Insertion of Internal Acetylenes into Orthopalladated α-Methylbenzylamine. Crystal Structure of $[Pd\{C(Ph){=}C(Ph)C(Ph){=}C(Ph)C_6H_4CH(Me)NH_2\}Br]$†

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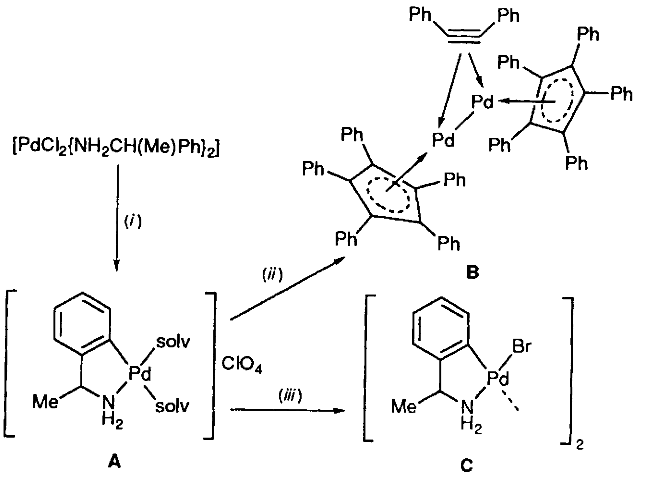
The complex $[Pd\{C_6H_4CH(Me)NH_2\}(Me_2CO)_2]ClO_4$ reacted with diphenylacetylene to give $[Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}\eta^2\text{-}PhC{\equiv}CPh)]$. A pathway for this reaction is suggested. Species related with the postulated intermediates can be isolated starting from $[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ which reacts with disubstituted alkynes ($RC{\equiv}CR$, R = CO_2Me or Ph) to afford $[Pd\{C(R){=}C(R)C(R){=}C(R)C_6H_4CH(Me)NH_2\}Br]$ (R = CO_2Me **1a** or Ph **1b**) through a double insertion of the alkyne into the Pd–C bond. Complex **1a** reacted with 1 equivalent of $MeO_2CC{\equiv}CCO_2Me$ to give the tri-insertion reaction product **2**. These are the first products of alkyne insertion into a cyclopalladated primary amine. Neutral ligands, such as pyridine (py) or CO, can break the Pd–π-olefinic bond in **1a** to give the corresponding adducts $[Pd\{C(R){=}C(R)C(R){=}C(R)C_6H_4CH(Me)NH_2\}Br(L)]$ (R = CO_2Me; L = py **3** or CO **4**). Complexes **1a** and **1b** reacted with $AgClO_4$ (1:1) in acetone to afford AgBr and $[Pd\{C(R){=}C(R)C(R){=}C(R)C_6H_4CH(Me)NH_2\}(solv)]ClO_4$ (R = CO_2Me, solv = H_2O **5a**; R = Ph, solv = Me_2CO **5b**). The reaction of complex **1a** with $AgClO_4$ (1:1) and excess of pyridine gave the cationic complex $[Pd\{C(R){=}C(R)C(R){=}C(R)C_6H_4CH(Me)NH_2\}(py)_2]ClO_4$ **6** (R = CO_2Me). The crystal structure of complex **1b** has been determined by X-ray diffraction. The palladium atom is bonded to Br, N, C(1) and to the midpoint of the C(3)–C(4) double bond in a distorted square-planar geometry.

The metal–carbon bond in orthopalladated tertiary amines undergoes insertion reactions with, for example, carbon monoxide,[2] alkenes,[3] acyl halides[4] and alkynes,[5-7] and, upon decomposition, can afford interesting organic compounds.[5,8,9] These compounds have therefore attracted great interest in organic synthesis.

Recently we have described the orthopalladation of α-methylbenzylamine.[1] We were interested in the reaction of these cyclometallated primary amines with alkynes, first because such reactions have not been reported yet and, secondly, because a different behaviour from their analogous complexes containing tertiary amines is expected. Thus, more stable insertion products are predicted due to their greater basic character and therefore there exists the possibility of studying the reactivity of such mono- or di-inserted complexes with different ligands to afford new types of organopalladium complexes. This is the main objective of the present work. The only reported reactions of cyclopalladated primary amines are those of CO or isocyanides with cyclopalladated benzylamine affording, after insertion and depalladation, phthalimidine or isoindolinimines, respectively. However, these results were published some time ago as a preliminary communication.[4]



Scheme 1 (*i*) +2 $AgClO_4$ + solv (acetone), −AgCl − $[PhCH(Me)NH_3]ClO_4$; (*ii*) +$PhC{\equiv}CPh$; (*iii*) +Br^-, −ClO_4^-

Results and Discussion

We have reported that $[PdCl_2\{NH_2CH(Me)Ph\}_2]$ reacts with $AgClO_4$ (1:2) in acetone to give AgCl, $[PhCH(Me)NH_3]ClO_4$ and the palladium complex $[Pd\{C_6H_4CH(Me)NH_2\}(Me_2CO)_2]ClO_4$ (complex **A** in Scheme 1).[1] This solvento complex reacts with $PhC{\equiv}CPh$ (1:5, acetone, room temperature, overnight) to give a dark green crystalline product which, after a crystal structure determination, proved to be the palladium(I) complex $[Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}\eta^2\text{-}PhC{\equiv}CPh)]$ (see **B** in Scheme 1) and a mixture of organic compounds which we could not separate. Complex **B** has been reported as one of the products of the reaction between $[\{Pd(O_2CMe)_2\}_3]$ and $PhC{\equiv}CPh$ and its crystal structure has been solved.[10] The proposed mechanism requires nucleophilic attack of MeO^-, probably generated by the reaction of the solvent (MeOH) and acetate, on the π-co-ordinated acetylene molecule. Since these are not

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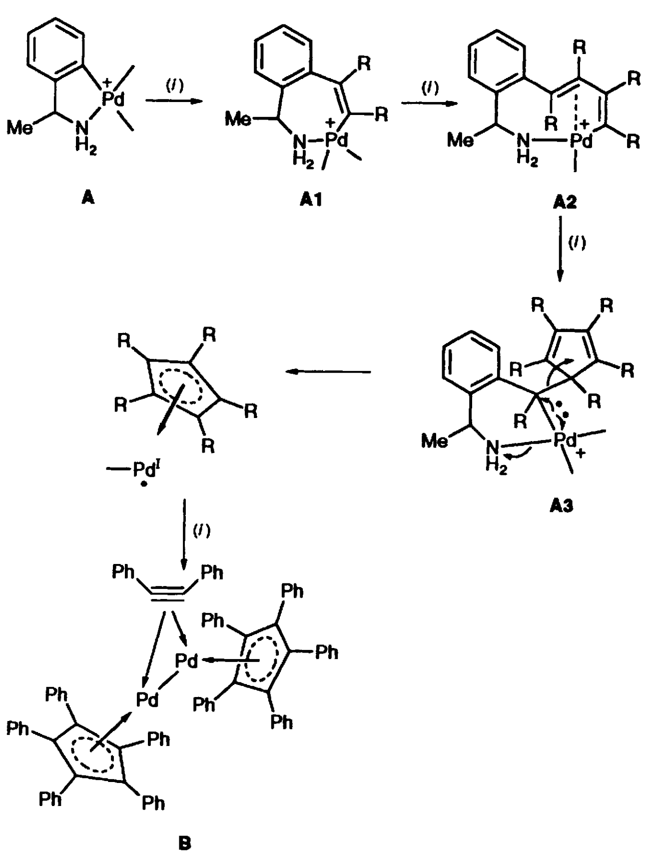
† Orthometallated Primary Amines. Part 2.[1]

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

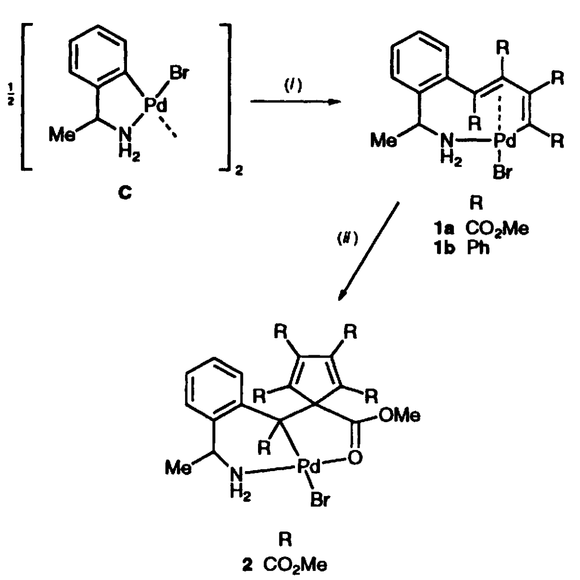


Scheme 2 (*i*) +RC≡CR

the conditions of our reaction we can adapt the proposed mechanism to our case as shown in Scheme 2. The low donor ability of the potential ligands in solution (Me_2CO, ClO_4^-, PhC≡CPh) to complete the four-co-ordination of Pd^{II} could be responsible for the instability of intermediates **A1**–**A3** and, therefore, for the formation of **B**. To get information on these intermediates we planned to study the insertion reactions of alkynes and the complex we reported as the result of the reaction of **A** and NaBr, *i.e.* $[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ (see **C** in Scheme 1).

The reaction of complex **C** with RC≡CR (R = CO_2Me or Ph) gives the nine-membered cyclometallated complexes $[Pd\{C(R){=}C(R)C(R){=}C(R)C_6H_4CH(Me)NH_2\}Br]$ (R = CO_2Me **1a** or Ph **1b**; see Scheme 3) resulting from insertion of two alkyne molecules into the Pd–C bond (type **A2**, see Scheme 2). Attempts to obtain the monoinsertion products (type **A1**, see Scheme 2) were unsuccessful. Thus, when the reaction between **C** and $MeO_2CC{\equiv}CCO_2Me$ was carried out in a 1 : 2 molar ratio (one alkyne per Pd atom) a 1 : 1 mixture of **C** and **1a** was obtained. When the reaction was carried out with PhC≡CPh an analogous mixture was obtained even when an excess of diphenylacetylene was used (1 : 4, that is, two alkynes per Pd atom). Only when 3 equivalents of PhC≡CPh were used, complex **1b** was obtained as a pure compound. Isolation of mono-[5,6a,h] and di-inserted[5,6c,e,f,h,7,9] compounds of the types **A1** and **A2** in reactions of cyclopalladated complexes and alkynes is well documented. The synthesis of the di-inserted compound, without isolation or observation of the monoinserted intermediate, has been reported to occur mainly with electron-rich acetylenes like hex-3-yne or PhC≡CPh.[5] Kinetic studies have shown that this is due to the fact that formation of the monoinserted compound is the rate-determining step.[6g]

Complex **1a** is very insoluble in all common organic solvents which prevented its characterization by NMR spectroscopy. Nevertheless, its IR spectrum shows three strong bands at 3290, 3203 and 3132 cm^{-1} corresponding to ν(NH), and four very



Scheme 3 (*i*) +2 RC≡CR; (*ii*) +RC≡CR

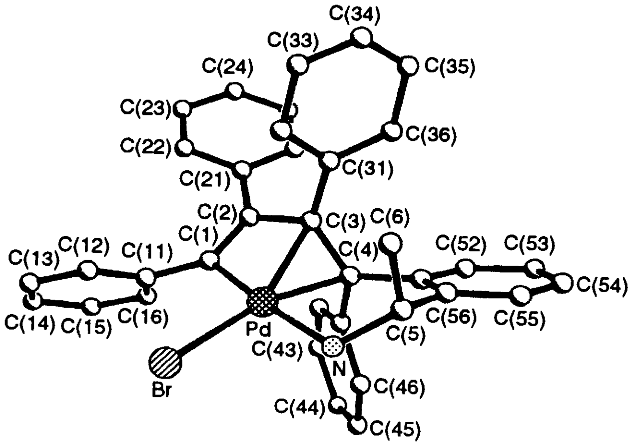


Fig. 1 Structure of complex **1b** in the crystal; H atoms are omitted for clarity

strong peaks at 1723, 1708, 1703 and 1671 cm^{-1} corresponding to $\nu(CO_2)$, which suggests that a di-insertion product was produced. On the other hand, the NMR spectra of its derivatives **2**–**6** showed four resonances in the range δ 3.14–3.90 corresponding to four different OMe groups.

Complex **1b** has been characterized by X-ray diffraction (Fig. 1). Table 1 gives crystal data and structure refinements, Table 2 atomic coordinates, and Table 3 selected bond lengths and angles. The palladium atom is bonded to Br, N, C(1) and to the midpoint of the C(3)–C(4) double bond in a distorted square-planar geometry. The deviations from the mean plane are: Pd, 0.0052; C(1), −0.0042; Br, 0.0011; N, −0.0037; midpoint C(3)–C(4), 0.0017 Å. The Pd–Br [2.439(1) Å], Pd–N [2.150(7) Å] and Pd–C(1) [2.009(7) Å] distances and related angles are similar to those in five-membered cyclopalladated compounds.[7] The Pd–C(3) [2.228(6) Å] and Pd–C(4) [2.215(6) Å] lengths are slightly different from one another, and the C(3)–C(4) bond [1.393(9) Å] is slightly longer than the C(1)–C(2) bond [1.322(9) Å] due to co-ordination to the palladium atom.

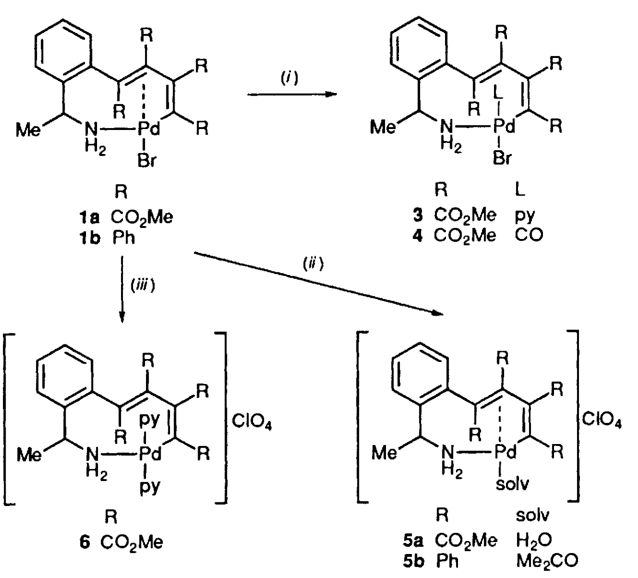
Since an excess of acetylene at room temperature does not give tri-inserted complexes from **1a** and **1b** we have tried this reaction using more severe reaction conditions. However, while **1a** reacted in refluxing $CHCl_3$ with more $MeO_2CC{\equiv}CCO_2Me$ to give a soluble compound **2**, complex **1b** does not react under the same conditions. The proton NMR spectrum of **2** revealed the presence of six inequivalent carboxylate groups. We propose for it the same structure (see Scheme 3) as that of analogous compounds prepared by Pfeffer and co-workers,[11] which is also the postulated structure for the intermediate **A3** (see Scheme 2) in the process of formation of compound **B** from **A**.

All reactions of the reported di-inserted complexes lead to palladium and organic products. These reactions occur at room or higher temperatures or after addition of maleic anhydride.[5] Complexes **1a** and **1b** are expected to be more stable than their homologues with tertiary amines. Thus, the reaction between $[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}Br]$ ($R = CO_2Me$) and neutral compounds such as pyridine (py) or CO afforded complexes $[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}Br(L)]$ ($R = CO_2Me$; L = py **3** or CO **4**; see Scheme 4), where the ligands broke the π-olefinic bond to give the corresponding adducts. Complex **4** [ν(CO) 2120s cm^{-1}] is stable at room temperature when solid, although it slowly decomposes in solution. This stability is remarkable because organopalladium(II) complexes usually react with carbon monoxide to give acyl derivatives,[12] and only a few aryl-[13a–e] and one divinyl-[13f] carbonyl palladium complexes have been reported. Therefore, as far as we are aware, complex **4** is the second isolated non-aryl carbonyl palladium(II) complex.

When complexes **1a** and **1b** reacted with $AgClO_4$ in acetone

Table 1 Crystal data and structure refinement details for compound **1b**

Empirical formula	$C_{36}H_{30}BrNPd$
M	662.9
T/K	290
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	13.468(3)
b/Å	15.528(3)
c/Å	14.092(3)
β/°	92.80(2)
U/Å^3	2943.3(11)
Z	4
D_c/Mg m^{-3}	1.496
μ(Mo-Kα)/mm^{-1}	2.013
F(000)	1336
Crystal size/mm	0.44 × 0.46 × 0.25
2θ range/°	5–45
h, k, l ranges	−4 to 14, −5 to 16, −15 to 15
Reflections collected	4387
Independent reflections	3875 (R_{int} = 0.0109)
Goodness of fit on F^2	1.32
$R(F)$, $wR(F^2)$	0.0495, 0.0577
(all data)	0.0695, 0.0622
Largest difference peak and hole/e Å^{-3}	0.63, −0.75
Maximum Δ/σ	0.001



Scheme 4 (*i*) +L; (*ii*) +$AgClO_4$, −AgBr, in acetone; (*iii*) +$AgClO_4$, −AgBr, +2 py

Table 3 Selected bond lengths (Å) and angles (°) for compound **1b**

Pd–Br	2.439(1)	Pd–N	2.150(7)
Pd–C(1)	2.009(7)	Pd–C(2)	2.603(7)
Pd–C(3)	2.228(6)	Pd–C(4)	2.215(6)
N–C(5)	1.489(12)	C(1)–C(2)	1.322(9)
C(2)–C(3)	1.510(10)	C(3)–C(4)	1.393(9)
Br–Pd–N	87.6(2)	Br–Pd–C(1)	97.0(2)
N–Pd–C(1)	175.3(3)	Br–Pd–C(2)	125.3(1)
N–Pd–C(2)	145.5(2)	C(1)–Pd–C(2)	29.9(1)
Br–Pd–C(3)	156.6(2)	N–Pd–C(3)	110.1(2)
C(1)–Pd–C(3)	65.3(3)	C(2)–Pd–C(3)	35.4(2)
Br–Pd–C(4)	165.1(2)	N–Pd–C(4)	88.4(2)
C(1)–Pd–C(4)	87.3(3)	C(2)–Pd–C(4)	62.4(2)
C(3)–Pd–C(4)	36.5(2)		

Table 2 Atomic coordinates (× 10^4) for compound **1b**

Atom	x	y	z	Atom	x	y	z
Pd	329(1)	3 299(1)	9 403(1)	C(26)	244(5)	1 137(5)	6 855(5)
Br	1 445(1)	3 808(1)	10 700(1)	C(31)	−985(5)	1 690(5)	8 767(5)
N	−823(5)	4 051(4)	10 005(4)	C(32)	−674(7)	1 232(5)	9 558(7)
C(1)	1 321(5)	2 558(4)	8 765(5)	C(33)	−1 246(11)	586(6)	9 911(9)
C(2)	722(5)	2 064(4)	8 229(5)	C(34)	−2 134(12)	369(7)	9 477(12)
C(3)	−333(5)	2 355(4)	8 363(4)	C(35)	−2 450(8)	794(7)	8 699(11)
C(4)	−632(5)	3 181(5)	8 088(5)	C(36)	−1 884(6)	1 458(6)	6 317(7)
C(5)	−1 891(7)	3 803(6)	9 905(6)	C(41)	−68(5)	3 771(4)	7 460(5)
C(6)	−2 113(9)	3 043(7)	10 485(7)	C(42)	507(5)	3 479(5)	6 730(5)
C(11)	2 411(5)	2 570(4)	8 826(5)	C(43)	941(6)	4 046(6)	6 121(6)
C(12)	2 962(7)	2 355(6)	9 637(6)	C(44)	800(6)	4 918(7)	6 234(7)
C(13)	3 975(8)	2 315(7)	9 649(8)	C(45)	256(6)	5 224(5)	6 960(7)
C(14)	4 475(7)	2 485(6)	8 864(9)	C(46)	−184(5)	4 658(5)	7 571(6)
C(15)	3 944(7)	2 723(5)	8 033(7)	C(51)	−1 713(5)	3 449(4)	8 113(5)
C(16)	2 919(6)	2 760(5)	8 032(6)	C(52)	−2 203(6)	3 412(5)	7 229(6)
C(21)	914(5)	1 331(4)	7 596(5)	C(53)	−3 179(6)	3 624(6)	7 063(7)
C(22)	1 746(6)	806(5)	7 719(5)	C(54)	−3 694(7)	3 903(6)	7 811(8)
C(23)	1 914(7)	135(5)	7 102(6)	C(55)	−3 250(6)	3 953(6)	8 689(7)
C(24)	1 240(7)	−27(5)	6 352(6)	C(56)	−2 259(6)	3 707(5)	8 869(6)
C(25)	405(6)	472(5)	6 235(6)				

AgBr was precipitated and from the resulting solution complexes $[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}(solv)]ClO_4$ (R = CO_2Me, solv = H_2O **5a**; R = Ph, solv = Me_2CO **5b**) were isolated. The IR spectra of both compounds showed bands characteristic of co-ordinated H_2O [ν(OH) 3480s (vbr) cm^{-1}] or acetone [ν(CO) 1656s cm^{-1}], respectively. The strong band around 1100 cm^{-1} corresponding to ν(ClO) of the ClO_4^- anion is split indicating interaction with co-ordinated H_2O or/and with the NH_2 group through hydrogen bonding. We have reported the crystal structure of the complex $[Pd\{C_6H_2(NO_2)_3\text{-}2,4,6\}(tht)(H_2O)]ClO_4$ (tht = tetrahydrothiophene) showing that each anion bridges, through hydrogen bonding, two cations and *vice versa* giving a *catena* structure.[14]

All complexes show two or three bands corresponding to ν(NH) in the region of 3320–3100 cm^{-1}.

The complex $[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}(py)_2]ClO_4$ **6** (R = CO_2Me) can be prepared by reaction of **1b**, $AgClO_4$ and pyridine in excess. Its ^1H NMR spectrum showed two different types of pyridine resonances. Some are normal while the others are broad. Apparently one of the ligands can be displaced by the olefinic bond in a rapid equilibrium.

Experimental

General Data.—The IR spectra, C, H and N analyses, conductance measurements and melting-point determinations were carried out as described elsewhere.[1] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ on a Varian Unity 300 spectrometer and conductivity measurements were carried out in acetone. Chemical shifts are referred to $SiMe_4$ or $(CD_3)_2CO$. The complexes $[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ and $[PdCl_2\{NH_2CH(Me)Ph\}_2]$ were prepared as previously described.[1]

Compound **B**.—The complex $[PdCl_2\{NH_2CH(Me)Ph\}_2]$ (500 mg, 1.19 mmol) was taken up in acetone (30 cm^3), treated with solid $AgClO_4$ (500 mg, 2.41 mmol) and stirred for 10 min. The resulting silver chloride was filtered off and the filtrate made up to a larger volume (100 cm^3) with acetone and stirred overnight at room temperature. Acetone was removed and the residue taken up in CH_2Cl_2 (20 cm^3) and filtered through a plug of $MgSO_4$. Solid PhC≡CPh (1062 mg, 5.958 mmol) was added and the resulting solution was stirred for 18 h. The resulting green solution was filtered through a plug of $MgSO_4$, solvent removed and acetone (30 cm^3) added. A deep green solid, insoluble in acetone, was collected, washed with acetone (2 × 20 cm^3), and air dried (292 mg, 0.228 mmol, 38%). Data for this compound match those previously reported.[10]

$[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}Br]$ **1a** (R = CO_2Me).—To a suspension of $[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ (439 mg, 0.716 mmol) in CH_2Cl_2 (30 cm^3) was added $MeO_2CC\equiv CCO_2Me$ (0.3 × 10^{-3} cm^3, 2.45 mmol). The yellow solution initially formed was stirred for 12 h. Complex **1a** precipitated from the reaction mixture as a pale yellow powder which was collected, washed with CH_2Cl_2 (2 × 20 cm^3), and air dried (737 mg, 1.25 mmol, 87%), m.p. 205 °C (decomp.) (Found: C, 40.50; H, 2.30; N, 3.75. Calc. for $C_{20}H_{22}BrNO_8Pd$: C, 40.65; H, 2.35; N, 3.75%). IR (cm^{-1}) ν(NH) 3290s, 3203s and 3132s; ν(CO) 1723vs, 1708vs, 1703vs and 1671vs.

$[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}Br]$ **1b** (R = Ph).—To a suspension of $[\{Pd[C_6H_4CH(Me)NH_2](\mu\text{-}Br)\}_2]$ (180 mg, 0.294 mmol) in CH_2Cl_2 (20 cm^3) was added PhC≡CPh (350 mg, 1.96 mmol). After 12 h a yellow solution was formed which was 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 **1b** as a bright yellow solid, which was collected, washed with diethyl ether (2 × 20 cm^3) and air dried (292 mg, 0.440 mmol, 75%), m.p. 217 °C (decomp.) (Found: C, 65.55; H, 4.65; N, 2.15. Calc. for $C_{36}H_{30}BrNPd$: C, 65.20; H, 4.55; N, 2.10%). Λ_M = 0 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}) ν(NH) 3292w, 3215w and 3137w. ^1H NMR: δ 0.65 (d, 3 H, Me, $^3J_{HH}$ = 6.9 Hz), 2.79–3.06 (m, 2 H, NH), 4.32 (m, 1 H, CH) and 6.80–7.57 (m, 24 H, Ph and C_6H_4).

Structure Determination of Complex **1b**.—A yellow prism was mounted on a glass fibre and transferred to the diffractometer (Siemens R3mV). Data were collected with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) to $2\theta_{max}$ = 45° and corrected for Lorentz and polarization effects and for absorption using a semiempirical ψ-scan method. The structure was solved by direct methods, and refined by full-matrix least-squares analysis on *F*. Hydrogen atoms were included using a riding model. In the final cycles of refinements a weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.0010F^2$ was used. Refinement continued until convergence was reached. The structure was solved and refined using the SHELXTL PLUS software package.[15] Final atomic coordinates for complex **1b** are listed in Table 2.

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

$[Pd\{C(CO_2Me)[C(CO_2Me)C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C(CO_2Me)]C_6H_4CH(Me)NH_2\}Br]$ **2**.—To a suspension of complex **1a** (60 mg, 0.102 mmol) in $CHCl_3$ (10 cm^3) was added $MeO_2CC\equiv CCO_2Me$ (0.05 cm^3, 0.408 mmol) and the resulting suspension was refluxed for 2 h. A yellow solution was formed which was filtered through a plug of $MgSO_4$. Solvent was removed until *ca.* 2 cm^3 remained and diethyl ether was added (25 cm^3) to precipitate complex **2** as a yellow solid, which was collected, washed with diethyl ether, and air dried (42.2 mg, 0.057 mmol, 56%), m.p. 160 °C (decomp.) (Found: C, 42.30; H, 4.05; N, 2.20. Calc. for $C_{26}H_{28}BrNO_{12}Pd$: C, 42.60; H, 4.60; N, 1.90%). Λ_M = 0 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}) ν(NH) 3289w and 3239w. ^1H NMR: δ 1.86 (d, 3 H, CH_3, $^3J_{HH}$ = 6.6 Hz), 3.28 (m, 1 H, NH or CH), 3.72, 3.76, 3.84, 3.85, 3.90, 3.95 (s, 19 H, 6 OMe; one NH or CH resonance obscured by the OMe groups), 4.21 (m, 1 H, NH or CH), and 7.03–7.33 (m, 4 H, C_6H_4).

$[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}Br(py)]$ **3** (R = CO_2Me).—To a suspension of complex **1a** (60 mg, 0.11 mmol) in CH_2Cl_2 (20 cm^3) was added pyridine (0.165 cm^3, 2.04 mmol). The resulting solution was stirred for 30 min 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 **3** as a very pale yellow solid which was collected, washed with ether and air dried (55 mg, 0.082 mmol, 77%), m.p. 192–193 °C (decomp.) (Found: C, 45.00; H, 4.05; N, 4.25. Calc. for $C_{25}H_{27}BrN_2O_8Pd$: C, 44.85; H, 4.05; N, 4.20%). Λ_M = 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}) ν(NH) 3320m, 3300m and 3240m; ν(CO) 1725vs and 1700vs. NMR: ^1H, δ 1.67 (d, 3 H, CH_3, $^3J_{HH}$ = 5.7 Hz), 3.03 (m, 1 H, NH), 3.14 (s, 3 H, OMe), 3.57 (s, 4 H, OMe and NH), 3.77 (s, 3 H, OMe), 3.90 (s, 3 H, OMe), 5.26 (m, 1 H, CH), 7.09 (dd, 1 H, H^3 of C_6H_4), 7.24–7.48 (m, 5 H, *m*-H of py; H^{2-4} of C_6H_4), 7.76 (m, 1 H, *p*-H of py) and 8.87 (m, 2 H, *o*-H of py); $^{13}C\text{-}\{^1H\}$, δ 22.9 (s, CH_3), 51.8 (s, OMe), 52.0 (s, OMe), 52.1 (s, OMe), 52.9 (s, OMe), 53.3 (s, $CHCH_3$), 124.6 (s, *m*-C of py), 125.7 (s, CH, C_6H_4), 127.6 (s, CH, C_6H_4), 127.8 (s, C=C), 128.6 (s, CH, C_6H_4), 130.2 (s, CH, C_6H_4), 133.3 (s, C=C), 135.1 (s, C=C), 137.9 (s, *p*-C of py), 138.5 (s, C, C_6H_4), 145.1 (s, C, C_6H_4), 154.2 (s, *m*-C of py), 159.9 (s, C, C=C), 164.7 (s, CO), 165.1 (s, CO), 167.8 (s, CO) and 171.5 (s, CO).

$[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2\}Br(CO)]$ **4** (R = CO_2Me).—Carbon monoxide was bubbled through a suspension of complex **1a** (100 mg, 0.169 mmol) in CH_2Cl_2 (30 cm^3) until it became a colourless solution which was stirred under an atmosphere of CO for 30 min, and then filtered through a plug of $MgSO_4$. Solvent was removed until *ca.* 2 cm^3 remained and diethyl ether was added (25 cm^3) to precipitate complex **4** as a white solid which was collected, washed with diethyl ether, and air dried (70 mg, 0.11 mmol, 67%), m.p. 186 °C (decomp.) (Found: C, 40.75; H, 3.55; N, 2.25. Calc. for $C_{21}H_{22}BrNO_9Pd$: C, 40.75; H, 3.60; N, 2.25%). $\Lambda_M = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (cm^{-1}) ν(NH) 3295s and 3243s; ν(CO) 2120s. NMR: ^{1}H, δ 1.67 (d, 3 H, CH_3, $^3J_{HH} = 6.6$ Hz), 3.25 (m, 1 H, NH), 3.65 (s, 4 H, OMe and NH), 3.73 (s, 3 H, OMe), 3.86 (s, 3 H, OMe), 3.88 (s, 3 H, OMe), 4.82 (m, 1 H, CH) and 7.13–7.52 (m, 4 H, C_6H_4); ^{13}C-{^{1}H}, δ 23.5 (s, CH_3), 52.2 (s, OMe), 52.4 (s, OMe), 52.5 (s, OMe), 52.9 (s, OMe), 53.1 (s, *C*HCH_3), 125.5 (s, CH, C_6H_4), 128.0 (s, CH, C_6H_4), 129.0 (s, C, C=C), 129.2 (s, CH, C_6H_4), 130.6 (s, CH, C_6H_4), 133.2 (s, C=C), 134.4 (s, C=C), 137.8 (s, C, C_6H_4), 144.8 (s, C, C_6H_4), 155.5 (s, PdCO), 160.6 (s, C, C=C), 164.3 (s, *C*O_2CH_3), 167.0 (s, *C*O_2CH_3), 169.9 (s, *C*O_2CH_3) and 170.9 (s, *C*O_2CH_3).

[Pd{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2}(OH_2)]ClO_4 **5a** (R = CO_2Me).—To a suspension of complex **1a** (400 mg, 0.677 mmol) in acetone (30 cm^3) was added solid $AgClO_4$ (145 mg, 0.699 mmol). The resulting suspension was stirred for 2 h, and then filtered through a plug of $MgSO_4$. Solvent was removed until *ca.* 2 cm^3 remained and diethyl ether was added (25 cm^3) to precipitate complex **5a** as a yellow solid which was collected, washed with diethyl ether, and air dried (361 mg, 0.575 mmol, 87%), decomposes 169 °C (Found: C, 38.30; H, 3.85; N, 2.65. Calc. for $C_{20}H_{24}ClNO_{13}Pd$: C, 38.25; H, 3.55; N, 2.25%). $\Lambda_M = 106\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (cm^{-1}) ν(NH) 3280s, 3210s and 3130s. ^{1}H NMR: δ 1.59 (d, 3 H, CH_3, $^3J_{HH}$ = 7.2), 3.51 (m, 1 H, NH), 3.56 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 4.58 (m, 1 H, NH), 5.12 (m, 1 H, CH), 7.12 (d, 1 H, H^3 of C_6H_4, $^3J_{HH}$ = 7.8), 7.35 (t, 1 H, H^4, C_6H_4), 7.44 (t, 1 H, H^5, C_6H_4) and 7.68 (d, 1 H, H^6, C_6H_4, $^3J_{HH}$ = 7.8 Hz).

[Pd{C(Ph)=C(Ph)C(Ph)=C(Ph)C_6H_4CH(Me)NH_2}(OCMe_2)]ClO_4 **5b**.—To a suspension of complex **1b** (150 mg, 0.226 mmol) in acetone (30 cm^3) was added solid $AgClO_4$ (47.0 mg, 0.227 mmol). The resulting suspension was stirred for 2 h, and then filtered through a plug of $MgSO_4$. Solvent was removed until *ca.* 2 cm^3 remained and diethyl ether was added (25 cm^3) to precipitate complex **5b** as a bright yellow solid, which was collected, washed with diethyl ether, and air dried (86.8 mg, 0.117 mmol, 52%), decomposes 162 °C (Found: C, 63.10; H, 4.95; N, 2.20. Calc. for $C_{39}H_{36}ClNO_5Pd$: C, 63.25; H, 4.90; N, 1.90%). $\Lambda_M = 107\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (cm^{-1}) ν(NH) 3277m, 3244m and 3159m. ^{1}H NMR: δ 0.68 (d, 3 H, CH_3, $^3J_{HH}$ = 6.9 Hz), 2.13 (s, 6 H, CH_3CO), 3.20–3.42 (m, 2 H, NH), 4.39 (m, 1 H, CH) and 6.66–7.66 (m, 24 H, Ph and C_6H_4).

[Pd{C(R)=C(R)C(R)=C(R)C_6H_4CH(Me)NH_2}$(py)_2$]ClO_4 **6** (R = CO_2Me).—To a suspension of complex **1a** (100 mg, 0.169 mmol) in acetone (30 cm^3) was added solid $AgClO_4$ (36.0 mg, 0.169 mmol). The resulting suspension was stirred for 2 h, and then filtered through a plug of $MgSO_4$. Pyridine (0.165 cm^3, 2.04 mmol) was added and the resulting colourless solution was stirred for 30 min. Solvent was removed until *ca.* 2 cm^3 remained and diethyl ether was added (25 cm^3) to precipitate complex **6** as a white solid, which was collected, washed with diethyl ether, and air dried (110 mg, 0.143 mmol, 85%), m.p. 135–137 °C (Found: C, 46.60; H, 4.30; N, 5.25. Calc. for $C_{30}H_{32}ClN_3O_{12}Pd$: C, 46.90; H, 4.20; N, 5.45%). $\Lambda_M = 111\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (KBr, cm^{-1}) ν(NH) 3238w and 3150w. ^{1}H NMR [$(CD_3)_2CO$]: δ 1.38 (d, 3 H, CH_3, $^3J_{HH}$ = 6.9), 3.22 (s, 3 H, OMe), 3.38 (m, 1 H, NH), 3.53 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 3.95 (s, 3 H, OMe), 4.58 (m, 1 H, NH), 5.27 (m, 1 H, CH), 7.14 (dd, 1 H, H^3 of C_6H_4, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2 Hz), 7.37 (dt, 1 H, H^4 of C_6H_4), 7.46 (dt, 1 H, H^5 of C_6H_4), 7.56 (apparent t, 2 H, *m*-H of py), 7.62 (dd, 1 H, H^6 of C_6H_4), 7.76 (m, 2 H, *m*-H of py), 8.01 (apparent t, 1 H, *p*-H of py), 8.12 (m, 1 H, *p*-H of py), 8.54 (apparent d, 2 H, *o*-H of py), and 8.93 (m, 2 H, *o*-H of py).

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