Orthometallated Primary Amines. Part 1. Facile Preparation of the First Optically Active Cyclopalladated Primary Amines†

José Vicente,*[a] Isabel Saura-Llamas[a] and Peter G. Jones*[b]

[a] *Grupo de Química Organometálica, Departamento de Química Inorgánica, Universidad de Murcia, Apdo 4021, Murcia, 30071 Spain*

[b] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany*

Reaction of $[PdCl_2\{NH_2CH(Me)Ph\}_2]$ **1** with $AgClO_4$ (1 : 2) gave a solution containing an orthopalladated complex **2**. Addition to this solution of neutral ligands or NaBr led to isolation of the complexes $[Pd\{C_6H_4[CH(Me)NH_2\text{-}2]\}(L_2)]ClO_4$ [L = pyridine **3a**, L_2 = cycloocta-1,5-diene(cod) **3b** or 2,2′-bipyridine **3c**] or $[\{Pd\{C_6H_4[CH(Me)NH_2\text{-}2]\}(\mu\text{-}Br)\}_2]$ **4**, respectively. Reaction of **4** with PPh_3 or Tl(acac) (Hacac = acetylacetone) gave $[Pd\{C_6H_4[CH(Me)NH_2\text{-}2]\}Br(PPh_3)]$ **5** or $[Pd\{C_6H_4[CH(Me)NH_2\text{-}2]\}(acac)]$ **6**, respectively. Complexes **1**, **4** and **5** can be obtained optically pure by using (*R*)-(+)- or (*S*)-(−)-α-methylbenzylamine as starting material. The solid-state crystal structures of **3b** and *R*-**5** were determined at low temperatures. In both complexes the palladium atom adopts the usual square-planar co-ordination. The major angular distortion is associated with the small bite of the chelating ligand (80.8 and 81.2°, respectively). The weaker *trans* influence of the cod ligand in **3b** accounts for *ca.* 0.02 Å longer Pd–N and Pd–C bonds in *R*-**5** than in **3b**. Short contacts between the perchlorate anion or bromo ligand in **3b** or *R*-**5** with the amino group (N ··· O 3.06 or N ··· Br 3.41 Å, respectively) probably represent hydrogen bonds.

We are interested in the synthesis of chiral orthopalladated primary amines, first because the metal–carbon bond in the corresponding complexes with tertiary benzylamines undergo insertion reactions with, for example, carbon monoxide,[1] electron-deficient alkenes,[2] alkynes,[3] and acyl halides[4] regiospecifically and for this reason they have attracted interest in organic synthesis. As far as we are aware, orthopalladated primary amines have not yet been studied and a different behaviour from the tertiary amines is expected because of their greater basic character and the possibility of giving neutral nitrogen heterocycles instead of cyclic ammonium salts.[2a,3] Karpeiskaya *et al.*[5] have postulated the formation of complexes containing orthometallated α-methylbenzylamine, which acted as catalysts when the reductive aminolysis of Δ^2-oxazolin-5-ones was carried out with (*S*)-α-methylbenzylamine and H_2 in the presence of $PdCl_2$. However, these species, described as a mixture of polynuclear zero-valent palladium(0) complexes, were very poorly defined. We have previously described the synthesis of indenols and indenones from arylpalladium complexes and acetylenes.[6]

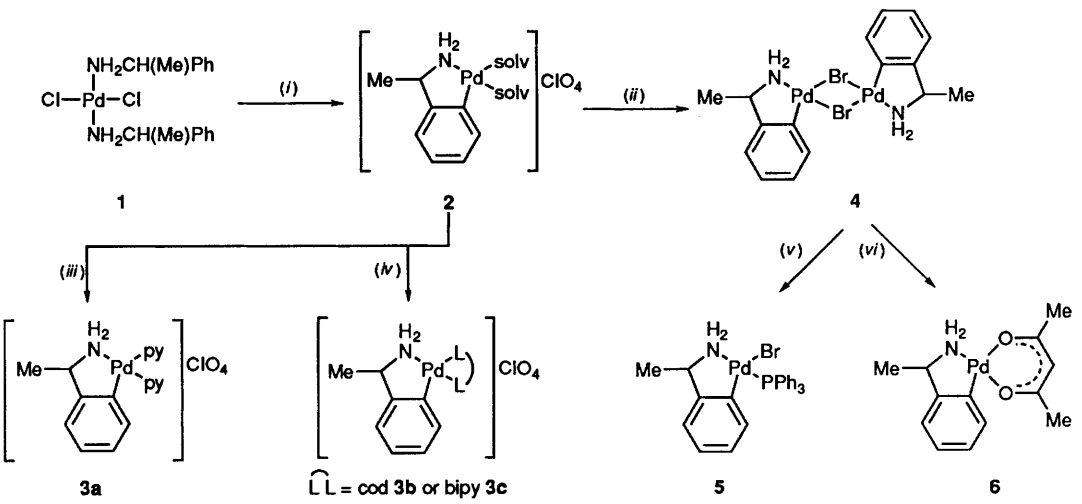
Secondly, chiral cyclopalladated complexes of tertiary amines have widely been used in the resolution of racemic amines, phosphines and arsines.[7] Orthopalladated primary amines should have the additional possibility of giving a second chiral centre on the nitrogen atom upon substituting a hydrogen atom by an alkyl group.

Many cyclopalladated amine complexes of palladium(II) have been reported.[8] They are mainly prepared by direct cyclopalladation of the amine (or orthopalladation, in the case of reactions involving the *ortho* position in the aromatic ring of the ligand).[9] However, since the early studies on this reaction by Cope and Friedrich[10] some limiting conditions have become generally accepted. One is that primary amines weaken the electrophilic properties of palladium, preventing attack on the aromatic ring. Only triphenylmethylamine[11] and benzylamine[12] have been orthopalladated. Therefore, the idea that primary amines are inert toward orthometallation is still generally accepted. Thus, in a recent review, Ryabov[9] comments 'Recent findings of . . . Avshu, who showed a way to palladacycles with primary amines, did not, however, change the general situation, since his approach has obvious limitations'. In this paper we also show that a modification of Avshu's method[12b] can be used to metallate other primary amines such as α-methylbenzylamine.

Results and Discussion

Synthesis of Complexes.—When $PdCl_2$ is stirred with α-methylbenzylamine the co-ordination of two molecules of the amine to the metallic centre takes place to give $[PdCl_2\{NH_2CH(Me)Ph\}_2]$ **1**. This complex did not undergo orthometallation on heating in acetone and decomposed when ethanol or methanol was used as solvent. Following a modification of a method previously described by Avshu *et al.*,[12b] we investigated the reaction of $[PdCl_2\{NH_2CH(Me)Ph\}_2]$ with $AgClO_4$ (1 : 2) in acetone. The quantitative amount of AgCl was produced and removed by filtration together with some of the ammonium salt $[PhCH(Me)NH_3]ClO_4$. We assume that the resulting solution contains the complex $[Pd\{C_6H_4[CH(Me)\text{-}NH_2\text{-}2]\}(Me_2CO)_2]ClO_4$ **2** (see Scheme 1) although we have been unable to isolate **2** or the MeCN complex presumably formed when acetonitrile is used as solvent. However, the addition to solutions of **2** of neutral mono- or bi-dentate ligands leads to the formation of the cationic orthometallated palladium(II) complexes $[Pd\{C_6H_4[CH(Me)NH_2\text{-}2]\}L_2]ClO_4$ [L =

* *Supplementary data available:* Further details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 380004/5.



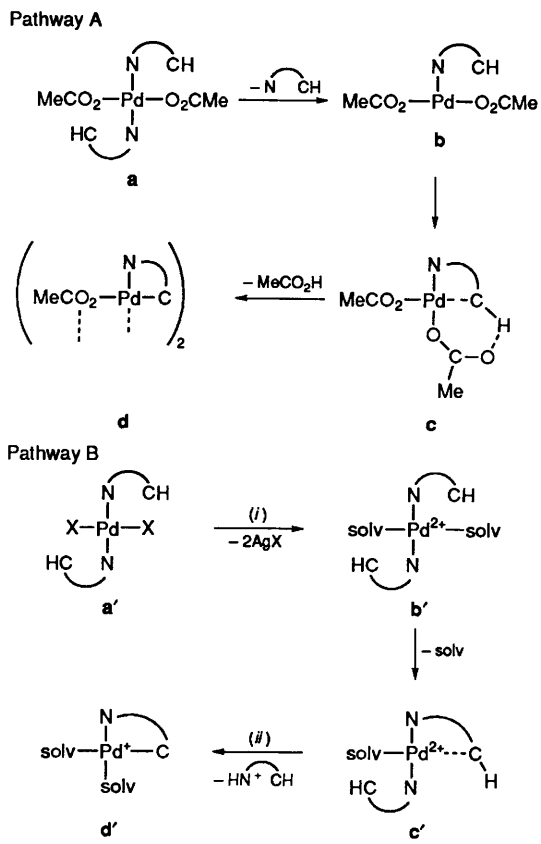
Scheme 1 (*i*) $2AgClO_4$, Me_2CO(solv); (*ii*) NaBr; (*iii*) 2 py; (*iv*) L–L; (*v*) PPh_3; (*vi*) Tl(acac)

pyridine (py) **3a**, L_2 = cycloocta-1,5-diene(cod) **3b**, or 2,2′-bipyridine (bipy) **3c**], whereas addition of NaBr (1.3 equivalents) gives the dimeric neutral complex [{Pd{C_6H_4[CH(Me)NH_2-2]}(μ-Br)}$_2$] **4**. When **4** was treated with PPh_3 (1:2) or Tl(acac) (Hacac = acetylacetone) the complex [Pd{C_6H_4[CH(Me)NH_2-2]}Br(PPh_3)] **5** or [Pd{C_6H_4[CH(Me)NH_2-2]}(acac)] **6** was obtained.

Complexes **1**, **4** and **5** in optically pure forms were easily obtained using the corresponding optically active amines. Thus, when $PdCl_2$ was treated with (*R*)-(+)- or (*S*)-(−)-α-methylbenzylamine the complex *RR*- or *SS*-**1** was obtained, respectively. These complexes are much more soluble than the racemic ones and so are their derivatives. When *RR*-**1** (or its enantiomer) was treated with $AgClO_4$ (1:2) in acetone following a procedure analogous to that given for the racemic mixture **1**, and NaBr was added to the resulting solution, *RR*-**4** (or its enantiomer) was isolated. The analogous chloro-complex with *N*,*N*, α-trimethylbenzylamine is known and has been used as a chiral agent for optical resolution of tertiary phosphines.[7] The addition of PPh_3 to suspensions of *RR*- or *SS*-**4** in CH_2Cl_2 gave the optically active complex *R*- or *S*-**5**, respectively.

Primary amines are inert towards orthopalladation because, according to kinetic data, the dissociative process **a** ⟶ **b** (see Scheme 2, pathway A) is very unfavourable for them, whereas secondary and, even better, tertiary amines can dissociate to give the three-co-ordinate intermediate **b**.[9] However, assuming that in our process the orthometallation also requires a three-co-ordinate intermediate, its formation only needs the easy dissociation of a solvent molecule (**b′** ⟶ **c′** in pathway B of Scheme 2) and, therefore, the success of the orthometallation reaction is independent of the basic character of the amine. For this reason, we do not agree with the comment of Ryabov,[2] on the 'obvious limitations' of the reaction of Avshu *et al.*,[12b] *trans*-[PdI_2(NH_2CH_2Ph)$_2$] + 2 $AgBF_4$ + KI ⟶ [{Pd[C_6H_4(CH_2-NH_2-2)](μ-I)}$_2$]. Additionally, in this way, the palladium centre becomes highly charged and electrophilic which should contribute to the C–H bond cleavage (**c′** ⟶ **d′**). However, as in 'normal' orthopalladation reactions, this bond breaking depends on the nucleophilicity of the aryl ring. No orthopalladation of (*S*)-α-methyl-4-nitrobenzylamine occurred following the method used for α-methylbenzylamine, which is attributable to the low nucleophilic character of the 4-nitrophenyl group. So, when a solution of [$PdCl_2L_2$] [L = (*S*)-α-methyl-4-nitrobenzylamine] in acetone was treated with $AgClO_4$ (1:2) and then with NaBr, [$PdBr_2L_2$] was isolated as shown by ^{1}H NMR spectroscopy.

Structure of Complexes.—The NMR data for complex **1** indicate that only the *cis* or *trans* isomer is obtained because only two different methyl resonances appear in the ^{13}C



Scheme 2 (*i*) $2Ag^+$, 2 solv; (*ii*) solv

spectrum, corresponding to the two possible diastereoisomers (*RR*/*SS* and *RS*). In the ^{1}H NMR spectrum the methyl protons are accidentally isochronous. The IR spectrum indicates that it is the *trans* isomer[13] because the observed band assignable to ν(PdCl) appears at 345 cm^{-1}. The same geometry could be assigned to *RR*- and *SS*-**1**.

It has been shown by IR[14] and X-ray studies[15] that halide-bridged dimers similar to **4** have the *trans* geometry shown in Scheme 1. Complex **4** is insoluble in CH_2Cl_2 and $CHCl_3$ but very soluble in acetone. Proton and ^{13}C-{^{1}H} NMR spectra were recorded in [$^2H_6$]acetone and, surprisingly, only one set of signals appeared in both. We assume that acetone breaks the bromo bridge leading to the formation of mononuclear species. This process is probably responsible for the high solubility of **4** in acetone and also for the absence of two sets of signals in the NMR spectra corresponding to a mixture of the two diastereo-

isomers of *trans*-**4** or four sets in the case of a mixture of *cis*- and *trans*-**4**. The isomers *RR*- and *SS*-**4** are soluble in CH_2Cl_2, $CHCl_3$ and acetone and only one set of signals is observed indicating that only one geometrical isomer is present.

Complex **5** was treated with a chiral NMR shift reagent, (+)-[EuL_3] [2 equivalents, $CDCl_3$; L = 3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]. The methyl ^1H NMR resonances of the enantiomers exhibited near-baseline resolution (0.05 ppm). When the shift reagent analysis was carried out on the optically active complexes, *R*- and *S*-**5**, no trace of the opposite enantiomer was observed. Hence, the optical purities of these complexes were > 98% enantiomeric excess.

All complexes show two or three bands corresponding to ν(NH) in the range 3100–3300 cm^{-1}.

Crystal structures of complexes **3b** and *R*-**5** were determined by X-ray diffraction. Table 1 gives crystal data and structure refinement, Tables 2 and 3 atomic coordinates, and Tables 4 and 5 selected bond lengths and angles, respectively. The palladium atom in **3b** (Fig. 1) adopts the usual planar co-ordination, if the midpoints of the double bonds C(1)–C(2) and C(5)–C(6) are considered as point ligands; the distances to Pd, 2.243 and 2.097 Å respectively, probably reflect the greater *trans* influence of the carbon donor C(9). The major angular distortion is associated with the small bite of the chelating ligand [N–Pd–C(9) 80.8°]. The short contact to the perchlorate anion N ··· O(4) ($-\frac{1}{2} + x$, $\frac{3}{2} - y$, $\frac{1}{2} + z$) 3.06 Å probably represents a hydrogen bond [H(0B) ··· O 2.38 Å, N–H ··· O 131°].

In complex *R*-**5** (Fig. 2) the bite of the chelating ligand is 81.2°; the Pd–N and Pd–C bonds are *ca.* 0.02 Å longer than in **3b**, presumably because the cod ligand in **3b** has a weak *trans* influence. A hydrogen bond N–H(0B) ··· Br ($1 - x$, $-\frac{1}{2} + y$, $1 - z$) is observed, with N ··· Br 3.41, H ··· Br 2.46 Å and N–H ··· Br 161°.

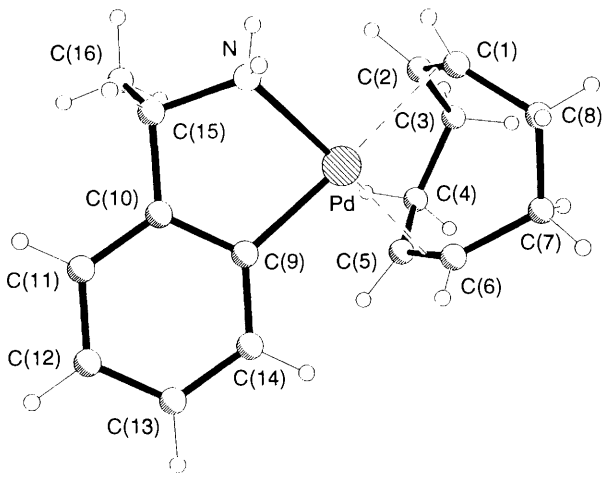


Fig. 1 The structure of the cation of complex **3b**

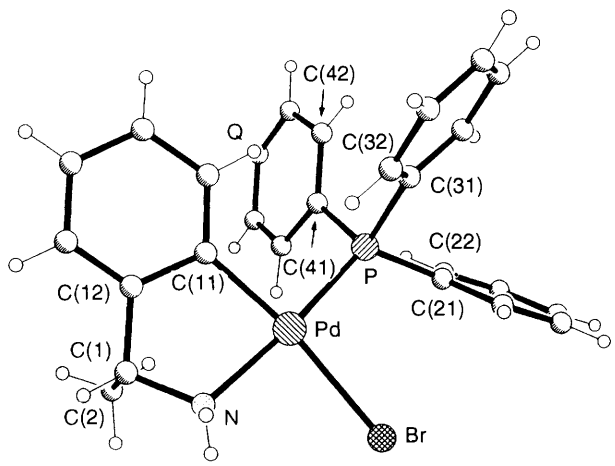


Fig. 2 The structure of complex *R*-**5**

Experimental

General Data.—Infrared spectra were recorded on a Perkin Elmer 1430 spectrometer using mineral oil mulls between polyethylene sheets. All NMR spectra were recorded on a Varian XL-300 spectrometer, using $CDCl_3$ solutions, and referenced to internal $SiMe_4$ (^1H), $CDCl_3$ (δ 77.1) or $(CD_3)_2CO$ (δ 29.8) (^{13}C), or external 85% H_3PO_4 (^{31}P). Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} solutions in acetone with a Philips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. The C, H and N

Table 1 Crystal data and structure refinement details for compounds **3b** and *R*-**5**

	3b	*R*-**5**
Empirical formula	$C_{16}H_{22}ClNO_4Pd$	$C_{26}H_{25}BrNPPd$
M	434.20	568.75
T/K	178(2)	143.0(10)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a/Å	9.514(4)	9.898(2)
b/Å	12.657(5)	8.452(2)
c/Å	14.868(5)	14.366(3)
β/°	107.88(3)	102.60(2)
U/Å^3	1703.9(11)	1172.9(4)
Z	4	2
D_c/Mg m^{-3}	1.693	1.610
μ(Mo-Kα)/mm^{-1}	1.264	2.576
F(000)	880	568
Crystal size/mm	0.40 × 0.30 × 0.25	0.75 × 0.35 × 0.15
2θ range/°	3.02–25.05	3.20–27.54
h, *k*, *l* ranges	−11 to 5, 0–15, −17 to 17	−1 to 12, −10 to 10, −18 to 18
Reflections collected	5019	5680
Independent reflections	3015 (R_{int} = 0.0277)	5324 (R_{int} = 0.0209)
Data, restraints, parameters	3014, 159, 208	5316, 162, 273
Goodness of fit on F^2	1.083	1.046
$R(F)$,$wR(F^2)$[$I > 2\sigma(I)$]	0.0405, 0.1033	0.0262, 0.0593
(all data)	0.0563, 0.1197	0.0295, 0.0642
Largest difference peak and hole/e Å^{-3}	1.160, −0.622	0.501, −0.595
Maximum Δ/σ	0.001	0.001

Table 2 Atomic coordinates ($\times 10^4$) for compound **3b**

Atom	*x*	*y*	*z*
Pd	6 778.8(4)	6 970.4(3)	5 067.5(3)
N	4 807(5)	6 932(4)	5 390(4)
C(1)	8 083(7)	7 808(5)	6 472(4)
C(2)	7 725(7)	8 575(4)	5 808(4)
C(3)	8 761(7)	9 019(5)	5 311(4)
C(4)	8 611(8)	8 483(5)	4 360(5)
C(5)	8 433(6)	7 306(5)	4 349(4)
C(6)	9 060(6)	6 608(5)	5 072(4)
C(7)	10 162(7)	6 891(5)	6 008(5)
C(8)	9 504(7)	7 198(5)	6 788(5)
C(9)	5 656(6)	5 960(4)	4 074(3)
C(10)	4 134(6)	5 948(4)	3 947(4)
C(11)	3 204(8)	5 301(5)	3 262(5)
C(12)	3 766(9)	4 674(5)	2 705(5)
C(13)	5 252(9)	4 682(5)	2 826(4)
C(14)	6 201(7)	5 305(4)	3 500(4)
C(15)	3 532(6)	6 663(5)	4 559(5)
C(16)	2 857(10)	7 657(7)	4 082(6)
Cl	8 960(2)	5 954.6(13)	1 922.1(12)
O(1)	9 571(10)	5 485(10)	1 308(7)
O(2)	7 469(6)	5 967(6)	1 593(6)
O(3)	9 333(7)	5 331(5)	2 751(5)
O(4)	9 669(10)	6 897(5)	2 163(6)

Table 3 Atomic coordinates ($\times 10^4$) for compound *R*-**5**

Atom	*x*	*y*	*z*
Pd	5 044.5(2)	4 927.4(2)	3 667.1(1)
Br	3 362.2(3)	4 970.0(6)	4 753.9(2)
P	3 703.1(8)	6 200.1(9)	2 433.3(5)
N	6 522(3)	3 934(4)	4 779(2)
C(1)	7 927(4)	4 152(5)	4 610(3)
C(2)	8 474(6)	5 781(6)	4 945(3)
C(11)	6 553(3)	4 510(3)	2 952(2)
C(12)	7 810(3)	4 002(4)	3 552(3)
C(13)	8 912(4)	3 499(4)	3 169(3)
C(14)	8 822(4)	3 521(4)	2 204(3)
C(15)	7 617(3)	4 060(4)	1 599(3)
C(16)	6 507(3)	4 520(3)	1 976(2)
C(21)	2 242(3)	7 406(4)	2 619(2)
C(22)	2 212(3)	9 040(4)	2 514(2)
C(23)	1 039(3)	9 884(7)	2 578(2)
C(24)	−109(4)	9 106(5)	2 746(3)
C(25)	−86(4)	7 508(5)	2 859(3)
C(26)	1 082(3)	6 642(4)	2 802(3)
C(31)	2 833(2)	4 935(6)	1 459(2)
C(32)	3 129(3)	3 321(4)	1 480(2)
C(33)	2 463(4)	2 341(4)	747(3)
C(34)	1 503(4)	2 948(5)	−6(3)
C(35)	1 187(3)	4 548(5)	−29(2)
C(36)	1 837(3)	5 530(4)	699(2)
C(41)	4 699(3)	7 673(4)	1 953(2)
C(42)	4 621(3)	7 926(4)	990(2)
C(43)	5 361(4)	9 166(4)	700(2)
C(44)	6 122(3)	10 179(5)	1 359(2)
C(45)	6 198(3)	9 960(6)	2 328(2)
C(46)	5 516(3)	8 680(4)	2 625(2)

analyses were carried out with a Carlo-Erba EA 1108 microanalyser. Reactions were carried out at room temperature in air with no special precautions.

Solvents and reagents were purified as follows: acetone, distilled from $KMnO_4$; diethyl ether, distilled from sodium–benzophenone; CH_2Cl_2, distilled from P_2O_5 and then from Na_2CO_3; hexane, distilled from $CaCl_2$. The compound Tl(acac) was prepared according to literature methods;[16] $PdCl_2$ (Engelhard), α-methylbenzylamine, (*R*)- and (*S*)-α-methylbenzylamine, (+)-[EuL_3] (Aldrich), NaBr (Probus), PPh_3 (Fluka), pyridine, cycloocta-1,5-diene and 2,2′-bipyridine (Merck) were used as received.

Table 4 Selected bond lengths (Å) and angles (°) for compound **3b**

Pd–C(9)	1.998(5)	C(1)–C(8)	1.502(9)
Pd–N	2.075(5)	C(2)–C(3)	1.511(8)
Pd–C(5)	2.198(5)	C(3)–C(4)	1.534(9)
Pd–C(6)	2.216(5)	C(4)–C(5)	1.499(8)
Pd–C(1)	2.331(5)	C(5)–C(6)	1.378(9)
Pd–C(2)	2.353(5)	C(6)–C(7)	1.507(9)
N–C(15)	1.481(8)	C(7)–C(8)	1.527(10)
C(1)–C(2)	1.351(8)		
C(9)–Pd–N	80.8(2)	C(5)–C(4)–C(3)	115.3(5)
C(9)–Pd–C(5)	93.7(2)	C(6)–C(5)–C(4)	127.4(6)
N–Pd–C(5)	161.8(2)	C(5)–C(6)–C(7)	125.5(5)
C(9)–Pd–C(6)	99.8(2)	C(6)–C(7)–C(8)	115.5(5)
N–Pd–C(6)	161.5(2)	C(1)–C(8)–C(7)	115.7(5)
C(5)–Pd–C(6)	36.4(2)	N–C(15)–C(16)	109.1(6)
C(9)–Pd–C(1)	166.0(2)	N–C(15)–C(10)	105.9(4)
N–Pd–C(1)	94.2(2)	C(2)–C(1)–Pd	74.1(3)
C(5)–Pd–C(1)	94.8(2)	C(8)–C(1)–Pd	103.1(4)
C(6)–Pd–C(1)	80.8(2)	C(1)–C(2)–C(3)	124.7(6)
C(9)–Pd–C(2)	160.0(2)	C(1)–C(2)–Pd	72.3(3)
N–Pd–C(2)	98.9(2)	C(3)–C(2)–Pd	107.8(4)
C(5)–Pd–C(2)	80.4(2)	C(2)–C(3)–C(4)	113.3(5)
C(6)–Pd–C(2)	86.8(2)	C(15)–N–Pd	112.3(4)
C(1)–Pd–C(2)	33.5(2)	C(2)–C(1)–C(8)	126.7(6)

Table 5 Selected bond lengths (Å) and angles (°) for compound *R*-**5**

Pd–C(11)	2.019(3)	P–C(31)	1.822(3)
Pd–N	2.092(3)	P–C(21)	1.836(3)
Pd–P	2.244(1)	N–C(1)	1.475(5)
Pd–Br	2.519(1)	C(1)–C(12)	1.504(5)
P–C(41)	1.815(3)	C(1)–C(2)	1.518(6)
C(31)–P–Pd	115.1(1)	C(11)–Pd–N	81.22(13)
C(21)–P–Pd	120.0(1)	C(11)–Pd–P	93.30(9)
C(1)–N–Pd	110.6(2)	N–Pd–P	172.0(1)
N–C(1)–C(12)	106.7(3)	C(11)–Pd–Br	168.5(9)
N–C(1)–C(2)	110.2(4)	N–Pd–Br	88.78(10)
C(12)–C(1)–C(2)	109.9(3)	P–Pd–Br	97.21(3)
C(41)–P–C(31)	108.4(2)	C(31)–P–C(21)	100.5(1)
C(41)–P–C(21)	100.7(1)	C(41)–P–Pd	110.6(1)

Preparations.—[$PdCl_2\{NH_2CH(Me)Ph\}_2$] **1**. Palladium(II) chloride (1.00 g, 5.64 mmol) and α-methylbenzylamine (2.00 cm^3, 15.5 mmol) were stirred in acetone (100 cm^3) until dissolved. The solution was filtered through $MgSO_4$, reduced in volume to *ca.* 2 cm^3 and diethyl ether (40 cm^3) added to precipitate complex **1** as a yellow solid, which was collected, washed with diethyl ether, and air dried (2.4 g, 5.2 mmol, 93%), m.p. 142–144 °C (Found: C, 45.75; H, 5.55; N, 6.40. Calc. for $C_{16}H_{22}Cl_2N_2Pd$: C, 45.80; H, 5.30; N, 6.65%). $\Lambda_M = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$) ν(NH) 3120s, 3210s and 3290s. NMR: ^1H, δ 1.71 (d, 3 H, Me, $^3J_{HH}$ = 6.8 Hz), 3.20 (m, 1 H, CH), 3.48 (m, 1 H, NH), 4.24 (m, 1 H, NH) and 7.26–7.39 (m, 5 H, Ph); ^{13}C-{^1H}, δ 23.1 and 23.2 (s, Me), 54.3 (s, CH), 126.4 (s, *o*-CH of C_6H_5), 128.2 (s, *p*-CH of C_6H_5), 129.0 (s, *m*-CH of C_6H_5) and 142.2 (s, *ipso*-C of C_6H_5).

RR-[$PdCl_2\{NH_2CH(Me)Ph\}_2$] *RR*-**1**. This compound was prepared from (*R*)-α-methylbenzylamine (2.00 cm^3, 15.5 mmol) in a manner identical with that for the racemate, as a yellow solid (2.5 g, 5.4 mmol, 98%), m.p. 131 °C (Found: C, 45.85; H, 5.40; N, 6.70%).

SS-[$PdCl_2\{NH_2CH(Me)Ph\}_2$] *SS*-**1**. This compound was prepared from (*S*)-α-methylbenzylamine (2.00 cm^3, 15.5 mmol) as above, as a yellow solid (2.6 g, 5.5 mmol, 99%), m.p. 131 °C (Found: C, 45.65; H, 5.70; N, 6.65%).

Solutions of complex **2**. Complex **1** (200 mg, 0.476 mmol) was taken up in acetone (20 cm^3), treated with solid $AgClO_4$ (200 mg, 0.965 mmol) and left to stand for 10 min. The resulting

precipitate of silver chloride was then filtered off. The filtrate was made up to a larger volume (75 cm^3) with acetone and allowed to stand overnight at room temperature. Acetone was removed and the residue taken up in CH_2Cl_2 (10 cm^3) and filtered through a plug of $MgSO_4$.

$[Pd\{C_6H_4CH(Me)NH_2\}(py)_2]ClO_4$ **3a**. To a solution of complex **2** (prepared from 200 mg, 0.476 mmol of **1**) pyridine (0.250 cm^3, 3.22 mmol) was added and the resulting colourless solution was stirred for 1 h and then filtered through $MgSO_4$. Its volume was reduced to *ca.* 2 cm^3 and diethyl ether was added (25 cm^3). The oily product obtained was stirred and washed with diethyl ether (3 × 25 cm^3) to give complex **3a** as a white solid which was collected, washed with diethyl ether, and air dried (124 mg, 0.255 mmol, 54%), m.p. 159–161 °C (Found: C, 44.65; H, 4.15; N, 8.60. Calc. for $C_{18}H_{20}ClN_3O_4Pd$: C, 44.65; H, 4.15; N, 8.70%). Λ_M = 126 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}) ν(NH) 3240s and 3280s. NMR: ^1H, δ 1.65 (d, 3 H, Me, $^3J_{HH}$ = 6.3), 3.75 (m, 1 H, NH), 4.53 (m, 1 H, CH), 4.71 (m, 1 H, NH), 5.99 (d, 1 H, C_6H_4, J = 6.9), 6.78 (t, 1 H, C_6H_4, J = 7.2), 6.85 (t, 1 H, C_6H_4, J = 7.5), 7.02 (t, 1 H, C_6H_4, J = 6.9 Hz), 7.43–7.53 (m, 4 H, *m*-H of py), 7.78 (m, 1 H, *p*-H of py), 7.95 (m, 1 H, *p*-H of py), 8.58 (m, 1 H, *o*-H of py) and 8.83 (m, 1 H, *o*-H of py); ^{13}C-$\{^1H\}$, δ 24.6 (s, Me), 60.2 (s, CH), 122.2 (s, CH of C_6H_4), 125.4 (s, CH of C_6H_4), 125.9 (s, CH of C_6H_4), 126.0, 126.4 (s, *m*-C of py), 132.9 (s, *p*-C of py), 138.7 (s, C of C_6H_4), 139.0 (s, CH of C_6H_4), 150.4, 152.3 (s, *o*-C of py) and 155.4 (s, C of C_6H_4).

$[Pd\{C_6H_4CH(Me)NH_2\}(cod)]ClO_4$ **3b**. To a solution of complex **2** (prepared from 500 mg, 1.19 mmol of **1** in 35 cm^3 of acetone) cod (0.250 cm^3, 2.63 mmol) was added and the resulting colourless solution stirred for 1 h and then filtered through $MgSO_4$. It was reduced in volume to *ca.* 2 cm^3 and diethyl ether added (25 cm^3). The oily product obtained was stirred with diethyl ether (3 × 25 cm^3) to give complex **3b** as a white solid which was collected, washed with diethyl ether, and air dried (251 mg, 0.578 mmol, 48%), m.p. 194–195 °C (decomp.) (Found: C, 44.60; H, 5.20; N, 3.35. Calc. for $C_{16}H_{22}ClNO_4Pd$: C, 44.25; H, 5.10; N, 3.25%). Λ_M = 127 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}) ν(NH) 3230vs and 3290vs. NMR: ^1H, δ 1.61 (d, 3 H, Me, $^3J_{HH}$ = 6.3), 2.68 (br s, 4 H, CH_2 of cod), 2.75 (br s, 4 H, CH_2 of cod), 4.60 (m, 1 H, CH), 4.72 (m, 1 H, NH), 5.42 (m, 1 H, NH), 5.89 (br s, 2 H, CH of cod), 6.28 (br s, 2 H, CH of cod), 6.67 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.8 Hz) and 6.95–7.26 (m, 3 H, C_6H_4); ^{13}C-$\{^1H\}$, δ 24.8 (s, Me), 28.3, 28.4, 29.9, 30.0 (s, CH_2 of cod), 60.5 (s, CH), 110.0, 110.3, 121.6, 121.8 (s, CH of cod), 124.2, 126.8, 127.2, 131.3 (s, CH of C_6H_4) and 149.4 and 156.7 (s, C of C_6H_4).

$[Pd\{C_6H_4CH(Me)NH_2\}(bipy)]ClO_4$ **3c**. To a solution of complex **2** (prepared from 100 mg, 0.238 mmol of **1** in 10 cm^3 of acetone) 2,2′-bipyridine (40 mg, 0.26 mmol) was added. The complex **3c**·H_2O precipitated from the reaction mixture as an off-white solid which was collected, washed with diethyl ether, and air dried (100 mg, 0.199 mmol, 84%), m.p. 186–188 °C (Found: C, 43.10; H, 4.05; N, 8.10. Calc. for $C_{18}H_{20}ClN_3O_5Pd$: C, 43.20; H, 4.05; N, 8.40%). IR (cm^{-1}) ν(NH) 3220s and 3260s.

$[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ **4**. To a solution of complex **2** (prepared from 500 mg, 1.19 mmol of **1** in 35 cm^3 of acetone) NaBr (160 mg, 1.55 mmol) was added and the resulting mixture stirred for 2 h. Acetone was removed and the residue taken up in CH_2Cl_2 (10 cm^3) and filtered through a plug of $MgSO_4$. While removing solvent, complex **4** precipitated as a yellow solid which was collected, washed with CH_2Cl_2, and air dried (252 mg, 0.411 mmol, 69%), m.p. 190 °C (decomp.) (Found: C, 31.75; H, 3.20; N, 4.50. Calc. for $C_{16}H_{20}Br_2N_2Pd_2$: C, 31.35; H, 3.30; N, 4.55%). Λ_M = 3 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}) ν(NH) 3230s and 3290s. NMR: ^1H, δ 1.58 (d, 3 H, Me, $^3J_{HH}$ = 6.3 Hz), 4.39 (m, 2 H, CH and NH), 5.21 (m, 1 H, NH) and 6.71–7.29 (m, 4 H, C_6H_4); ^{13}C-$\{^1H\}$, δ 24.2 (s, Me), 60.9 (s, CH), 122.2, 124.6, 125.6, 135.6 (s, CH of C_6H_4), 146.3 and 156.2 (s, C of C_6H_4).

RR-$[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ *RR*-**4**. This compound was prepared from *RR*-**1** (500 mg, 1.19 mmol), $AgClO_4$ (500 mg, 2.41 mmol) and NaBr (160 mg, 1.55 mmol) in a manner identical with that for the racemate, as a yellow solid (146 mg, 0.238 mmol, 40%), decomposes 187 °C (Found: C, 31.70; H, 3.65; N, 4.35%).

SS-$[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ *SS*-**4**. This compound was prepared from *SS*-**1** (500 mg, 1.19 mmol), as above, as a yellow solid (131 mg, 0.214 mmol, 36%), decomposes 185 °C (Found: C, 31.60; H, 3.55; N, 4.45%).

$[Pd\{C_6H_4CH(Me)NH_2\}Br(PPh_3)]$ **5**. To a suspension of complex **4** (100 mg, 0.163 mmol) in CH_2Cl_2 (20 cm^3) solid PPh_3 (90 mg, 0.34 mmol) was added. The resulting solution was stirred for 1 h and then filtered through a plug of $MgSO_4$. Its volume was reduced to *ca.* 2 cm^3 and diethyl ether (25 cm^3) added to precipitate complex **5** as a white solid which was collected and air dried (150 mg, 0.264 mmol, 81%), m.p. 216–218 °C (Found: C, 55.30; H, 4.50; N, 2.40. Calc. for $C_{26}H_{25}BrNPPd$: C, 54.90; H, 4.45; N, 2.45%). Λ_M = 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}) ν(NH) 3180m and 3260m. NMR: ^1H, δ 1.72 (d, 3 H, Me, $^3J_{HH}$ = 6.6 Hz), 3.52 (m, 1 H, NH), 4.13 (m, 1 H, NH), 4.54 (m, 1 H, CH), 6.35–6.45 (m, 2 H, C_6H_4), 6.82–6.94 (m, 2 H, C_6H_4), 7.32–7.46 (m, 9 H, Ph) and 7.69–7.77 (m, 6 H, Ph); ^{13}C-$\{^1H\}$, δ 25.8 (s, Me), 60.1 (d, CH, J_{PC} = 2.6), 122.2 (s, CH of C_6H_4), 124.2 (s, CH of C_6H_4), 125.5 (d, CH of C_6H_4, J_{PC} = 5.6), 128.1 (d, *o*-CH of PPh_3, J_{PC} = 10.6), 130.7 (d, *p*-CH of PPh_3, J_{PC} = 2.5), 131.5 (d, *ipso*-C of PPh_3, J_{PC} = 49.3), 135.4 (d, *m*-CH of PPh_3, J_{PC} = 11.6), 138.1 (d, CH of C_6H_4, J_{PC} = 10.6), 150.8 (s, C of C_6H_4) and 156.2 (d, C of C_6H_4, J_{PC} = 1.1 Hz); ^{31}P-$\{^1H\}$, δ 41.5 (s).

R-$[Pd\{C_6H_4CH(Me)NH_2\}Br(PPh_3)]$ *R*-**5**. This compound was prepared from *RR*-**4** (100 mg, 0.163 mmol) and PPh_3 (90 mg, 0.34 mmol) as above, as a white solid (148 mg, 0.261 mmol, 80%), m.p. 215 °C (decomp.) (Found: C, 54.45; H, 4.90; N, 2.55%).

S-$[Pd\{C_6H_4CH(Me)NH_2\}Br(PPh_3)]$ *S*-**5**. This compound was prepared from *SS*-**4** (100 mg, 0.163 mmol) as above, as a white solid (144 mg, 0.254 mmol, 78%), m.p. 217 °C (decomp.) (Found: C, 54.20; H, 5.05; N, 2.50%).

$[Pd\{C_6H_4CH(Me)NH_2\}(acac)]$ **6**. To a solution of $[\{Pd\{C_6H_4CH(Me)NH_2\}(\mu\text{-}Br)\}_2]$ (152 mg, 0.248 mmol) in acetone (20 cm^3) solid Tl(acac) (151 mg, 0.497 mmol) was added. The resulting white suspension was stirred for 1 h and then solvent was removed. The residue was taken up in diethyl ether (2 × 30 cm^3) and filtered through a plug of $MgSO_4$. Its volume was reduced to *ca.* 2 cm^3 and hexane (25 cm^3) added to precipitate complex **6** as a white solid which was collected and air dried (118 mg, 0.361 mmol, 73%), m.p. 111–113 °C (Found: C, 47.75; H, 5.60; N, 4.30. Calc. for $C_{13}H_{17}NO_2Pd$: C, 47.95; H, 5.25; N, 4.30%). Λ_M = 2 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}) ν(NH) 3210m and 3250s. NMR: ^1H, δ 1.54 (d, 3 H, Me, $^3J_{HH}$ = 6.6 Hz), 1.92 (s, 3 H, Me), 2.04 (s, 3 H, Me), 3.10 (m, 1 H, NH), 4.00 (m, 1 H, NH), 4.25 (m, 1 H, CH), 6.74 (m, 1 H, C_6H_4), 7.00 (m, 2 H, C_6H_4) and 7.32 (m, 1 H, C_6H_4); ^{13}C-$\{^1H\}$, δ 24.8 (s, Me), 27.8, 27.9 (s, *Me*CO), 59.4 (s, CH), 100.3 (s, *C*HCO), 121.1, 124.6, 125.3, 140.0 (s, CH of C_6H_4), 144.4, 154.4 (s, C of C_6H_4) and 187.2 and 187.3 (s, CO).

Structure Determinations.—Compound **3b**. A colourless prism was mounted on a glass fibre with inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). Data were collected with Mo-Kα radiation (λ 0.710 73 Å) to $2\theta_{max}$ 50°. Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–23°. An attempted absorption correction based on ψ scans did not improve the merging R value. The structure was solved by the heavy-atom method and refined on F^2 (program SHELXL 92[17]). The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants adjusted by the program. Hydrogen atoms were included using a riding model.

Compound R-**5**. A pale yellow prism was mounted as above on a Stoe STADI-4 diffractometer equipped with a Siemens

LT-2 low-temperature attachment. Data, including a full set of Friedel opposites, were collected to $2\theta_{max}$ 55°. Cell constants were refined from $\pm\omega$ angles of 68 reflections in the 2θ range 20–23°. An absorption correction based on ψ scans gave transmission factors 0.67–0.89. The structure was solved and refined as for complex **3b**. Additionally the absolute configuration was confirmed by an x refinement, with $x = -0.009(9)$. An extinction correction of the form $F_{corr} = F/[1 + 0.001xF^2\lambda^3/\sin(2\theta)]^{\frac{1}{4}}$ was applied: the refined value of x was 0.0061(5).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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