Processing Center of Kyoto University. We also express our appreciation to Toshiba Silicon Co., Ltd., and Shin-etsu Chemical Co., Ltd., for a gift of organochlorosilanes.

Registry No. 1, 61851-11-4; **2**, 69307-60-4; **3a**, 63261-73-4; **3b**, 65568-79-8; **4**, 83077-05-8; **5**, 85443-38-5; **6a**, 83077-06-9; **6b**, 85452-99-9; **7**, 65568-82-3; **8**, 83077-07-0; **9**, 85443-39-6; **10**, 79628-11-8; **11a**, 79628-07-2; **11b**, 85443-41-0; **12**, 81142-39-4; **13**, 22843-39-6; **14**, 79628-12-9; **15a**, 79628-08-3; **15b**, 85443-42-1; **16**, 83095-62-9; **17**, 79628-13-0; **18**, 79628-09-4; $PhC{\equiv}CSiMe_2Bu\text{-}t$, 85443-40-9; $PhC{\equiv}CSiMe_3$, 2170-06-1; $HMe_iSiSiMe_2H$, 814-98-2; $PhC{\equiv}CSiMe_2Et$, 4131-45-7; $PhC{\equiv}CSiMe_2Ph$, 79628-15-2.

Synthesis of Di-*tert*-butyl(cyclopropylmethyl)phosphine, *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$, and $\overline{PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$. The Intramolecular Activation of C–C and C–H Bonds of a Cyclopropyl Phosphine

Wiley J. Youngs and James A. Ibers*

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

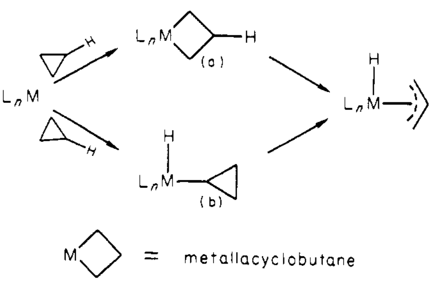
Received December 28, 1982

The synthesis of the cyclopropyl phosphine $(t\text{-}Bu)_2PCH_2\overline{CHCH_2CH_2}$ (**1**) is described. When this new phosphine is combined with dichlorobis(benzonitrile)platinum(II) in toluene, the resulting product is *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$ (**2**). In refluxing 2-methoxyethanol, compound **2** undergoes an intramolecular cyclometalation reaction in which both a C–C and a C–H bond of one of the cyclopropane rings are cleaved to form the chelating σ-allyl complex $\overline{PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$ (**3**). Complex **3** crystallizes in the monoclinic space group C_{2h}^5—$P2_1/c$, with four formula units in a cell of dimensions a = 11.847 (5) Å, b = 15.451 (7) Å, c = 16.802 (8) Å, β = 116.70 (2)°, and V = 2747 Å^3. The final agreement indices for 4630 reflections having $F_o^2 > 3\sigma(F_o^2)$ are $R(F)$ = 0.044 and $R_w(F)$ = 0.047 (253 variables). Bond lengths in the five-atom chelate ring $\overline{Pt—P—C{=}C—C}$ are Pt—P = 2.279 (2) Å, P—C = 1.824 (8) Å, C=C = 1.386 (11) Å, C—C = 1.432 (10) Å, and C—Pt = 2.018 (6) Å. Possible mechanims for the formation of **3** involve either initial C–H or C–C bond activation of the cyclopropane ring.

The activation of C–H and C–C bonds, especially in saturated systems, is of considerable interest.[1] Recent results have shown that alkane C–H bonds can be activated intermolecularly by selected metal complexes.[2-4] A more extensive literature clearly demonstrates that intramolecular C–H bond activation by a transition-metal complex occurs with relative ease, particularly when the C–H group is part of a phosphine.[5] This intramolecular C–H bond activation is very sensitive to the phosphine (bulky phosphines promote metalation) and the metal (group 8 metals are very reactive).[5a]

Intermolecular activation of C–C bonds has also been observed in strained ring compounds.[6] One example of C–C bond activation is the formation of metallacyclobutanes from the interaction of cyclopropanes with transition-metal complexes.[6b] The formation of allyl hydrides from the interaction of cyclopropanes with transition-metal complexes also occurs and may proceed through initial C–C bond activation (Scheme Ia), followed by hydride migration,[6c] or may arise from initial C–H bond activation with the intermediacy of a σ-bound cyclopropane complex (Scheme Ib).

Scheme I



Our general interest in C–H and C–C bond activation has led us to investigate the interaction with transition-

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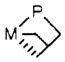
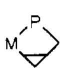
metal complexes of phosphines that contain appended cyclopropyl substituents. With cyclopropyl phosphines one might expect C–C bond activation to produce chelating metallacyclobutanes



or C–H bond activation to produce chelating σ-bound cyclopropanes



either as intermediates or as isolable products. The metallacyclobutanes and the σ-bound cyclopropanes could react further to produce η^1 or η^3 allylic systems.

We have reported the reaction of di-*tert*-butyl(cyclopropylmethyl)phosphine with Ir(I) to afford σ-bound cyclopropanes[7] and with Pd(II) to afford $[PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2]_2$.[8] Here we report the synthesis of di-*tert*-butyl(cyclopropylmethyl)phosphine, its reaction with Pt(II) compounds to afford *trans*-bis(di-*tert*-butyl(cyclopropylmethyl)phosphine)dichloroplatinum(II), and the intramolecular metalation of this compound to afford the chelating σ-allyl complex $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CCH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$. A preliminary account of some of these results has appeared.[7]

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of prepurified nitrogen with the use of standard Schlenk-line techniques.[9] Di-*tert*-butylphosphine was prepared, as described previously,[10] from di-*tert*-butylchlorophosphine (Strem Chemicals Inc.). Platinum metal salts were used as received from Johnson Matthey, Inc. Solvents were purified by standard methods.

Elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL, or by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra were obtained with a Perkin-Elmer 283 spectrometer from samples prepared as mulls in Nujol or Fluorolube and pressed between KBr, CsBr, or CsI windows. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on either a JEOL FX90Q or a JNM-FX 270 FTNMR spectrometer. ^{31}P positive chemical shifts are downfield from 85% H_3PO_4.

Synthesis of Di-*tert*-butyl(cyclopropylmethyl)phosphine. One equivalent of di-*tert*-butylphosphine[10] was added to a solution of cyclopropylmethyl bromide (5 g) in isobutyl methyl ketone, and the mixture was refluxed for 5.5 h. A white precipitate of the phosphonium hydrobromide formed. Solvent was removed under vacuum, and the precipitate was washed with hexane. Anal. Calcd for $C_{12}H_{26}BrP$: C, 51.25; H, 9.32; Br 28.41; P, 11.01. Found: C, 51.45; H, 9.03; Br, 27.58; P, 11.07.

The phosphonium hydrobromide was dissolved in a mixture of 25 mL of water and 20 mL of diethyl ether. Saturated sodium hydroxide solution was added dropwise, until no further reaction was evident. Removal of solvent and distillation (bp 60 °C (1 mm)) gave the product in 95% yield (isolated): IR 3078 cm^{-1}; ^1H NMR (C_6D_6) δ 1.3 (m, P-CH$_2$), 0.8 (m, cyclopropyl methine), 0.53 (m, cyclopropyl methylene), 0.11 (m, cyclopropyl methylene), 1.1 (d, J = 10.6 Hz, CCH$_3$); ^{13}C NMR (C_6D_6) δ 30.8 (d, J = 20.8 Hz), 29.7 (d, J = 13.4 Hz), 26.8 (d, J = 19.5 Hz), 11.2 (d, J = 25.6 Hz), 7.2 (d, J = 8.5 Hz); ^{31}P NMR (C_6D_6) δ 28.5 (s).

Table I. Crystallographic Details for $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$

formula	$C_{24}H_{49}ClP_2Pt$
formula mass, amu	630.15
space group	C^5_{2h}–$P2_1/c$
a, Å	11.847 (5)
b, Å	15.451 (7)
c, Å	16.802 (8)
β, deg	116.70 (2)
vol, Å^3	2747
Z	4
ρ_{calcd}, g/cm^3	1.523
cryst dimensions, mm	0.23 × 0.43 × 0.43
cryst shape	8-sided; faces {001}, $(0\bar{1}0)$, {100}, $(10\bar{2})$, (110), $(\bar{1}10)$
cryst vol, mm^3	0.0275
radiation	Mo Kα (λ(Mo Kα_1) = 0.709 30 Å) from monochromator
linear abs coeff, cm^{-1}	53.79
transmission factors	0.174–0.410
temp, °C	–155[a]
takeoff angle	3.6°
scan mode	θ–2θ
scan speed	2° in 2θ/min
scan range	1.0° below Kα_1 to 1.0° above Kα_2
background counts	10 s total with rescan option[b]
2θ limits, deg	3.0–54.0
unique data	6020
unique data with $F_0^2 > 3\sigma(F_0^2)$	4630
final no. of variables	136
$R(F^2)$	0.066
$R_w(F^2)$	0.094
$R(F)$ ($F_0^2 > 3\sigma(F_0^2)$)	0.044
$R_w(F)$ ($F_0^2 > 3\sigma(F_0^2)$)	0.047
error in observn of unit weight, e^2	1.64

[a] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974.
[b] The diffractometer was run under the Vanderbilt disk oriented system (Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570).

Synthesis of *trans*-Bis(di-*tert*-butyl(cyclpropylmethyl)phosphine)dichloroplatinum(II), *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)_2$. Dichlorobis(benzonitrile)platinum(II)[11] (0.41 g) and di-*tert*-butyl(cyclopropylmethyl)phosphine (0.50 g) were stirred in toluene for 24 h. Recrystallization from hexane gave the product in ~95% yield: mp 142 °C; IR 3050, 328 cm^{-1}; ^1H NMR (C_7D_8) δ 2.07 (m, P-CH$_2$), 1.37 (m, cyclopropyl methine), 0.57 (m, cyclopropyl methylene), 0.36 (m, cyclopropyl methylene), 1.52 (t, J = 6.4 Hz, CCH$_3$); ^{13}C NMR (C_7D_8) δ 36.2 (t, J = 10.7 Hz), 30.9 (s), 8.8, 8.7; ^{31}P NMR (C_7D_8) δ 30.8 (J_{Pt-P} = 2470.7 Hz). Anal. Calcd for $C_{24}H_{50}Cl_2P_2Pt$: C, 43.24; H, 7.56; Cl, 10.64. Found: C, 43.66; H, 7.58; Cl, 10.11.

Synthesis of $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$. *trans*-Bis(di-*tert*-butyl(cyclopropylmethyl)phosphine)dichloroplatinum(II) (0.5 g) was heated under reflux in 2-methoxyethanol (10 mL) for 2 h. A color change from yellow to white occurred. The solvent was removed and the product recrystallized from hexane in ~50% yield: IR 1615, 257 cm^{-1}; ^1H NMR (C_6D_6) δ 5.33 (m, vinyl H), 2.78 (m, Pt-CH$_2$), 2.07 (s, allylic CH$_3$), 1.97 (s, P-CH$_2$), 1.41 (distorted t, C(CH$_3$)$_3$, J = 13.6 Hz), 0.35 + 0.60 (m, cyclopropyl methylene); ^{31}P NMR (C_7D_8) δ 72.41 (J_{Pt-P} = 2992 Hz), 45.28 (J_{Pt-P} = 2834 Hz) (J_{P-P} = 403.4 Hz), 69.30 (J_{Pt-P} = 3081 Hz), 43.00 (J_{Pt-P} = 2776 Hz) (J_{P-P} = 401.7 Hz). Anal. Calcd for $C_{24}H_{49}ClP_2Pt$: C, 45.75; H, 7.84; Cl, 5.63. Found: C, 45.08; H, 7.52; Cl, 5.69.

X-ray Study of $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$. Crystals suitable for diffraction study were obtained upon recrystallization of the material from hexane. Preliminary film work revealed the crystal to be monoclinic with

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Table II. Positional Parameters[a] for the Non-Hydrogen Atoms of

$\mathrm{PtCl(P(}t\mathrm{\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(}t\mathrm{\text{-}Bu)_2CH_2CHCH_2CH_2)}$

atom	*x*	*y*	*z*
Pt	−0.29738 (2)	0.35280 (1)	0.25520 (2)
Cl	−0.3136 (2)	0.2201 (1)	0.3237 (2)
P(1)	−0.4867 (2)	0.4029 (1)	0.2407 (1)
P(2)	−0.0994 (2)	0.3191 (1)	0.2654 (1)
C(1)	−0.5141 (8)	0.4997 (6)	0.1724 (8)
C(2)	−0.4085 (8)	0.5210 (4)	0.1612 (5)
C(3)	−0.2990 (7)	0.4665 (4)	0.1956 (5)
C(4)	−0.4133 (10)	0.6000 (4)	0.1077 (5)
C(5)	−0.6265 (7)	0.3331 (5)	0.1741 (5)
C(6)	−0.6433 (9)	0.2607 (6)	0.2252 (7)
C(7)	−0.7483 (8)	0.3820 (8)	0.1348 (9)
C(8)	−0.599 (1)	0.294 (1)	0.0998 (7)
C(9)	−0.4839 (8)	0.4400 (6)	0.3474 (6)
C(10)	−0.590 (1)	0.4905 (6)	0.3370 (8)
C(11)	−0.462 (1)	0.3664 (8)	0.4112 (6)
C(12)	−0.372 (1)	0.507 (1)	0.384 (1)
C(13)	−0.0511 (6)	0.3817 (4)	0.1922 (4)
C(14)	−0.1231 (9)	0.3688 (6)	0.0923 (6)
C(15)	−0.118 (1)	0.4289 (7)	0.0303 (6)
C(16)	−0.229 (2)	0.414 (2)	0.0317 (9)
C(17)	0.0265 (6)	0.3534 (4)	0.3785 (4)
C(18)	−0.0035 (8)	0.3159 (5)	0.4523 (5)
C(19)	0.1595 (7)	0.3305 (5)	0.3963 (5)
C(20)	0.0184 (8)	0.4525 (4)	0.3830 (5)
C(21)	−0.0714 (7)	0.2031 (4)	0.2408 (5)
C(22)	−0.0453 (8)	0.1433 (4)	0.3173 (6)
C(23)	0.0352 (7)	0.1951 (5)	0.2142 (6)
C(24)	−0.1953 (7)	0.1743 (4)	0.1624 (5)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) strongly indicative of the centrosymmetric space group C_{2h}^5—$P2_1/c$.

Lattice parameters were obtained and intensity data collected on a Picker FACS-1 diffractometer in a manner previously described.[12] Details relevant to the present structure appear in Table I.

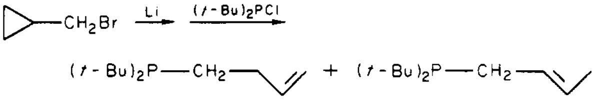
The positions of the Pt, Cl, and two P atoms were found by direct methods.[13] All remaining non-hydrogen atoms were obtained from a series of electron density syntheses. After two cycles of isotropic and one cycle of anisotropic least-squares refinement, some but not all hydrogen atoms were apparent in a difference electron density map. All hydrogen atoms whose approximate positions could be obtained from the electron density map were placed in idealized positions (C–H = 0.95 Å, tetrahedral or trigonal angles) with idealized thermal parameters (B = 1.0 Å^2 greater than the equivalent B of the atom to which it is attached) and held fixed during subsequent refinement.

Initial cycles of refinement were based on F and involved only those reflections having $F_o^2 > 3\sigma(F_o^2)$. Final refinements were carried out on F_o^2 with the use of all unique data including those with $F_o^2 < 0$. The final cycle of anisotropic refinement converged to values of $R(F^2) = 0.066$ and $R_w(F^2) = 0.094$ for 6020 observations and 253 variables. The corresponding agreement indices on F for those 4630 reflections for which $F_o^2 > 3\sigma(F_o^2)$ are 0.044 and 0.047, respectively. Table II presents the final positional parameters, Table III[14] the thermal parameters, Table IV[14] the hydrogen atom positions, and Table V[14] a listing of $10|F_o|$vs. $10|F_c|$.

Results and Discussion

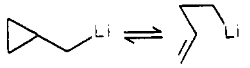
Synthesis of Di-*tert*-butyl(cyclopropylmethyl)phosphine.

Two of the usual approaches[15] were used unsuccesfully in initial attempts to synthesize the phosphine. When one reacts 2 equiv of lithium metal with cyclopropylmethyl bromide and combines the resulting product with di-*tert*-butylchlorophosphine, a mixture of alkene phosphines is obtained (eq 1). These products



(1)

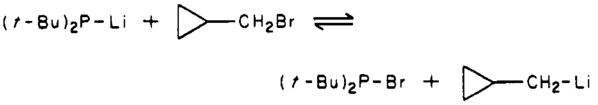
presumably result form a cyclopropyl ring opening reaction for the (cyclopropylmethyl)lithium[16a] compound to produce the (alkene)lithium reagent.[16b,c]



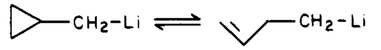
In a second approach we combined di-*tert*-butyllithium phosphide with cyclopropylmethyl bromide. This reaction afforded an approximately 50% yield of the desired phosphine, 25% yield of alkene phosphines, and 25% yield of tetra-*tert*-butyldiphosphine. Issleib et al.[17] had previously observed that di-*tert*-butyllithium phosphide undergoes lithium–halogen exchange with various alkyl halides to produce di-*tert*-butylhalophosphine and the alkyllithium reagent (eq 2). With cyclopropylmethyl

$$(t\text{-Bu}_2)\text{P–Li} + \text{R–X} \rightleftharpoons (t\text{-Bu})_2\text{P–X} + \text{R–Li} \qquad (2)$$

bromide and di-*tert*-butyllithium phosphide lithium–halogen exchange would produce di-*tert*-butylbromophosphine and (cyclopropylmethyl)lithium (eq 3) which could then undergo a ring opening (eq 4).

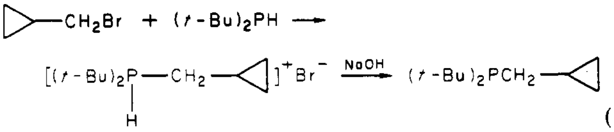


(3)



(4)

The following route proved to be successful. When a mixture of di-*tert*-butylphosphine[10] and cyclopropylmethyl bromide is heated in refluxing isobutyl methyl ketone, the formation of the phosphonium hydrobromide salt is observed. This salt is converted to the (cyclopropylmethyl)phosphine in virtually quantitative yield by the addition of a solution of NaOH (eq 5).



(5)

The ^{31}P{^{1}H} NMR spectrum of the final product consists of a singlet at 28.5 ppm. The ^{1}H NMR spectrum shows a multiplet at δ 1.3 for the methylene group between the phosphorus atom and the cyclopropane ring. Multiplets at δ 0.8, 0.53, and 0.11 are assigned to the cyclopropyl protons. The resonance assigned to the *tert*-butyl protons is a doublet (J = 10.6 Hz) at δ 1.1. The IR spectrum shows

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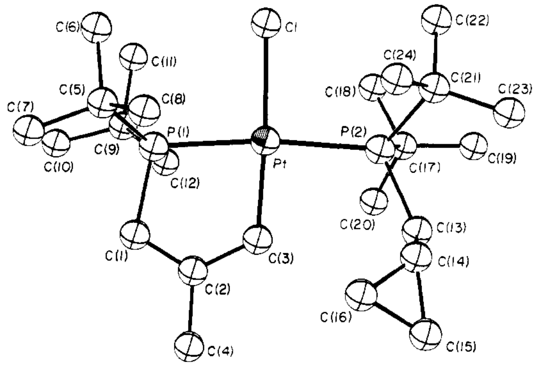
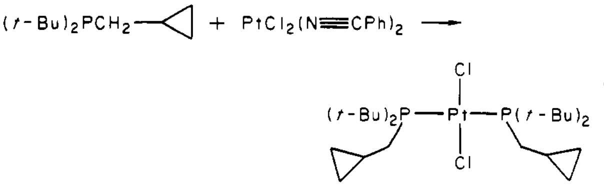


Figure 1. Drawing of the $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$ molecule. The atoms have been drawn as spheres with arbitrary radii.

the cyclopropyl C-H stretching band at 3078 cm^{-1}.

Synthesis of *trans*-Bis(di-*tert*-butyl(cyclopropylmethyl)phosphine)dichloroplatinum(II). Di-*tert*-butyl(cyclopropylmethyl)phosphine reacts with $PtCl_2(N{\equiv}CPh)_2$ in benzene to produce the desired product in high yield (eq 6). The occurrence of a triplet pattern in the ^1H NMR spectrum, δ 1.52 (t, J = 6.4 Hz), is typical of trans *tert*-butyl phosphines.[17] The ^{31}P NMR spectrum shows the expected peak at 30.8 ppm with its ^{195}Pt satellites ($J_{Pt\text{-}P}$ = 2470.7 Hz). Similarly the observation of the one band at 328 cm^{-1} in the region expected for ν(Pt–Cl) vibrations is characteristic of a trans Cl–Pt–Cl group.[18] Examination of the cyclopropane region of the proton NMR spectrum shows clearly that the cyclopropane rings are intact.



(6)

Synthesis and Characterization of $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$.

When *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)_2$ is heated in refluxing 2-methoxyethanol for 2 h, a color change from yellow to white occurs. Although elemental analysis and spectroscopic study of the product suggested that cyclometalation and loss of HCl had occurred, unambiguous characterization proved impossible. Accordingly a crystal structure analysis was carried out. The product is $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$. Its molecular structure consists of a slightly distorted square-planar Pt(II) center surrounded by a chloro and a phosphine ligand and by a cyclometalated phosphine ligand. The $Pt(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)$ portion of this molecule is very similar to the analogous Pd portion in $[PdCl(P(t\text{-}Bu_2)CH{=}C(CH_3)CH_2)]_2$.[8]

Figure 1 shows the labeling scheme. Figure 2 is a stereodrawing of the molecule, while Figure 3 displays the packing. Metrical details are given in Table VI. All intermolecular distances are normal, the shortest between nonhydrogen atoms being 3.58 (1) Å.

The coordination about the Pt atom is essentially planar, with the average deviation from the best weighted least-squares plane being 0.017 Å. The largest deviation is that of carbon atom C(3) of the cyclometalated phosphine (0.026 Å). The cyclometalated phosphine causes significant distortion from the idealized 90° for angles around the Pt. The relevant angles are P(1)–Pt–C(3) = 82.05 (20)°, P(2)–Pt–C(3) = 90.91 (20)°, P(1)–Pt–Cl = 93.12 (6)°, P(2)–Pt–Cl = 93.94 (6)°. The angles Cl–Pt–C(3) and P(1)–Pt–P(2) differ significantly from the usual 180° for trans ligands, being 172.12 (20)° and 172.79 (6)°, respectively. The difference in the Pt–P(1) and Pt–P(2) bond distances, 2.279 (2) and 2.333 (2) Å, respectively, arise from the chelating nature of the phosphine of which atom P(1) is a part. Distorted metal centers are typical of cyclometalated complexes.[19] The long Pt–Cl distance of 2.401 (2) Å is consistent with the large trans influence of the allyl moiety observed in $[PdClP(t\text{-}Bu)_2CH{=}C(CH_3)CH_2]_2$[8] and in *trans*-$PtCl(\eta^1\text{-}C_3H_5)(PEt_3)_2$.[20]

The Pt–C(3) distance of 2.018 (6) Å is typical of Pt(II)–C(sp^3) bonds (cf. 2.079 (14) Å in *trans*-$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$ and 2.07 (1) Å in *trans*-$PtClMe(PMePh_2)_2$[21]) and is slightly shorter than the Pt–σ-allyl bond distance of 2.090 (4) Å observed in *trans*-$PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2$.[20] The Pt–C(3) distance is comparable with the Pd–C(3) distance of 2.016 (3) Å observed in the closely related palladium dimer $[PdClP(t\text{-}Bu)_2CH{=}C(CH_3)CH_2]_2$.[8] The C(1)–C(2) distance (1.386 (11) Å), formally the double bond of the σ-allyl system, when compared with the double bond in *trans*-$PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2$ (1.311 (9) Å) and $[PdClP(t\text{-}Bu)_2CH{=}C(CH_3)CH_2]_2$ (1.328 (5) Å) may be slightly longer. Consistent with this possible lengthening is the single C–C bond of the allyl system (C(2)–C(3) = 1.432 (10) Å) as compared with the C–C bond in *trans*-$PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2$ (1.487 (7) Å) and $[PdClP(t\text{-}Bu)_2CH{=}C(CH_3)CH_2]_2$ (1.493 (5) Å). Methyl group C(4) is bound to atom C(2) with an sp^2–sp^3 bond of 1.502 (9) Å compared with 1.505 (5) Å in $[PdClP(t\text{-}Bu)_2CH{=}C(CH_3)CH_2]_2$.

In the di-*tert*-butyl(cyclopropylmethyl)phosphine group the CH_2 group connecting the phosphorus atom with the cyclopropane is 1.845 (6) Å (P(2)–C(13)) from the phosphorus atom and 1.516 (11) Å (C(13)–C(14)) from the cyclopropane group. Bond distances in the cyclopropane are C(14)–C(15) = 1.418 (12) Å, C(14–C(16) = 1.395 (17) Å, and C(15)–C(16) = 1.352 (20) Å, compared with 1.488 (7)–1.527 (6) Å in *cis*-$Pt(CHCH_2CH_2)_2(PMe_2Ph)_2$.[22] Clearly, the C–C bonds of the cyclopropyl group in the present structure are foreshortened, and their standard deviations are grossly underestimated. The thermal parameters on atoms C(14), C(15), and C(16) are very high for a data set collected at −155 °C (equivalent isotropic thermal parameters are 6.0, 8.8, and 19.6 $Å^2$, respectively). We presume that there is some disorder associated with the cyclopropyl ring but no clear model for such disorder could be derived from difference electron density maps.

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Figure 2. Stereoscopic view of the $\overline{\mathrm{PtCl(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH_2}\overline{\mathrm{CHCH_2C}}\mathrm{H_2)}$ molecule. Thermal ellipsoids have been drawn at the 50% probability level.

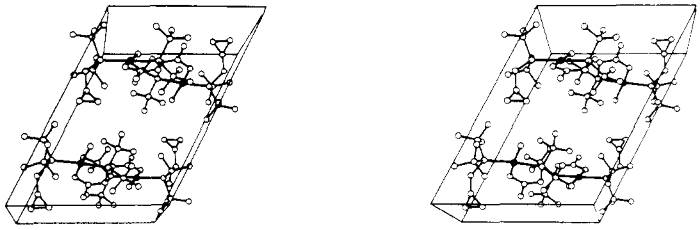

Figure 3. Stereoscopic packing diagram for $\overline{\mathrm{PtCl(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH_2}\overline{\mathrm{CHCH_2C}}\mathrm{H_2)}$. The atoms have been drawn as spheres with arbitrary radii.

Table VI. Distances (Å) and Angles (deg) in $\overline{\mathrm{PtCl(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH_2}\overline{\mathrm{CHCH_2C}}\mathrm{H_2)}$

Bond Distances

Pt-Cl	2.401 (2)	C(5)-C(6)	1.476 (11)	C(14)-C(15)	1.418 (12)
Pt-P(1)	2.299 (2)	C(5)-C(7)	1.495 (12)	C(14)-C(16)	1.395 (17)
Pt-P(2)	2.333 (2)	C(5)-C(8)	1.546 (14)	C(15)-C(16)	1.352 (20)
Pt-C(3)	2.018 (6)	C(9)-C(10)	1.502 (11)	C(17)-C(18)	1.548 (10)
P(1)-C(1)	1.824 (8)	C(9)-C(11)	1.504 (14)	C(17)-C(19)	1.508 (10)
P(1)-C(5)	1.869 (8)	C(9)-C(12)	1.567 (14)	C(17)-C(20)	1.538 (9)
P(1)-C(9)	1.868 (9)	P(2)-C(13)	1.845 (6)	C(21)-C(22)	1.498 (10)
C(1)-C(2)	1.386 (11)	P(2)-C(17)	1.889 (7)	C(21)-C(23)	1.521 (9)
C(2)-C(3)	1.432 (10)	P(2)-C(21)	1.902 (6)	C(21)-C(24)	1.533 (10)
C(2)-C(4)	1.502 (9)	C(13)-C(14)	1.516 (11)		

Bond Angles

Cl-Pt-P(1)	93.12 (6)	C(6)-C(5)-C(7)	106.5 (7)	C(13)-C(14)-C(16)	128.2 (10)
Cl-Pt-P(2)	93.94 (6)	C(6)-C(5)-C(8)	107.6 (9)	C(15)-C(14)-C(16)	57.4 (10)
Cl-Pt-C(3)	172.12 (20)	C(7)-C(5)-C(8)	110.6 (9)	C(14)-C(15)-C(16)	60.4 (9)
P(1)-Pt-P(2)	172.79 (6)	P(1)-C(9)-C(10)	114.9 (7)	C(14)-C(16)-C(15)	62.1 (9)
P(1)-Pt-C(3)	82.05 (20)	P(1)-C(9)-C(11)	112.1 (6)	P(2)-C(17)-C(18)	109.8 (4)
P(2)-Pt-C(3)	90.91 (20)	P(1)-C(9)-C(12)	103.2 (7)	P(2)-C(17)-C(19)	114.6 (5)
Pt-P(1)-C(1)	103.6 (3)	C(10)-C(9)-C(11)	109.4 (8)	P(2)-C(17)-C(20)	106.8 (5)
Pt-P(1)-C(5)	115.7 (3)	C(10)-C(9)-C(12)	105.1 (9)	C(18)-C(17)-C(19)	110.4 (6)
Pt-P(1)-C(9)	114.1 (3)	C(11)-C(9)-C(12)	111.9 (11)	C(18)-C(17)-C(20)	107.0 (6)
P(1)-C(1)-C(2)	111.3 (6)	Pt-P(2)-C(13)	115.9 (2)	C(19)-C(17)-C(20)	107.8 (6)
C(1)-C(2)-C(3)	121.1 (6)	Pt-P(2)-C(17)	109.0 (2)	P(2)-C(21)-C(22)	112.5 (5)
C(1)-C(2)-C(4)	118.7 (8)	Pt-P(2)-C(21)	117.5 (2)	P(2)-C(21)-C(23)	112.9 (5)
C(3)-C(2)-C(4)	120.1 (8)	C(13)-P(2)-C(17)	100.5 (3)	P(2)-C(21)-C(24)	105.5 (5)
Pt-C(3)-C(2)	121.1 (5)	C(13)-P(2)-C(21)	102.2 (3)	C(22)-C(21)-C(23)	108.9 (6)
P(1)-C(5)-C(6)	113.8 (6)	C(17)-P(2)-C(21)	110.3 (3)	C(22)-C(21)-C(24)	107.9 (6)
P(1)-C(5)-C(7)	113.1 (7)	P(2)-C(13)-C(14)	118.7 (5)	C(23)-C(21)-C(24)	109.0 (6)
P(1)-C(5)-C(8)	105.1 (6)	C(13)-C(14)-C(15)	122.6 (8)		

In the final difference electron density map the five largest peaks are near the platinum atom with the sixth peak near atom C(16). Distances and angles in the *tert*-butyl groups of both phosphines are slightly distorted from normal. This may be related to the disorder of the cyclopropyl ring.

The ^{1}H NMR spectrum of $\overline{\mathrm{PtCl(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH_2}\overline{\mathrm{CHCH_2C}}\mathrm{H_2)}$ shows small multiples at δ 5.33 (vinyl H) and δ 2.78, a singlet at δ 2.07, a distorted triplet for the *tert*-butyl groups, δ 1.413 (J = 13.6 Hz), and three multiplets in the cyclopropane region. Compared with the IR spectrum of the starting material, the IR spectrum shows a new band at 1615 cm^{-1}, which is characteristic of ν(C=C), loss of the band at 328 cm^{-1}, and gain of a band at 257 cm^{-1}, which is typical of a chloro ligand trans to carbon in platinum(II) complexes.[18]

The ^{31}P NMR spectrum of $\overline{\mathrm{PtCl(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)(P}(t\text{-}\mathrm{Bu})_2\mathrm{CH_2}\overline{\mathrm{CHCH_2C}}\mathrm{H_2)}$ is more complex than we would expect from the crystal structure. Four different phosphorus signals are observed in this spectrum; these are split into doublets owing to ^2J(P-P) coupling, with satellites because of coupling with the ^{195}Pt nucleus. The two phosphorus signals at 72.43 ppm ($J_{\mathrm{Pt-P}}$ = 2991.6 Hz) and 45.28 ppm ($J_{\mathrm{Pt-P}}$ = 2834.3 Hz) are coupled to each other (J_{PP} = 403.4 Hz). Similarly the two phosphorus signals at 69.30 ppm ($J_{\mathrm{Pt-P}}$ = 3080.5 Hz) and 43.00 ppm ($J_{\mathrm{Pt-P}}$ = 2776.2 Hz) are coupled to each other (J_{PP} = 401.7 Hz), indicating that the phosphorus nuclei are in mutually trans positions.[23,24] The signals at 45.28 and 43.00 ppm

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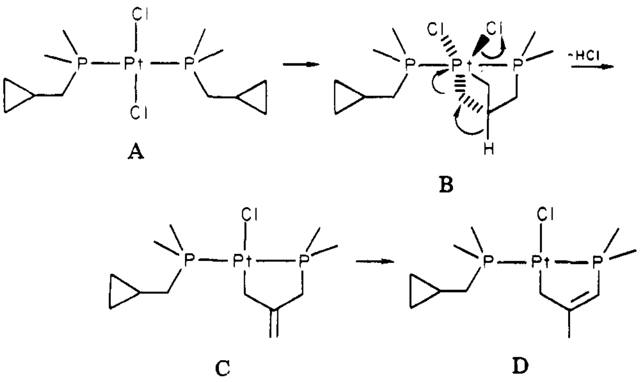
are assigned to monodentate phosphines, while the signals at 72.43 and 69.30 ppm are assigned to chelating phosphines. The assignment of phosphine signals is consistent with the empirical observation of a strong correlation between the size of a chelate ring and the ^{31}P chemical shift of the phosphorus nucleus in that chelate ring,[25] the signal of a phosphorus atom in a five-membered ring being shifted downfield relative to an acyclic phosphine. On the basis of the ^{31}P NMR spectrum this material appears to be a mixture of two different species. On repeated recrystallizations, in which well-shaped crystals are formed, no separation is observed. A variable-temperature ^{31}P NMR study shows that the downfield phosphines in both species collapse into the base line at about 24 °C. At higher temperatures (up to 95 °C) the differences between the absorptions at 45.28 and 43.00 ppm and between those at 72.43 and 69.50 ppm narrow, but they do not coalesce in the solvents used nor do their relative intensities vary from the approximately 1:1 ratio observed at 24 °C.

On the basis of the crystal structure it is possible that the two species are different geometrical isomers that result from rotation about the metal–phosphorus bond of the acyclic phosphine group. There is evidence for the existence of such rotamers in metal complexes of *tert*-butylphosphines.[26] Alternatively, there may be an $\eta^1 \leftrightarrow \eta^3$ conversion in solution. Such processes, with the resultant signal broadening, have been observed previously.[27] In fact the compound $PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2$ was isolated in the attempt to grow crystals of $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]Cl$.[21] In the present compound the allyl proton resonances appear as broad signals in which the fine structure is lost. They do not provide conclusive evidence for the η^1-allyl complex being the only species in solution. However, the similarity between the ^{31}P NMR resonances for the two species leads us to favor the existence of rotamers.

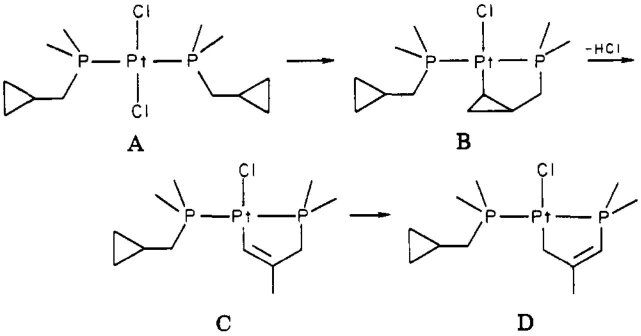
Possible Mode of Formation of $PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$. It has been previously observed that platinum(II) complexes that contain bulky phosphines undergo internal C–H bond activation reactions with much greater ease than do the corresponding palladium(II) complexes.[18b] This has been attributed in part to the reluctance of a palladium(II) complex to undergo oxidative addition to give a palladium(IV) intermediate. Similarly we have found dichlorobis(di-*tert*-butyl(cyclopropylmethyl)phosphine)platinum(II) undergoes cyclopropane ring opening much more readily than does the analogous palladium compound (refluxing in 2-methoxyethanol for 2 h (Pt) vs. 32 h (Pd)). The monomer is isolated with the platinum compound, whereas the dimer is isolated with the palladium complex. Under extended refluxing, conditions necessary for the formation of the palladium complex, the platinum complex does not form a dimer.

McQuillin and Powell[28] observed a general preference for fission of the less substituted carbon–carbon bond of cyclopropanes in the formation of (propane-1,3-diyl)$PtCl_2$ complexes. The formation of the present product is consistent with activation of the less substituted C–C bond as β-hydride elimination and a 1,3 hydride migration would give the final product (Scheme II). There is probably a preference for a [1.1.2] bicyclic intermediate relative to the [0.2.2] bicyclic intermediate required for activation of the more substituted C–C cyclopropane bonds. The Pt(IV) intermediate (B), formed from C–C bond activation of the cyclopropane, would be extremely strained owing to its bicyclic nature.

Scheme II



Scheme III



This mechanistic scheme differs from that which we have previously proposed[8] for the formation of $[PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2]_2$. The essential difference is that in the palladium scheme preliminary phosphine dissociation before C–C bond activation is proposed, thereby avoiding an intermediate similar to B. Since in the present instance both phosphines are bound to the platinum atom in the final product D, preliminary phosphine dissociation would require eventual association. Moreover, since in the overall reaction HCl is liberated, phosphonium hydrochloride would result if there were phosphine dissociation.

Alternatively it may be that C–H bond activation is the intitial step (Scheme III). This scheme involves the formation of an intermediate σ-cyclopropane with the concerted elimination of HCl in a mechanism similar to that proposed for C–H activation in other alkyls.[1b] Formation of the final product would result from ring opening of this intermediate followed by a 1,3 hydride migration. The conversion of a σ-cyclopropyl platinum complex into an (η^3-allyl)platinum complex has been previously observed.[29]

At this time it is not possible to decide whether these reactions proceed through C–C or C–H bond activation. We are currently synthesizing and investigating the reactivity of a series of other new cyclopropyl phosphines in which the number of methylene groups that link the cyclopropyl group to the phosphorus atom is varied. Such variations, because of the ring sizes of potential metalla-

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cycles formed, may lead to the stabilization of some of the intermediates proposed in the above reaction schemes.

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Supplementary Material Available: Table III, thermal parameters, Table IV, a listing of parameters for the non-hydridic hydrogen atoms, and Table V, a listing of $10|F_o|$ andd $10|F_c|$ (23 pages). Ordering information is given on any current masthead page.

Decomposition of High-Oxygen Content Organoaluminum Compounds. The Formation and Structure of the $[Al_7O_6Me_{16}]^-$ Anion

Jerry L. Atwood,* Duane C. Hrncir, Ralph D. Priester, and Robin D. Rogers

Department of Chemistry, University of Alabama, University, Alabama 35486

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The unusual anion $[Al_7O_6Me_{16}]^-$ has been encountered in the decomposition pathways of two different high-oxygen content organoaluminum compounds, $K[Al_2Me_6O_2]$ and presumably $Cs_2[Al_2Me_6O]$. It is likely that these two compounds pass through the same intermediate and that the $[Al_7O_6Me_{16}]^-$ ion is a thermodynamic sink. In both cases crystalline material has been isolated, and X-ray structural determinations have been carried out. $K[Al_7O_6Me_{16}]\cdot C_6H_6$ crystalizes in the triclinic space group $P\bar{1}$ with lattice parameters $a = 12.095$ (5) Å, $b = 12.222$ (5) Å, $c = 13.893$ (5) Å, $\alpha = 105.56$ (3)°, $\beta = 94.52$ (2)°, $\gamma = 83.98$ (2)°, and $\rho_{calcd} = 1.09$ g cm^{-3} for $Z = 2$. Least-squares refinement gave a final R value of 0.042 for 2509 independent observed reflections. $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$ belongs to the cubic space group $P2_13$ with $a = 17.512$ (8) Å and $\rho_{calcd} = 1.16$ g cm^{-3} for $Z = 4$. Refinement based on 460 observed reflections gave a final R of 0.075. The anion for the cesium salt lies on a crystallographic threefold axis. The structure consists of an open Al_6O_6 cage capped by the seventh Al atom which is bonded to three alternate O atoms in the cage. The six Al atoms are bonded to two terminal methyl groups each, while the unique Al is bonded to only one methyl group. Each O atom is three coordinate: the ones on the exterior (not bonded to the unique Al atom) bridge two Al atoms and are also bonded to one methyl group each.

Introduction

In the course of numerous investigations of the reaction of aluminum alkyls with alkali-metal halides and related MX compounds, several high-oxygen content anions have been explored. Compounds such as $K[Al_2Me_6NO_3]$,[1] $K[AlMe_3NO_3]$,[1] [K·dibenzo-18-crown-6]$[Al_2Me_6O_2]$,[2] $[NMe_4][Al_2Me_6(MeCOO)]$,[3] and $K_2[Al_4Me_{12}SO_4]$[4] have resulted. The reactions leading to the formation of the substances are surprisingly mild. For example, KNO_3 reacts smoothly with $AlMe_3$ in refluxing toluene to form $K[Al_2Me_6NO_3]$, and the resulting liquid clathrate[5] $K[Al_2Me_6NO_3]\cdot nC_6H_5Me$ is stable indefinitely at 80 °C in a nitrogen atmosphere. One would expect a much more vigorous result, given the relative Al–C and Al–O bond strengths. Indeed, $K[Al_2Me_6NO_3]$ is violently air sensitive and has been found to detonate photolytically in the $K[Al_2Me_6NO_3]\cdot nC_6H_6$ form.[6] All the substances listed above may be classified as high-energy content compounds which are apparently stabilized by kinetic not thermodynamic factors. Under what conditions do such compounds decompose, and what species may be encountered upon rearrangement? In this contribution we demonstrate the presence of the unexpected $[Al_7O_6Me_{16}]^-$ anion in the decomposition pathway of two different high-oxygen content parent compounds.

Results and Discussion

Potassium superoxide reacts with trimethylaluminum in toluene in the presence of dibenzo-18-crown-6[7] to form a liquid clathrate of composition [K·dibenzo-18-crown-6]$[Al_2Me_6O_2]\cdot nC_6H_5Me$. This liquid can be heated for days at 80 °C with no evidence of decomposition. The crystal structure of the compound from a benzene liquid clathrate has been reported.[2] However, without the crown ether different results are obtained. No liquid layering (liquid clathrate) is observed if KO_2 and $AlMe_3$ (in a 1·2 ratio) are placed in refluxing benzene. Instead, a slow reaction ensues, and large, colorless crystals are deposited on the walls of the flask. X-ray diffraction studies have shown the product to be $K[Al_7O_6Me_{16}]\cdot C_6H_6$. The structure of this surprising anion is shown in Figure 1. Equally surprising, $[Al_7O_6Me_{16}]^-$ is not an isolated crystallographic curiosity.

In parallel with superoxide studies, we have investigated alkali-metal oxides. Cesium oxide reacts smoothly with trimethylaluminum at room temperature in toluene to yield a liquid clathrate, presumably of composition $Cs_2[Al_2Me_6O]\cdot nC_6H_5Me$. Slow cooling to −10 °C affords colorless, air-sensitive needles in ca. 15% yield. X-ray

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