The First Orthopalladation of a Primary Nitrobenzylamine. Synthesis of Chiral Cyclopalladated Complexes derived from (*S*)-α-Methyl-4-nitrobenzylamine†

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

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

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

By refluxing a mixture of (*S*)-α-methyl-4-nitrobenzylamine and $Pd(O_2CMe)_2$ (1:1) in acetone, complexes (*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-X)}$_2$] (X = $MeCO_2$ **1a** or Cl **1b**) are obtained. Complex **1b** can also be obtained by treating (*S*)-α-methyl-4-nitrobenzylamine hydrochloride with $Pd(O_2CMe)_2$ (1:1) in acetone. These complexes are the first orthometallated complexes containing a primary amine with an electron-withdrawing group in the benzene ring. Complex **1a** reacted with an excess of NaBr or NaI to give (*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-X)}$_2$] (X = Br **1c** or I **1d**). Triphenylphosphine reacted with **1b** or **1c** to give (*S*)-[Pd{C_6H_3[CH(Me)NH_2]-2-NO_2-5}X(PPh_3)] (X = Cl **2a** or Br **2b**). The reaction of complex **1b** with $AgClO_4$ (1:1) and an excess of pyridine (py) gave (*S*)-[Pd{C_6H_3[CH(Me)NH_2]-2-NO_2-5}(py)$_2$]ClO_4 **3**. Complex **1c** reacted with 3 equivalents of RC≡CR (R = CO_2Me) to give a tri-insertion reaction product, the crystal structure of which has been determined: space group $P2_12_12_1$, a = 11.0969(14), b = 17.197(2), c = 19.604(3) Å, $R(F)$ = 0.041. The planar co-ordination at palladium is not significantly disturbed by a short contact of 2.600 Å to the C atom of a CO_2Me group. A cationic derivative of this complex has also been prepared.

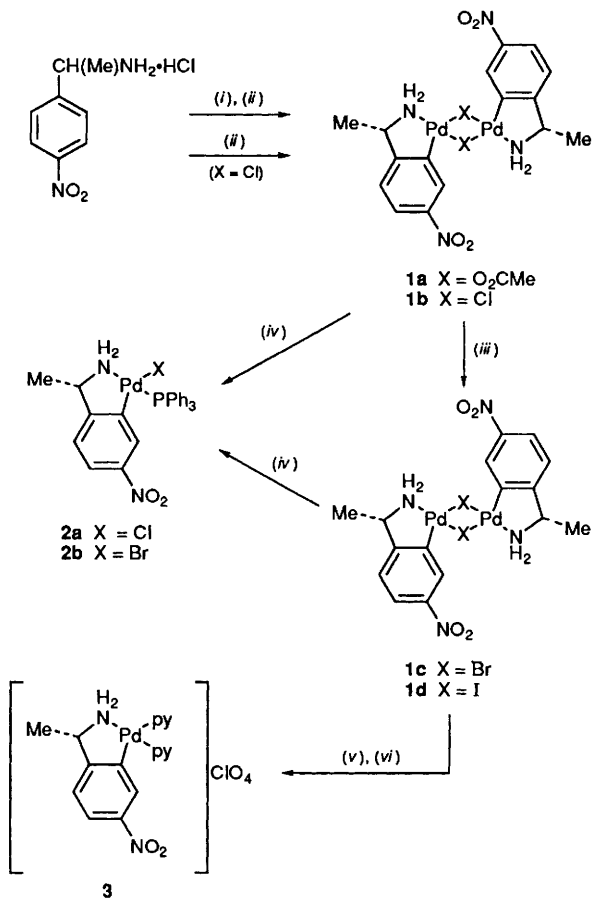
Ryabov[2] points out in his recent review on cyclometallation reactions that 'there is a fundamental rule in the chemistry of orthopalladated compounds: direct activation of C–H bonds by palladium(II) to afford corresponding palladacycles is the most feasible in the case of tertiary amines, whereas primary and secondary amines are usually inert toward such activation'. This behaviour, first established by Cope and Friedrich[3] and now generally accepted,[4] has been explained in terms of the stronger nitrogen co-ordination of primary and secondary compared with tertiary amines, thus preventing electrophilic attack of palladium(II) on the aromatic ring.[4] Ryabov[2] proposes, based on kinetic data, that cyclopalladation requires dissociation of the amine from the initially formed adduct with two co-ordinated amines to form a three-co-ordinate reactive intermediate. Therefore, the less basic tertiary amines are more easily orthometallated. The same mechanism can explain the orthopalladation of benzylamine when treating [PdI_2(NH_2-CH_2Ph)$_2$] with $AgBF_4$ and KI:[5] silver(I) abstracts iodide and the required three-co-ordinate reactive intermediate is thus formed. We have used a similar method to orthometallate α-methylbenzylamine.[1] Steric effects have been invoked to explain the orthometallation of α,α-diphenylbenzylamine.[6] However, orthopalladation of benzylamine has been achieved by reaction of the amine with palladium acetylacetonate[7] or acetate.[8] We are interested in the synthesis of orthopalladated primary amines, not only from a synthetic point of view, but also because we plan to study the reactivity of these complexes with acetylenes and other unsaturated species. Tertiary benzylamines undergo insertion reactions with, for example, carbon monoxide, electron-deficient alkenes, alkynes and acyl halides and for this reason they have attracted interest in organic synthesis.[9] As far as we are aware, cyclopalladated primary amines have not yet been studied. Karpeiskaya *et al.*[10] have postulated the formation of catalytically active complexes containing orthometallated α-methylbenzylamine when the reductive aminolysis of Δ^2-oxazolin-5-ones is carried out with (*S*)-α-methylbenzylamine and H_2 in the presence of $PdCl_2$. However, these complexes, described as a mixture of polynuclear zerovalent palladium(0) complexes, were very poorly defined.

Another well established rule in orthopalladation reactions is that, because of the electrophilic character of palladium(II), C–H activation is favoured by the presence in the aryl ring of electron-releasing substituents, whereas electron-withdrawing substituents deactivate the aryl ring. Thus, reactions of unsymmetrically substituted azobenzenes with $PdCl_2$ lead to complexes cyclopalladated at the benzene ring bearing the electron-releasing group.[11] In addition, *N*,*N*-dimethyl-4-X-benzylamine undergoes orthopalladation when X = MeO but not when X = NO_2.[3] As far as we are aware, the only reported orthopalladation of an aryl derivative containing an electron-withdrawing substituent, such as nitro, is that of a tertiary amine, but the metallation occurs in acetic acid, in which the mechanism is different from that in usual solvents.[12] Orthopalladated nitroaryl ligands have been prepared by other routes, *e.g.*, those involving the reaction of *o*-bromobenzylamines with bis(dibenzylideneacetone)palladium(0)[13] or ligand-exchange reactions,[12,14] but none of these complexes involves a primary amine such as we describe in this paper.

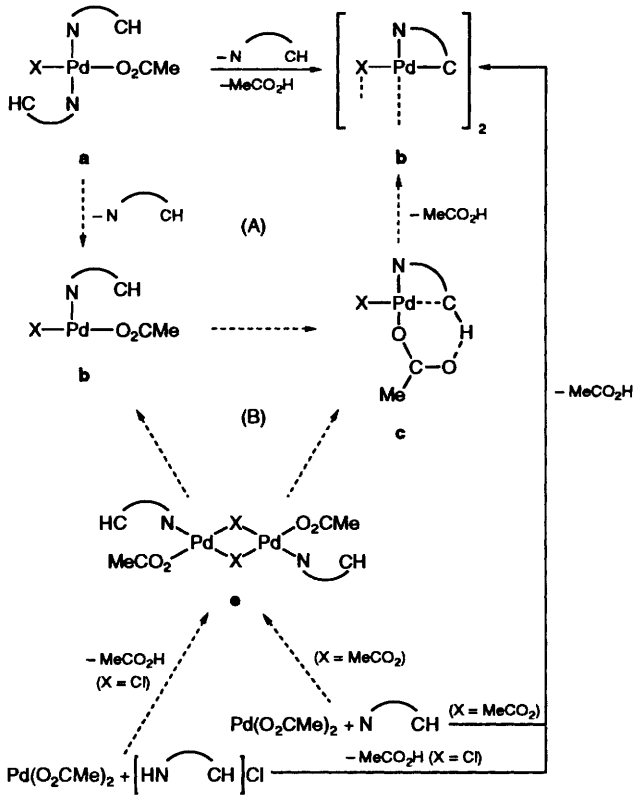
Chiral cyclopalladated complexes have been widely used in the resolution of racemic amines, phosphines and arsines.[15] In this paper, we describe the synthesis of orthometallated complexes from the chiral α-methyl-4-nitrobenzylamine.

† Orthometallated Primary Amines. Part 3.[1]

Supplementary data available: Full details of the crystal structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, 76344 Eggenstein-Leopoldshafen, Germany, and can be obtained on quoting a full literature citation and the reference number CDS 401665.



Scheme 1 (*i*) NaOH; (*ii*) $Pd(O_2CMe)_2$; (*iii*) +NaX, $-NaO_2CMe$; (*iv*) $+PPh_3$; (*v*) + $AgClO_4$, −AgCl; (*vi*) +pyridine (py)



Scheme 2 N CH = (*S*)-α-Methyl-4-nitrobenzylamine

Results and Discussion

Following our method of orthometallation, which modifies that of Avshu *et al.*,[5] we were not able to obtain the orthometallation product of (*S*)-α-methyl-4-nitrobenzylamine.[1] Thus, 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 ^1H NMR spectroscopy.

We then tried the reaction of $Pd(O_2CMe)_2$ and the free amine, obtained *in situ* by treating the amine hydrochloride with aqueous NaOH. After refluxing the 1:1 mixture in acetone for 4 h, the orange (*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5}](μ-O_2CMe)$\}_2$] **1a** precipitated (see Scheme 1). From the mother-liquor a yellow solid could be isolated and characterized as (*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-Cl)$\}_2$] **1b**. Complex **1b** can also be prepared directly by refluxing the amine hydrochloride with $Pd(O_2CMe)_2$. These compounds are the first orthometallated complexes containing a primary amine with an electron-withdrawing group in the benzene ring. As mentioned above and according to Ryabov's mechanism,[2] the orthometallation of primary amines when using a 2:1 molar ratio of amine to palladium is rendered difficult because the dissociative process **a** ⟶ **b** (see Scheme 2, pathway A) is very unfavourable. The presence of a nitro group on the aryl ring makes the metallation even more difficult.

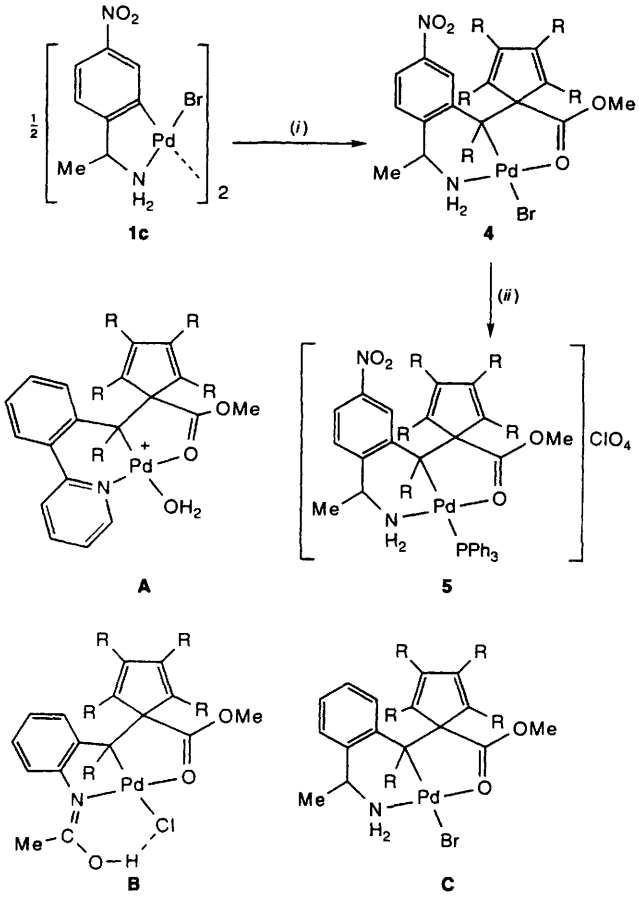
We believe that our success was simply due to the use of a 1:1 molar ratio. In fact the reaction using 2 mol amine per mol of palladium acetate does not lead to orthometallation. We assume that a dimeric acetato- or chloro-bridged intermediate **e** (see pathway B in Scheme 2) is formed, such as have been found in other orthopalladation reactions.[4c] When the hydrochloride is treated with $Pd(O_2CMe)_2$ the dimeric chloride-bridged intermediate could be formed. The bridge splitting of this complex could give the three-co-ordinate intermediate **b** or, directly, the intermediate **c**. Here the 4-nitrophenyl group is probably palladated, because the acetate ligand, acting as a base, assists the C–H bond breaking. Therefore, the success of the orthometallation reaction seems to be independent of the basic character of the amine.

Complex **1a** reacts with an excess of NaBr or NaI to give (*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-X)$\}_2$] (X = Br **1c**, or I **1d**. Triphenylphosphine can split the halide bridge in **1b** or **1c** to give (*S*)-[Pd{C_6H_3[CH(Me)NH_2]-2-NO_2-5}-X(PPh_3)] (X = Cl **2a** or Br **2b**. The reaction of complex **1b** with $AgClO_4$ (1:1) and an excess of pyridine gave (*S*)-[Pd{C_6H_3[CH(Me)NH_2]-2-NO_2-5}$(py)_2$]ClO_4 **3**.

It has been shown by IR[16] and X-ray diffraction studies[17] that bridged dimers similar to **1a–1d** have the *trans* geometry assumed for these complexes in Scheme 1. Similarly, we have described the crystal structure of (*R*)-[Pd{C_6H_3[CH(Me)-NH_2]-2}Br(PPh_3)][1] which shows the same geometry as assumed for **2a** and **2b**. This is also the expected geometry according to the antisymbiotic effect.[18]

Cyclopalladated complexes usually react with alkynes to give complexes containing one or two molecules of alkyne inserted into the Pd–C bond.[9] Tri-insertion products have been isolated (see **A**, **B**[19] and **C**[1b] in Scheme 3) only in a few cases. Complex **1c** reacts with 3 equivalents of RC≡CR (R = CO_2Me) to give the tri-insertion reaction product **4** (see Scheme 3).

The crystal structure of complex **4** (see Fig. 1) has been determined by X-ray diffraction, and shows similar features to analogous compounds **A** and **B**.[19] An additional feature in **4** is a weak interaction between Pd and C(201); the distance is 2.600(6) Å and the angle C(201)–C(20)–Pd is 92.6°. The interaction is not strong enough to disturb the planar co-ordination at palladium; the mean deviation from the best plane through Pd, Br, N(1), O(211) and C(20) is only 0.01 Å, and C(201) lies 1.5 Å out of the plane. The co-ordination of O(211) to palladium promotes a slight lengthening of the C–O(211) bond



Scheme 3 R = CO_2Me. (*i*) +3 RC≡CR; (*ii*) +$AgClO_4$, −AgBr, +PPh_3

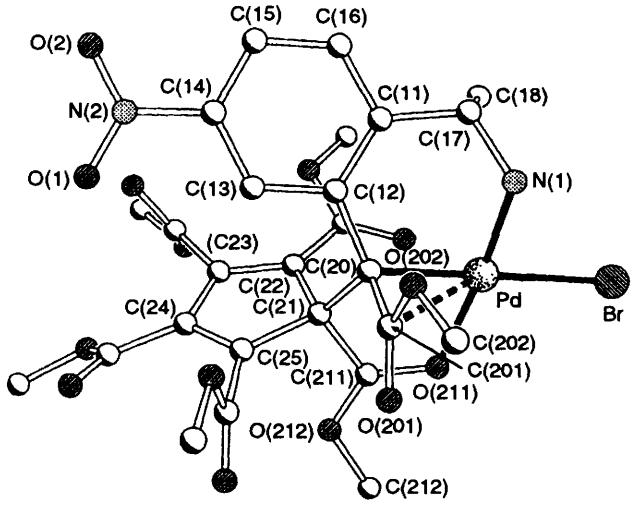


Fig. 1 Structure of complex **4** in the crystal. Radii are arbitrary; H atoms omitted

[1.235(7) Å, mean value for the other C–O bond distances, 1.198 Å]. The neutral complexes **4** and **B** show similar Pd–O bond distances [2.091(4) and 2.096(2) Å, respectively] but **4** shows a shorter Pd–N bond distance [1.996(5) Å] than **B** [2.031(2) Å] because primary amines are better donor ligands. The Pd–O bond distance in **A** [2.063(1) Å] is shorter than that in **4** or **B** probably because of its cationic nature. Table 1 gives atomic coordinates, and Table 2 selected bond lengths and angles for **4**.

When complex **4** reacted with $AgClO_4$ and PPh_3, AgBr precipitated and the corresponding cationic product **5** could be isolated (see Scheme 3).

All complexes show two or three bands corresponding to ν(NH) in the range 3100-3300 cm^{-1}. They are non-conducting in acetone solutions except for the cationic complexes **3** and **5**, the molar conductivities of which (106 and 109 Ω^{-1} cm^2 mol^{-1}) are typical of 1 : 1 electrolytes.[20] The diastereotopic NH protons in complexes **2** are *ca.* 1 ppm more shielded than those in the dimeric complexes **1**, probably because the *trans* ligand PPh_3 releases more electron density than do the *trans* halide ligands in **1**. The deshielding of NH protons in complex **3** by more than 1 ppm with respect to **2** is attributable to the cationic nature of **3**.

Experimental

Infrared spectra were recorded on Perkin-Elmer 1430 and 16F-PC-FT spectrometers. The C, H and N analyses, conductance measurements in acetone and melting-point determinations were carried out as described elsewhere.[1] Unless otherwise stated, NMR spectra were recorded in $(CD_3)_2CO$ on a Varian Unity 300 spectrometer. Chemical shifts are referenced to $SiMe_4$ (^1H and ^{13}C-{^1H}) or H_3PO_4 (^{31}P-{^1H}).

(*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-O_2CMe)}$_2$] **1a**.—(*S*)-α-Methyl-4-nitrobenzylamine hydrochloride (808 mg, 4.00 mmol) was treated with aqueous NaOH (8 cm^3 of 0.5 mol dm^{-3} solution, 4 mmol) in acetone (20 cm^3) and left to stand for 10 min. Palladium(II) acetate (900 mg, 4 mmol) was added and the resulting mixture refluxed for 6 h. After cooling, complex **1a** precipitated as an orange powder which was collected, washed with acetone, and air dried (493.7 mg, 0.747 mmol, 37%), decomp. 267 °C (Found: C, 36.50; H, 3.80; N, 8.25. Calc for $C_{20}H_{24}N_4O_8Pd_2$: C, 36.35; H, 3.65; N, 8.45%). IR (cm^{-1}) ν(NH) 3110s, 3200s and 3300s.

From the mother-liquors, removal of solvent and addition of CH_2Cl_2 (20 cm^3) allowed the isolation of complex **1b** as a yellow solid which was collected, washed with CH_2Cl_2, and air dried (201 mg, 0.327 mmol, 16%).

(*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-Cl)}$_2$] **1b**.—(*S*)-α-Methyl-4-nitrobenzylamine hydrochloride (808 mg, 4.00 mmol) was treated with $Pd(O_2CMe)_2$ (900 mg, 4 mmol) in acetone (20 cm^3) and the resulting mixture refluxed for 4 h. Solvent was removed and CH_2Cl_2 added to obtain complex **1b** as a yellow powder which was collected, washed with CH_2Cl_2, and air dried (697.4 mg, 1.14 mmol, 57%), decomp. 240 °C (Found: C, 31.40; H, 2.95; N, 8.65. Calc. for $C_{16}H_{18}Cl_2N_4O_4Pd_2$: C, 31.30; H, 2.95; N, 9.10%). IR (cm^{-1}) ν(NH) 3210s and 3300s. ^1H NMR: δ 1.65 (d, 3 H, Me, $^3J_{HH}$ = 6.6), 4.52 (m, 1 H, CH), 4.84 (m, 1 H, NH), 5.58 (m, 1 H, NH), 7.08 (d, 1 H, H^3, $^3J_{HH}$ = 8.1), 7.83 (dd, 1 H, H^4, $^4J_{HH}$ = 2.1 Hz) and 7.92 (d, 1 H, H^6); ^{13}C-{^1H}, δ 23.8 (s, Me), 60.8 (d, CH), 120.3 (s, CH, C_6H_3), 122.9 (s, CH, C_6H_3), 127.7 (s, CH, C_6H_3), 144.6 (s, C, C_6H_3), 145.3 (s, C, C_6H_3) and 164.5 (d, C, C_6H_3).

(*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-Br)}$_2$] **1c**.—To a suspension of complex **1a** (103 mg, 0.155 mmol) in acetone (20 cm^3) was added solid NaBr (178 mg, 1.73 mmol). After 18 h a yellow solution was formed, which was filtered through a plug of $MgSO_4$. Solvent was removed and the residue was collected, washed with water (3 × 30 cm^3) and diethyl ether (3 × 30 cm^3) and air dried to afford complex **1c** as a yellow solid (87.3 mg, 0.124 mmol, 80%), decomp. 230 °C (Found: C, 27.50; H, 2.50; N, 7.55. Calc. for $C_{16}H_{18}Br_2N_4O_4Pd_2$: C, 27.35; H, 2.60; N, 7.95%). IR (cm^{-1}) ν(NH) 3220s and 3282s. ^1H NMR: δ 1.65 (d, 3 H, Me, $^3J_{HH}$ = 6.9), 4.57 (m, 1 H, CH), 4.65 (m, 1 H, NH), 5.45 (m, 1 H, NH), 6.98 (d, 1 H, H^3, $^3J_{HH}$ = 8.1), 7.72 (dd, 1 H, H^4, $^4J_{HH}$ = 2.4 Hz) and 8.73 (d, 1 H, H^6).

(*S*,*S*)-[{Pd[C_6H_3{CH(Me)NH_2}-2-NO_2-5](μ-I)}$_2$] **1d**.—To a suspension of **1a** (467 mg, 0.706 mmol) in acetone (30 cm^3) was added solid NaI (1051 mg, 7.06 mmol). After 4 h a yellow

Table 1 Atomic coordinates (× 10^4) for compound **4**

Atom	x	y	z	Atom	x	y	z
Pd	8 133.4(4)	7 644.5(3)	4 471.0(2)	C(221)	10 120(5)	9 214(4)	4 467(3)
Br	8 550.3(6)	6 613.3(4)	5 338.4(3)	C(222)	10 880(8)	9 949(5)	5 390(4)
C(11)	6 682(5)	9 339(4)	4 642(3)	O(221)	10 290(4)	8 623(3)	4 782(2)
C(12)	7 115(5)	9 209(4)	3 975(3)	O(222)	10 294(4)	9 918(3)	4 718(2)
C(13)	7 015(5)	9 811(4)	3 501(3)	C(23)	10 095(6)	9 799(4)	3 300(3)
C(14)	6 564(6)	10 526(4)	3 685(3)	C(231)	10 689(7)	10 558(5)	3 439(3)
C(15)	6 152(7)	10 681(4)	4 332(3)	C(232)	12 458(8)	11 238(5)	3 700(5)
C(16)	6 193(7)	10 076(4)	4 797(3)	O(231)	10 119(5)	11 149(3)	3 407(3)
C(17)	6 670(5)	8 769(4)	5 217(3)	O(232)	11 863(4)	10 502(3)	3 589(2)
C(18)	7 712(6)	8 898(4)	5 710(3)	C(24)	9 636(6)	9 604(4)	2 624(3)
N(1)	6 642(4)	7 957(3)	4 970(2)	C(241)	9 960(6)	10 007(4)	1 975(3)
N(2)	6 517(6)	11 137(4)	3 171(3)	C(242)	11 531(7)	10 683(4)	1 425(3)
O(1)	6 896(5)	11 004(3)	2 600(3)	O(241)	9 366(5)	9 988(3)	1 468(2)
O(2)	6 126(7)	11 769(3)	3 345(3)	O(242)	11 021(4)	10 354(3)	2 038(2)
C(20)	7 764(5)	8 470(4)	3 743(3)	C(25)	8 953(5)	8 959(4)	2 657(3)
C(201)	7 047(6)	7 906(4)	3 319(3)	C(251)	8 346(6)	8 603(4)	2 051(3)
C(202)	5 139(6)	7 318(5)	3 167(4)	C(252)	6 555(7)	8 525(6)	1 445(4)
O(201)	7 475(4)	7 476(3)	2 902(2)	O(251)	8 824(4)	8 170(3)	1 659(2)
O(202)	5 853(4)	7 939(3)	3 469(2)	O(252)	7 213(4)	8 836(3)	2 021(2)
C(21)	8 990(5)	8 629(4)	3 384(3)	C(98)	8 748(11)	5 683(6)	7 201(6)
C(211)	9 726(5)	7 880(4)	3 386(3)	Cl(1)	8 081(4)	6 293(2)	7 797(3)
C(212)	11 218(6)	7 133(4)	2 822(4)	Cl(2)	9 330(2)	4 859(2)	7 582.1(14)
O(211)	9 614(3)	7 396(3)	3 848(2)	C(99)	4 103(11)	2 494(6)	5 666(5)
O(212)	10 472(4)	7 828(3)	2 880(2)	Cl(3)	3 525(5)	1 543(4)	5 566(2)
C(22)	9 752(5)	9 250(4)	3 750(3)	Cl(4)	5 024(4)	2 737(2)	4 951(2)

Table 2 Selected bond lengths (Å) and angles (°) for complex **4**

Pd–N(1)	1.996(5)	Pd–C(20)	2.054(6)
Pd–O(211)	2.091(4)	Pd–Br	2.5001(8)
Pd–C(201)	2.600(6)	C(12)–C(20)	1.530(9)
C(14)–N(2)	1.457(9)	C(17)–N(1)	1.478(8)
C(17)–C(18)	1.525(9)	C(11)–C(17)	1.493(9)
N(2)–O(2)	1.218(8)	N(2)–O(1)	1.219(7)
C(20)–C(21)	1.556(8)	C(21)–C(25)	1.535(8)
C(21)–C(22)	1.540(9)	C(22)–C(23)	1.346(9)
C(23)–C(24)	1.460(9)	C(24)–C(25)	1.345(9)
N(1)–Pd–C(20)	89.4(2)	C(20)–Pd–O(211)	83.8(2)
N(1)–Pd–Br	90.6(2)	O(211)–Pd–Br	96.17(12)
C(201)–C(20)–C(21)	109.0(5)	C(12)–C(20)–C(21)	113.6(5)
C(201)–C(20)–Pd	92.6(4)	C(12)–C(20)–Pd	117.5(4)
C(201)–C(20)–C(12)	116.8(5)	C(21)–C(20)–Pd	105.1(4)
C(17)–N(1)–Pd	113.4(4)	O(2)–N(2)–O(1)	123.2(6)
O(2)–N(2)–C(14)	117.6(6)	O(1)–N(2)–C(14)	119.1(6)
C(211)–C(21)–C(25)	109.3(5)	C(211)–C(21)–C(22)	106.9(5)
C(25)–C(21)–C(22)	100.9(5)	C(211)–C(21)–C(20)	108.6(5)
C(25)–C(21)–C(20)	117.5(5)	C(22)–C(21)–C(20)	113.1(5)
C(23)–C(22)–C(21)	109.7(5)	C(22)–C(23)–C(24)	109.6(6)
C(25)–C(24)–C(23)	109.9(6)	C(24)–C(25)–C(21)	109.6(5)

solution was formed, which was filtered through a plug of $MgSO_4$. Solvent was removed and the residue was collected, washed with water (3 × 30 cm^3) and diethyl ether (3 × 30 cm^3) and air dried to afford complex **1d** as a yellow solid (510 mg, 0.640 mmol, 91%), decomp. 209 °C (Found: C, 24.30; H, 2.20; N, 6.90. Calc. for $C_{16}H_{18}I_2N_4O_4Pd_2$: C, 24.10; H, 2.30; N, 7.05%). IR (cm^{-1}) ν(NH) 3240s and 3286s. ^1H NMR: δ 1.68 (d, 3 H, Me, $^3J_{HH}$ = 6.6), 4.66 (m, 1 H, CH), 4.90 (m, 1 H, NH), 5.63 (m, 1 H, NH), 7.18 (d, 1 H, H^3, $^3J_{HH}$ = 8.4), 7.83 (dd, 1 H, H^4, $^4J_{HH}$ = 2.4 Hz) and 8.47 (d, 1 H, H^6).

(*S*)-[Pd{C_6H_3[CH(Me)NH_2]-2-NO_2-5}Cl(PPh_3)] **2a**.—To a suspension of complex **1b** (100 mg, 0.163 mmol) in CH_2Cl_2 (10 cm^3) was added solid PPh_3 (85.4 mg, 0.326 mmol). The resulting solution was stirred for 1 h and then filtered through a plug of $MgSO_4$. Solvent was removed to *ca.* 2 cm^3 and diethyl ether (25 cm^3) was added to precipitate complex **2a** as a pale yellow solid which was collected and air dried (131 mg, 0.229 mmol, 70%), m.p. 236 °C (decomp.) Found: C, 54.80; H, 4.30; N, 4.85. Calc. for $C_{26}H_{24}ClN_2O_2PPd$: C, 54.85; H, 4.25; N, 4.90%. IR (cm^{-1}) ν(NH) 3110m, 3175s and 3314s. NMR ($CDCl_3$): ^1H, δ 1.61 (d, 3 H, Me, $^3J_{HH}$ = 6.6), 3.60 (m, 1 H, NH), 4.44 (m, 1 H, NH), 4.78 (m, 1 H, CH), 6.89 (m, 1 H, H^3), 7.21 (m, 1 H, H^4), 7.23–7.44 (m, 10 H) and 7.62–7.70 (m, 6 H, Ph); ^{13}C-{^1H}, δ 25.2 (s, Me), 58.9 (d, CH, $^3J_{PC}$ = 2.6), 119.3 (s, CH, C_6H_3), 122.1 (s, CH, C_6H_3), 128.3 (d, *o*-CH, PPh_3, $^2J_{PC}$ = 11.1), 129.9 (d, *ipso*-C, PPh_3, $^1J_{PC}$ = 50.4), 131.0 (d, *p*-CH, PPh_3, $^4J_{PC}$ = 2.0), 131.9 (d, CH, C_6H_3, J_{PC} = 11.5), 135.0 (d, *m*-CH, PPh_3, $^3J_{PC}$ = 12.4), 144.7 (d, C, C_6H_3, J_{PC} = 5.5), 149.8 (d, C, C_6H_3, J_{PC} = 1.5) and 164.6 (d, C, C_6H_3, J_{PC} = 1.5 Hz); ^{31}P-{^1H}, δ 43.3 (s).

(*S*)-[Pd{C_6H_3[CH(Me)NH_2]-2-NO_2-5}Br(PPh_3)] **2b**.—To a suspension of complex **1c** (100 mg, 0.142 mmol) in CH_2Cl_2 (20 cm^3) was added solid PPh_3 (75 mg, 0.29 mmol). The resulting solution was stirred for 1 h and then filtered through a plug of $MgSO_4$. Solvent was removed until *ca.* 2 cm^3 remained and diethyl ether (25 cm^3) was added to precipitate complex **2b** as a pale yellow solid which was collected and air dried (142 mg, 0.232 mmol, 80%), m.p. 230–232 °C (decomp.) (Found: C, 50.80; H, 3.90; N, 4.50. Calc. for $C_{26}H_{24}BrN_2O_2PPd$: C, 50.90; H, 3.95; N, 4.55%). IR (cm^{-1}) ν(NH) 3250s and 3310s. NMR ($CDCl_3$): ^1H, δ 1.72 (d, 3 H, Me, $^3J_{HH}$ = 6.6), 3.58 (m, 1 H, NH), 4.40 (m, 1 H, NH), 4.57 (m, 1 H, CH), 7.00 (m, 1 H, H^3), 6.20–7.23 (m, 1 H, H^4), 7.26 (m, 1 H, H^6), 7.39–7.46 (m, 9 H, Ph) and 7.67–7.74 (m, 6 H); ^{13}C-{^1H}, δ 25.5 (s, Me), 60.0 (d, CH, $^3J_{PC}$ = 2.8), 119.5 (s, CH, C_6H_3), 122.0 (s, CH, C_6H_3), 128.4 (d, *o*-CH, PPh_3, J_{PC} = 11.1), 130.4 (d, *ipso*-CH, PPh_3, J_{PC} = 50.8), 131.1 (d, *p*-CH, PPh_3, J_{PC} = 2.5), 131.7 (s, CH, C_6H_3), 135.2 (d, *m*-CH, PPh_3, J_{PC} = 11.6), 144.9 (d, C, C_6H_3, J_{PC} = 5.6), 152.1 (s, C, C_6H_3) and 163.4 (d, C, C_6H_3, J_{PC} = 1.3 Hz); ^{31}P-{^1H}, δ 40.1 (s).

(*S*)-[Pd{C_6H_3[CH(Me)NH_2]-2-NO_2-5}$(py)_2$]ClO_4 **3**.—To a solution of complex **1b** (200 mg, 0.326 mmol) in acetone (20 cm^3) was added solid $AgClO_4$ (135 mg, 0.651 mmol). The resulting precipitate of silver chloride was filtered off. Pyridine (0.250 cm^3, 3.22 mmol) was added to the filtrate and the resulting colourless solution stirred for 1 h and then filtered again through a plug of $MgSO_4$. Solvent was removed to *ca.* 2 cm^3 and diethyl ether (25 cm^3) was added. The oily product thus

obtained was stirred and washed with diethyl ether (3 × 25 cm^3) to yield complex **3** as an off-white solid which was collected, washed with diethyl ether, and air dried (278.6 mg, 0.526 mmol, 81%), m.p. 132–134 °C (Found: C, 40.60; H, 3.50; N, 10.30. Calc. for $C_{18}H_{19}ClN_4O_6Pd$: C, 40.85; H, 3.60; N, 10.60%) Λ_M = 106 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}) ν(NH) 3240s and 3280s. NMR: ^1H, δ 1.71 (d, 3 H, Me, $^3J_{HH}$ = 6.6), 4.66 (m, 1 H, CH), 4.99 (m, 1 H, NH), 5.67 (m, 1 H, NH), 6.84 (d, 1 H, C_6H_3, J = 2.4), 7.22 (dd, 1 H, C_6H_3, J = 8.4, 0.9), 7.59 (m, 2 H, *m*-H of py), 7.73 (m, 2 H, *m*-H of py), 7.86 (dd, 1 H, C_6H_3, J = 8.4, 2.4), 8.01 (m, 1 H, *p*-H of py), 8.18 (m, 1 H, *p*-H of py), 8.83 (m, 2 H, *o*-H of py) and 9.12 (m, 2 H, *o*-H of py); ^{13}C-{^1H}, δ 24.0 (s, Me), 60.6 (s, CH), 120.6 (s, CH, C_6H_3), 123.0 (s, CH, C_6H_3), 126.6 (s, CH, C_6H_3), 127.5, 127.6 (s, *m*-C of py), 139.9 (s, C, C_6H_3), 140.5 (s, *p*-C of py), 145.9 (s, C, C_6H_3), 151.4, 153.2 (s, *o*-C of py) and 164.9 (s, C, C_6H_3).

[Pd{C(CO_2Me)[C(CO_2Me)C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C(CO_2Me)]C_6H_3[CH(Me)NH_2]-2-NO_2-5}Br] **4**.—To a suspension of complex **1c** (100 mg, 0.142 mmol) in $CHCl_3$ (20 cm^3) was added $MeO_2CC{\equiv}CCO_2Me$ (0.4 cm^3, 3.26 mmol) and the resulting suspension was refluxed for 3 h. A yellow solution was formed, which was filtered through a plug of $MgSO_4$. Solvent was removed to *ca.* 2 cm^3 and diethyl ether added (25 cm^3) to complete the precipitation of complex **4** as a yellow solid, which was collected, washed with diethyl ether (2 × 25 cm^3), and air dried (208.1 mg, 0.267 mmol, 94%), m.p. 170–172 °C (decomp.) (Found: C, 39.90; H, 3.75; N, 3.60. Calc. for $C_{26}H_{27}BrN_2O_{14}Pd$: C, 40.15; H, 3.50; N, 3.60%). Λ_M = 5 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}) ν(NH) 3289vw and 3235vw. NMR ($CDCl_3$): ^1H, δ 1.86 (d, 3 H, CH_3, $^3J_{HH}$ = 6.6), 3.41 (m, 1 H, NH or CH), 3.71, 3.77, 3.82, 3.89, 3.93, 3.98 (s, 19 H, 6 OMe; one NH or CH resonance obscured by the OMe groups), 4.54 (m, 1 H, NH or CH), 7.31 (d, 1 H, C_6H_3, H^3, $^3J_{HH}$ = 8.7), 8.03 (dd, 1 H, C_6H_3, H^4, $^4J_{HH}$ = 2.1 Hz) and 8.34 (d, 1 H, C_6H_3, H^6).

[Pd{C(CO_2Me)[C(CO_2Me)C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C(CO_2Me)]C_6H_3[CH(Me)NH_2]-2-NO_2-5}(PPh_3)]-ClO_4 **5**.—To a suspension of complex **4** (150 mg, 0.193 mmol) in acetone (15 cm^3) was added solid $AgClO_4$ (40 mg, 0.193 mmol). The resulting suspension was stirred for 15 min then filtered through a plug of $MgSO_4$. Solid PPh_3 (52 mg, 0.198 mmol) was added to the resulting solution, which was stirred for 2 h and then filtered again through a plug of $MgSO_4$. Solvent was removed to *ca.* 2 cm^3 and diethyl ether (25 cm^3) added to precipitate complex **5** as a yellow solid, which was collected, washed with diethyl ether (2 × 25 cm^3) and air dried (163 mg, 0.154 mmol, 80%), m.p. 155 °C (decomp.) (Found: C, 50.00; H, 4.00; N, 2.30. Calc. for $C_{44}H_{42}ClN_2O_{18}PPd$: C, 49.85; H, 4.00; N, 2.65%). Λ_M = 109 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}) ν(NH) 3279vw and 3225vw. NMR ($CDCl_3$): ^1H, δ 1.65 (d, 3 H, CH_3, $^3J_{HH}$ = 6.9), 3.52 (m, 1 H, NH or CH), 3.62, 3.65, 3.72, 3.84, 3.90, 3.94 (s, 19 H, 6 OMe; one NH or CH resonance obscured by the OMe groups), 4.64 (m, 1 H, NH or CH), 7.20 (d, 1 H, C_6H_3, H^3, $^3J_{HH}$ = 8.7), 7.93 (dd, 1 H, C_6H_3, H^4, $^4J_{HH}$ = 2.4 Hz), 7.54–7.77 (m, 15 H, PPh_3) and 8.22 (d, 1 H, C_6H_3, H^6). ^{31}P-{^1H}, δ 22.9 (s).

Crystal Structure Determination of Complex **4**·$2CH_2Cl_2$.—*Crystal data.* $C_{28}H_{31}BrCl_4N_2O_{14}Pd$, M_r = 947.66, orthorhombic, space group $P2_12_12_1$, a = 11.0969(14), b = 17.197(2), c = 19.604(3) Å, U = 3741.0(9) $Å^3$, Z = 4, D_c = 1.683 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 1.9 mm^{-1}, F(000) = 1896, T = 173 K.

Data collection and reduction. A yellow prism 0.8 × 0.25 × 0.25 mm was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Siemens *P*4 with LT2 low-temperature attachment). A total of 6013 intensity data were collected to 2θ 50°. An absorption correction based on ψ scans was applied, with transmissions 0.70–0.92. Merging equivalents gave 5665 unique data (R_{int} = 0.031), which were used for all calculations.

Structure solution and refinement. The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL 93).[21] Hydrogen atoms were included using a riding model or as rigid methyl groups. The final $wR(F^2)$ was 0.099, with conventional $R(F)$ 0.041, for 458 parameters and 364 restraints (to light atom U values). The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. S = 0.98; maximum Δ/σ = 0.001; maximum $\Delta\rho$ = 1.8 e $Å^{-3}$ in the solvent region. The absolute configuration was confirmed by an x refinement; x = −0.013(11).

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

Acknowledgements

We thank Dirección General de Investigación Científica y Técnica (PB92-0982-C) and the Fonds der Chemischen Industrie for financial support and the Human Capital and Mobility research Program of the Commission of the European Communities for a research training fellowship to M. G. P. (contract No. ERBCHBGCT920143).

References

1 (*a*) Part 1, J. Vicente, I. Saura-Llamas and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1993, 3619; (*b*) Part 2, J. Vicente, I. Saura-Llamas and M. Carmen Ramírez-de-Arellano, preceding paper.
2 A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403 and refs. therein.
3 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.
4 (*a*) J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327; (*b*) I. Omae, *Coord. Chem. Rev.*, 1988, **83**, 137; (*c*) V. V. Dunina, O. A. Zalevskaya and V. M. Potapov, *Russ. Chem. Rev.*, 1988, **57**, 250 and refs. therein.
5 A. Avshu, R. D. O'Sullivan, A. W. Parkins, N. W. Alcock and R. M. Countryman, *J. Chem. Soc., Dalton Trans.*, 1983, 1619.
6 B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1973, 404.
7 S. Baba and S. Kawaguchi, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 415.
8 Y. Fuchita and H. Tsuchiya, *Polyhedron*, 1993, **12**, 2079.
9 A. D. Ryabov, *Synthesis*, 1985, 233; M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567 and refs. therein.
10 E. I. Karpeiskaya, E. S. Levitina, L. F. Godunova and E. I. Klabunovskii, *J. Mol. Catal.*, 1986, **34**, 129.
11 H. Takahashi and J. Tsuji, *J. Organomet. Chem.*, 1967, **10**, 511.
12 A. D. Ryabov, *Inorg. Chem.*, 1987, **26**, 1252.
13 P. W. Clark and S. F. Dyke, *J. Organomet. Chem.*, 1985, **281**, 389.
14 A. D. Ryabov and A. K. Yatsimirsky, *Inorg. Chem.*, 1984, **23**, 789; J. Granell, D. Sainz, J. Sales, X. Solans and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, 1986, 1785.
15 S. Otsuka, A. Nakamura, T. Kano and K. Tani, *J. Am. Chem. Soc.*, 1971, **93**, 4301; K. Tani, L. D. Brown, J. Ahmed, J. A. Ibers, M. Yokota, A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, 1977, **99**, 7976; N. K. Roberts and S. B. Wild, *J. Am. Chem. Soc.*, 1979, **101**, 6254; *J. Chem. Soc., Dalton Trans.*, 1979, 2015; D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem and S. B. Wild, *Inorg. Chem.*, 1982, **21**, 1007; S. Y. M. Chooi, P. Leung, C. C. Lim, K. F. Mok, G. H. Quek, K. Y. Sim and M. K. Tan, *Tetrahedron: Asymmetry*, 1992, **3**, 529.
16 J. Dehan, M. Pfeffer and J. Shamir, *Spectrochim. Acta, Part A*, 1977, **33**, 1101.
17 R. C. Elder, R. D. P. Cruea and R. F. Morrison, *Inorg. Chem.*, 1976, **15**, 1623.
18 R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712; J. Dehand, J. Jordanov, M. Pfeffer and M. Zinsius, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1975, **281**, 651; M. Pfeffer, D. Grandjean and G. Le Borgne, *Inorg. Chem.*, 1981, **20**, 4426; C. Arlen, M. Pfeffer, O. Bars and G. Le Borgne, *J. Chem. Soc., Dalton Trans.*, 1986, 359.
19 J. Dupont, M. Pfeffer, J. C. Daran and J. Gauteron, *J. Chem. Soc., Dalton Trans.*, 1988, 2421; F. Maassarani, M. Pfeffer and G. Le Borgne, *Organometallics*, 1987, **6**, 2043.
20 W. J. Geary, *Coord. Chem. Rev.*, 1981, **7**, 81.
21 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

Received 6th February 1995; *Paper* 5/00667H