Reactions of Arylpalladium Complexes with Ammonia and Chelating Amines. Crystal and Molecular Structure of $[\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NCH_2CH_2NH_2})(\mathrm{NH_2CH_2CH_2NH_2})][\mathrm{PF_6}]$,† a Product of Transamination and Ligand Substitution

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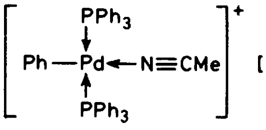
Reaction of *trans*-$[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$ with $\mathrm{NH_3}$, $\mathrm{NH_2CH_2CH_2NH_2}$ (en), and $\mathrm{NH_2(CH_2)_3NH_2}$ (pn) afforded *trans*-$[\mathrm{Pd(Ph)(PPh_3)_2(NH_3)}]^+$ and $[\mathrm{Pd(Ph)(PPh_3)(N{-}N)}]^+$ where N–N = en or pn. Treatment of $[\{\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NPh})\mathrm{X}\}_2]$ (X = Cl or $\mathrm{O_2CMe}$) with ammonia gave $[\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NPh})(\mathrm{NH_3})\mathrm{X}]$, but with an excess of $\mathrm{NH_3}$, $[\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NPh})(\mathrm{NH_3})_2]\mathrm{Cl}$ and $[\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NPh})(\mathrm{NH_3})_3][\mathrm{O_2CMe}]$ were formed. With 1,2-bis(dimethylamino)ethane, $[\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NPh})(\mathrm{Me_2NCH_2CH_2NMe_2})]^+$ was isolated whereas with en, a transamination reaction occurred giving $[\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NCH_2CH_2NH_2})(\mathrm{en})]^+$. The structure of this cation (as the $\mathrm{PF_6}^-$ salt) was determined crystallographically. Crystals are triclinic, space group $P\bar{1}$, a = 8.109(16), b = 11.027(27), c = 18.93(4) Å, α = 88.30(19), β = 83.19(18), γ = 81.05(18)°, and Z = 4. The $\mathrm{NH_2}$ group of the o-$\mathrm{C_6H_4CH{=}NCH_2CH_2NH_2}$ ligand is not co-ordinated to palladium.

As part of a programme directed towards new syntheses of aromatic amines, we have investigated the reactions of certain arylpalladium complexes with ammonia and chelating aliphatic amines. It has previously been reported that nickel(II) salts and complexes catalyse the amination of aryl halides under vigorous conditions,[1] and in view of the ability of palladium both to metallate aromatic compounds directly [2] and to promote nucleophilic aromatic substitution reactions,[3] the amination of a number of pre-formed arylpalladium compounds was attempted. Amination of the aromatic ring was not in fact observed in these reactions, but a variety of novel arylpalladium ammines were obtained, and are described in this report.

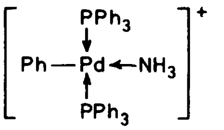
RESULTS AND DISCUSSION

The yellow cationic phenylpalladium–acetonitrile complex (1), prepared by reaction of silver tetrafluoroborate with *trans*-$[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$[4] in acetonitrile, reacted rapidly with ammonia in dichloromethane to give the colourless ammine complex (2), isolated as its tetrafluoroborate and hexafluorophosphate salts. This same ammine was, however, prepared more simply by direct ammonolysis of *trans*-$[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$ in methanol, followed by precipitation as the hexafluorophosphate, and a similar reaction was observed with 1,2-diaminoethane. In this case, however, a molecule of triphenylphosphine was also displaced to give the cationic complex (3). 1,3-Diaminopropane reacted in analogous fashion, whereas 1,2-bis(dimethylamino)ethane failed to give any reaction with *trans*-$[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$, presumably for steric reasons.



$$\left[\mathrm{Ph{-}\underset{\underset{PPh_3}{\uparrow}}{\overset{\overset{PPh_3}{\downarrow}}{Pd}}{\leftarrow}N{\equiv}CMe}\right]^+ [\mathrm{BF_4}]^-$$

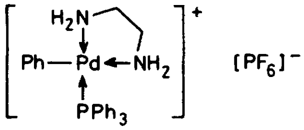
(1)



$$\left[\mathrm{Ph{-}\underset{\underset{PPh_3}{\uparrow}}{\overset{\overset{PPh_3}{\downarrow}}{Pd}}{\leftarrow}NH_3}\right]^+ \mathrm{X}^-$$

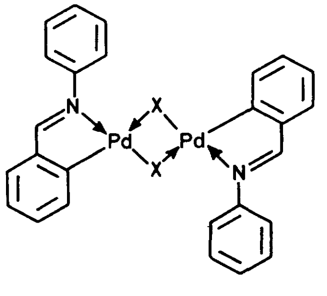
(2a) $\mathrm{X = BF_4}$

(2b) $\mathrm{X = PF_6}$



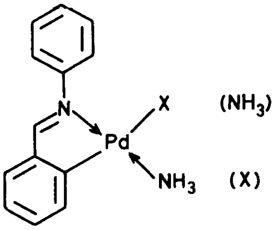
(3a)

Bridge-splitting reactions of the cyclometallated arylpalladium complexes (4)[5] with ammonia in dichloromethane initially yielded the neutral ammines (5), although the stereochemistry of these complexes was not determined.



(4a) X = Cl

(4b) $\mathrm{X = O_2CMe}$



(5a) X = Cl

(5b) $\mathrm{X = O_2CMe}$

With an excess of ammonia, however, the chloro- or acetato-ligand was displaced to give the salt of a cationic ammine. The chloride analysed as a bis-ammine (6a) but the acetate salt contained three molecules of ammonia per palladium. The third molecule is only weakly held, however, since the bis-ammine (6b) is precipitated on

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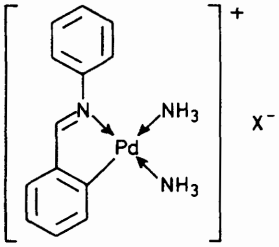
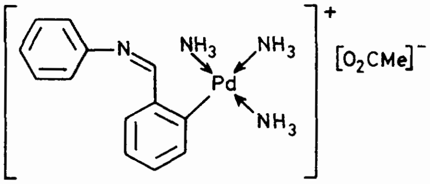
† [2-(4-Amino-2-azabut-1-enyl)phenyl-C^1,N^2](1,2-diaminoethane)palladium(II) hexafluorophosphate.

addition of ammonium hexafluorophosphate to methanol solutions of both the chloride and acetate salts.

It is possible that the acetate salt could have a tris-ammine structure (7), which is stabilised in solution only by the presence of an excess of ammonia, and in the solid state by hydrogen bonding of the acetate ion to ammine ligands. Somewhat analogous structures have previously been suggested for the tris-phosphine derivatives of a cyclometallated azobenzenepalladium complex.[6]

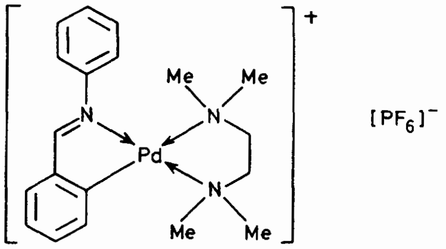


(6a) X = Cl
(6b) X = PF_6



(7)

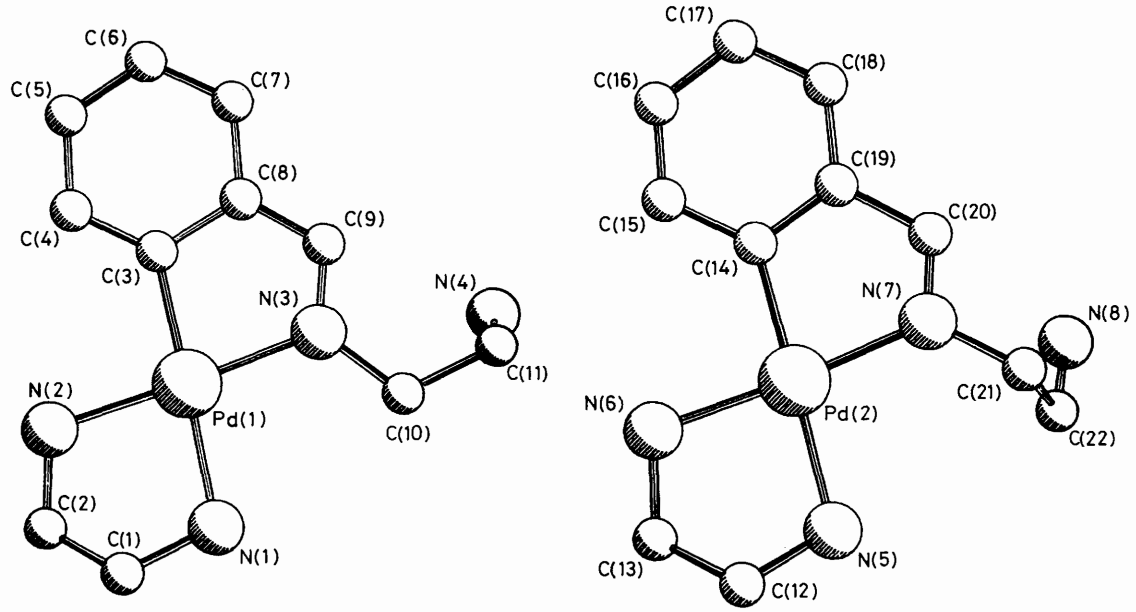
Reaction of the bridged complexes (4) with the di-tertiary amine *NN'*-tetramethyl-1,2-diaminoethane gave a simple bis-ammine, isolated as its yellow, crystalline hexafluorophosphate salt (8). The two different pairs of N-methyl groups in complex (8) give rise to ^1H n.m.r. signals separated by almost 1 p.p.m. (Table 2), and a space-filling molecular model strongly suggests that the high-field resonance is due to methyl groups adjacent to the unco-ordinated aromatic ring. This ring lies in a plane perpendicular to the co-ordination plane of palladium, so that the adjacent methyl groups are shielded by the aromatic ring-current, whereas the aryl group bonded to the metal lies within the co-ordination plane, and produces no such effect.



(8)

Reaction of the complexes (4) with 1,2-diaminoethane however, gave a very different result. Elemental analysis (Table 1) and ^1H n.m.r. (Table 2) suggested that not only had the diamine cleaved the bridge and then replaced the anionic ligand X, but also that a metal-promoted transamination had occurred whereby the aniline residue of the cyclometallated ligand was replaced by 1,2-diaminoethane.

The resulting complex could, in principle, adopt one of two structures, having either a five-membered chelate ring, (9a), or an eight-membered ring in which the imino-nitrogen is displaced by an amino-group, (10). A



Molecule 1 Molecule 2

FIGURE Molecular geometry and atom labelling for the cation $[Pd(o\text{-}C_6H_4CH{=}NCH_2CH_2NH_2)(H_2NCH_2CH_2NH_2)]^+$

single-crystal *X*-ray study of the complex, as its hexafluorophosphate salt, in fact revealed structure (9a) to be the one adopted.

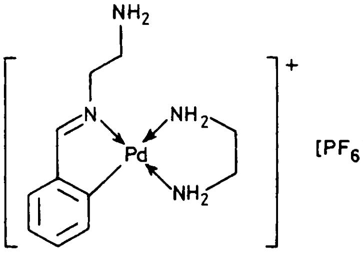
Crystallographic Studies.—The structures of the two crystallographically independent cations are illustrated in the Figure, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (with estimated standard deviations) and details of planar fragments and torsion angles are compared in Tables 3 and 4.

TABLE 1

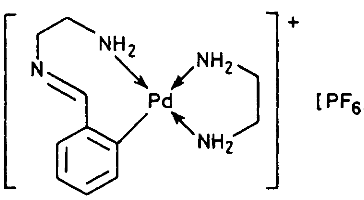
Analytical data

	Analysis [a] (%)			
Complex	C	H	N	P/Cl
(1)	63.0 (63.2)	4.5 (4.6)	1.7 (1.7)	
(2a)	61.8 (62.1)	4.4 (4.7)	1.8 (1.7)	7.5 (7.6) [b]
(2b)	57.7 (58.0)	4.6 (4.4)	1.7 (1.6)	—
(3a)	47.5 (48.0)	4.3 (4.3)	4.1 (4.3)	9.4 (9.5) [b]
(3b)	49.1 (48.8)	4.8 (4.5)	4.2 (4.2)	—
(4b)	51.8 (52.1)	4.0 (3.7)	4.0 (4.1)	—
(5b)	50.3 (49.7)	4.6 (4.5)	8.0 (7.7)	—
(5a)	46.5 (46.1)	3.8 (3.9)	8.1 (8.3)	10.6 (10.5) [c]
(8)	41.7 (41.7)	4.6 (4.8)	7.4 (7.7)	5.6 (5.7) [b]
(9a)	28.8 (28.8)	4.3 (4.2)	12.1 (12.2)	6.9 (6.8) [b]
(9b) [d]	32.4 (32.1)	5.1 (4.8)	11.8 (11.5)	—
(6a)	43.5 (43.8)	4.2 (4.5)	11.5 (11.8)	—
(6b)	33.6 (33.5)	3.2 (3.5)	9.2 (9.0)	—

[a] Calculated values are in parentheses. [b] Phosphorus analysis. [c] Chlorine analysis. [d] [Pd(o-$C_6H_4CH{=}NCH_2CH_2CH_2NH_2$)($NH_2CH_2CH_2CH_2NH_2$)][$PF_6$].



(9a)



(10)

The asymmetric unit comprises two hexafluorophosphate anions and two crystallographically independent but chemically very similar cations. Each cation comprises an approximately square-planar co-ordinated palladium(II) atom with a bidentate 1,2-diaminoethane ligand and a bidentate 1-amino-2-benzylidene-iminoethane ligand which utilises the imine-nitrogen atom for co-ordination to the palladium; the terminal primary amine residue is not involved in co-ordination and the cations differ only in the conformation adopted by the terminal aminoethane chain [see the Figure and Table 4]. The principal features of the cation geometry are the relatively short palladium–carbon bond and the markedly different palladium–nitrogen (primary amine) bond lengths which may be attributed to the different natures of the *trans* ligands. The co-ordination around the palladium is not exactly square planar; the chelate rings, neither of which is symmetrically positioned with respect to the co-ordination plane of the metal, both exhibit ' bite ' angles which are considerably less than 90° and the polyhedron shows small out-of-plane distortions, principally involving the imino-nitrogen atom (Table 4). The closest palladium–palladium contacts are between symmetry-related cations; both independent cations show such contacts at 3.62 and 3.71 Å respectively. The two independent hexafluorophosphate anions exhibit normal O_h symmetries [mean P–F 1.568(22) ± 0.035 Å; maximum bond angle deviation 3.4(12)°] and show a variety of non-bonded (ion-dipole) contacts to the co-ordinated and unco-ordinated primary amine residues of both cations. Table 3 includes a selection of the shorter such interactions; it seems probable that this different nature of the intermolecular environments of the cations accounts for the different conformations adopted by the unco-ordinated aminoethane residues.

TABLE 2

Spectroscopic data

Complex	^{1}H n.m.r. ($CDCl_3$) (δ)	I.r. (KBr) (cm^{-1})
(1)	1.34, s, 3 H (MeCN); 6.3—6.7, m, 5 H (Ph–Pd); 7.0—7.8, m, 15 H (PPh_3)	2 300w, ν(C≡N); 1 560m, δ(CH, Ph–Pd)
(2b)	1.15, br, 3 H (NH_3); 6.3—6.8, m, 5 H (Ph–Pd); 7.0—7.6, m, 15 H (PPh_3)	3 280, 3 360w, ν(NH); 1 660w, δ(NH); 1 560m, δ(CH, Ph–Pd)
(3a)	2.08, t, 2 H; 2.92, t, 2 H ($-CH_2CH_2-$); 2.97, m, 2 H; 3.09, m, 2 H ($-NH_2$); 6.85—3.09, m, 5 H (Ph–Pd); 7.34—7.46, m, 15 H (PPh_3)	3 370—3 285m, ν(NH); 1 585m, δ(NH); 1 560m, δ(CH, Ph–Pd)
(5a)		3 370—3 115m, ν(NH); 1 620w, δ(NH); 1 600s, ν(C=N);
(6b)		3 380, 3 320m, ν(NH); 1 600m, ν(C=N)
(8)	2.12, s, 6 H ($-NMe_2$); 3.03, s, 6 H ($-NMe_2$); 7.2—7.7, m, 9 H (aromatic); 8.03, s, 1 H (–CH=N–)	
(9a)	2.82, s, 4 H ($\overline{\text{NCH}_2\text{CH}_2\text{NPd}}$); 2.94, t, 2 H ($-CH_2-NH_2$); 3.64, t, 2 H ($CH_2-N{=}C$); 6.86—7.42, m, 5 H (aromatic); 8.15, s, 1 H, (CH=N)	

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations for the two independent cations [Pd(*o*-$C_6H_4CH{=}NCH_2CH_2NH_2)(H_2NCH_2CH_2NH_2)]^+$

(*a*) Bond lengths

Pd(1)–N(1)	2.14(2)	Pd(2)–N(5)	2.15(2)
Pd(1)–N(2)	2.05(2)	Pd(2)–N(6)	2.04(2)
Pd(1)–N(3)	2.03(2)	Pd(2)–N(7)	2.01(2)
Pd(1)–C(3)	1.97(2)	Pd(2)–C(14)	1.99(2)
N(1)–C(1)	1.50(4)	N(5)–C(12)	1.50(4)
N(2)–C(2)	1.47(4)	N(6)–C(13)	1.52(4)
C(1)–C(2)	1.42(5)	C(12)–C(13)	1.52(4)
C(3)–C(4)	1.37(4)	C(14)–C(15)	1.39(3)
C(4)–C(5)	1.40(4)	C(15)–C(16)	1.35(4)
C(5)–C(6)	1.39(4)	C(16)–C(17)	1.39(4)
C(6)–C(7)	1.39(4)	C(17)–C(18)	1.40(4)
C(7)–C(8)	1.45(4)	C(18)–C(19)	1.41(4)
C(8)–C(3)	1.42(4)	C(19)–C(14)	1.38(4)
C(8)–C(9)	1.36(4)	C(19)–C(20)	1.46(4)
C(9)–N(3)	1.28(3)	C(20)–N(7)	1.22(3)
N(3)–C(10)	1.50(3)	N(7)–C(21)	1.49(3)
C(10)–C(11)	1.54(4)	C(21)–C(22)	1.56(4)
C(11)–N(4)	1.46(4)	C(22)–N(8)	1.48(4)

(*b*) Bond angles

N(1)–Pd(1)–N(2)	82.6(9)	N(5)–Pd(2)–N(6)	84.6(9)
N(1)–Pd(1)–N(3)	100.3(8)	N(5)–Pd(2)–N(7)	100.0(9)
N(1)–Pd(1)–C(3)	178.7(9)	N(5)–Pd(2)–C(14)	177.8(9)
N(2)–Pd(1)–N(3)	175.1(9)	N(6)–Pd(2)–N(7)	173.4(9)
N(2)–Pd(1)–C(3)	96.2(10)	N(6)–Pd(2)–C(14)	94.2(9)
N(3)–Pd(1)–C(3)	80.9(9)	N(7)–Pd(2)–C(14)	81.4(9)
Pd(1)–N(1)–C(1)	103.5(17)	Pd(2)–N(5)–C(12)	104.1(17)
Pd(1)–N(2)–C(2)	111.2(18)	Pd(2)–N(6)–C(13)	108.4(16)
N(1)–C(1)–C(2)	113(3)	N(5)–C(12)–C(13)	107(2)
N(2)–C(2)–C(1)	109(3)	N(6)–C(13)–C(12)	109(2)
Pd(1)–C(3)–C(4)	128(2)	Pd(2)–C(14)–C(15)	131(2)
Pd(1)–C(3)–C(8)	109(2)	Pd(2)–C(14)–C(19)	110(2)
C(4)–C(3)–C(8)	122(2)	C(15)–C(14)–C(19)	118(2)
C(3)–C(4)–C(5)	120(3)	C(14)–C(15)–C(16)	120(2)
C(4)–C(5)–C(6)	120(3)	C(15)–C(16)–C(17)	124(3)
C(5)–C(6)–C(7)	120(3)	C(16)–C(17)–C(18)	115(3)
C(6)–C(7)–C(8)	121(3)	C(17)–C(18)–C(19)	122(3)
C(3)–C(8)–C(7)	116(2)	C(14)–C(19)–C(18)	119(2)
C(3)–C(8)–C(9)	119(2)	C(14)–C(19)–C(20)	116(2)
C(7)–C(8)–C(9)	123(2)	C(18)–C(19)–C(20)	124(2)
C(8)–C(9)–N(3)	115(2)	C(19)–C(20)–N(7)	116(2)
Pd(1)–N(3)–C(9)	115(2)	Pd(2)–N(7)–C(20)	116(2)
Pd(1)–N(3)–C(10)	122(2)	Pd(2)–N(7)–C(21)	128(2)
C(9)–N(3)–C(10)	123(2)	C(20)–N(7)–C(21)	115(2)
N(3)–C(10)–C(11)	116(2)	N(7)–C(21)–C(22)	111(2)
C(10)–C(11)–N(4)	110(2)	C(21)–C(22)–N(8)	114(2)

(*c*) Inter-ionic fluorine–nitrogen contacts (Å)

F(1) · · · N(4)[$-x, -y, -z$]	3.38(3)
F(1) · · · N(5)[x, y, z]	3.21(3)
F(2) · · · N(1)[$-x, 1 - y, -z$]	3.40(3)
F(2) · · · N(5)[x, y, z]	3.29(3)
F(3) · · · N(5)[x, y, z]	3.34(3)
F(5) · · · N(2)[x, y, z]	3.19(3)
F(6) · · · N(1)[$-x, 1 - y, -z$]	3.39(3)
F(7) · · · N(4)[$1 - x, -y, -z$]	3.38(3)
F(8) · · · N(4)[$1 - x, -y, -z$]	3.39(3)
F(10) · · · N(4)[$1 - x, -y, -z$]	3.25(3)
F(11) · · · N(6)[$-x, 1 - y, 1 - z$]	3.18(3)
F(11) · · · N(8)[x, y, z]	3.20(3)
F(12) · · · N(6)[$1 + x, -1 + y, z$]	3.14(3)

TABLE 4

Best planes and selected torsion angles in the molecular ions [Pd(*o*-$C_6H_4CH{=}NCH_2CH_2NH_2)(NH_2CH_2CH_2NH_2)]^+$. The equations of the mean planes are of the form $pX + qY + rZ = d$, where the direction cosines are referred to orthogonal axes a, b^*, c'. Deviations of atoms (Å) from the mean planes are given in square brackets

Molecule 1

Plane A N(1), N(2), N(3), C(3)
$0.8983X - 0.3997Y - 0.1825Z = 1.8465$
[N(1) 0.031, N(2) −0.033, N(3) −0.032, C(3) 0.035, Pd(1) 0.038]

Plane B Pd(1), N(1), N(2)
$0.9108X - 0.3825Y - 0.1555Z = 1.9462$
[N(3) −0.140, C(1) −0.431, C(2) 0.186, C(3) −0.009]

Plane C C(3)—C(8)
$0.8926X - 0.3590Y - 0.2728Z = 1.6832$
[C(3) 0.040, C(4) −0.019, C(5) 0.005, C(6) −0.015, C(7) 0.036, C(8) −0.047, Pd(1) 0.201, C(9) 0.102]

Plane D Pd(1), N(3), C(3)
$0.8848X - 0.4158Y - 0.2102Z = 1.8210$
[C(8) −0.082, C(9) −0.031]

Molecule 2

Plane A N(5), N(6), N(7), C(14)
$-0.8951X + 0.4207Y - 0.1476Z = 0.9571$
[N(5) −0.054, N(6) 0.058, N(7) 0.058, C(14) −0.063, Pd(2) −0.026]

Plane B Pd(2), N(5), N(6)
$-0.9091X + 0.3823Y - 0.1653Z = 0.5366$
[N(7) 0.164, C(12) 0.561, C(13) −0.170, C(14) −0.064]

Plane C C(14)—C(19)
$-0.8794X + 0.4589Y - 0.1270Z = 1.3972$
[C(14) −0.050, C(15) 0.036, C(16) 0.002, C(17) −0.026, C(18) 0.011, C(19) 0.027, Pd(2) −0.047, C(20) 0.059]

Plane D Pd(2), N(7), C(14)
$-0.8790X + 0.4603Y - 0.1249Z = 1.3771$
[C(19) 0.076, C(20) 0.105]

Angles between planes (°)

	Molecule 1	Molecule 2
A—B	2.0	2.5
A—C	5.7	2.6
A—D	2.0	2.8
B—C	6.9	5.2
B—D	4.0	5.3
C—D	4.9	0.1

Torsion angles (°)

Molecule 1

N(1)–C(1)–C(2)–N(2)	−51.7
C(9)–N(3)–C(10)–C(11)	−13.1
Pd(1)–N(3)–C(10)–C(11)	+168.7
N(3)–C(10)–C(11)–N(4)	−67.7

Molecule 2

N(5)–C(12)–C(13)–N(6)	−56.8
C(20)–N(7)–C(21)–C(22)	−109.5
Pd(2)–N(7)–C(21)–C(22)	+82.5
N(7)–C(21)–C(22)–N(8)	+60.4

EXPERIMENTAL

The complexes *trans*-[Pd(Ph)$(PPh_3)_2$Cl], *trans*-[Pd(Ph)$(PPh_3)_2$(NCMe)][BF_4], and [{Pd(*o*-$C_6H_4CH{=}NPh)X\}_2$](X = Cl or O_2CMe) were prepared as described in the literature. Yields are quoted relative to the starting palladium complex, and microanalyses were determined by the Microanalytical Laboratories of the Chemistry Departments of the Universities of Sheffield and Birmingham, and of the Analytical Group of the then Corporate Research Laboratory at I.C.I., Runcorn. Infrared spectral data were obtained using PE291 and PE180 spectrophotometers, and ^1H n.m.r. spectra were measured using Varian HA100, PE 34, and Brucker WH400 instruments.

Acetonitrilephenylbis(triphenylphosphine)palladium(II) *Tetrafluoroborate*, [Pd(Ph)$(PPh_3)_2$(NCMe)][BF_4] (1).—A solution of $AgBF_4$ (0.52 g, 2.7 mmol) in acetonitrile (45 cm^3)

was added to a stirred suspension of $[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$ (2.0 g, 2.7 mmol) in acetonitrile (30 $\mathrm{cm^3}$). After stirring for 30 min, the precipitated AgCl was filtered off and the pale yellow filtrate evaporated *in vacuo* to low volume (*ca.* 10 $\mathrm{cm^3}$). Diethyl ether was then added to precipitate the *complex* which was filtered off and recrystallised from dichloromethane–diethyl ether mixtures, giving pale yellow crystals (2.1 g, 93%).

Amminephenylbis(triphenylphosphine)palladium(II) *Tetrafluoroborate*, $[\mathrm{Pd(Ph)(PPh_3)_2(NH_3)}][\mathrm{BF_4}]$ (2a).—Ammonia in ethanol (0.7 $\mathrm{cm^3}$, 3 mol $\mathrm{dm^{-3}}$ solution) was added to a stirred solution of $[\mathrm{Pd(Ph)(PPh_3)_2(NCMe)}][\mathrm{BF_4}]$ (1.0 g, 1.33 mmol) in dichloromethane (25 $\mathrm{cm^3}$). The solution changed rapidly from yellow to colourless, n-pentane was then added, and the *complex* formed as a white solid which was filtered off and air-dried (0.76 g, 78%).

Amminephenylbis(triphenylphosphine)palladium(II) *Hexafluorophosphate*, $[\mathrm{Pd(Ph)(PPh_3)_2(NH_3)}][\mathrm{PF_6}]$ (2b).—$[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$ (1.0 g) was stirred in a saturated solution of ammonia in methanol (50 $\mathrm{cm^3}$). To the resulting clear solution was added $\mathrm{NH_4PF_6}$ (excess) in water. The *complex* precipitated as a white solid which was filtered off and recrystallised from dichloromethane–hexane (1.12 g, 96%).

(1,2-*Diaminoethane)phenyl(triphenylphosphine)palladium*(II) *Hexafluorophosphate*, $[\mathrm{Pd(Ph)(NH_2CH_2CH_2NH_2)(PPh_3)}][\mathrm{PF_6}]$ (3a).—1,2-Diaminoethane (4 $\mathrm{cm^3}$) was added dropwise to a stirred suspension of $[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$ (0.5 g) in degassed methanol (30 $\mathrm{cm^3}$). To the resulting colourless solution was added $\mathrm{NH_4PF_6}$ (excess) in water. The *complex* precipitated as a white solid which was filtered off and recrystallised from dichloromethane–hexane (0.33 g, 76%).

(1,3-*Diaminopropane)phenyl(triphenylphosphine)palladium*(II) *Hexafluorophosphate*, $[\mathrm{Pd(Ph)(NH_2CH_2CH_2CH_2NH_2)(PPh_3)}][\mathrm{PF_6}]$ (3b).—This *complex* was prepared in the same way as its 1,2-diaminoethane analogue above, using 1,3 diaminopropane (4 $\mathrm{cm^3}$) and $[\mathrm{Pd(Ph)(PPh_3)_2Cl}]$ (1.0 g). It was obtained as white crystals from dichloromethane–diethyl ether–hexane mixtures (0.66 g, 74%).

Acetatoammine[2-(*phenyliminomethyl)phenyl*-$\mathrm{C^1}$,N]*palladium*(II), $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(NH_3)(O_2CMe)}]$ (5b).—Ammonia gas in dichloromethane (5 $\mathrm{cm^3}$) was added to a stirred solution of $[\{\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(\mu\text{-}O_2CMe)}\}_2]$ (0.5 g) in dichloromethane (30 $\mathrm{cm^3}$). Diethyl ether was then added to the dark yellow-orange solution until crystallisation of the *complex* occurred (0.47 g, 90%).

Amminechloro[2-(*phenyliminomethyl)phenyl*-$\mathrm{C^1}$,N]*palladium*(II), $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(NH_3)Cl}]$ (5a).—This compound was prepared in the same way as its acetato analogue, using $[\{\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(\mu\text{-}Cl)}\}_2]$ (0.29 g), and was obtained as a yellow solid (0.21 g, 69%).

Diammine[2-(*phenyliminomethyl)phenyl*-$\mathrm{C^1}$,N]*palladium*(II) *Chloride*, $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(NH_3)_2}]\mathrm{Cl}$ (6a).—Ammonia gas in dichloromethane (15 $\mathrm{cm^3}$) was added to a stirred solution of $[\{\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(\mu\text{-}Cl)}\}_2]$ (0.5 g) in dichloromethane (20 $\mathrm{cm^3}$). The *complex* precipitated as a pale yellow powder which was filtered off and air-dried (0.54 g, 98%).

Triammine[2-(*phenyliminomethyl)phenyl*]*palladium*(II) *Acetate*, $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(NH_3)_3}][\mathrm{O_2CMe}]$ (7).—Ammonia (D = 0.88 g $\mathrm{cm^{-3}}$, large excess) in dichloromethane (15 $\mathrm{cm^3}$) was added to a stirred solution of $[\{\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(\mu\text{-}O_2CMe)}\}_2]$ (0.8 g) in dichloromethane (20 $\mathrm{cm^3}$). The *complex* precipitated as a white powder which was filtered off and air-dried (0.65 g, 71%).

Diammine[2-(*phenyliminoethyl)phenyl*-$\mathrm{C^1}$,N]*palladium*(II) *Hexafluorophosphate*, $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(NH_3)_2}][\mathrm{PF_6}]$, (6b).—A solution of $\mathrm{NH_4PF_6}$ (0.2 g) in methanol (10 $\mathrm{cm^3}$) was added to a stirred solution of $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(NH_3)_2}]\mathrm{Cl}$ (0.35 g) in methanol (20 $\mathrm{cm^3}$). The methanol was then reduced in volume to *ca.* 5 $\mathrm{cm^3}$ and water (50 $\mathrm{cm^3}$) was then added to effect precipitation of the *complex*. This was recrystallised from methanol–water mixtures, giving yellow crystals (0.2 g, 42%). The same product was obtained from the reaction of $\mathrm{NH_4PF_6}$ with $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(NH_3)_3}][\mathrm{O_2CMe}]$.

TABLE 5

Atomic positional parameters with estimated standard deviations for the molecule $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NCH_2CH_2NH_2)(NH_2CH_2CH_2NH_2)}]^+[\mathrm{PF_6}]^-$

	X/a	Y/b	Z/c
Pd(1)	0.302 2(3)	0.102 99(18)	0.017 36(12)
Pd(2)	−0.199 5(3)	0.559 88(17)	0.462 60(11)
P(1)	−0.123 7(11)	0.446 9(7)	0.157 9(4)
P(2)	0.417 1(11)	−0.024 7(6)	0.370 5(4)
F(1)	−0.197(3)	0.392 0(18)	0.230 7(10)
F(2)	−0.208(3)	0.577 9(16)	0.185 2(11)
F(3)	0.042(3)	0.458 4(17)	0.190 2(10)
F(4)	−0.288(3)	0.432 3(19)	0.127 8(10)
F(5)	−0.043(3)	0.314 4(16)	0.130 5(11)
F(6)	−0.050(3)	0.506 7(18)	0.087 2(10)
F(7)	0.313(3)	0.072 3(15)	0.321 1(10)
F(8)	0.501(3)	−0.096 3(17)	0.299 9(10)
F(9)	0.265(3)	−0.098 3(23)	0.374 5(14)
F(10)	0.567(3)	0.049 0(18)	0.364 8(11)
F(11)	0.332(3)	0.049 9(20)	0.436 8(11)
F(12)	0.521(2)	−0.123 1(14)	0.417 9(9)
N(1)	0.352(3)	0.264(2)	−0.042 2(12)
N(2)	0.348(3)	0.204(2)	0.100 7(12)
N(3)	0.238(3)	0.001(2)	−0.060 4(12)
N(4)	0.370(3)	−0.140(2)	−0.199 9(12)
N(5)	−0.118(3)	0.569(2)	0.350 4(12)
N(6)	−0.140(3)	0.733(2)	0.463 8(12)
N(7)	−0.283(3)	0.396(2)	0.468 5(11)
N(8)	−0.061(4)	0.153(2)	0.437 0(13)
C(1)	0.335(5)	0.361(2)	0.013 6(17)
C(2)	0.410(5)	0.317(2)	0.075 4(16)
C(3)	0.256(4)	−0.044(2)	0.074 4(12)
C(4)	0.270(4)	−0.067(2)	0.145 0(13)
C(5)	0.248(4)	−0.183(3)	0.174 5(15)
C(6)	0.198(5)	−0.271(3)	0.133 6(15)
C(7)	0.182(4)	−0.248(3)	0.062 1(15)
C(8)	0.197(3)	−0.127(2)	0.030 7(15)
C(9)	0.195(4)	−0.103(2)	−0.040 1(11)
C(10)	0.237(4)	0.048(2)	−0.135 8(12)
C(11)	0.219(4)	−0.047(3)	−0.191 4(14)
C(12)	−0.135(4)	0.704(2)	0.333 7(15)
C(13)	−0.055(4)	0.763(2)	0.390 2(15)
C(14)	−0.266(3)	0.553(2)	0.567 4(11)
C(15)	−0.269(3)	0.639(3)	0.620 2(14)
C(16)	−0.319(4)	0.613(2)	0.688 8(14)
C(17)	−0.381(4)	0.506(3)	0.711 4(16)
C(18)	−0.392(4)	0.425(2)	0.657 2(15)
C(19)	−0.339(4)	0.449(2)	0.585 2(15)
C(20)	−0.348(4)	0.367(2)	0.526 8(14)
C(21)	−0.306(3)	0.316(2)	0.409 3(15)
C(22)	−0.134(4)	0.236(3)	0.381 8(16)

1,2-*Bis(dimethylamino)ethane*[2-(*phenyliminomethyl)phenyl*-$\mathrm{C^1}$,N]*palladium*(II) *Hexafluorophosphate*, $[\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(Me_2NCH_2CH_2NMe_2)}][\mathrm{PF_6}]$ (8).—1,2-Bis(dimethylamino)ethane (4 $\mathrm{cm^3}$) was added dropwise to a stirred suspension of $[\{\mathrm{Pd(\mathit{o}\text{-}C_6H_4CH{=}NPh)(\mu\text{-}O_2CMe)}\}_2]$ (0.8 g) in methanol (25 $\mathrm{cm^3}$) giving a clear pale yellow solution. To this was added $\mathrm{NH_4PF_6}$ (excess) dissolved in methanol (25 $\mathrm{cm^3}$) and the *complex* precipitated as a yellow solid. This was recrystallised from dichloromethane–ether mixtures (0.76 g, 60%).

$[Pd(o\text{-}C_6H_4CH{=}NCH_2CH_2NH_2)(H_2NCH_2CH_2NH_2)][PF_6]$ (9a).—1,2-Diaminoethane (4 cm^3) was added dropwise to a stirred suspension of $[\{Pd(o\text{-}C_6H_4CH{=}NPh)(\mu\text{-}O_2CMe)\}_2]$ (0.5 g) in methanol (25 cm^3) giving a clear yellow-green solution. To this was added NH_4PF_6 (excess) in methanol (25 cm^3), and the resulting mixture was concentrated *in vacuo* and allowed to stand at −3 °C until the yellow-green *complex* had precipitated. The compound was filtered off and recrystallised from methanol–diethyl ether–hexane mixtures (0.45 g, 68%).

X-*Ray Crystallography*.—*Crystal data*. $[Pd(C_9H_{11}N_2)(H_2NCH_2CH_2NH_2)]^+[PF_6]^-$: $C_{11}H_{19}F_6N_4PPd$, $M = 458.66$, crystallises from methanol–diethyl ether–hexane as fine, yellow needles; Triclinic, $a = 8.109(16)$, $b = 11.027(27)$, $c = 18.93(4)$ Å, $\alpha = 88.30(19)$, $\beta = 83.19(18)$, $\gamma = 81.05(18)°$, $U = 1\,660(7)$ Å^3, $D_m = 1.81$, $Z = 4$, $D_c = 1.835$ g cm^{-3}, space group $P\bar{1}$ (assumed and confirmed by the analysis), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 12.58 cm^{-1}, $F(000) = 912$; crystal dimensions 0.80 × 0.10 × 0.05 mm.

Structure solution and refinement. Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer by the omega-scan method; 1 725 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.95, N–H 0.91 Å, C–N–H 110°); their contributions were included in structure factor calculations ($B = 8.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0672 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of palladium. Table 5 lists the atomic positional parameters with estimated standard deviations. Tables of anisotropic thermal vibrational parameters with estimated standard deviations, predicted hydrogen atom positional parameters, and observed structure amplitudes and calculated structure factors are deposited in Supplementary Publication No. SUP 23289 (19 pp.).* Scattering factors were taken from ref. 7, and unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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