttt*-CDT ⇄ *ctt*-CDT ⇌ *cct*-CDT ⇄ *ccc*-CDT. Irradiation of similar solutions at wavelength >240 nm induced irreversible rearrangement of CDT to 9-vinyl-*cis,cis*-1,5-cyclodecadiene (VCDD) in addition to the reversible cis–trans photoisomerizations. The rearrangement was most likely caused by photoexcitation of CuCl·*ccc*-CDT with the light energy corresponding to 240–290 nm, and its mechanisms are proposed.

Introduction

Chemical reactions caused by sensitized, and less frequently direct, excitations of nonconjugated cyclic polyenes have attracted extensive investigations and are known to involve cis–trans isomerization, cycloaddition, and other assorted rearrangements.[1] Nonconjugated polyenes are known to form π-complexes with copper(I) salts;[2,3] the structure and bonding of some of these Cu(I) complexes are well-defined.[2] Owing to the tendency of coordination, photocatalyzed cycloadditions and rearrangements of such polyenes in the presence of Cu(I) salts have been extensively investigated;[4,8] an excellent review on these subjects has been published.[14] Recently we have provided evidence of the isomerization and cycloaddition of 1,5-cyclooctadienes (1,5-COD) complexed with copper(I) salts and, further, a wavelength dependence of these photoreactions in the Cu(I) complexes.[8] This work led us to examine similar CuCl complexes of readily available *trans,trans,trans*-1,5,9-cyclododecatriene (*ttt*-CDT) and *cis,trans,trans*-1,5,9-cyclododecatriene (*ctt*-CDT); their photorearrangements are described here.

Sensitized photorearrangements of CDT's have been investigated occasionally in the past.[9-11] The major pathway is the cis–trans isomerization of the olefinic bonds to give a mixture of all possible isomers, e.g., photolysis of *ctt*-CDT to *ttt*-CDT, *cct*-CDT, and *ccc*-CDT, although the disagreement on the presence of the last isomer has

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