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PHENYL-PHENYL COUPLING IN TRIPHENYLANTIMONY CATALYSED BY PALLADIUM(0)

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Summary. The Pd(0) induced coupling of phenyl groups in triphenylantimony to afford diphenyl and Sb(0) has been studied in a search for possible intermediates. Two complexes containing antimony and palladium have been isolated. Their structures have been determined by X-ray crystallography. Complex **1** is made up of triphenylantimony coordinated to palladium diacetate. It affords diphenyl nearly quantitatively on pyrolysis. Complex **2** contains a phenyl-palladium σ-bond as well as two coordinated triphenylantimony residues.

We have recently reported[1] that certain compounds including Bi(III), Bi(V), Sb(III), Sb(V), and Pb(IV) derivatives, bearing aryl groups, undergo nearly quantitative aryl-aryl coupling when treated with Pd(0). The other product of the reaction is the parent element Bi(0), Sb(0) and Pb(0). The driving force for this reaction is due to the strength of the aryl-aryl bond and the weakness of the aryl- -Bi, -Sb and -Pb bonds. When the aryl-metalloid bond is stronger, no coupling is observed. For example, triphenylarsine is perfectly stable to treatment with Pd(0).

As we have also reported, Pd(0) induced aryl-aryl coupling[2] is seen also with tellurides, but diphenyl selenide is also perfectly stable to this reagent.

We decided to look for intermediates in this coupling process using triphenylantimony. First, we established that a stoichiometric quantity of Pd(0) is required and that both Sb(0) and Pd(0) are formed in the reaction. The Pd(0) was initially produced, as before, by adding triethylamine to palladium acetate. Entries 1 and 2 in Table 1 show typical results. In hexamethylphosphoramide (HMPA) at 60° or in tetrahydrofuran at 70° a high yield of diphenyl was obtained in 1-2 hours. When we omitted the triethylamine (entries 3-9 in Table 1) Pd(0) was again formed and a high yield coupling took place in THF, $CHCl_3$ CCl_4, CH_3CN and C_2Cl_4, but not in pyridine (entry 7).

At room temperature, using the same conditions as for entry 2, the reaction was too slow (27% after 24 hrs.), but on heating the same solution at 70° for 3 hrs., the usual yield (95%) was obtained.

The formation of Pd(0) in the presence of triethylamine is usually regarded as an electron transfer reduction, with 2 moles of acetic acid being formed by dehydrogenation of the base. We have studied the reaction in dry carbon tetrachloride as for entry 5 using anisole as an internal standard. By n.m.r. analysis, the usual yield of diphenyl is seen as well as formation of a mixture of acetic acid and acetic anhydride (total 100%). No diacetyl peroxide was formed. It seems, therefore, improbable that the Pd(0) is formed by homolysis of the palladium-acetate bond. At the temperature used, the acetate radical would at once decarboxylate.[3] It seems probable that palladium diacetate decomposes into palladium oxide and acetic anhydride. Since palladium acetate heated under reflux in tetrahydrofuran for 48 hrs. is stable, the complexing with the substrate Ph_3Sb must give rise to the formation of the Pd(0). However, we still do not know what is oxidized by the palladium oxide.

Table 1. Phenyl-phenyl coupling in triphenylantimony under various conditions[a]

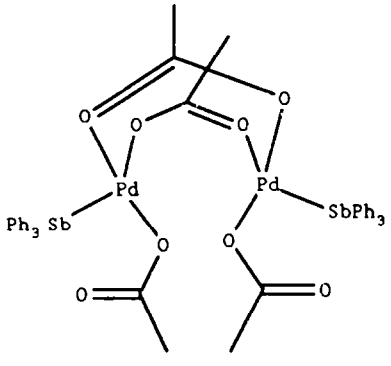
Entry	Et_3N (mmol)	Solvent	Temp.(°C)/ Time (hr)	Ph_2(%)
1	2	HMPA	60/1	90
2	2	THF	70/2	95
3	0	THF	70/14	97
4	0	$CHCl_3$	70/14	99
5	0	CCl_4	70/14	98
6	0	CH_3CN	70/14	98
7	0	Pyr	70/24	<5
8	0	C_2Cl_4	70/2.5	96
9	0	$CHCl_3$	40/24	97

[a] 1.0 mmole of Ph_3Sb and $Pd(OAc)_2$ was used. See experimental section.

The addition of triphenylantimony to palladium acetate in $CDCl_3$ in an n.m.r. tube immediately indicates the formation of a complex. Addition of pentane afforded a crystalline complex between $Pd(OAc)_2$ and Ph_3Sb of the composition $Pd_2(OAc)_4.(SbPh_3)_2$. The addition of triethylamine before or after the other compounds gave the same complex. Heating the complex in $CDCl_3$ at 60° afforded smoothly diphenyl (96%) as well as Pd(0) and Sb(0). This complex was shown by X-ray crystallography to have structure **1**.

The range of solvents used in diphenyl formation makes it improbable that phenyl radicals are involved. The addition of diphenyl diselenide, a potent radicophile, had no effect on the reaction. The addition of dimethylaniline also left the reaction unchanged and the dimethylaniline was recovered quantitatively. This amine is rapidly oxidized by peroxides, thus this confirms that diacetyl peroxide is not formed.

In the search for intermediates, we carried out reactions at lower temperatures. At 47° in THF diphenyl formation had reached 70% after 1 hr. In a second experiment in THF-dioxane at 45° for 1 hr. there was formed on addition of hexane, a new complex. This had a very interesting and unique structure **2**. We have proposed[1] that the aryl coupling reactions involving



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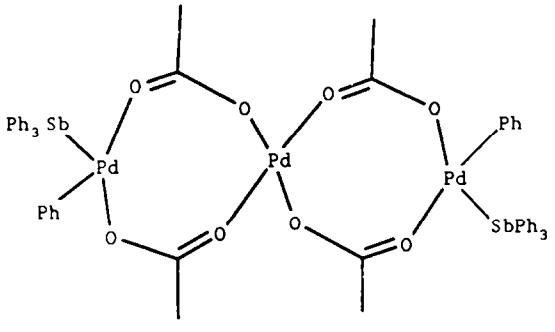

2

Pd(0) and suitable aryl donors proceed by migration of aryl from the metalloid onto palladium. The migration of two aryl groups would give $Pd^{II}Ar_2$ which, by ligand coupling, would furnish again Pd(0). In the first complex **1**, the Ph_3Sb is already complexed to palladium so that when Pd^{II} changes to Pd(0) the rest of the reaction can take place. In the second complex **2**, both phenyl and Ph_3Sb are bonded to palladium^{II} and the same sequence will lead to the coupling of four aryl groups. It would be reasonable to suppose that the single aryl-palladium bonds in **2** represent

one of the odd number of aryl groups in Ph_3Sb. However, it is not certain that this complex **2** is a real intermediate in the reaction. Thus on heating at 70° in tetrahydrofuran for several hours, only 45% of the phenyl groups present were coupled.

Crystallographic Structures of Complexes **1** and **2**:

The perspective views of the complexes **1** and **2** with the atom numbering system are depicted in Fig. 1 and 2, respectively. The corresponding bond lengths and angles are listed in Tables 2 and 3.[4]

Complex **1** and the chloroform molecule of solvation are unique (not laying on or about special positions). The coordination sphere of the Pd atoms in **1** is best described as square pyramidal with three basal positions occupied by oxygen atoms of two bridging acetato ligands and a terminal acetato ligand and the remaining basal site occupied by an Sb atom. The apical site is occupied by an adjacent Pd atom. The basal atoms for Pd1 coordination sphere and Pd2 coordination sphere form a plane (the equation of the plane for Pd1 coordination sphere : $-0.807 = 19.369x - 5.742y - 10.619z$ and for the Pd2 coordination sphere : $-0.0139 = 20.548x + 4.842y - 9.627z$). The Pd atoms deviate from these planes toward the apical atom by 0.099Å and 0.0649Å for Pd1 and Pd2, respectively. The two planes are not parallel with the normal of the two planes forming an angle of 30.5°. The Pd-Pd distance [Pd1-Pd2 = 2.892(4)Å] is less than the sum of their covalent radii and similar to other previously reported Pd-Pd distances in linear complexes.[5] The dihedral angle which describes the geometric position of the triphenylantimony ligands with one another (Sb1-Pd1-Pd2-Sb2)is 107.7° while the dihedral angle which describes the geometric positions of the terminal acetato ligands (O7-Pd1-Pd2-O6) is -92.2°. The chloroform solvation molecule is isolated with nearest neighbor at 3.34(1)Å (chloroform C to O8).

Only one-half of complex **2** and one-half of the dioxan molecule of solvation are unique. Complex **2** sits on a crystallographic inversion center about the special position 1/2,0,1. The remaining half of the dioxan molecule is generated by the inversion operation. The coordination sphere with Pd2 occupying the special position (0,0,0). The remaining half of the complex is generated by the inversion operation. The dioxan molecule sits about the special position 1/2,0,1. The remaining half of the dioxan molecule is generated by the inversion operation. The coordination sphere

Table 2. Selected bond lengths and bond angles for complex **1**

Bond lengths (Å)

Pd(1)-Pd(2)	2.892 (4)	Pd(1)-Sb(1)	2.508 (4)
Pd(1)-O(2)	2.001 (20)	Pd(1)-O(4)	2.087 (21)
Pd(1)-O(7)	1.985 (24)	Pd(2)-Sb(2)	2.509 (4)
Pd(2)-O(1)	2.133 (21)	Pd(2)-O(3)	2.018 (21)
Pd(2)-O(6)	1.980 (25)	Sb(1)-C(6)	2.120 (27)
Sb(1)-C(12)	2.075 (30)	Sb(1)-C(18)	2.144 (27)
Sb(2)-C(24)	2.082 (34)	Sb(2)-C(30)	2.138 (22)
Sb(2)-C(36)	2.119 (23)	C(37)-C(38)	1.522 (47)
C(37)-O(3)	1.299 (43)	C(37)-O(4)	1.229 (42)
C(39)-C(40)	1.533 (47)	C(39)-O(1)	1.256 (41)
C(39)-O(2)	1.252 (42)	C(41)-C(42)	1.493 (56)
C(41)-O(5)	1.222 (50)	C(41)-O(6)	1.243 (51)
C(43)-C(44)	1.558 (52)	C(43)-O(7)	1.208 (46)
C(43)-O(8)	1.256 (48)		

Bond angles (°)

Pd(2)-Pd(1)-Sb(1)	109.6(1)	Pd(2)-Pd(1)-O(2)	84.4(6)
Sb(1)-Pd(1)-O(2)	87.4(6)	Pd(2)-Pd(1)-O(4)	77.7(6)
Sb(1)-Pd(1)-O(4)	171.4(6)	O(2)-Pd(1)-O(4)	88.8(8)
Pd(2)-Pd(1)-O(7)	96.6(6)	Sb(1)-Pd(1)-O(7)	97.6(7)
O(2)-Pd(1)-O(7)	174.3(9)	O(4)-Pd(1)-O(7)	85.8(9)
Pd(1)-Pd(2)-Sb(2)	105.4(1)	Pd(1)-Pd(2)-O(1)	77.9(6)
Sb(2)-Pd(2)-O(1)	175.2(6)	Pd(1)-Pd(2)-O(3)	84.0(6)
Sb(2)-Pd(2)-O(3)	89.2(6)	O(1)-Pd(2)-O(3)	87.8(8)
Pd(1)-Pd(2)-O(6)	97.4(7)	Sb(2)-Pd(2)-O(6)	96.9(7)
O(1)-Pd(2)-O(6)	85.9(9)	O(3)-Pd(2)-O(6)	173.0(10)
Pd(1)-Sb(1)-C(6)	127.2(6)	Pd(1)-Sb(1)-C(12)	114.4(6)
C(6)-Sb(1)-C(12)	105.3(8)	Pd(1)-Sb(1)-C(18)	108.3(6)
C(6)-Sb(1)-C(18)	97.4(8)	C(12)-Sb(1)-C(18)	99.7(8)
Pd(2)-Sb(2)-C(24)	120.3(8)	Pd(2)-Sb(2)-C(30)	106.2(6)
C(24)-Sb(2)-C(30)	100.7(10)	Pd(2)-Sb(2)-C(36)	122.2(5)
C(24)-Sb(2)-C(36)	104.1(9)	C(30)-Sb(2)-C(36)	99.1(9)
Sb(1)-C(6)-C(1)	119.0(6)	Sb(1)-C(6)-C(5)	120.4(6)
Sb(1)-C(12)-C(7)	120.0(6)	Sb(1)-C(12)-C(11)	120.0(6)
Sb(1)-C(18)-C(13)	119.7(6)	Sb(1)-C(18)-C(17)	120.3(6)
Sb(2)-C(24)-C(19)	120.1(8)	Sb(2)-C(24)-C(23)	119.9(8)
Sb(2)-C(30)-C(25)	121.3(6)	Sb(2)-C(30)-C(29)	118.6(5)
Sb(2)-C(36)-C(31)	120.4(5)	Sb(2)-C(36)-C(35)	119.3(6)
C(38)-C(37)-O(3)	111.0(29)	C(38)-C(37)-O(4)	120.9(31)
O(3)-C(37)-O(4)	127.4(32)	C(40)-C(39)-O(1)	116.0(29)
C(40)-C(39)-O(2)	111.1(27)	O(1)-C(39)-O(2)	130.3(31)
C(42)-C(41)-O(5)	113.2(36)	C(42)-C(41)-O(6)	118.8(36)
O(5)-C(41)-O(6)	127.5(39)	C(44)-C(43)-O(7)	119.8(34)
C(44)-C(43)-O(8)	114.6(32)	O(7)-C(43)-O(8)	125.6(35)
Pd(2)-O(1)-C(39)	123.5(21)	Pd(1)-O(2)-C(39)	120.6(19)
Pd(2)-O(3)-C(37)	121.3(20)	Pd(1)-O(4)-C(37)	126.2(22)
Pd(2)-O(6)-C(41)	124.3(26)	Pd(1)-O(7)-C(43)	123.4(24)

Table 3. Selected bond lengths and bond angles for complex **2**

Bond lengths (Å)

Pd(1)-Pd(2)	3.012 (3)	Pd(1)-O(4)	2.006 (25)
Pd(1)-O(6)	1.942 (27)	Pd(1)-Pd(2A)	3.012 (3)
Pd(1)-O(4A)	2.006 (25)	Pd(1)-O(6A)	1.942 (27)
Pd(2)-Sb	2.473 (4)	Pd(2)-O(3)	2.181 (26)
Pd(2)-O(5)	2.146 (26)	Pd(2)-C(12)	1.992 (26)
Sb-C(18)	2.132 (25)	Sb-C(24)	2.119 (29)
Sb-C(30)	2.110 (18)	O(3)-C(3)	1.275 (35)
O(4)-C(3)	1.196 (40)	C(3)-C(4)	1.579 (58)
O(5)-C(5)	1.296 (33)	O(6)-C(5)	1.256 (40)
C(5)-C(6)	1.500 (58)		

Bond angles (°)

Pd(2)-Pd(1)-O(4)	82.0(5)	Pd(2)-Pd(1)-O(6)	82.7(5)
O(4)-Pd(1)-O(6)	89.8(10)	Pd(2)-Pd(1)-Pd(2A)	180.0(1)
O(4)-Pd(1)-Pd(2A)	98.0(5)	O(6)-Pd(1)-Pd(2A)	97.3(5)
Pd(2)-Pd(1)-O(4A)	98.0(5)	O(4)-Pd(1)-O(4A)	180.0(1)
O(6)-Pd(1)-O(4A)	90.2(10)	Pd(2A)-Pd(1)-O(4A)	82.0(5)
Pd(2)-Pd(1)-O(6A)	97.3(5)	O(4)-Pd(1)-O(6A)	90.2(10)
O(6)-Pd(1)-O(6A)	180.0(1)	Pd(2A)-Pd(1)-O(6A)	82.7(5)
O(4A)-Pd(1)-O(6A)	89.8(10)	Pd(1)-Pd(2)-Sb	114.7(1)
Pd(1)-Pd(2)-O(3)	76.1(5)	Sb-Pd(2)-O(3)	169.1(5)
Pd(1)-Pd(2)-O(5)	74.3(6)	Sb-Pd(2)-O(5)	91.1(7)
O(3)-Pd(2)-O(5)	91.4(10)	Pd(1)-Pd(2)-C(12)	110.4(6)
Sb-Pd(2)-C(12)	85.8(7)	O(3)-Pd(2)-C(12)	91.0(10)
O(5)-Pd(2)-C(12)	175.1(8)	Pd(2)-Sb-C(18)	113.9(5)
Pd(2)-Sb-C(24)	125.2(8)	C(18)-Sb-C(24)	100.9(10)
Pd(2)-Sb-C(30)	110.6(7)	C(18)-Sb-C(30)	102.4(9)
C(24)-Sb-C(30)	101.0(8)	Pd(2)-O(3)-C(3)	119.8(25)
Pd(1)-O(4)-C(3)	122.5(23)	O(3)-C(3)-O(4)	134.5(40)
O(3)-C(3)-C(4)	109.0(29)	O(4)-C(3)-C(4)	116.5(27)
Pd(2)-O(5)-C(5)	129.5(23)	Pd(1)-O(6)-C(5)	129.7(21)
O(5)-C(5)-O(6)	121.0(33)	O(5)-C(5)-C(6)	118.6(29)
O(6)-C(5)-C(6)	120.5(25)	Pd(2)-C(12)-C(7)	119.0(6)
Pd(2)-C(12)-C(11)	120.4(6)	Sb-C(18)-C(13)	116.2(5)
Sb-C(18)-C(17)	123.8(5)	Sb-C(24)-C(19)	119.8(7)
Sb-C(24)-C(23)	120.2(7)	Sb-C(30)-C(25)	118.5(6)
Sb-C(30)-C(29)	121.5(6)		

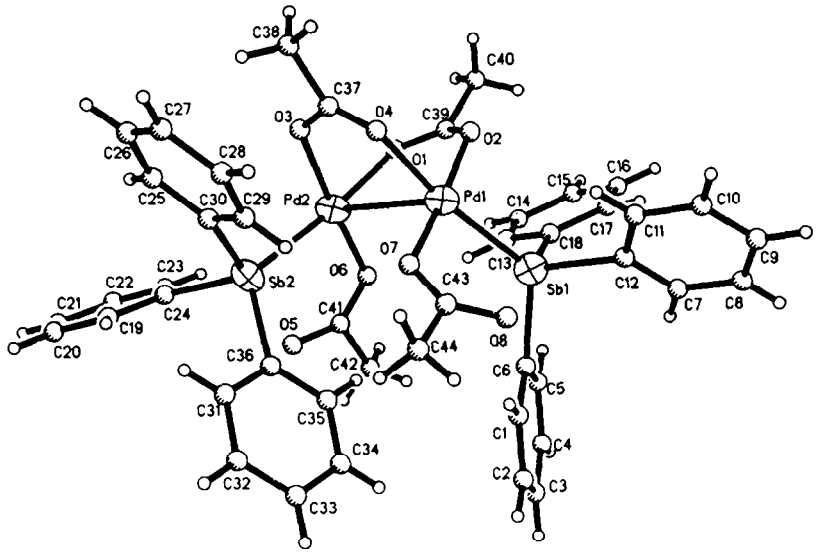
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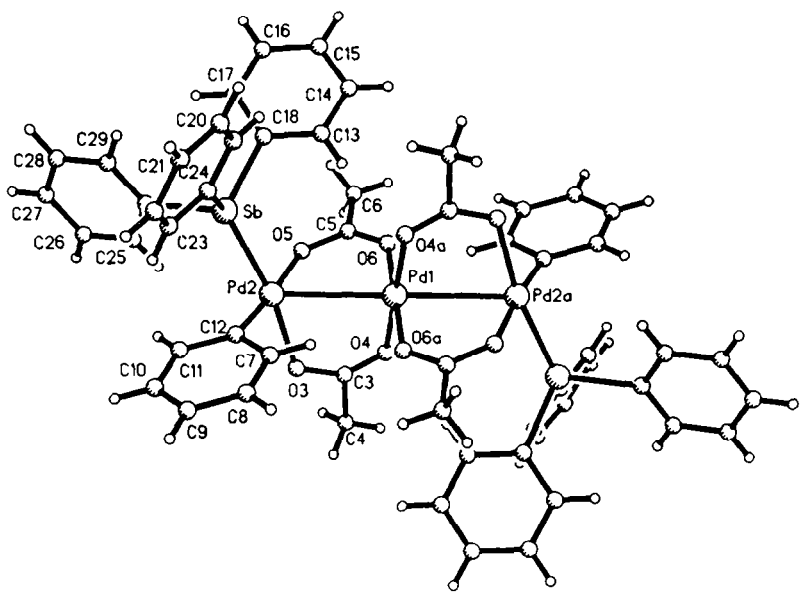
Fig. 1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C26
C25
C23
O6
Pd1
Pd2
Pd2a
C12
O4
O6a
C10
C11
C7
O3
C3
C8
C9
C4

Fig. 2

for Pd1 in complex **2** is best described as a distorted octrahedron. The four meridial sites of the octrahedral are occupied by oxygen atoms of bridging acetato ligands. The remaining apical sites are occupied by adjacent Pd atoms (Pd2 and Pd2a). The Pd1-Pd2 vector is not normal to the plane formed by the meridianal oxygen atoms but bent toward O4 and O6 [Pd2-Pd2-O4 = 81.9(5)° and Pd2-Pd1-O6 = 83.0(5)°]. The coordination sphere for Pd2 in complex **2** is best described as square pyramidal. The adjacent Pd1 atom occupies the apical position. The basal sites are occupied by two oxygen atoms from bridging acetato ligands, Sb and a carbon atom of the coordinated phenyl ring. The four basal atoms form a plane (equation of the plane : 2.819 = - 4.600x + 7.624y + 5.529z). The Pd2 atom deviates 0.138Å from this plane toward the apical Pd1 atom. The meridianal plane of the coordination sphere for Pd1 and the basal plane for the coordination sphere for Pd2 are not parallel and the angle between the normals of the two planes intersect at 37.7°. The Pd-Pd separation 3.013(3)Å is less than the sum of the covalent radii for Pd but significantly longer than that seen for complex **1**. The phenyl group is seen coordinated to the Pd2 atom. Large, but not significant differences, were seen for aromatic carbon-carbon bond distances in the phenyl ring [1.43(7)Å (C7-C8) to 1.31(6)Å (C7-C12) on average 1.36(4)Å] which may have been due to the crystal quality, data collection and/or structure refinement quality rather than chemical effects. It was decided that a chemically correct phenyl ring with idealized bond distances would be a more suitable model. The idealized ring was included in the final refinement cycles. The dioxan molecule of solvation is isolated with nearest neighbors 3.79Å (O100-C27), 3.79Å (C100-C21) and 3.80Å (C200-O4).

Experimental

General: ^{1}H-NMR spectra were recorded with a Varian EM 390 or a Varian Gemini-200 spectrometer (δ scale, TMS as an internal standard). The IR spectra were measured with a Perkin-Elmer 881 spectrometer; only the most significant absorptions were listed. Analytical g.c. was performed on a Chrompack 439 equipped with a FID detector using a fused silica capillary column CP5-Sil-5 CB, 20x0.22 mm id. (N_2 as carrier gas). Preparative t.l.c. separations were performed using Analtech silica gel GF (1000 microns) plates. Melting points were determined on a Kofler hot stage and are uncorrected.

Procedure for the Formation of Diphenyl from the Reaction of Triphenylantimony with Palladium Diacetate: A solution of triphenylantimony (0.36 g; 1.0 mmol), palladium diacetate (0.22 g; 1.0 mmol) and cyclododecane (internal standard, 6.7×10^{-2} g; 0.40 mmol) in a solvent (10 ml) was stirred at room temperature (see Table 1). In a few minutes, triphenylantimony disappeared with the formation of a polar product (t.l.c.; hexane:ether, 9:1). The solution was then kept at 70° until deposition of the black precipitate was complete. This was removed by filtration. The quantity of diphenyl formed was determined by g.c. analysis of an aliquot from the filtrate (0.5 ml) dissolved in hexane (5.0 ml). The retention times (min) at 85° (isothermal) was 2.18 for cyclododecane and 2.67 for diphenyl. Analytical sample of diphenyl obtained by preparative t.l.c. (hexane:ether, 9:1) (mp. 69-71°) was compared with the authentic sample (mixed mp. 69-72°).

Preparation of Complex **1**: A solution of triphenylantimony (0.36 g; 1.0 mmol) and palladium diacetate (0.22 g; 1.0 mmol) in $CHCl_3$ (10 ml) was stirred at room temperature for 45 min. Then pentane was added slowly to induce formation of orange crystals. The solution was kept at room temperature for complete deposition of the crystals which were filtered (0.56 g; 95%), washed with pentane and air dried. Mp. 106-109 (dec.); ^{1}H-NMR ($CDCl_3$) δ: 7.1-7.8 (30H, m), 1-2 (12H, m); IR ($CHCl_3$) ν: 1557 and 1380 cm^{-1}.

Decomposition of Complex **1**: A solution of the complex **1** (0.20 g; 0.17 mmol) and cyclododecane (internal standard, 0.084 g; 0.5 mmole) in THF (20 ml) was stirred at 70° for 1 hr. The solution was freed from the black precipitate by filtration. An aliquot from the filtrate was dissolved in hexane and analyzed by g.c. The yield of diphenyl was 94%.

Preparation of Complex **2**: A solution of triphenylantimony (0.36 g; 2.0 mmol) and palladium diacetate (0.22 g; 1.0 mmol) in dioxan (10 ml) was stirred at 45° for 45 min. During this time, a color change from dark red to dark green was observed. Hexane was added slowly to the cooled (ice-bath) solution until formation of a brown precipitate. This precipitate was removed by filtration and the filtrate was kept in a refrigerator for 3 days. The deposited crystals were filtered and washed with hexane (0.5g; 50%). Mp. 127-131°; ^{1}H-NMR ($CDCl_3$) δ: 7.2-7.7 (34H, m), 6.7-6.82 (6H, m), 1.94 (3H, s), 1.70 (3H, s), 1.33 (3H, s), 1.12 (3H, s); IR ($CHCl_3$) ν: 1557 and 1415 cm^{-1}.

Decomposition of Complex **2**: Complex **2** (300 mg; 0.21 mmol) and cyclododecane

(internal standard, 0.084 g; 0.50 mmol) were dissolved in THF (10 ml). The solution was stirred at 70° for 8 hrs. An aliquot (0.5 ml) was extracted with hexane (5.0 ml); g.c. analysis of the hexane solution showed the formation of 45% of diphenyl.

X-Ray Structure Analysis: Only very small plates of **1** and **2** could be grown from solution. Finally after several repeated attempts, small but suitable crystals of **1** and very small crystals of **2** were chosen. Preliminary X-ray single-crystal diffraction analysis by omega scanning techniques indicated poor crystal quality for **1** and **2**. The best samples were eventually chosen and submitted to X-ray analysis. Crystals of **2** proved too small to be analyzed on a conventional sealed-tube X-ray diffractometer and were submitted for analysis on a rotating anode X-ray diffractometer.

An orange plate [0.03mm x 0.11mm x 0.21mm] for **1** and a dark orange plate [0.034mm x 0.067mm x 0.11mm] for **2** were mounted on glass fibers with epoxy cement at room temperature.

Data Collection: Preliminary examination and data collection for **1** was performed on a Nicolet R3m/V X-ray diffractometer. Examination and data collection for **2** were performed on a Rigaku AFC5R rotating anode X-ray diffractometer. Both diffractometers employed a oriented graphite monochromator; MoKα λ = 0.71073 Å radiation.

Data were collected for $4.0° \leq 2\theta \leq 50.0°$ for **1** [ω-2θ scans; $-26 \leq h \leq 0$, $-21 \leq k \leq 0$m $0 \leq l \leq 20$] and $4.0° \leq 2\theta \leq 50.0°$ for **2** [ω scans, Lehmann-Larsen processing[6]; $0 \leq h \leq 14$, $-16 \leq k \leq 15$, $-11 \leq k \leq 11$] at room temperature. Scan range for data collection was 1.2° for **1** and 1.75° for **2** plus the Kα separation. Scan rate for **1** was variable (2.0° min^{-1} to 30.0° min^{-1}) and constant for **2** (4.0° min^{-1}). Three control reflections collected every 97 and 150 reflections for **1** and **2** respectively, showed no significant trends. Lorentz and polarization corrections were applied to 6955 reflections for **1** and 5434 reflections for **2**. A semi-emperical[7] absorption correction was applied (ellipsoidal approximation, μr = 0.04; T_{max} = 0.910; T_{min} = 0.836). No absorption correction was applied to **2**. Reflections were profiled for **1** by employing a learnt profile technique.[8] A total of 1610 unique observed reflections for **1** and 1378 reflections for **2** both with $|I| \geq 4\sigma|I|$, were used in further calculations.

Crystal Data for Complex **1**: Chemical formula: $C_{45}H_{43}O_8Cl_3Pd_2Sb_2$; formula weight: 1274.4 amu; space group and unit cell dimensions: Orthorhombic Pbca, a = 24.682(7)Å, b = 20.296(6)Å, c = 19.255(4)Å; volume: 9646(4)Å^3; Density

(calc.): 1.755 g/cm^3; absorption coefficient: 2.056 mm^{-1}; F(000): 4976e$^-$; formula units per cell: 8.

Crystal Data for Complex **2**: Chemical formula: $C_{30}H_{26}O_5Pd_{1.5}Sb$; formula weight: 747.9 amu; space group and unit cell dimensions: Triclinic P 1-BAR a = 12.615(6)Å, b = 13.471(4)Å, c = 9.632(3)Å, α = 110.13(2)° β = 96.04(5)°, γ = 102.03(4)°; volume : 1474.9(9)Å^3; density (calc.) = 1.684 g/cm^3; absorption coefficient = 1.849 mm^{-1}; F(000) : 732 e$^-$; formula units per cell : 2.

Structure Solution and Refinement: The structures were solved by Direct Methods [SHELXS, SHELXTL-PLUS program package, Sheldrick, G.M. (1988)].[9] Full-matrix least squares anisotropic refinement for Pd1, Pd2, Sb1 and Sb2 and isotropic refinement for all remaining non-hydrogen atoms for **1** and full-matrix least squares anisotropic refinement for Pd1, Pd2 and Sb and isotropic refinement for all non-hydrogen atoms for **2** yielded R = 0.058; wR = 0.060 and S = 1.76 for **1** and R = 0.071; wR = 0.082 and S = 1.94 for **2** at convergence [SHELXLS, SHELXLS program package, Sheldrick, G.M. (1988); 189 and 165 least squares parameters for **1** and **2**, respectively; quantity minimized $\Sigma w (F_o-F_c)^2$; $w = \sigma^2F + gF^2$ where g = 0.0001 for **1** and **2**; largest Δ/σ was 0.0003 for **1** and 0.045 for **2** while the average Δ/σ was 0.0001 for **1** and 0.0001 for **2**; largest positive peak in the final Fourier difference map was 0.97 e$^-$Å^{-3} for **1** and 1.21 e$^-$Å^{-3} for **2**; largest negative peak was -0.64e$^-$Å^{-3} for **1** and -1.34e$^-$Å^{-3} for **2**][4]. Hydrogen atoms were placed in idealized positions with isotropic thermal paramaters fixed at 0.08 for **1** and **2**. In the final models, all phenyl rings were constrained to idealized hexagons (C-C bond distances fixed at 1.395Å) for **1** and **2**. The constrained models were included in the final refinement cycles. Near the end of the refinement a molecule of chloroform was located in the unique volume of the unit cell for **1** and one-half of a molecule of dioxan was located to rest about the inversion center (1/2,0,1) in the unique volume of the unit cell of **2**. Atoms C50, Cl1, Cl2 and Cl3 were included in the atom list for **1** and their atomic distances were fixed to idealized values with the routine DFIX.[9] Atoms O100, C100 and C200 were included in the atom list for **2** and their atomic distances and the distances to the inversion center were fixed to idealized values with the routine DFIX.[9] The constrained models were then included in the final refinement cycles for **1** and **2**. Neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ were taken from reference 10.[10]

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