Addition of Tin(II) Chloride to $Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$. The Crystal and Molecular Structure of $Pd_2(Ph_2PCH_2PPh_2)_2(SnCl_3)Cl$

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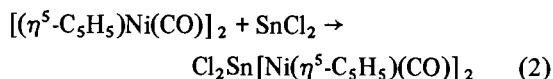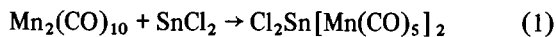
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Addition of tin(II) chloride to $Pd_2(dpm)_2Cl_2$ (dpm is $Ph_2PCH_2PPh_2$) produces $Pd_2(dpm)_2(SnCl_3)Cl$. The crystal structure of the latter complex reveals that the tin(II) chloride has inserted into the Pd–Cl bond and that a nearly linear Pd–Pd–Sn unit is present. Infrared and electronic spectral evidence indicates that carbon monoxide and sulfur dioxide insert into the Pd–Pd bond of $Pd_2(dpm)_2(SnCl_3)Cl$. Spectroscopic evidence for the formation of $Pd_2(dpm)_2(SnCl_3)_2$ is described.
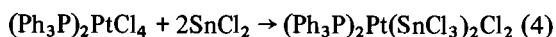
Introduction

The metal–metal bond of $Pd_2(dpm)_2Cl_2$ (dpm is bis(diphenylphosphino)methane) exhibits unusual reactivity toward insertion reactions. Carbon monoxide [1, 2], isocyanides [1, 2] and sulfur dioxide [3] cleave this bond to form adducts (1) in which the two metals have moved about 0.5 Å

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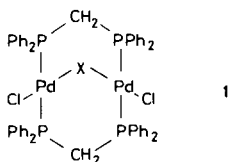
farther apart from their directly bonded positions in $Pd_2(dpm)_2Cl_2$. Another small molecule known to participate in insertion reactions is tin(II) chloride, which can insert into metal–metal bonds as shown in equations 1 [4] and 2 [5]. However, it can also insert into metal–halogen bonds to form the trichlorostan-

$$Mn_2(CO)_{10} + SnCl_2 \rightarrow Cl_2Sn[Mn(CO)_5]_2 \quad (1)$$

$$[(\eta^5\text{-}C_5H_5)Ni(CO)]_2 + SnCl_2 \rightarrow$$
$$Cl_2Sn[Ni(\eta^5\text{-}C_5H_5)(CO)]_2 \quad (2)$$

nate ligand. Characteristic reactions are given in equations 3 [6] and 4 [7]. A review documents numerous examples of both types of insertion reactions [8]. Here we

$$PdCl_4^{-2} + 4SnCl_2 \rightarrow Pd(SnCl_3)_4^{-2} \quad (3)$$

$$(Ph_3P)_2PtCl_4 + 2SnCl_2 \rightarrow (Ph_3P)_2Pt(SnCl_3)_2Cl_2 \quad (4)$$

describe the reactions of $Pd_2(dpm)_2Cl_2$ with tin(II) chloride and report crystal structure data for $Pd_2(dpm)_2(SnCl_3)Cl$.

Experimental

General

The dimer $Pd_2(dpm)_2Cl_2$ was prepared by a previously reported method [2]. Anhydrous tin(II) chloride (Ventron), carbon monoxide (Matheson), and sulfur dioxide (Matheson) were used without further purification. Reactions involving CO and SO_2 were routinely carried out under prepurified nitrogen using deoxygenated solvents.

$Pd_2(dpm)_2(SnCl_3)Cl$

A methanol solution of $SnCl_2$ (0.044 g, 0.23 mmol) was added to a dichloromethane solution of $Pd_2(dpm)_2Cl_2$ (0.110 g, 0.105 mmol). The resulting red solution was filtered and concentrated to *ca.* 5 ml. Upon addition of methanol, the product precipitated. Recrystallization from dichloromethane/methanol afforded pure red-orange crystals in 75% yield. Infrared data: ν(Pd–Cl), 287 cm^{-1}; ν(Sn–Cl), 325 cm^{-1}. *Anal.* Found: C, 47.58; H, 3.67; P, 9.93; Cl, 12.50%. $C_{50}H_{44}Cl_4P_4Pd_2Sn\cdot1/4CCl_2H_2$. Calcd.: C, 47.77; H, 3.55; P, 9.81; Cl, 12.63%.

$Pd_2(dpm)_2(SnCl_3)_2$

Using a mol ratio of 1:12, solutions of $Pd_2(dpm)_2$-Cl_2 in dichloromethane and $SnCl_2$ in methanol were mixed and filtered. The resulting purple solution was allowed to slowly evaporate to form a purple glass which was collected by filtration. Infrared datum: ν(Sn–Cl), 314 cm^{-1}.

Physical Measurements

Infrared spectra of nujol mulls were recorded on a Perkin Elmer 180 spectrophotometer. Electronic spectra were obtained on a Cary 17 spectrophotometer. Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

X-ray Data Collection

Crystals of Pd$_2$(dpm)$_2$(SnCl$_3$)Cl were obtained by slow diffusion of anhydrous methanol into a dichloromethane solution of the complex A red-orange plate measuring 0.25 X 0 15 X 0 025 mm was selected for data collection

Intensity data were collected at 150 K on a Syntex P2$_1$ automated diffractometer using CuK$_\alpha$ radiation (λ = 1 5418 Å) and a graphite monochromator A variable speed (0.5 to 29 3° min^{-1}) ω-scan of the most intense 15% of the ω range and a 1° offset for background were used During data collection, the intensities of 2 standard reflections were measured every 118 reflections and showed only random fluctuation Of the 6481 total reflections measured with $2\theta \leqslant 115°$, 5836 with $I_{net} > 3\sigma(I_{net})$ were used in final refinement The data were corrected for Lorentz and polarization effects but not for absorption Crystal data are reported in Table I

TABLE I Crystal Data for Pd$_2$(dpm)$_2$(SnCl$_3$)Cl

Pd$_2$SnCl$_4$P$_4$C$_{50}$H$_{44}$	Monoclinic
FW = 1242 1	Space Group P2$_1$/c (No 14)
a = 16 238(31) Å	CuK$_\alpha$ radiation
b = 13 274(23) Å	μ_{CuK_α} = 136 7 cm^{-1}
c = 23 449(23) Å	Z = 4
β = 108 28(12)°	D$_{exptl}$(298 K) $\approx$ 1 677 g cm^{-3}
V = 4799 3 Å^3	D$_{calcd}$(150 K) $\approx$ 1 720 g cm^{-3}

## Solution and Refinement of the Structure

The one tin and two palladium atoms were located on a sharpened three-dimensional Patterson map. A Fourier map, calculated with phases from these three atoms, indicated the positions of the eight other heavy atoms Following two cycles of full-matrix least-squares refinement of these eleven atoms, a second Fourier map revealed the locations of the fifty carbon atoms Two cycles of full-matrix refinement of sixty-one isotropic atoms brought R to 0 128 ($R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$) The absence of solvent was verified by a difference Fourier map which only contained electron density attributable to the three metal atoms No effort was made to locate hydrogen atoms An additional cycle of refinement brought R to 0 124 Inspection of the data indicates that this relatively high R value to a large extent is related to the lack of absorption correction Since all of the significant features of the molecule were defined at this point, and since there is no doubt about the essential correctness of the structure, further refinement (which would include absorption corrections) is not warranted Final atomic shifts were <1/10 the corresponding e s d for the heavy atoms and $\leqslant$1/4 the e s d for the carbons except for C(14) which

shifted about 1/2 e s.d Final fractional coordinates and e s d,s are listed in Table II

Results and Discussion

Synthetic Studies

The addition of a methanolic solution of tin(II) chloride to an orange dichloromethane solution of Pd$_2$(dpm)$_2$Cl$_2$ produces a deep red color when the Sn to Pd$_2$ ratio is in the range 2 to 6 and a purple color when that ratio exceeds 10 A red-orange crystalline solid, Pd$_2$(dpm)$_2$(SnCl$_3$)Cl, may be isolated from either the red or the purple solution by the addition of methanol If the purple solution is allowed to slowly evaporate, a purple solid with clean facets but showing no diffraction evidence of crystallinity is deposited along with some white tin(II) chloride We believe that this purple solid contains molecules of Pd$_2$(dpm)$_2$(SnCl$_3$)$_2$ although it has not been obtained in pure form These observations suggest that the successive equilibria 1 and 2 govern this system Which species predominates in solution depends on the tin(II) chloride

1 Pd$_2$(dpm)$_2$Cl$_2$ + SnCl$_2$ = Pd$_2$(dpm)$_2$(SnCl$_3$)Cl

2 Pd$_2$(dpm)$_2$(SnCl$_3$)Cl + SnCl$_2$ = Pd$_2$(dpm)$_2$(SnCl$_3$)$_2$
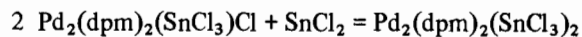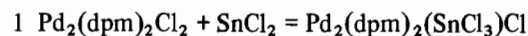
concentration and on the solvent Electronic spectral data for these compounds are reproduced in Figure 1 and reported in Table III In dichloromethane solution Pd$_2$(dpm)$_2$(SnCl$_3$)$_2$ appears to undergo slow dissociation of tin(II) chloride The shoulder at 500 nm which is seen in trace C of Figure 1 grows as the solution is aged and appears to be due to Pd$_2$(dpm)$_2$-(SnCl$_3$)Cl Addition of methanol to such a dichloromethane solution hastens the dissociation of tin(II) chloride and causes the precipitation of Pd$_2$(dpm)$_2$-(SnCl$_3$)Cl An analogous stepwise insertion of tin(II) chloride into the two metal—halogen bonds of (Ph$_3$P)$_2$PtCl$_2$ occurs in acetone solution [9]

When carbon monoxide is bubbled into a dichloromethane solution of Pd$_2$(dpm)$_2$(SnCl$_3$)Cl the presence of a new infrared absorption band at 1688 cm^{-1} indicates that carbon monoxide has inserted into the Pd—Pd bond The product is identified as Pd$_2$(dpm)$_2$(μ-CO)(SnCl$_3$)Cl by analogy with Pd$_2$-(dpm)$_2$(μ-CO)Cl$_2$ [1, 2] Moreover, the presence of a weak shoulder at 1707 cm^{-1} indicates that some Pd$_2$(dpm)$_2$(μ-CO)Cl$_2$ [1] forms during the reaction of carbon monoxide with Pd$_2$(dpm)$_2$(SnCl$_3$)Cl Eventually the slightly soluble Pd$_2$(dpm)$_2$(μ-CO)Cl$_2$ precipitates from this solution The electronic spectra of the two carbonyl complexes are recorded in Table III It was not possible to isolate Pd$_2$(dpm)$_2$(μ-CO)-(SnCl$_3$)Cl as a solid In part this is due to the ease with which this complex loses carbon monoxide When a solution of Pd$_2$(dpm)$_2$(μ-CO)(SnCl$_3$)Cl is

TABLE II. Final Atomic Fractional Coordinates and Isotropic Temperature Factors (A^2).

Atom	x/a	y/b	z/c	B$_{iso}$
SN	0.5002(1)	0.5559(1)	0.2055	1.73(3)
PD(1)	0.6434(1)	0.6458(1)	0.2102	1.52(3)
PD(2)	0.7909(1)	0.7037(1)	0.1950	1.52(3)
CL(1)	0.9174(2)	0.7798(3)	0.1817(2)	2.23(7)
CL(2)	0.3869(3)	0.6316(3)	0.2345(2)	2.90(8)
CL(3)	0.4208(3)	0.4906(3)	0.1075(2)	2.81(8)
CL(4)	0.4984(3)	0.3948(3)	0.2508(2)	2.99(8)
P(1)	0.5974(2)	0.7074(3)	0.1139(2)	1.60(7)
P(2)	0.7070(2)	0.6343(3)	0.3128(2)	1.62(7)
P(3)	0.7477(2)	0.5926(3)	0.1134(2)	1.70(7)
P(4)	0.8345(2)	0.7742(3)	0.2892(2)	1.59(7)
C(1)	0.6343(10)	0.6209(11)	0.0661(7)	1.83(27)
C(2)	0.4817(9)	0.7287(11)	0.0757(6)	1.49(24)
C(3)	0.4309(10)	0.7638(12)	0.1102(7)	2.10(28)
C(4)	0.3428(11)	0.7803(12)	0.0833(8)	2.28(29)
C(5)	0.3055(11)	0.7605(12)	0.0231(8)	2.41(29)
C(6)	0.3551(12)	0.7270(13)	−0.0124(8)	2.78(32)
C(7)	0.4431(11)	0.7082(12)	0.0152(7)	2.17(29)
C(8)	0.6709(11)	0.8559(13)	0.0579(8)	2.66(32)
C(9)	0.7046(13)	0.9511(14)	0.0555(9)	3.28(36)
C(10)	0.7155(11)	1.0196(13)	0.1020(8)	2.53(30)
C(11)	0.6888(11)	0.9899(13)	0.1520(8)	2.53(30)
C(12)	0.6565(9)	0.8953(10)	0.1541(6)	1.37(24)
C(13)	0.6457(10)	0.8297(12)	0.1079(7)	1.95(27)
C(14)	0.6755(11)	0.3238(13)	0.1762(7)	2.30(29)
C(15)	0.6727(11)	0.4202(12)	0.1507(7)	2.26(28)
C(16)	0.7447(10)	0.4621(11)	0.1387(7)	1.55(25)
C(17)	0.8206(11)	0.4055(12)	0.1519(7)	2.29(28)
C(18)	0.8257(13)	0.3107(15)	0.1769(9)	3.39(36)
C(19)	0.7540(11)	0.2707(12)	0.1900(7)	2.36(29)
C(20)	0.8768(14)	0.6293(15)	0.0589(9)	3.63(38)
C(21)	0.8034(10)	0.5780(11)	0.0565(7)	1.85(26)
C(22)	0.7723(12)	0.5052(13)	0.0121(8)	2.87(32)
C(23)	0.8136(12)	0.4886(14)	−0.0302(8)	3.04(33)
C(24)	0.8866(12)	0.5436(13)	−0.0289(8)	2.82(32)
C(25)	0.9172(15)	0.6127(17)	0.0151(10)	4.47(44)
C(26)	0.6323(10)	0.6292(11)	0.3576(7)	1.83(27)
C(27)	0.6099(11)	0.5372(13)	0.3763(8)	2.49(30)
C(28)	0.5488(12)	0.5347(13)	0.4062(8)	2.59(31)
C(29)	0.5098(13)	0.6200(15)	0.4173(9)	3.34(36)
C(30)	0.5310(12)	0.7135(13)	0.3987(8)	2.91(33)
C(31)	0.5924(10)	0.7184(12)	0.3684(7)	2.03(27)
C(32)	0.8042(13)	0.4636(15)	0.3103(9)	3.49(36)
C(33)	0.7876(11)	0.5371(12)	0.3466(7)	2.17(28)
C(34)	0.8301(11)	0.5393(13)	0.4083(8)	2.45(30)
C(35)	0.8927(12)	0.4679(14)	0.4328(8)	2.94(33)
C(36)	0.9103(13)	0.3916(15)	0.3967(9)	3.67(38)
C(37)	0.8679(14)	0.3894(17)	0.3360(10)	4.14(41)
C(38)	0.7601(10)	0.7577(11)	0.3330(7)	1.71(26)
C(39)	0.8059(11)	0.9790(13)	0.3108(8)	2.46(30)
C(40)	0.8292(11)	1.0770(13)	0.3206(8)	2.58(30)
C(41)	0.9102(12)	1.1116(13)	0.3198(8)	2.86(32)
C(42)	0.9656(11)	1.0418(12)	0.3057(8)	2.40(30)
C(43)	0.9427(12)	0.9407(13)	0.2963(8)	2.70(32)
C(44)	0.8624(9)	0.9069(11)	0.2994(7)	1.58(25)
C(45)	0.9657(10)	0.6257(12)	0.3169(7)	2.01(27)
C(46)	1.0396(12)	0.5798(13)	0.3539(8)	2.67(31)
C(47)	1.0822(12)	0.6143(14)	0.4109(9)	3.19(35)
C(48)	1.0514(12)	0.7040(13)	0.4291(8)	2.87(33)
C(49)	0.9778(11)	0.7545(13)	0.3921(8)	2.55(30)
C(50)	0.9340(10)	0.7140(11)	0.3362(7)	1.82(26)

allowed to stand open to the atmosphere, carbon monoxide is lost and $Pd_2(dpm)_2(SnCl_3)Cl$ is re-formed. Consequently, $Pd_2(dpm)_2(\mu\text{-}CO)(SnCl_3)Cl$ appears to be less stable toward decarbonylation than is $Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$. We have previously reported [2] that the terminal anions affect the stability of the bridging carbonyl in $Pd_2(dpm)_2(\mu\text{-}CO)X_2$, and that effect is seen again here.

Addition of sulfur dioxide to a dichloromethane solution of $Pd_2(dpm)_2(SnCl_3)Cl$ produces a purple solution whose electronic spectrum is similar to that of $Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$ [3]. The purple compound, which has not been isolated, is believed to be $Pd_2\text{-}(dpm)_2(\mu\text{-}SO_2)(SnCl_3)Cl$. When this purple solution is purged with nitrogen, sulfur dioxide is lost and $Pd_2(dpm)_2(SnCl_3)Cl$ is regenerated. All of these chemical reactions are summarized in the chart.

Figure 1. Electronic spectra of A) a 0.29 mmolar solution of $Pd_2(dpm)_2Cl$, B) a 0.37 mmolar solution of $Pd_2(dpm)_2$-$(SnCl)_3Cl$, and C) a 0.40 mmolar solution of $Pd_2(dpm)_2$-$(SnCl_3)_2$. The solvent is dichloromethane.

TABLE III. Electronic Spectra.

Compound	Solvent	λ_{max}, nm(ϵ_{max}, M^{-1} cm^{-1}) at 25 °C
$Pd_2(dpm)_2Cl_2$ [a]	CH_2Cl_2	416(7550), 347(16,800), 293(25,900)
$Pd_2(dpm)_2(SnCl_3)Cl$	CH_2Cl_2	495(14,200), 422(8640), 340(18,200), 294sh(18,100), 260sh(31,700)
	mull [b]	525(0.84), 427(0.89), 383(0.92), 312(1.00)
$Pd_2(dpm)_2(SnCl_3)_2$	CH_2Cl_2	536(21,200), 500sh(17,900), 417sh(6120), 353(19,000), 261sh(35,000)
	mull [b]	610(1.00), 434(0.92), 371(0.96)
$Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$ [a,c]	CH_2Cl_2	468(0.37), 404(0.20), 306(0.47), 250sh(1.00)
$Pd_2(dpm)_2(\mu\text{-}CO)(SnCl_3)Cl$ [c]	CH_2Cl_2	490(0.74), 414(0.41), 340(0.75), 294sh(1.00)
$Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$ [c,d]	CH_2Cl_2	511(0.44), 345(1.00)
$Pd_2(dpm)_2(\mu\text{-}SO_2)(SnCl_3)Cl$ [c]	CH_2Cl_2	521(0.76), 350(1.00)

[a] Data from reference 2. [b] Values listed as ϵ_{max} are relative absorbance values. [c] The complex was generated in solution by purging the parent solution with CO or SO_2 gas. Values listed as ϵ_{max} are relative absorbance values. [d] Data from reference 3.
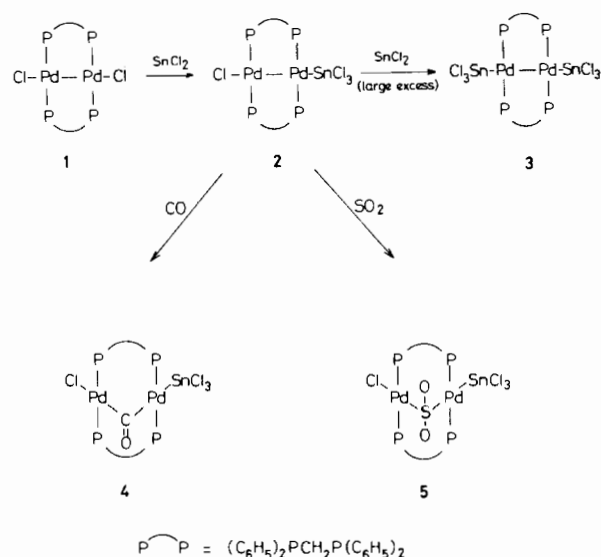
TABLE IV. Equations of Least-Squares Planes[a] and Distances (Å) of Atom from These Planes.

Plane	Defining Atoms	Distances (Å)		
I	Pd(1), Pd(2),[b] Cl(1) P(3), P(4)	Pd(1) 0.1949 Pd(2) 0.0452	P(3) -0.2155 P(4) -0.2246	Cl(1) 0.2000
II	Pd(1),[b] Pd(2), Sn P(1), P(2)	Pd(1) 0.0027 Pd(2) -0.2969	P(1) 0.2962 P(2) 0.2541	Sn -0.2561

Plane I: $-5.9795x + 10.5586y - 8.0097z - 1.0932 = 0$
Plane II: $-5.9747x + 12.0085y + 7.4948z - 0.2075 = 0$

Dihedral Angle: 41.3°

[a]Equations have the form $Ax + By + Cz - D = 0$ where x, y, and z are fractional monoclinic coordinates. [b]Central atom of the square plane.

Structural Characterization of Pd₂(dpm)₂(SnCl₃)Cl

The complex crystallizes with one discrete molecule per asymmetric unit, or four per unit cell, thus there is no crystallographically imposed symmetry. An ORTEP drawing of the molecule is shown in Figure 2. It is clear that the tin(II) chloride has
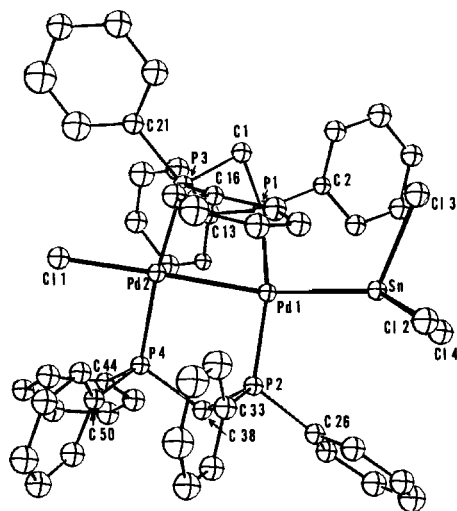
Figure 2. An ORTEP drawing of the Pd₂(dpm)₂(SnCl₃)Cl molecule showing 50% thermal ellipsoids.

inserted into the Pd—Cl rather than the Pd—Pd bond. The molecular structure of the resulting complex is similar to that previously reported for Pd₂(dpm)₂-Br₂ [10] and Pt₂(dpm)₂Cl₂ [11]. The coordination geometry about each palladium is approximately planar, but the coordination planes about the two different palladium atoms are twisted so that the dihedral angle between them is 41.3°. In Pd₂(dpm)₂-Br₂ the comparable dihedral angle is 39°. Additionally, the four atoms bonded to each palladium are displaced slightly toward tetrahedral geometry so that

the ligating atoms alternate above and below the least-squares plane about each metal. This distortion is significantly greater around the Pd which is coordinated to the bulky SnCl₃ group. Table IV summarizes the equations for these least-squares planes and the distances of atoms from them.

The interatomic distances and angles for Pd₂-(dpm)₂(SnCl₃)Cl are essentially normal and are reported in Tables V and VI. The metal—metal bond length of 2.699 Å is comparable to that in both

TABLE V. Selected Interatomic Distances.

Pd(1)—Pd(2)	2.644(2)	P(1)—C(1)	1.83(2)
Sn—Pd(1)	2.585(2)	P(1)—C(2)	1.83(2)
Pd(2)—Cl(1)	2.396(4)	P(1)—C(13)	1.83(2)
Sn—Cl(2)	2.374(5)	P(2)—C(26)	1.84(2)
Sn—Cl(3)	2.415(4)	P(2)—C(33)	1.83(2)
Sn—Cl(4)	2.393(4)	P(2)—C(38)	1.84(2)
Pd(1)—P(1)	2.295(4)	P(3)—C(1)	1.87(2)
Pd(1)—P(2)	2.307(4)	P(3)—C(16)	1.84(2)
Pd(2)—P(3)	2.343(4)	P(3)—C(21)	1.84(2)
Pd(2)—P(4)	2.296(4)	P(4)—C(38)	1.83(2)
P(1)—P(3)	2.880(6)	P(4)—C(44)	1.82(2)
P(2)—P(4)	2.960(6)	P(4)—C(50)	1.83(2)

Pd₂(dpm)₂Br₂ (2.644 Å) [10] and Pt₂(dpm)₂Cl₂ (2.652 Å) [11], but is longer than found in unbridged Pd₂(CNCH₃)₆²⁺ (2.531) [12]. The short Pd—Pd distance requires that adjacent phosphorus atoms also have close interatomic contacts. These P—P distances in 2 are 2.88 and 2.96 Å. In an insertion product such as 1, the Pd—Pd distance has increased to 3.22 Å and the P—P distance has increased to 3.11 Å. Consequently the formation of adducts such as 1 appears to relieve steric strain in these bridged dpm complexes. The other close non-bonded interatomic

TABLE VI. Selected Interatomic Angles.

Pd(1)–Sn–Cl(2)	124.0(1)	Pd(1)–P(2)–C(26)	116.0(5)
Pd(1)–Sn–Cl(3)	114.3(1)	Pd(1)–P(2)–C(33)	121.6(5)
Pd(1)–Sn–Cl(4)	122.0(1)	Pd(1)–P(2)–C(38)	103.3(5)
Cl(2)–Sn–Cl(3)	101.2(2)	C(26)–P(2)–C(33)	103.7(7)
Cl(2)–Sn–Cl(4)	97.6(2)	C(26)–P(2)–C(38)	103.0(7)
Cl(3)–Sn–Cl(4)	91.4(1)	C(33)–P(2)–C(38)	107.5(7)
Sn–Pd(1)–Pd(2)	165.8(1)	Pd(2)–P(3)–C(1)	110.2(5)
Sn–Pd(1)–P(1)	96.4(1)	Pd(2)–P(3)–C(16)	111.2(5)
Sn–Pd(1)–P(2)	96.7(1)	Pd(2)–P(3)–C(21)	124.6(5)
Pd(2)–Pd(1)–P(1)	78.1(1)	C(1)–P(3)–C(16)	105.1(7)
Pd(2)–Pd(1)–P(2)	91.8(1)	C(1)–P(3)–C(21)	102.0(7)
Pd(1)–Pd(2)–Cl(1)	172.0(1)	C(16)–P(3)–C(21)	101.8(7)
Pd(1)–Pd(2)–P(3)	82.8(1)	Pd(2)–P(4)–C(38)	115.6(5)
Pd(1)–Pd(2)–P(4)	90.5(1)	Pd(2)–P(4)–C(44)	120.8(5)
Cl(1)–Pd(2)–P(3)	102.0(1)	Pd(2)–P(4)–C(50)	110.4(5)
Cl(1)–Pd(2)–P(4)	86.3(1)	C(38)–P(4)–C(44)	102.9(7)
Pd(1)–P(1)–C(1)	108.1(5)	C(38)–P(4)–C(50)	102.9(7)
Pd(1)–P(1)–C(2)	120.2(5)	C(44)–P(4)–C(50)	102.0(7)
Pd(1)–P(1)–C(13)	112.2(5)	P(1)–C(1)–P(3)	102.4(8)
C(1)–P(1)–C(2)	106.3(7)	P(2)–C(38)–P(4)	107.5(8)
C(1)–P(1)–C(13)	106.2(7)		
C(2)–P(1)–C(13)	103.0(7)		

contacts are at distances of 2.83 [C(44)–C(50)] and 2.85 Å [C(16)–C(20)] between carbons on adjacent phenyl rings.

The geometry of the trichlorostannate ligand is similar to that observed in the complexes $(\eta^3\text{-}C_3H_5)$-$(Ph_3P)Pd(SnCl_3)$ [10], $(1,5\text{-}C_8H_{12})_2Ir(SnCl_3)$ [11], and $Ru_2(\mu\text{-}Cl)_3(CO)_5(SnCl_3)$ [12]. The tin–palladium bond length (2.585 Å) is similar to the 2.563 Å distance found in $(\eta^3\text{-}C_3H_5)(Ph_3P)Pd(SnCl_3)$ [10]. The coordination about tin is slightly distorted from tetrahedral. As is characteristic of this ligand the Cl–Sn–Cl angles, which range from 91 to 101°, are compressed relative to ideal tetrahedral values, while the Pd–Sn–Cl angles, which fall in the range 114–124°, are correspondingly expanded. The tin–chlorine bond lengths are normal.

The observations shown in Chart 1 provide additional evidence for the ability of the bridging bis(diphenylphosphino)methane ligands to adapt to a variety of different structural changes [2]. Despite the crowded geometry resulting from the placing of the eight phenyl rings about the two metals in $Pd_2(dpm)_2Cl_2$, this molecule still is able to accommodate reactions at both the metal–metal bond and at the terminal metal–halogen bonds. Moreover Pd_2-$(dpm)_2(SnCl_3)Cl$ with its steric congestion near the trichlorostannate ligand has the ability to undergo insertion of carbon monoxide or sulfur dioxide into its Pd–Pd bond.

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