Cationic η^5-Cyclopentadienylpalladium(II) Complexes. Compounds of Type $[Pd(\eta^5-C_5H_5)L_2]PF_6$ containing Tertiary Phosphines, Arsines, and Stibines. Crystal and Molecular Structure of $[Pd(\eta^5-C_5H_5)(SbPh_3)_2]PF_6{\cdot}CH_2Cl_2$ ‡

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The complexes $[Pd(\eta^5-C_5H_5)L_2]PF_6$ [where L = PMe_2Ph, PPh_3, $AsMe_2Ph$, $AsPh_3$, or $SbPh_3$ and L_2 = (*SS*)-, (*RR,SS*)-, (*RS*)-$C_6H_4(PMePh)_2$-*o* or (*SS*)-, (*RR,SS*)-, (*RS*)-$C_6H_4(AsMePh)_2$-*o*] have been prepared in high yield from the appropriate complexes $[PdCl_2L_2]$ and cyclopentadiene in Me_2CO in the presence of $AgPF_6$, or with $AgNO_3$ followed by metathesis with NH_4PF_6. The brightly coloured compounds conduct as uni-univalent electrolytes in Me_2CO and CH_2Cl_2 and have spectroscopic properties consistent with η^5 co-ordination of the cyclopentadienyl moiety in solution. The molecular structure of $[Pd(\eta^5-C_5H_5)(SbPh_3)_2]PF_6{\cdot}CH_2Cl_2$ has been determined by a single-crystal *X*-ray analysis. The crystals are monoclinic, space group $P2_1/c$ with a = 12.506(6), b = 19.002(7), c = 18.575(5) Å, β = 106.53(3)°, and Z = 4. The structure was solved by heavy-atom methods at 295(1) K and refined by least-squares methods to R = 0.051 for 4 384 observed reflections. The arrangement of the two antimony atoms and the centre of the cyclopentadienyl ring about the palladium atom is approximately trigonal. The co-ordinated cyclopentadienyl moiety shows no significant deviations from planarity.

Although complexes of the type $[Pd(\eta^5-C_5H_5)L_2]X$ containing chelating di-olefins have been known for some time,[1,2] the preparation of similar compounds involving chelating ditertiary-arsines and -phosphines has not hitherto been reported. The only related work appears to be that of Cross and Wardle [3] who isolated $[Pd(\eta^5-C_5H_5)(PEt_3)_2]Br$ from the reaction between $[PdBr(\eta^5-C_5H_5)(PEt_3)]$ and triethylphosphine. However, the nature of the added ligand was critical for the success of the reaction: triphenylphosphine did not produce an ionic product [although evidence of a σ-cyclopentadienylpalladium(II) species was found] and carbon monoxide apparently did not react. Because of our interest in bivalent palladium systems containing dissymmetric ditertiary-arsines and -phosphines [4] we have developed a convenient method of synthesis for the compounds $[Pd(\eta^5-C_5H_5)L_2]PF_6$, which we believe to be of considerable generality.

Results and Discussion

The addition of two equivalents of $AgPF_6$ to a suspension of *cis*- or *trans*-$[PdCl_2L_2]$ [where L = PMe_2Ph, PPh_3, $AsMe_2Ph$, $AsPh_3$, or $SbPh_3$ and L_2 = (*SS*)-, (*RR,SS*)-, (*RS*)-$C_6H_4(PMePh)_2$-*o* [5] or (*SS*)-, (*RR,SS*)-, (*RS*)-$C_6H_4(AsMePh)_2$-*o* [6]] in acetone led to the rapid precipitation of silver chloride [equation (i)].

$$[PdCl_2L_2] + 2AgPF_6 \xrightarrow{Me_2CO} [Pd(Me_2CO)_2L_2][PF_6]_2 + 2AgCl \quad (i)$$

The bis-acetone species were reasonably stable in acetone solution, but could not be isolated in a crystalline state. The product derived from *cis*-$[PdCl_2(SbPh_3)_2]$ was the least stable, decomposing within several minutes of formation. Conductivity measurements on the reaction mixtures (after removal of AgCl) were consistent with the presence of di-univalent electrolytes in each case.

Treatment of the yellow coloured acetone solutions of the respective hexafluorophosphate salts with cyclopentadiene resulted in a rapid change in colour of the reaction mixtures due to the formation of the corresponding η^5-cyclopentadienylpalladium(II) derivatives [equation (ii)].

$$[Pd(Me_2CO)_2L_2][PF_6]_2 + C_5H_6 \xrightarrow{Me_2CO} [Pd(\eta^5-C_5H_5)L_2]PF_6 + HPF_6 \quad (ii)$$

High yields of the brightly coloured air-stable products, (1)—(11) were obtained from the reaction mixture by the addition of diethyl ether (Table 1). Because of the instability of the intermediate containing triphenylstibine, the cyclopentadiene was added to the reaction mixture before the $AgPF_6$ in the preparation of (5). Use of $AgNO_3$ was also found satisfactory. For example, reaction of $[PdCl_2\{(SS)\text{-}C_6H_4(AsMePh)_2\text{-}o\}]$ with two equivalents of $AgNO_3$ in aqueous methanol led to the immediate precipitation of AgCl, which was filtered off. Cyclopentadiene was then added to the pale yellow filtrate, followed by aqueous NH_4PF_6. Recrystallization of the precipitate from acetone by the addition of diethyl ether afforded $[Pd(\eta^5-C_5H_5)\{(SS)\text{-}C_6H_4(AsMePh)_2\text{-}o\}]PF_6{\cdot}0.5Me_2CO$ (9) in 92% yield.

Crystal and Molecular Structure of $[Pd(\eta^5-C_5H_5)(SbPh_3)_2]PF_6{\cdot}CH_2Cl_2$ (5).—The asymmetric unit of the crystal consists of the complex cation and associated anion, as well as a solvent molecule (Figure 1). The crystal was obtained from dichloromethane solution by the addition of diethyl ether. The stereochemical arrangement of the atoms in the cation is depicted in Figure 2 and the corresponding distances and angles associated with the palladium and antimony atoms are

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‡ η^5-Cyclopentadienylbis(triphenylstibine)palladium(II) hexafluorophosphate-dichloromethane (1/1).

Supplementary data available (No. SUP 23368, 28 pp.): observed and calculated structure factors, thermal parameters, hydrogen atom parameters, least-squares planes, anion geometry. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Physical properties and analytical data (%) for the complexes $[Pd(\eta^5\text{-}C_5H_5)L_2]PF_6$

				Λ_M [a]		Analysis (%)			
						Found		Calc.	
Complex	Colour	M.p. (°C)	Yield (%)	Acetone	Dichloromethane	C	H	C	H
(1) $[Pd(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]PF_6$ [b]	Red	166—167	94	132	47	43.2	4.7	43.5	4.9
(2) $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)_2]PF_6$ [c]	Purple	194—196	78	128	59	54.8	3.8	54.5	4.0
(3) $[Pd(\eta^5\text{-}C_5H_5)(AsMe_2Ph)_2]PF_6$ [b]	Purple	173—174	98	137	45	38.2	4.1	38.1	4.3
(4) $[Pd(\eta^5\text{-}C_5H_5)(AsPh_3)_2]PF_6$ [c]	Blue	191—192	84	129	54	49.6	3.6	49.8	3.7
(5) $[Pd(\eta^5\text{-}C_5H_5)(SbPh_3)_2]PF_6$ [c]	Blue	145—148	85	128	55	45.7	3.4	45.6	3.4
(6) $[Pd(\eta^5\text{-}C_5H_5)\{(SS)\text{-}C_6H_4(PMePh)_2\text{-}o\}]PF_6$ [d]	Orange	216—220	39 [e]	135	48	46.6	4.0	47.0	3.9
(7) $[Pd(\eta^5\text{-}C_5H_5)\{(RR,SS)\text{-}C_6H_4(PMePh)_2\text{-}o\}]PF_6$	Orange	188—190	85	133	48	46.7	4.0	47.0	3.9
(8) $[Pd(\eta^5\text{-}C_5H_5)\{(RS)\text{-}C_6H_4(PMePh)_2\text{-}o\}]PF_6$	Orange	224—225	88	128	49	47.4	4.1	47.0	3.9
(9) $[Pd(\eta^5\text{-}C_5H_5)\{(SS)\text{-}C_6H_4(AsMePh)_2\text{-}o\}]PF_6$ [b,f]	Violet	155—160	84	127	49	42.1	3.7	42.1	3.7
(10) $[Pd(\eta^5\text{-}C_5H_5)\{(RR,SS)\text{-}C_6H_4(AsMePh)_2\text{-}o\}]PF_6$ [b]	Violet	142—143	92	130	48	42.5	3.8	42.1	3.7
(11) $[Pd(\eta^5\text{-}C_5H_5)\{(RS)\text{-}C_6H_4(AsMePh)_2\text{-}o\}]PF_6$	Violet	196—200	85	129	47	41.4	3.5	41.3	3.5

[a] Conductance in Ω^{-1} cm^2 mol^{-1} for 10^{-3} mol dm^{-3} solutions at 293 K; all complexes behave as 1 : 1 electrolytes. [b] Isolated as acetone hemisolvates. [c] Recrystallized from CH_2Cl_2–Et_2O and isolated as dichloromethane monosolvates. [d] α[589.3 nm, 20 °C, (6), 22 g dm^{-3} in CH_2Cl_2, 10 cm] = +835°. [e] Crystallized from cold methanol with difficulty. [f] α[589.3 nm, 20 °C, (9), 22 g dm^{-3} in CH_2Cl_2, 10 cm] = +390°.

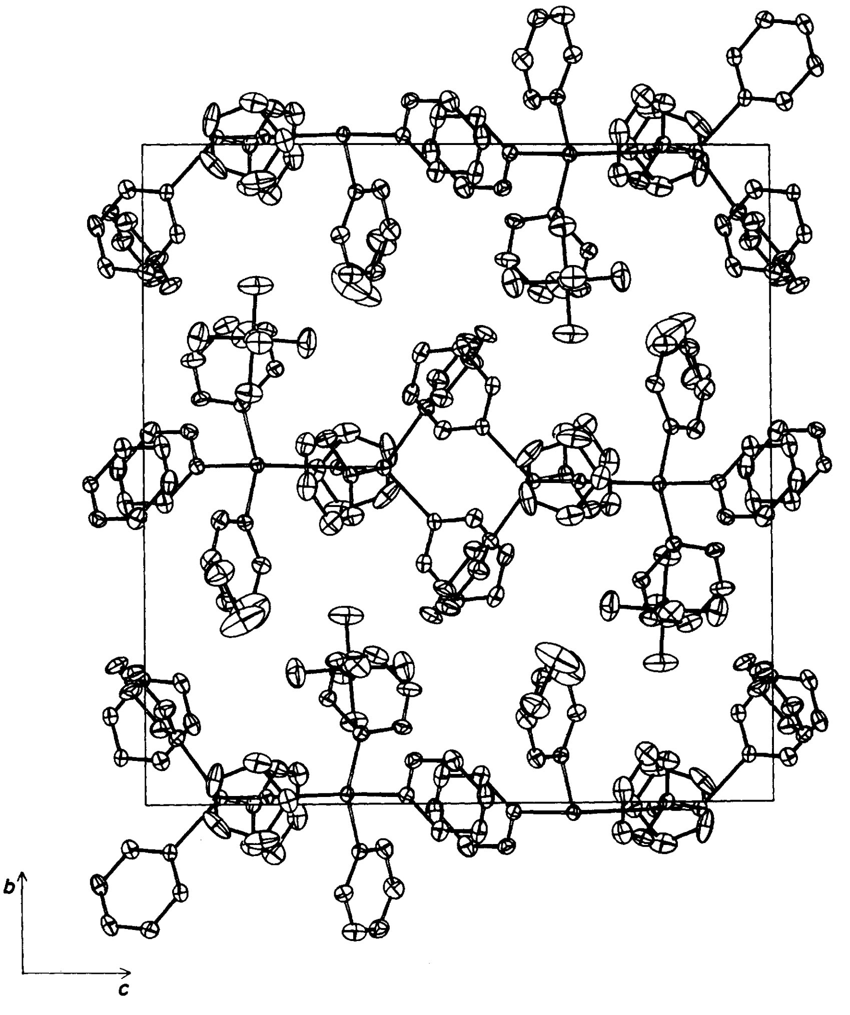

Figure 1. Unit cell contents projected normal to *bc*. Non-hydrogen atoms are shown with 20% thermal ellipsoids

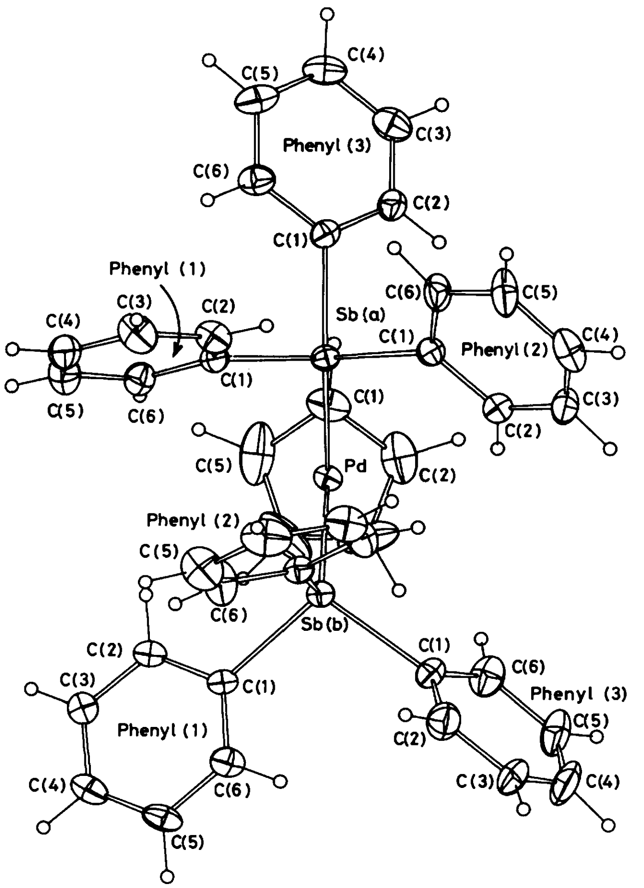

Figure 2. The molecular structure and atom numbering scheme of the cation $[Pd(\eta^5-C_5H_5)(SbPh_3)_2]^+$

Table 2. The palladium environment: the first column (*r*) in the matrix is the Pd-ligand distance (Å); other entries are the angles subtended at the palladium by the relevant atoms

	r(Pd-X)	Sb(b)	C(1)	C(2)	C(3)	C(4)	C(5)
Sb(a)	2.506(1)	96.47(5)	98.9(3)	114.9(5)	150.3(4)	151.8(4)	117.4(4)
Sb(b)	2.527(1)		164.4(3)	133.5(5)	150.8(4)	107.5(4)	135.5(4)
C(1)	2.23(1)			35.0(3)	58.9(5)	58.4(5)	35.7(5)
C(2)	2.30(1)				35.6(6)	57.2(6)	57.8(5)
C(3)	2.25(1)					33.3(6)	57.1(5)
C(4)	2.28(1)						34.4(5)
C(5)	2.31(1)						

Table 3. The antimony environments (presentation as for Table 2): the two values in each entry are for Sb(a,b), respectively

	r(Sb-X)	C(11)	C(21)	C(31)
Pd	2.506(1), 2.527(1)	111.9(2), 113.3(3)	115.0(3), 122.5(3)	118.7(2), 115.8(3)
C(11)	2.10(1), 2.13(1)		107.9(4), 100.1(3)	101.9(4), 101.9(4)
C(21)	2.11(1), 2.12(1)			100.1(4), 100.0(4)
C(31)	2.11(1), 2.15(1)			

presented in Tables 2 and 3 respectively. The palladium atom is symmetrically co-ordinated to the η^5-cyclopentadienyl moiety. The Pd-C distances lie between 2.23(1) and 2.31(1) Å. The slight deviation of the ring from planarity may be accounted for by unsymmetrical packing forces. The arrangement between the centre of the cyclopentadienyl ring and the two antimony atoms is essentially trigonal planar [Sb-Pd-Sb = 96.47(5)°]. Within the triphenylstibine species the Sb-C bond lengths of 2.1_2 Å are *ca.* 0.2 Å longer than corresponding As-C distances, which are typically 1.9_3 Å.[7] Considerable variation was observed in the C-Sb-C angles, *viz.*, 100.0(4)—122.5(3)°. The variation in the Pd-Sb-C angles [111.9(2)—122.5(3)°] may be due to interaction between the triphenylstibine ligands, where C(a22) • • • H(b22) = 2.6_8 Å.

Properties of the Complexes $[Pd(\eta^5-C_5H_5)L_2]PF_6$.—The complexes are appreciably soluble in acetone and dichloromethane in which they behave as uni-univalent electrolytes (Table 1). The compound $[Pd(\eta^5-C_5H_5)(SbPh_3)_2]PF_6$ (5) was the least stable and a solution of it in dichloromethane deposited metal over a 24 h period. The complexes were rapidly decomposed by dilute mineral acids producing $[PdX_2L_2]$. However, they appeared to be quite stable towards concentrated perchloric acid.

Selected spectroscopic properties of the complexes are summarized in Table 4. The cyclopentadienyl resonance in the ^1H n.m.r. spectra of the compounds containing tertiary-arsenic or -antimony donors appears as a sharp singlet in the region *ca.* δ 6 p.p.m., but is split into a triplet (J_{PH} *ca.* 2 Hz) for the phosphine complexes. The PMe resonances in the complexes (1) and (6)—(8) occurred as ' filled-in ' doublets due to the virtual coupling effect characteristic of *cis* co-ordinated methylated tertiary phosphines.[8]

The electronic spectra of the complexes in dichloromethane contain three to four distinguishable bands (Table 4). The low intensity absorption appears to be a *d-d* transition. Its position (475—600 nm) is particularly sensitive to the nature of the ligands present. The high-energy bands have intensities and positions commonly associated with charge transfer and intraligand absorptions.

The method of synthesis of the complexes $[Pd(\eta^5-C_5H_5)L_2]PF_6$ appears to be quite general. For example, use of $[PdCl_2(cod)]$ (cod = cyclo-octa-1,5-diene) as precursor led to $[Pd(\eta^5-C_5H_5)(cod)]PF_6$ in 87% yield. It has been reported that this reaction does not proceed in dichloromethane.[9] Acetylacetone forms the expected complexes $[Pd\{CH(COMe)_2\}L_2]PF_6$ by deprotonation under the conditions we describe.

Experimental

Proton n.m.r. spectra were recorded at 34 °C using a Bruker HX-90 spectrometer. Electronic spectra were obtained on

Table 4. Selected spectroscopic properties of the complexes $[Pd(\eta^5\text{-}C_5H_5)L_2]PF_6$

	^{1}H n.m.r. ($[^2H_6]Me_2CO$) [a]		
Compound	δ(C_5H_5)	δ(PMe) or δ(AsMe)	u.v.–visible (CH_2Cl_2) [b] $\lambda_{max.}(\varepsilon)$
(1) [c]	6.07 (t, *J* 1.9)	1.79 (fd, '*J*' 11)	245 (10 600), 314 (10 500), 505 (118)
(2) [c]	5.67 (t, *J* 2.1)		245 (10 700), 349 (9 800), 555 (87)
(3) [c]	6.12 (s)	1.75 (s)	240 (10 600), 320 (10 100), 565 (77)
(4) [c]	5.94 (s)		245 (10 700), 347 (10 200), 595 (70)
(5) [c]	6.29 (s)		250 (10 600), 356 (10 000), 597 (93)
(6)	5.95 (t, '*J*' 1.9)	2.64 (fd, '*J*' 12.8)	245 (10 700), 280 (10 600), ~300 (sh), 475 (146)
(7)	5.95 (t, '*J*' 1.9)	2.64 (fd, '*J*' 12.8)	245 (10 700), 280 (10 600), ~300 (sh), 475 (145)
(8)	6.02 ('*J*' 1.9)	2.62 (fd, '*J*' 12.8)	243 (10 600), 286 (10 600), ~300 (sh), 475 (170)
(9) [c]	6.17 (s)	2.48 (s)	235 (10 700), 270 (10 700), 322 (9 600), 525 (90)
(10) [c]	6.17 (s)	2.48 (s)	235 (10 700), 270 (10 700), 323 (9 600), 525 (90)
(11)	6.21 (s)	2.49 (s)	240 (10 600), 270 (10 600), 326 (9 700), 530 (99)

[a] Chemical shift values in p.p.m. relative to $SiMe_4$; fd = 'filled in' doublet; '*J*' = $^2J_{PH} + {}^5J_{PH}$ (virtual coupling), *J* values in Hz. [b] For 10^{-3} mol dm^{-3} solutions; absorption coefficients in $dm^3\ mol^{-1}\ cm^{-1}$. [c] Presence of solvent of crystallization confirmed in ^{1}H n.m.r. spectrum.

Table 5. Fractional atomic co-ordinates for complex (5) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	*x*	*y*	*z*
Pd	0.152 49(6)	0.011 19(4)	0.192 07(4)			
(*a*) Cyclopentadienide						
C(1)	−0.004 6(9)	0.005 7(7)	0.226 2(6)			
C(2)	−0.006 0(11)	−0.053 7(7)	0.184 5(11)			
C(3)	−0.006 6(11)	−0.030 6(9)	0.113 1(9)			
C(4)	−0.016 5(10)	0.037 5(10)	0.110 2(7)			
C(5)	−0.019 5(9)	0.063 4(7)	0.177 8(9)			
	Ligand part a			Ligand part b		
(*b*) Triphenylstibine						
Sb	0.290 10(5)	0.015 28(4)	0.319 86(4)	0.294 38(5)	0.010 51(4)	0.118 68(4)
(*i*) Phenyl (1)						
C(1)	0.397 5(8)	−0.072 1(5)	0.339 4(5)	0.269 5(7)	−0.072 2(5)	0.038 5(5)
C(2)	0.513 1(9)	−0.068 2(6)	0.378 9(6)	0.226 3(9)	−0.134 5(6)	0.055 3(5)
C(3)	0.575 6(10)	−0.128 9(7)	0.393 9(7)	0.213 4(10)	−0.191 6(6)	0.005 8(6)
C(4)	0.527 6(11)	−0.192 0(6)	0.369 7(7)	0.244 9(10)	−0.184 9(6)	−0.058 3(6)
C(5)	0.415 7(11)	−0.196 9(6)	0.330 4(8)	0.290 0(9)	−0.122 2(6)	−0.074 5(6)
C(6)	0.351 8(9)	−0.136 6(6)	0.314 1(6)	0.300 9(8)	−0.067 2(6)	−0.024 7(6)
(*ii*) Phenyl (2)						
C(1)	0.389 3(8)	0.106 9(5)	0.342 7(5)	0.468 0(8)	−0.000 3(5)	0.171 1(5)
C(2)	0.369 8(10)	0.161 2(6)	0.290 5(6)	0.532 0(9)	0.054 6(6)	0.209 6(7)
C(3)	0.438 0(11)	0.219 9(6)	0.304 4(7)	0.644 7(10)	0.046 2(7)	0.242 4(7)
C(4)	0.523 5(10)	0.227 0(6)	0.367 5(8)	0.695 6(10)	−0.017 7(8)	0.240 4(7)
C(5)	0.541 3(11)	0.174 4(6)	0.420 3(8)	0.632 9(10)	−0.073 8(8)	0.202 5(8)
C(6)	0.474 0(10)	0.116 3(5)	0.408 5(6)	0.519 2(9)	−0.063 3(6)	0.169 4(7)
(*iii*) Phenyl (3)						
C(1)	0.229 6(8)	0.013 4(5)	0.415 1(5)	0.295 0(8)	0.101 6(5)	0.050 5(6)
C(2)	0.160 4(9)	0.066 1(5)	0.426 6(6)	0.386 8(11)	0.116 0(6)	0.025 9(7)
C(3)	0.121 2(10)	0.065 2(7)	0.488 9(7)	0.385 0(13)	0.172 9(6)	−0.022 7(8)
C(4)	0.147 6(10)	0.010 6(7)	0.540 4(6)	0.293 6(14)	0.213 0(7)	−0.044 7(8)
C(5)	0.219 8(11)	−0.042 8(7)	0.529 5(6)	0.203 9(11)	0.201 3(6)	−0.017 8(8)
C(6)	0.257 8(9)	−0.041 6(6)	0.467 0(6)	0.205 7(10)	0.144 8(6)	0.031 2(7)
(*c*) Solvent						
C	0.035 5(15)	0.278 7(12)	0.155 4(16)			
Cl(1)	0.165 4(5)	0.292 6(5)	0.167 4(5)			
Cl(2)	−0.046 7(4)	0.352 1(3)	0.119 6(3)			
(*d*) Anion						
P	0.896 3(3)	0.207 1(2)	0.325 3(2)			
F(1)	0.894 6(7)	0.124 6(4)	0.332 2(5)			
F(2)	0.776 9(6)	0.212 9(5)	0.337 6(5)			
F(3)	0.843 4(8)	0.200 1(5)	0.239 8(4)			
F(4)	0.948 8(7)	0.209 4(5)	0.412 1(4)			
F(5)	0.899 6(8)	0.287 1(4)	0.320 7(6)			
F(6)	1.016 3(6)	0.200 3(4)	0.315 4(5)			

10^{-3} mol dm^{-3} solutions of the complexes in dichloromethane using a Beckman ACTA MIV spectrophotometer. Conductance measurements were carried out on the same solutions with a Phillips GM 4249 conductivity bridge. Optical rotations were determined in a 10 cm cell at 20 °C by use of a Perkin-Elmer model 141 polarimeter.

Silver hexafluorophosphate was purchased from the Ozark-Mahoning Company, Tulsa, Oklahoma 74119. The complexes containing the diastereoisomers and enantiomers of *o*-phenylenebis(methylphenylphosphine) and its arsenic analogues were prepared according to ref. 4. Analytical data for the complexes are presented in Table 1.

Preparations.—[$PdCl_2L_2$] (L = PMe_2Ph, PPh_3, $AsMe_2Ph$, $AsPh_3$, *or* $SbPh_3$). Palladium(II) chloride (10 mmol) was dissolved in 10 mol dm^{-3} HCl (4 cm^3) by gentle warming on a steam-bath and the solution diluted with ethanol (25 cm^3). This solution was then treated with *ca.* 25 mmol of the appropriate ligand. The products precipitated in 90—95% yield and were recrystallized from dichloromethane by the addition of diethyl ether.

[$Pd(\eta^5\text{-}C_5H_5)L_2$]$PF_6$. A solution of $AgPF_6$ (1 mmol) in acetone (1 cm^3) was added to a suspension of [$PdCl_2L_2$] (0.5 mmol) in acetone (5 cm^3). The mixture was stirred until all of the initial dichloropalladium complex had dissolved. The AgCl was then filtered off and an excess of freshly distilled cyclopentadiene (*ca.* 0.2 cm^3) added to the yellow filtrate. Dilution of the brightly coloured reaction mixture with diethyl ether (*ca.* 30 cm^3) produced the desired complexes as crystalline solids, except for compound (6), which precipitated as a red oil in high yield. The latter was crystallized from cold methanol with considerable loss of material. Compounds (1), (3), and (7)—(11) were recrystallized from acetone by the addition of diethyl ether, (1), (3), (9), and (10) being isolated as acetone hemisolvates. However, (2) and (4) were better recrystallized from a dichloromethane–diethyl ether mixture (*ca.* 1 : 1) from which they were isolated as dichloromethane solvates. Details concerning the properties and yields of the various complexes are collected in Table 1.

Alternative method. A mixture of the appropriate complex [$PdCl_2L_2$] (0.05 mmol) and $AgNO_3$ (1 mmol) was stirred in aqueous methanol (1 : 1, 20 cm^3) until the initial palladium complex had dissolved. The mixture was then treated with an excess of cyclopentadiene (*ca.* 0.2 cm^3) and the resultant brightly coloured solution filtered to remove AgCl. The addition of an excess of aqueous NH_4PF_6 led to the precipitation of the crystalline products, which were purified by recrystallization as outlined above.

(η^5-*Cyclopentadienyl*)*bis*(*triphenylstibine*)*palladium*(II) *hexafluorophosphate–dichloromethane* (1/1), (5). A suspension of [$PdCl_2(SbPh_3)_2$] (0.46 g) in acetone (10 cm^3) was treated with cyclopentadiene (0.2 cm^3) followed by $AgPF_6$ (0.26 g) in acetone (1 cm^3). The reaction mixture turned blue. Stirring was continued for 0.5 h, at which time the AgCl was filtered off and the filtrate diluted with diethyl ether. The crude product was recrystallized from dichloromethane by the addition of diethyl ether yielding blue cubes of the pure compound as a dichloromethane solvate (0.49 g, 85%).

Collection of X-Ray Intensity Data; Solution and Refinement of [$Pd(\eta^5\text{-}C_5H_5)(SbPh_3)_2$]$PF_6 \cdot CH_2Cl_2$ (5).—*Crystal data.* $C_{42}H_{37}Cl_2F_6PPdSb_2$, M = 1 107.5, Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 12.506(6), b = 19.002(7), c = 18.575(5) Å, β = 106.53(3)°, U = 4 332(3) Å^3, D_c = 1.74 g cm^{-3}, Z = 4, $F(000)$ = 2 160, $\lambda(\text{Mo-}K_\alpha)$ = 0.7107 Å, $\mu(\text{Mo-}K_\alpha)$ = 17.9 cm^{-1}, T = 295(1) K. Specimen size: 0.08 × 0.45 × 0.20 mm.

Data collection and structural analysis. Diffraction data were collected and unit cell dimensions were determined on Syntex $P\bar{1}$ and $P2_1$ diffractometers using graphite single-crystal monochromated Mo-K_α radiation. A unique data set was measured within the limit $2\theta_{\text{max.}} = 50°$ yielding 7 493 independent reflections; of these 4 384 with $I > 3\sigma(I)$ were considered observed and used in the structure determination and refinement after analytical absorption correction. Refinement of the structure was by 9 × 9 block-diagonal least squares, non-hydrogen atom thermal parameters being refined anisotropically. Hydrogen atoms were included as invariants in calculated trigonal and tetrahedral positions with U_H set at 1.25 U_{ii} (parent C). Residuals at convergence were R 0.051, R' 0.062, reflection weights being set at $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[10] Computation was carried out using a local variant of the *X*-RAY 76 program system [11] implemented on a Perkin-Elmer 8/32 computer. The atomic co-ordinates and their standard deviations are shown in Table 5.

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