residue was extracted with dichloromethane and chromatographed on alumina. Two components were isolated from the column: (1) $[C_5H_5Fe(CO)_2]_2$ (1.734 g, 80%, eluted with benzene) and (2) **10** (0.504 g, 15%, eluted with 50% diethyl ether–benzene). Recrystallization of **10** from CH_2Cl_2–hexane gave air-stable yellow crystals: mp 122–123 °C; IR (THF) 2015 (vs), 1950 (vs), 1640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s, 6 H), 3.15 (s, 4 H), 4.80 (s, 10 H). Anal. Calcd for $C_{21}H_{20}Fe_2O_6$: C, 52.50; H, 4.16; Fe, 23.28. Found: C, 52.17; H, 4.35; Fe, 22.86.

Photolysis of $[C_5H_5(CO)_2Fe(C{=}O)\{CH_2C(CH_3)_2CH_2\}(C{=}O)Fe(CO)_2C_5H_5]$ (10). A solution of **10** (0.200 g, 0.41 mmol) in THF (15 mL) was photolyzed for 3 h at 45 °C. VPC analysis revealed the presence of 1,1-dimethylcyclopropane (70%) and isobutylene (6%). The infrared analysis of the solution revealed $[C_5H_5Fe(CO)_2]_2$ (65%) as well as **10** (10%) as the products.

Photolysis of $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (12). A solution of **12** (0.300 g, 0.73 mmol) in THF (30 mL) was subjected to photolysis for 3 h at 45 °C. VPC analysis revealed the presence of 1-butene (40%), *cis*-2-butene (1.5%), and *trans*-2-butene (10%). The infrared of the solution was checked, and the major products were found to be $[C_5H_5Fe(CO)_2]_2$ (60%) and **12** (30%).

Thermolysis of $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (12). A solution of **12** (0.200 g, 0.48 mmol) in THF (15 mL) was placed in an autoclave and heated at 120 °C for 3 h. The gas phase over the final product mixture was analyzed by VPC, and only a trace amount of 1-butene was found. The infrared of the solution indicated that almost all the starting material was intact.

Thermolysis of $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (12) under CO. A solution of **12** (0.500 g, 1.22 mmol) in THF (15 mL) was charged with CO (450 psi) and heated at 120 °C for 5 h. VPC analysis of the gas phase over the product mixture found only trace amounts of C_4 hydrocarbon. The liquid phase concentrated to give a dark yellow solid. This dark yellow solid was recrystallized from THF–hexane to give yellow crystals of **13** (70%).[21]

Photolysis of $[C_5H_5(CO)_2Fe(C{=}O)(CH_2)_4(C{=}O)Fe(CO)_2C_5H_5]$ (13). A solution of **13** (0.500 g, 1.07 mmol) in THF (30 mL) was subjected to photolysis at 45 °C for 2 h. VPC analysis of the gas phase over the resulting solution revealed the presence of 1-butene (25%), *cis*-2-butene (1.2%), and *trans*-2-butene (6%). The liquid phase was concentrated and chromatographed on alumina. Three components were isolated from the column: (1) $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (0.176 g, 40%, eluted with 50% hexane–benzene), (2) $[C_5H_5Fe(CO)_2]_2$ (0.150 g, 40%, eluted with benzene), and **13** (0.085 g, 17%, eluted with 50% diethyl ether–benzene).

Acknowledgment. We are grateful to the Robert A. Welch Foundation, the National Science Foundation, and the Department of Energy for support. C.H.T. would like to thank NATO/DAAD for a Postdoctoral Fellowship during the period of this research. We also thank Professor Evan P. Kyba for many helpful discussions.

Registry No. *cis*-1, 79839-80-8; *trans*-1, 79896-43-8; 5, 85293-84-1; 7, 12117-43-0; 8, 85293-85-2; 10, 85293-86-3; 12, 36655-41-1; 13, 36655-42-2; $C_5H_5Fe(CO)_2K$, 60039-75-0; $C_5H_5Fe(CO)_2(CH_2Cl)$, 12107-38-9; Fe, 7439-89-6; succinyl chloride, 543-20-4; 3,3-dimethylglutaryl, 53120-75-5.

Formation of a Chelating σ-Allyl by the Intramolecular Activation of a Cyclopropylphosphine. Synthesis and Crystal Structure of $[PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)]_2$

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The cyclopropyl-containing phosphine di-*tert*-butyl(cyclopropylmethyl)phosphine, $P(t\text{-}Bu_2CH_2\text{-}CHCH_2CH_2$, reacts with $PdCl_2$ to afford *trans*-$PdCl_2(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)_2$. When this complex is refluxed in $MeOCH_2CH_2OH$ or glacial acetic acid, a cyclometalated dimer, $[PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)]_2$, is formed, as deduced from spectroscopic and X-ray analysis. This complex crystallizes in the monoclinic space group C_{2h}^5—$P2_1/n$ (a = 7.957 (4) Å, b = 15.780 (2) Å, c = 12.169 (1) Å, and β = 99.11 (2)°) with two molecules per unit cell (imposed crystallographic symmetry, $\bar{1}$). The final agreement indices for 2493 reflections having $F_o^2 > 3\sigma(F_o^2)$ are $R(F)$ = 0.031 and $R_w(F)$ = 0.041 (136 variables). The five-atom chelate ring Pd—P—C=C—C is planar to within 0.011 (4) Å with a bond length pattern of Pd—P = 2.218 (1) Å, P—C = 1.781 (4) Å, C=C = 1.328 (5) Å, C—C = 1.493 (5) Å, and C—Pd = 2.016 (3) Å. The Pd-Cl distance trans to the P atom is 2.416 (1) Å and that trans to the C atom is 2.457 (1) Å. In the formation of the complex the chelating σ-allyl group probably results from C-C bond activation of the cyclopropyl group.

Introduction

A variety of strained ring molecules have been shown to undergo rearrangements in the presence of transition-metal complexes. The metal-assisted conversion of cyclopropanes to olefins (eq 1)[1] and the metal-assisted isomerizations of olefins (eq 2)[2] have received much at-

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[1] Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461–486.

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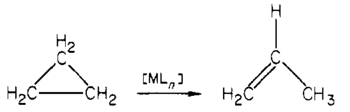
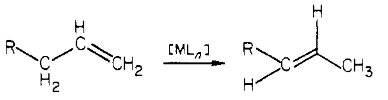


(1)



(2)

tention. Both transformations have been proposed to go through allyl metal hydride complexes. The ring opening of cyclopropanes has been proposed to proceed via the mechanism presented in Scheme I, with the initial step being activation of a C–C bond of the cyclopropane by the metal center to form a metallacyclobutane complex. Metallacyclobutane[3] and allyl metal hydride complexes[4] have been previously isolated from reactions of cyclopropanes with transition-metal complexes. Following our general interest in C–C and C–H bond activation and in the reactions of cyclopropane derivatives with transition-metal complexes, we have synthesized a number of phosphines that contain cyclopropyl substituents and we have studied the reactions of these phosphines with group 8 transition-metal complexes. Here we report the synthesis of $\mathrm{PdCl_2(P}(t\text{-Bu})_2\mathrm{CH_2\overline{CHCH_2CH_2}})_2$ and its conversion to the σ-allyl dimer $[\mathrm{\overline{PdCl(P}(t\text{-Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)}]_2$.

Experimental Section

All manipulations involving free tertiary phosphines or heating under reflux in 2-methoxyethanol were carried out under purified nitrogen or argon with the use of standard Schlenk techniques. Solvents were rigorously purified and dried by standard techniques. ^{1}H NMR and ^{31}P NMR spectra were obtained on JEOL FX90 and JNM-FX270 spectrometers. All infrared (IR) data were recorded on a Perkin-Elmer 283 spectrometer and are from solid samples in Nujol.

***trans*-$\mathrm{PdCl_2(P}(t\text{-Bu})_2\mathrm{CH_2\overline{CHCH_2CH_2}})_2$.** Palladium dichloride (0.221 g, 1.248 mmol) was combined with di-*tert*-butyl(cyclopropylmethyl)phosphine[5] (0.500 g, 2.496 mmol) in aqueous EtOH and stirred under N_2 for 3 days at room temperature. The resulting product was recrystallized from hexane to yield large, well-formed orange crystals (95% yield): IR (Nujol mull) 345 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.04 (m, CH_2), 1.52 (t, CCH_3, J = 6.60 Hz), 0.39–0.61 (m, $\overline{\mathrm{CHCH_2CH_2}}$); ^{31}P NMR ($C_6D_6$) δ 42.2 (s). Anal. Calcd: C, 49.88; H, 8.72; Cl, 12.27. Found: C, 50.44; H, 8.43; Cl, 12.22.

$[\mathrm{\overline{PdCl(P}(t\text{-Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)}]_2$. *trans*-$\mathrm{PdCl_2(P}(t\text{-Bu})_2\mathrm{CH_2\overline{CHCH_2CH_2}})_2$ was refluxed in acetic acid (glacial) for 2 h. The solution was cooled, water was added, and a white precipitate formed. Recrystallization from hexane/toluene gave transparent, pale yellow crystals (45% yield, isolated): IR (Nujol mull) C=C, 1610 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.91 (vinyl H, J = 10.99 Hz), 3.08 (CH_2, J = 6.10 Hz), 1.62 (br s, CH_3), 1.28 (CCH_3, J = 14.16 Hz); ^{31}P δ 89.9 (s). Anal. Calcd: C, 42.25; H, 6.99; Cl, 10.39; P, 9.08. Found: C, 40.75; H, 6.98; Cl, 10.01; P, 8.35. If 2-methoxyethanol is used and the solution is refluxed for 32 h, the same product results. When $\mathrm{PdCl_2(P}(t\text{-Bu})_2\mathrm{CH_2\overline{CHCH_2CH_2}})_2$ is refluxed for an extended period of time in $\mathrm{MeOCH_2CH_2OCH_2CH_2OMe}$, only starting material is recovered.

Scheme I

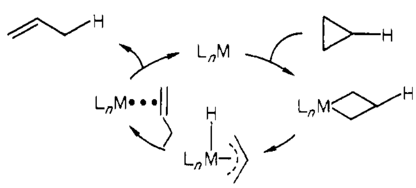


Table I. Crystallographic Details for $[\mathrm{\overline{PdCl(P}(t\text{-Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)}]_2$

formula	$C_{24}H_{48}Cl_2P_2Pd_2$
formula mass, amu	682.30
space group	C^5_{2h}—$P2_1/n$
a, Å	7.957 (4)
b, Å	15.780 (2)
c, Å	12.169 (1)
β, deg	99.11 (2)
vol, Å^3	1509
Z	2
ρ_{calcd}, g/cm^3	1.502
cryst dimens, mm	0.3 × 0.4 × 0.6
radiation	Mo Kα (graphite monochromator)
linear abs coeff, cm^{-1}	14.7
rel transmissn factors	0.91-1.00
temp, °C	22
scan mode	θ-2θ
2θ limits, deg	2.0-52.0
scan range, deg	0.45 + 0.35 tan θ
data collected	±h, +k, +l
unique data	2957
unique data with $F_0^2 > 3\sigma(F_0^2)$	2493
final no. of variables	136
$R(F)$	0.031
$R_w(F)$	0.041
error in an observn of unit weight (e)	1.26

X-ray Study of $[\mathrm{\overline{PdCl(P}(t\text{-Bu})_2\mathrm{CH{=}C(CH_3)C}}\mathrm{H_2)}]_2$. Crystals of the compound suitable for X-ray work were obtained through recrystallization from a 75:25 hexane/toluene solvent mixture. Data collection was performed on an Enraf-Nonius CAD4 diffractometer. The monoclinic symmetry inferred from the unit cell parameters was confirmed by an analysis of symmetry equivalent intensities. Systematic extinctions were consistent with the space group $C_{2h}{}^5$—$P2_1/n$. Crystal or instrumental instability was monitored through the measurement of two standard reflections that were collected after every hour of data collection. Experimental details are given in Table I.

The solution, refinement, and analysis of the crystal structure was carried out with the SDP[6] crystallographic computing package on a DEC 11/70 computer. An empirical absorption correction[7] was applied from averaged transmission factors determined from psi scans of six Bragg reflections. Neutral atom scattering factors[8] were used with anomalous dispersion corrections[9] being applied to the Pd, Cl, P, and C atoms.[10] The coordinates of the Pd atom were determined from a three-dimensional Patterson synthesis and the subsequent model was extended through standard least-squares and difference electron density techniques. Hydrogen atoms were included in idealized positions (except for hydrogen atoms bonded to atom C(4)) with thermal parameters of B_{iso} = 5.0 Å^2 and added as fixed contributions to the structure

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(2) For reviews of transition-metal-catalyzed olefin isomerizations see: (a) Tolman, C. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1976; pp 271–312. (b) Hubert, A. J.; Reimlinger, H. *Synthesis* **1970**, *2*, 405–430. (c) Davies, N. R. *Rev. Pure Appl. Chem.* **1967**, *17*, 83–93.

(3) (a) Rajaram, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 829–838. (b) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045–2046. (c) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *Ibid.* **1961**, 738–742.

(4) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252–3254; *Ibid.* **1979**, *101*, 4201–4211.

(5) Youngs, W. J.; Ibers, J. A. *Organometallics*, in press.

(6) Enraf-Nonius Structure Determination Package, Revision 3A (1979).

(7) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A* **1968**, *A24*, 351–359.

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(9) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781–782.

(10) Cromer, D. T., "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table II. Positional Parameters[a] for the Non-Hydrogen Atoms of $[\overline{PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)C}H_2)]_2$

atom	x	y	z
Pd	0.31236 (3)	0.48080 (2)	0.40238 (2)
Cl	0.5867 (1)	0.41052 (6)	0.46345 (9)
P	0.1862 (1)	0.39413 (6)	0.27119 (7)
C(1)	−0.0178 (5)	0.4398 (3)	0.2265 (3)
C(2)	−0.0457 (5)	0.5108 (2)	0.2796 (3)
C(3)	0.0919 (5)	0.5453 (2)	0.3656 (3)
C(4)	−0.2077 (5)	0.5616 (3)	0.2595 (4)
C(5)	0.2912 (5)	0.3934 (3)	0.1436 (3)
C(6)	0.3000 (7)	0.4864 (4)	0.1104 (4)
C(7)	0.1891 (7)	0.3458 (4)	0.0462 (4)
C(8)	0.4699 (6)	0.3590 (4)	0.1669 (4)
C(9)	0.1424 (5)	0.2856 (2)	0.3213 (4)
C(10)	0.0230 (7)	0.2344 (3)	0.2423 (6)
C(11)	0.3035 (7)	0.2355 (3)	0.3530 (6)
C(12)	0.0700 (9)	0.2999 (4)	0.4265 (5)

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

factors. Positions for the hydrogen atoms of atom C(4) were determined from a difference electron density map. The final cycle of full-matrix least-squares refinement on F_o involved 136 variables and 2493 unique data with $F_o^2 > 3\sigma(F_o^2)$. The final residuals are $R(F) = 0.031$ and $R_w(F) = 0.041$ and the error in an observation of unit weight is 1.26 e. The four largest peaks (0.51 (4)–0.47 (4) e/Å^3) in the final difference electron density map are located in the vicinity of the Pd atom.

The positional parameters for the non-hydrogen atoms are listed in Table II. Table III[11] presents the anisotropic thermal parameters, Table IV[11] presents the hydrogen atom parameters, and Table VI[11] presents the final values of $10|F_o|$ and $10|F_c|$.

Results and Discussion

Synthesis of *trans*-$PdCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2C}H_2)_2$. The reaction of $PdCl_2$ with di-*tert*-butyl(cyclopropylmethyl)phosphine in aqueous EtOH affords *trans*-$PdCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2C}H_2)_2$ in high yield and purity. The trans configuration for this complex is confirmed by its yellow color, the occurrence of only one band assignable to ν(Pd–Cl) (345 cm^{-1}) in the IR region, and a virtual triplet for the *tert*-butyl protons in the ^1H NMR spectrum. The ^1H NMR spectrum also shows that the cyclopropane of the phosphine is still intact and has not been activated by interaction with the Pd atom.

Synthesis and Structure of $[\overline{PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)C}H_2]_2$. When *trans*-$PdCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2C}H_2)_2$ is refluxed in $MeOCH_2CH_2OH$ for 32 h or glacial acetic acid for 2 h the formation of a cyclometalated product is observed. Owing to the domination of the ^1H NMR spectrum by the *tert*-butyl hydrogen atoms and the variety of possible bonding modes that a cyclopropyl group or an activated cyclopropyl group might have, it was not possible to assign a unique structure from spectroscopic data. Accordingly we turned to a crystallographic study in order to establish unequivocally the molecular connectivity of this complex.

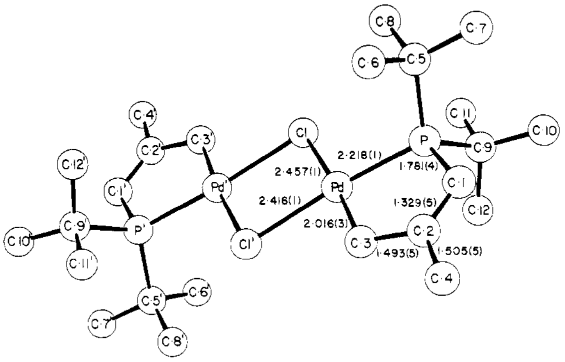

Figure 1. Drawing of the $[\overline{PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)C}H_2)]_2$ molecule. The hydrogen atoms have been omitted for clarity, and the atoms have been drawn as spheres with arbitrary radii. Selected bond distances (Å) have been included in the figure. Primed and unprimed atoms are related by a crystallographic inversion center.

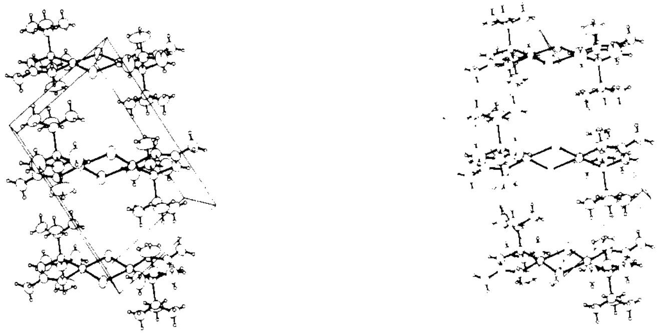

Figure 2. Stereoscopic packing diagram for $[\overline{PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)C}H_2)]_2$ Thermal ellipsoids are drawn at the 50% probability level except for hydrogen atoms which have been drawn artificially small.

As illustrated in Figure 1, the molecular structure of this compound consists of a centrosymmetric dimer in which each Pd atom has a four-coordinate square-planar geometry. Each metal center belongs to a five-membered $\overline{Pd{-}P{-}C{=}C{-}C}$ chelate ring in addition to being bonded to two bridging chloro ligands. These results are consistent with the ^1H NMR and ^{31}P NMR spectroscopic data. The protons of the *tert*-butyl groups occur at δ 1.28 and are split into a doublet (14.16 Hz), consistent with a P atom being bound to each Pd atom. The resonance for the vinyl H atom is at δ 4.91 and is split into a doublet ($J_{P-H} = 10.99$ Hz) by the adjacent P atom. The proton resonance for the allylic methylene group bonded to the Pd atom occurs at δ 3.08 and is also split into a doublet ($J_{P-H} = 6.10$ Hz) while the allylic methyl proton signal is a singlet at δ 1.62. The ^{31}P NMR spectrum shows a singlet at δ 89.9.

Bond distances involving the Pd coordination sphere and the metallacycle are given in Figure 1 while Table V contains a list of intramolecular bond distances and angles. The crystal packing for $[\overline{PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)}\text{-}\overline{C}H_2)]_2$ is displayed in Figure 2. The crystal structure consists of individual dimeric molecules with the shortest intermolecular non-hydrogen separation (3.703 (6) Å) being between methyl carbon atoms C(4) and C(10) of neighboring molecules. The dimer is situated on a crystallographic inversion center and thus only half of the molecule is unique.

The four-coordinate Pd atom has a cis configuration and is bonded to the P atom of a cyclometalated phosphine, an allyl carbon atom (in a σ fashion) of a phosphine substituent, and two bridging chloro ligands. The Cambridge Crystallographic Database[12] was used for the location and tabulation of comparative molecular parameters. The

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(11) Supplementary material.

(12) Cambridge Crystallographic Database, 1982, Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

Table V. Distances (Å) and Angles (deg) in [PdCl(P(*t*-Bu)$_2$CH=C(CH$_3$)CH$_2$)]$_2$

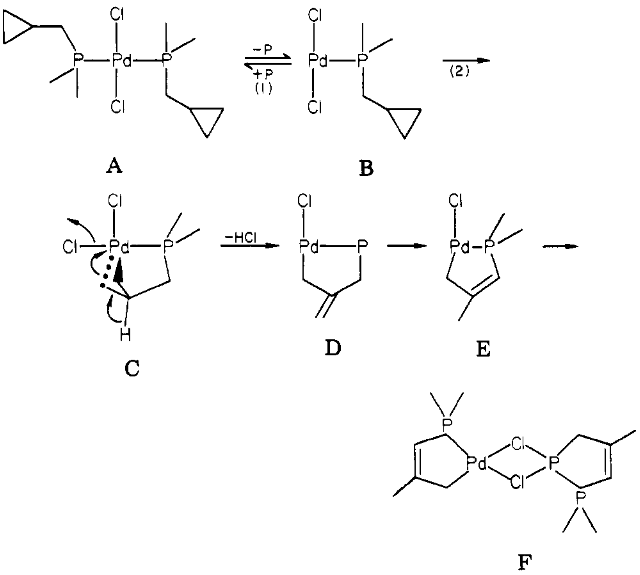
Bond Distances					
Pd-Cl	2.457 (1)	P-C(5)	1.876 (3)	C(5)-C(7)	1.524 (5)
Pd-Cl′	2.416 (1)	P-C(9)	1.869 (4)	C(5)-C(8)	1.506 (5)
Pd-P	2.218 (1)	C(1)-C(2)	1.329 (5)	C(9)-C(10)	1.481 (6)
Pd-C(3)	2.016 (3)	C(2)-C(3)	1.493 (5)	C(9)-C(11)	1.504 (6)
Pd···Pd′	3.561 (1)	C(2)-C(4)	1.505 (5)	C(9)-C(12)	1.501 (6)
P-C(1)	1.781 (4)	C(5)-C(6)	1.527 (6)		
Bond Angles					
Cl-Pd-Cl′	86.08 (3)	C(1)-P-C(5)	104.7 (2)	P-C(5)-C(8)	112.2 (3)
Cl-Pd-P	102.63 (3)	C(1)-P-C(9)	105.3 (2)	C(6)-C(5)-C(7)	108.0 (4)
Cl′-Pd-P	171.23 (3)	C(5)-P-C(9)	113.3 (2)	C(6)-C(5)-C(8)	108.3 (4)
Cl-Pd-C(3)	174.5 (1)	P-C(1)-C(2)	114.0 (3)	C(7)-C(5)-C(8)	109.9 (4)
Cl′-Pd-C(3)	88.6 (1)	C(1)-C(2)-C(3)	119.2 (3)	P-C(9)-C(10)	114.9 (3)
P-Pd-C(3)	82.7 (1)	C(1)-C(2)-C(4)	125.1 (4)	P-C(9)-C(11)	111.8 (3)
Pd-Cl-Pd′	93.92 (3)	C(2)-C(3)-Pd	119.1 (2)	P-C(9)-C(12)	104.9 (3)
Pd-P-C(1)	104.9 (1)	C(3)-C(2)-C(4)	115.7 (3)	C(10)-C(9)-C(11)	108.2 (4)
Pd-P-C(5)	112.9 (1)	P-C(5)-C(6)	105.0 (3)	C(10)-C(9)-C(12)	110.0 (5)
Pd-P-C(9)	114.6 (1)	P-C(5)-C(7)	113.2 (3)	C(11)-C(9)-C(12)	106.7 (5)

Pd–P bond length of 2.218 (1) Å falls within the range of previously reported values for this structural fragment in other chloro-bridged Pd dimers (range 2.15–2.21 Å; three examples) as does the Pd–C(3) bond distance of 2.016 (3) Å (range 2.00–2.18 Å; six examples). The two Pd–Cl distances (Pd–Cl = 2.457 (1) Å and Pd–Cl′ = 2.416 (1) Å) also fall within their expected range of 2.27–2.52 Å (18 examples). The 0.041-Å difference between the two Pd–Cl distances we attribute to the stronger trans influence of the σ-bonded C atom relative to the coordinated P atom. A very similar bond length distribution that shows the same ordering of trans influences has recently been reported for the chloro-bridged dinuclear complex [PdCl(P(*t*-Bu)$_2$C(CH$_3$)$_2$CH$_2$)]$_2$.[13,14] In the present structure the PdClCl′PC(3) fragment is essentially planar with the largest deviation from the least-squares plane being 0.033 (5) Å for atom Cl.

Deviations from idealized square-planar geometry appear to arise more from intramolecular repulsions than from the geometric constraint of the five-membered metallacycle. The P–Pd–C(3) bond angle of 82.7 (1)° is an indication of only a slight distortion imposed by the ring when compared with a P–Pd–C angle of 70.0 (2)° found for the four-membered metallacycle in [PdCl(P(*t*-Bu)$_2$C(CH$_3$)$_2$CH$_2$)]$_2$.[13] In contrast to the P–Pd–C(3) angle the Cl–Pd–P angle (102.63 (3)°) has no bonding constraint imposed upon it and yet it deviates more from 90°. This angle increases perhaps to relieve the close contacts between the Cl atom and the atoms C(8) (3.672 (3) Å) and C(11) (3.681 (3) Å). These distances are close to the sum of the van der Waals' radii for a Cl and a methyl group,[15] and thus it seems possible that intramolecular repulsions involving the phosphine *tert*-butyl groups play a role in determining geometric distortions about the Pd center.

The five-membered metallacycle Pd—P—C=C—C is planar to within 0.011 (4) Å (for atoms C(2) and C(3)) and is similar to the five-membered chelate rings (Pd–P–C–C–C) in [Pd(OAc)(P(*t*-Bu)(*o*-tolyl)C$_6$H$_4$CH$_2$)].[16] The metrical parameters of the present metallacycle are consistent with those found in other σ-bonded transition-metal allyl systems. For example, the C(1)–C(2) double bond (1.328 (5) Å) and the C(2)–C(3) single bond (1.493 (5) Å) are comparable with the corresponding bonds (1.298 (10) and 1.486 (9) Å) found in the complex *trans*-PtBr(η^1-C$_3$H$_5$)(PEt$_3$)$_2$.[17]

Scheme II



A mechanism for the formation of [PdCl(P(*t*-Bu)$_2$CH=C(CH$_3$)CH$_2$)]$_2$ consistent with the usually observed C–C bond activation of cyclopropanes by transition-metal complexes and similar to the cyclopropane-to-olefin isomerization mechanism proposed by McQuillin and Powell[18] is shown in Scheme II. This mechanism involves initial dissociation of phosphine (1) followed by C–C bond activation (2) to produce intermediate C. Intermediate C can then undergo rapid β-hydride elimination to produce D which, with a 1,3 hydride shift and dimerization, produces the observed product F.

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Registry No. $trans$-$\text{PdCl}_2(\text{P}(t\text{-Bu})_2\text{CH}_2\overline{\text{CHCH}_2\text{C}}\text{H}_2)_2$, 85318-43-0; $[\overline{\text{PdCl}(\text{P}(t\text{-Bu})_2\text{CH}{=}\text{C}(\text{CH}_3)\text{C}}\text{H}_2)]_2$, 85318-44-1.

Supplementary Material Available: Table III, the thermal parameters, Table IV, a listing of parameters for the hydrogen atoms, and Table VI, a listing of $10|F_o|$ and $10|F_c|$ (13 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Some *P*-Mesityl-Substituted Phosphorus Compounds

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The preparation and characterization of a series of *P*-mesityl-substituted phosphorus compouds containing the Si–N–P and/or Si–C–P linkages are described. The reaction of RPCl_2 (R = 2,4,6-$\text{Me}_3\text{C}_6\text{H}_2$) with 1 equiv of $(\text{Me}_3\text{Si})_2\text{NLi}$ affords the thermally unstable chlorophosphine $(\text{Me}_3\text{Si})_2\text{NP(R)Cl}$ (**1**) in nearly quantitative yield. Substitution reactions of **1** are used to prepare the stable derivatives $(\text{Me}_3\text{Si})_2\text{NP(R)X}$ (**2**, X = Me; **3**, X = H; **4**, X = CH_2SiMe_3), while treatment with Me_3SiN_3 yields the unstable azidophosphine $(\text{Me}_3\text{Si})_2\text{NP(R)N}_3$ (**5**). The methylphosphine **2** reacts smoothly with CCl_4 via elimination of CHCl_3 and a [1,3]-silyl shift to form the chlorophosphinimine $\text{Me}_3\text{SiN}{=}\text{P(R)}(\text{CH}_2\text{SiMe}_3)\text{Cl}$ (**6**), which is readily converted to the P–Me analogue **7** by reaction with MeLi. Depending on the reaction stoichiometry, treatment of RPCl_2 with $\text{Me}_3\text{SiCH}_2\text{MgCl}$ gives either the chlorophosphine $\text{Me}_3\text{SiCH}_2\text{P(R)Cl}$ (**8**) as an unstable product from which **4** is produced by reaction with $(\text{Me}_3\text{Si})_2\text{NLi}$ or the stable disubstituted phosphine $(\text{Me}_3\text{SiCH}_2)_2\text{PR}$ (**9**). Decomposition of the azidophosphine **5** proceeds with elimination of nitrogen and formation of the dimeric forms of the bis(imino)phosphorane $\text{RP}({=}\text{NSiMe}_3)_2$ (**5a**). Either the cis (**10**) or trans (**11**) four-membered ring dimer can be isolated under appropriate conditions. Proton, ^{13}C, and ^{31}P NMR data are reported for the new compounds.

Introduction

Currently, there is considerable interest in the chemistry of "low-coordinate" phoshorus compounds such as the two-coordinate phosphines[1] R—P═E and the three-coordinate phosphoranes[2] R—P(═E)$_2$ where E = NR′ or CR′$_2$. Several examples of stable compounds of each type now exist, and some reports of their derivative chemistry[3] have appeared recently. Our interest in such compounds stems mainly from the possibility that they might be useful precursors to new classes of phosphorus-containing polymers or cyclic oligomers. It seems reasonable that systems suited to this purpose should contain: (1) a sterically bulky, unreactive group on phosphorus to provide kinetic stability and (2) functional linkages such as Si–N–P and/or Si–C–P which could serve as sites for condensation–polymerization reactions.[4,5]

As the initial phase of this project, we report here on the synthesis and reactivity of a series of silylated, *P*-mesityl-substituted compounds. The potential uses of some of these reagents in the preparation of low-coordinate species and new oligomers will be described in subsequent papers.

Results and Discussion

Mesityldichlorophosphine RPCl_2 (R = 2,4,6-$\text{Me}_3\text{C}_6\text{H}_2$) was selected as the starting material in this study for essentially two reasons: (1) it provides an unreactive P–C bond with a substantial amount of steric hinderance around phosphorus and (2) it is easily prepared in relatively large quantity (~100 g) and good yield (~80%) from PCl_3 and mesityl Grignard reagent. The reactions described herein were primarily intended to introduce Si–N–P or Si–C–P linkages in various arrangements for the purpose outlined above.

Treatment of RPCl_2 (R = mesityl) with 1 equiv of lithium bis(trimethylsilyl)amide (eq 1) in ether solution gave the important reagent [bis(trimethylsilyl)amino]chloromesitylphosphine (**1**). Compound **1** was obtained in ca.

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