Palladium(II) Complexes Containing ' Mixed ' Nitrogen–Arsenic Polydentate Ligands

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Palladium(II) dihalides (Cl, Br, or I) react with $R_2NC_2H_4AsPh_2$ and $[R_2NC_2H_4]_2AsPh$, where R = H, Me, and Et, to form a series of four-co-ordinate, square planar complexes of stoicheiometry PdX_2L, when X = Cl, Br, and I and L represents any one of the aforementioned ligands. In addition, the *S*-bonded thiocyanate complexes, $Pd(SCN)_2L$, were prepared for all three bidentate ligands. The explanations for the isolation of only the *S*-bonded isomer and the inability to prepare five-co-ordinate complexes are discussed.

DIVALENT palladium generally forms four-co-ordinate, square planar complexes with a variety of ligands. However, five-co-ordinate palladium(II) complexes, although by no means as numerous, have been known for some time, primarily as a result of the preliminary work in this area by Venanzi,[1] Nyholm,[2] and Chatt.[3] In 1965, Westland [4] found in the case of Group V donor atoms the tendency to promote five-co-ordination for Pd^{II} increased in the order $N < P < As < Sb$ for the ligands investigated. It was suggested that the increased π-acceptor behaviour of the heavier members of Group V removes the excess of negative charge from the metal which has been built up by the σ-bonding. This process enables the palladium(II) ion to add a fifth ligand resulting in a trigonal bipyramidal or square pyramidal complex. Subsequently, further work in this laboratory [5] and elsewhere [6] examined the stereochemistry of the complexes resulting from the reaction of palladium(II) dihalides with various other Group V donors. The polydentate ligands employed in these studies contained both a ' hard ' base, the nitrogen atom in an amine, and

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[1] L. M. Venanzi, *Angew. Chem. Internat. Edn.*, 1964, **3**, 453, and references therein.

[2] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.

[3] J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 1962, 2537.

[4] A. D. Westland, *J. Chem. Soc.*, 1965, 3060.

[5] R. C. Taylor, G. R. Dobson, and R. A. Kolodny, *Inorg. Chem.*, 1968, **7**, 1886.

[6] H. P. Fritz, I. R. Gordon, K. E. Schwarzhans, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 5210.

a ' soft ' base, the phosphorus atom in a tertiary phosphine. All attempts to isolate five-co-ordinate palladium(II) complexes containing these ligands were unsuccessful. The presence of the non-π-accepting nitrogen atom in the co-ordination sphere apparently prevents the addition of a fifth ligand. This may also be due, in part, to the inability of the phosphorus atom effectively to remove, *via* d_π–d_π bonding, excess negative charge built up on the metal by the halides and the amine. Westland's[4] suggestion that ligands containing arsenic and/or antimony exhibit greater tendency to promote five-co-ordination prompted us to investigate structurally analogous ligands (replacement of P by As or Sb) with the hope of isolating stable five-co-ordinate palladium(II) complexes. The necessary ' mixed ' nitrogen–antimony polydentate ligand could not be synthesized, therefore, the work is restricted to the ' mixed ' nitrogen–arsenic ligands. We report the results of these studies.

RESULTS AND DISCUSSION

The elemental analyses, i.r., n.m.r., and electronic absorption spectra for the ligands and complexes prepared in this study are listed in the Tables.

TABLE 1

Analysis, colour, melting point, and yield of ligands and complexes

Compound	Colour	M.p. °C	Yield %	Λ_M [b]	Analyses [a] C	H	N	As	Pd	Electronic spectral data (*ca.* 10^{-3}M solution in dichloromethane, molar extinction coefficients in parentheses)
$H_2NC_2H_4AsPh_2$	Pale yellow	140, 0·4 mmHg [c]	27		61·0 (61·6)	5·9 (5·9)	5·0 (5·1)			
$Me_2NC_2H_4AsPh_2$	Pale yellow	155, 0·4 mmHg [c]	50		63·5 (63·8)	6·6 (6·7)	4·6 (4·6)			
$Et_2NC_2H_4AsPh_2$	Pale yellow	138—140, 0·3 mmHg [c]	51		65·5 (65·5)	7·3 (7·4)	4·2 (4·2)			
$PdCl_2(H_2NC_2H_4AsPh_2)$	Yellow	209—211 [d]	70	6·6	37·6 (37·2)	3·6 (3·5)	3·1 (3·1)			27,200 (1100); 37,800 (8100)
$PdI_2(H_2NC_2H_4AsPh_2)$	Red	270—273	50	7·9	26·8 (26·5)	2·5 (2·5)	2·3 (2·2)			21,600 (2000); 25,800 (1400); 32,500 (16,000)
$PdCl_2(Me_2NC_2H_4AsPh_2)$	Yellow	166—169 [d]	70	6·0	40·4 (40·2)	4·2 (4·2)	2·9 (2·4)			26,700 (1350); 31,400sh; 36,000 (12,000)
$PdBr_2(Me_2NC_2H_4AsPh_2)$	Orange	157—160 [d]	50	6·8	33·8 (33·8)	3·5 (3·5)	2·4 (2·5)			25,600 (2100); 34,600 (10,000)
$PdI_2(Me_2NC_2H_4AsPh_2)$	Red	176—177	60	8·1 ,	30·1 (29·0)	3·0 (3·0)	1·9 (2·1)	10·8 (11·4)	17·4 (16·5)	20,800 (3040); 29,000 (2500); 31,200 (6500); 37,000sh
$PdCl_2(Et_2NC_2H_4AsPh_2)$	Yellow	159—162 [d]	60	3·7	43·0 (42·6)	4·7 (4·8)	2·6 (2·8)	12·2 (14·9)		28,100 (1350); 32,200 (5700); 36,400 (12,000)
$PdBr_2(Et_2NC_2H_4AsPh_2)$	Orange	145—148 [d]	30	7·2	36·2 (36·3)	4·0 (4·1)	2·4 (2·4)	12·6 (13·3)	20·6 (17·9)	25,200 (1820); 30,000 (2100); 35,700 (14,000)
$Pd(SCN)_2(H_2NC_2H_4AsPh_2)$	Reddish orange	215—218 [d]	45	0·9	39·4 (38·7)	3·4 (3·2)	8·1 (8·5)			22,500 (2450); 32,200 (10,000); 37,400 (15,000)
$Pd(SCN)_2(Me_2NC_2H_4AsPh_2)$	Orange	165—167 [d]	45	1·0	41·0 (41·3)	3·8 (3·8)	8·0 (8·0)			23,000 (2500); 33,000 (11,000); 36,900 (16,000)
$Pd(SCN)_2(Et_2NC_2H_4AsPh_2)$	Orange	150—151 [d]	55	1·2	43·6 (43·6)	4·4 (4·4)	7·4 (7·6)			23,200 (3200); 35,800 (13,000)
$PdCl_2(Me_2NC_2H_4)_2AsPh$	Yellow	178—179	70	15	35·2 (35·5)	5·2 (5·3)	5·8 (5·9)	13·5 (15·8)		27,300 (1540); 34,000 (8200); 38,200 (19,100)
$PdBr_2(Me_2NC_2H_4)_2AsPh$	Orange	174—177 [d]	70	10	31·1 (30·0)	4·6 (4·5)	5·2 (5·0)	13·3 (13·3)	21·0 (19·0)	26,000 (1730); 30,200sh
$PdI_2(Me_2NC_2H_4)_2AsPh$	Red	155—157	45	12	25·6 (25·6)	3·8 (3·8)	4·2 (4·3)			21,800 (1750); 25,500 (9250); 31,800 (4000); 37,600 (9000)
$PdCl_2(Et_2NC_2H_4)_2AsPh$	Yellow	161—162	70	18	40·8 (40·8)	6·2 (6·3)	5·4 (5·3)			26,600 (1500); 33,000 (4000); 38,400 (11,000)
$PdBr_2(Et_2NC_2H_4)_2AsPh$	Orange	147—149	60	14	33·5 (34·9)	5·1 (5·4)	4·4 (4·5)	12·6 (12·1)	18·6 (17·7)	25,200 (2000); 27,600 (2560); 35,800 (8500)
$PdI_2(Et_2NC_2H_4)_2AsPh$	Red	139—143	40	14	28·9 (30·3)	4·4 (4·7)	3·7 (3·9)	10·2 (10·5)	14·7 (14·9)	21,800 (3700); 25,000 (1900); 32,400 (10,000); 38,400 (19,000)

[a] Calculated values in parentheses. [b] Molar conductance in Ω^{-1} cm^2 mol^{-1}; listed values are for *ca.* 10^{-3} M solutions of the compound in nitromethane at 23—25° C. Reference value in nitromethane for a 1 : 1 electrolyte Et_4NBr is 100. [c] Boiling points. [d] Decomposition.

TABLE 2

^{1}H N.m.r. spectra of the ' mixed As–N ' ligands [a]

Ligand	Solvent	Chemical shifts [b] δ(NH)	δ(CH)$_3$	δ(C_2H_5)	δ(NCH_2)	δ($AsCH_2$)	δ(C_6H_5)
$H_2NC_2H_4AsPh_2$	Neat	1·25(s)			2·71(m)	2·03(m)	7·08(m), 7·37(m)
$Me_2NC_2H_4AsPh_2$	Neat		1·75(s)		2·10(m)	1·90(m)	6·84(m), 7·16(m)
$Et_2NC_2H_4AsPh_2$	Neat			0·82(t) 2·36(q) [c]	2·55(m)	2·12(m)	7·07(m), 7·38(m)
$(Ph_2AsC_2H_4)_2NMe$	$CDCl_3$		2·18(s)		2·56(m)	2·12(m)	7·24(m), 7·41(m)
$(H_2NC_2H_4)_2AsPh$	$CDCl_3$	1·97(s)			2·96(m)	2·04(m)	7·42(m), 7·65(m)
$(Me_2NC_2H_4)_2AsPh$	Neat		1·96(s)		2·25(m)	1·79(m)	7·08(m), 7·39(m)
$(Et_2NC_2H_4)AsPh$	Neat			0·82(t) 2·34(q) [c]	2·50(m)	1·78(m)	7·12(m), 7·42(m)

[a] At 100 MHz. [b] In p.p.m. from TMS as internal standard. [c] $J_{CH_2-CH_3}$ 7·0—7·5 Hz.

The ' Mixed ' Nitrogen–Arsenic Ligands, $R_2NC_2H_4AsPh_2$, $(R_2NC_2H_4)_2AsPh$, *and* $(Ph_2AsC_2H_4)_2NR$ (R = H, Me, and Et).—The only ligand of this type that has been reported in the literature is bis(2-diphenylarsinoethyl)amine, $(Ph_2AsC_2H_4)_2NH$.[7] The bidentate ligands prepared in this study were purified by fractional distillation at low pressures and characterized by elemental analysis (Table 1) and ^{1}H n.m.r. spectra (Table 2). The tridentate ligands containing two arsenic atoms were prepared by the method employed by Sacconi *et al.*[7] The syntheses of the ' mixed ' tri-

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[7] L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1968, **7**, 1417.

dentate nitrogen–arsenic–nitrogen ligands have not been described previously in the literature. They were prepared, albeit in low yield (Table 1), by the reaction of disodium phenylarsenide, $PhAsNa_2$,[8] with 2-chloroethyldialkylamines (2 mol) in 1,2-dimethoxyethane–ether. Neither series of tridentate ligands could be purified by fractional distillation because of excessive thermal decomposition. The ^1H n.m.r. spectra (Table 2) are consistent with the proposed formulations both in terms of chemical shifts, integrated intensities, and spin–spin coupling constants.

The Palladium(II) *Complexes*.—All three bidentate ligands and all three nitrogen–arsenic–nitrogen tridentate ligands prepared in this study react with palladium(II) dihalides in ethanol to form highly crystalline compounds of stoicheiometry, PdX_2L, where L represents any one of the aforementioned ligands. On the other hand, the arsenic–nitrogen–arsenic tridentate ligands react with palladium(II) halides to form highly insoluble brown to brownish-grey powders. Apparently these materials are polymeric and they could not be characterized adequately.

Complexes of the Bidentate Ligands.—Elemental analyses, conductivity measurements, and electronic absorption data (Table 1) support the formulation of these compounds as normal, four-co-ordinate, square planar palladium(II) complexes. All are non-electrolytes in nitromethane. The electronic absorption spectra consists of one low energy absorption, which may be assigned to the lowest *d–d* ligand field transition in square planar $4d^8$ complexes, and a number of intense high-energy charge-transfer bands. The relative positions of the *d–d* absorption bands are as expected based on the spectrochemical series for the halides. Thus in any series, PdX_2L, the energy of the lowest absorption decreases from chloride to iodide. The data is also consistent when compared with the electronic absorption spectra for the corresponding palladium complexes containing ' mixed ' nitrogen–phosphorus bidentate ligands.[5] The ' mixed ' nitrogen–phosphorus ligands produce a slightly greater ligand field compared with the corresponding nitrogen–arsenic ligands. This suggests that phosphorus is either a better σ-donor or π-acceptor or both. In an effort to provide some additional information about the relative π-acceptor strengths of P *versus* As in palladium(II) complexes it was decided to synthesize the thiocyanate complexes of palladium(II) containing these mixed ligands. It is well known that the mode of bonding of the thiocyanate ligand is subject to several directive influences such as the nature of the co-ordinated metal atom, the electronic character of other ligands in the co-ordination sphere, steric factors involving other ligands, the physical state of the complex, the reaction conditions employed for the synthesis of the complex, and in certain instances the nature of a non-co-ordinated group in the complex.[9] In order to focus solely on the directive influence of the electronic character of the ligands in the co-ordination sphere, it was necessary to compare the mode of bonding of the thiocyanate ligand in the structurally analogous nitrogen–phosphorus and nitrogen–arsenic palladium(II) complexes. Meek *et al.*[10] showed, by examination of the i.r. spectrum in the $\nu(C\equiv N)$ region of the complex $[Pd(SCN)_2(Me_2NC_2H_4PPh_2)]$ that it contained both *N*- and *S*-bonded thiocyanate groups. A preliminary *X*-ray determination of an analogous complex, $[Pd(SCN)_2(Me_2NC_3H_6PPh_2)]$, confirmed this and further indicated that the *N*-bonded thiocyanate was *trans* to the phosphine. This result is consistent with the idea that phosphorus effectively competes with the S atom of SCN^- for the same π-orbital on Pd^{II}; consequently *N*-bonding of SCN^- is favoured *trans* to the phosphorus. However, it was not possible for these authors to ascertain whether the mixed mode of thiocyanate co-ordination was due to steric factors or to the *trans*-directing influence of the donor atom. The analogous nitrogen–arsenic ligands would be subject to the same steric factors so that any difference in the mode of thiocyanate bonding in the two systems would be a direct result of electronic factors alone. Accordingly, the complexes $Pd(SCN)_2(R_2NC_2H_4AsPh_2)$ were prepared by two different methods, either the reaction of $Pd(SCN)_4{}^{2-}$ with the ligand or by metathesis of $PdCl_2(R_2NC_2H_4AsPh_2)$ with NaSCN. The complexes prepared by the two methods were identical. The i.r. spectra of these complexes, taken either as Nujol mulls of the solids or in dichloromethane solution, show one strong sharp absorption in the $C\equiv N$ stretching region (Table 3). The peak position (>2100 cm^{-1}) and the peak width at half height ($\nu_{\frac{1}{2}} = 13$—15 cm^{-1}) are typical of *S*-bonded thiocyanates.[12] Intense ligand absorptions prevented the location of the C–S stretching frequency. The lowest energy transition in the visible spectrum of these complexes (Table 1) indicates the SCN^- ligand occupies a position in the spectrochemical series between Br^- and I^-. This result also suggests *S*-bonded thiocyanates and is consistent with other studies.[10,13]

TABLE 3

Infrared spectral data in the $\nu(C\equiv N)$ region of the $Pd(SCN)_2L$ complexes

Complex	$\nu(C\equiv N)$ cm^{-1} Nujol mull	Solution[a]	$\nu_{\frac{1}{2}}$ cm^{-1}
$Pd(SCN)_2(H_2NC_2H_4AsPh_2)$	2120	2119	15
$Pd(SCN)_2(Me_2NC_2H_4AsPh_2)$	2128	2126	13
$Pd(SCN)_2(Et_2NC_2H_4AsPh_2)$	2130	2127	13

[a] In spectral grade dichloromethane (*ca.* 10^{-2} M).

These data, together with the results obtained by Meek *et al.*,[10] suggest that the phosphorus atom is a better π-acceptor toward Pd^{II} than arsenic when present in identical ligand environments. Hence, thiocyanates

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[8] J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, 1957, **22**, 375.

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[11] G. R. Clark, G. J. Palenik, and D. W. Meek, *J. Amer. Chem. Soc.*, 1970, **92**, 1077.

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trans to P are generally *N*-bonded in the absence of any steric factors, whereas they are *S*-bonded when *trans* to the weaker π-acceptor arsenic. That the difference between P and As is small is shown by the ability to isolate the *S*-bonded thiocyanate complex $Pd(SCN)_2(Ph_3As)_2$, which undergoes isomerization to the *N*-bonded isomer at high temperature.[14] Further, the differences in the electronic absorption spectra for analogous palladium(II) complexes are very small. As in the case of the analogous phosphorus–nitrogen bidentate ligands,[5,6] all attempts to prepare five-co-ordinate Pd^{II} complexes containing the arsenic–nitrogen bidentate ligands were unsuccessful.

Tridentate Ligands.—Based on the conductivity measurements and the electronic absorption data the complexes of stoicheiometry PdX_2L, where L represents the potential tridentate nitrogen–arsenic–nitrogen ligands, are also four-co-ordinate, square planar palladium(II) complexes both in the solid state and in solution. All these complexes are non-electrolytes. The close agreement of the lowest energy electronic absorption in these complexes as compared with the complexes containing the bidentate ligands indicates a four-co-ordinate, square planar geometry as well as strongly suggesting that the arsenic atom and one of the nitrogen atoms are co-ordinated. Unfortunately, ^1H n.m.r. spectra of these compounds could not be obtained because of solubility limitations.

As with the analogous nitrogen–phosphorus–nitrogen tridentate ligands,[5] five-co-ordination could not be achieved presumably because of the destabilizing influence of the strong σ-donor amine. Attempts to prepare the arsenic analogue of $[PdCl_2(Et_2NCH_2)_2PPh](BPh_4)$ in which all three donor atoms of the ligand are co-ordinated led only to reduction of palladium(II) to metallic palladium.

EXPERIMENTAL

All manipulations involving the preparation of the ligands were performed under a nitrogen atmosphere. The palladium complexes were sufficiently stable toward oxidation in solution and in the solid state to be handled in air. Sodium tetrachloropalladate(II) (Englehard), triphenylarsine (Metal and Thermite Chemicals), ethylenimine (Dow), and all the amine chloride hydrochlorides (Aldrich) were obtained from the indicated sources.

The free amine chlorides were prepared by the procedure outlined by the Michigan Chemical Corporation.[15] Potassium diphenylarsenide dioxanate, was prepared by the method of Tzschach and Lange.[16] Arsenobenzene, Ph_2As_2, was synthesized from benzenearsonic acid (Eastman) by the procedure of Reesor and Wright.[8] The solvents, dioxan, 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and nitromethane were purified prior to use. Dioxan and DME were distilled from metallic sodium whereas THF was distilled from lithium aluminium hydride. Spectral grade nitromethane for conductance measurements was dried over predried (300 °C) 4A molecular sieves for 48 h.

Microanalyses (C, H, N) of the ligands were determined by Pascher Microanalytisches Laboratorium, Bonn, Germany. Microanalyses (C, H, N) of the complexes were determined by M. M. Kshatriya and M. W. Swanson of this Department using a Perkin-Elmer 240 Analyser. Arsenic and palladium analyses were performed by Dr. J. McCall using *X*-ray fluorescence techniques.[17] Palladium cyanide (Alfa) and monosodium orthoarsenate (Baker) were used as primary standards for the palladium and arsenic analyses, respectively. The analytical results, colours, m.p.s, and yields are listed in Table 1. The i.r. were recorded on a Perkin-Elmer 621 grating spectrometer calibrated with polystyrene. Spectra were obtained as Nujol mulls or in spectral grade dichloromethane (1 mm pathlength). Solution and solid state electronic transmittance spectra were recorded on a Cary 14 spectrophotometer. Solution spectra were run in dichloromethane in matched 1 cm quartz cells. The solid state transmittance spectra in the visible region were obtained as Nujol mulls supported on filter paper according to the technique of Lee, Griswold, and Kleinberg.[18] ^1H n.m.r. spectra (Table 2) were recorded at 100 MHz on a Varian HA-100 spectrometer with tetramethylsilane as internal reference. Conductance measurements in nitromethane were performed at room temperature (23—25 °C) with an Industrial Instruments RC-16-B2 conductivity bridge using a cell with constant $k = 0{\cdot}1792\ cm^{-1}$. The conductance data was treated according to the method of Feltham and Hayter.[19] All the palladium(II) complexes prepared in this study are non-electrolytes (see Table 1).

Preparation of Ligands.—*2-Aminoethyldiphenylarsine*, $H_2NC_2H_4AsPh_2$. The preparation of the ligand is based on the procedure reported by Issleib and Haferberg [20] for the synthesis of the analogous 'mixed' nitrogen–phosphorus ligand.

2-Dimethylaminoethyldiphenylarsine, $Me_2NC_2H_4AsPh_2$ and *2-diethylaminoethyldiphenylarsine*, $Et_2NC_2H_4AsPh_2$, were prepared in an analogous fashion using 2-dimethyl and 2-diethylaminoethylchlorides in place of ethylenimine.

Bis-(2-diphenylarsinoethyl)amine, $(Ph_2AsC_2H_4)_2NH$, *bis-(2-diphenylarsinoethyl)methylamine*, $(Ph_2AsC_2H_4)_2NMe$, and *bis-(2-diphenylarsinoethyl)ethylamine*, $(Ph_2AsC_2H_4)_2NEt$, were prepared by the reaction of potassium diphenylarsenide dioxanate with $(ClC_2H_4)_2NR$, where R = H, Me, or Et. This procedure has been described in detail by Sacconi *et al.*[7] Attempts to purify these ligands by fractional distillation under reduced pressure led to excessive decomposition. In all subsequent reactions, the crude product was used after removal of solvent.

Bis-(2-aminoethyl)phenylarsine, $(H_2NC_2H_4)_2AsPh$, *bis-(2-dimethylaminoethyl)phenylarsine*, $(Me_2NC_2H_4)_2AsPh$, and *bis-(2-diethylaminoethyl)phenylarsine*, $(Et_2NC_2H_4]_2AsPh$, were prepared by the reaction of disodium phenylarsenide with the appropriate 2-chloroethylamine in DME. Arsenobenzene (3·07 g, 0·01 mol) and freshly distilled DME (40 ml) were placed in a 125 ml Erlenmeyer flask. Metallic sodium (2·0 g, 0·11 mol) was added, the flask stoppered, and stirred magnetically for 5 days. After removal of the excess of sodium from the greenish-yellow solution, $R_2NC_2H_4Cl$ (0·09 mol) was added dropwise. The mixture was stirred

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overnight and subsequently hydrolysed with deaerated water (50 ml). The organic layer was separated and dried over anhydrous potassium carbonate. The solvent was removed under reduced pressure. Because of difficulties encountered during fractional distillation the crude product was used without further purification. In the case of $(H_2NC_2H_4)_2AsPh$ the yield was only 5%.

Preparation of Palladium Complexes.—The palladium(II) halides form complexes of stoicheiometry PdX_2L, where L = any one of the aforementioned bidentate ligands. The preparations given below are typical.

Dichloro(2-diethylaminoethyldiphenylarsino)palladium(II), $PdCl_2(Et_2NC_2H_4AsPh_2)$.—A solution of $Et_2NC_2H_4AsPh_2$ (1 mmol) in absolute ethanol (10 ml) was added to a boiling ethanolic solution (50 ml) containing sodium tetrachloropalladate(II) (0·294 g, 1 mmol). The yellow precipitate which separated upon cooling was filtered and washed with cold ethanol. The complex was recrystallized from hot ethanol yielding yellow needles.

The dibromo-, di-iodo-, and dithiocyanato-analogues were prepared by metatheses: $PdCl_2(R_2NC_2H_4AsPh_2)$ (1 mmol) in ethanol (50 ml) was mixed with a solution containing NaX (X = Br, I, SCN; 10 mmol) dissolved in hot ethanol (25 ml). After refluxing for 30 min, the volume of solvent was reduced to half and filtered hot to remove NaCl. Upon cooling, the appropriate $PdX_2(R_2NC_2H_4AsPh_2)$ complexes were obtained. All complexes were recrystallized from hot ethanolic solutions that contained additional NaX to ensure complete conversion of the chloride. The thiocyanate complexes were also obtained by adding $R_2NC_2H_4AsPh_2$ (1 mmol) to an ethanolic solution of sodium tetrathiocyanatopalladate(II) (1 mmol). The latter was prepared by the addition of excess of NaSCN to an ethanolic solution of Na_2PdCl_4. The products obtained by both methods were identical (see text).

Dichloro[bis(dimethylaminoethyl)phenylarsine]palladium(II), $PdCl_2[(Me_2NC_2H_4)_2AsPh]$.—The ligand (1·3 mmol) was dissolved in methylene chloride (10 ml) and the solution added to Na_2PdCl_4 (1·3 mmol) in ethanol (25 ml). After stirring overnight at room temperature, yellow crystals were deposited. Recrystallization was carried out in hot ethanol. The dibromo- and di-iodo-complexes were prepared by metatheses.

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