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A New Method for High Yield Cyclopalladation of Primary and Secondary Amines. Atom-Efficient Open-to-Air Inexpensive Synthesis of Buchwald-Type Precatalysts

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ABSTRACT: A new method for high yield cyclopalladation of primary and secondary amines involving the corresponding ammonium triflates, instead of the amines generally employed is reported. The method is applied for the synthesis of Buchwald-type precatalysts [Pd(*C*,*N*-$C_6H_4CH_2CH(R')NHR$-2)X(phosphine)] that can be easily prepared by reaction of $Pd(OAc)_2$, one equiv of the ammonium

triflate [$PhCH_2CH(R')NH_2R$]OTf and an excess of NaX, and then treating the resulting complexes [$Pd_2(C,N\text{-}C_6H_4CH_2CH(R')NHR\text{-}2)_2(\mu\text{-}X)_2$] with the appropriate phosphine. This new method has several advantages over Buchwald´s reported synthesis.

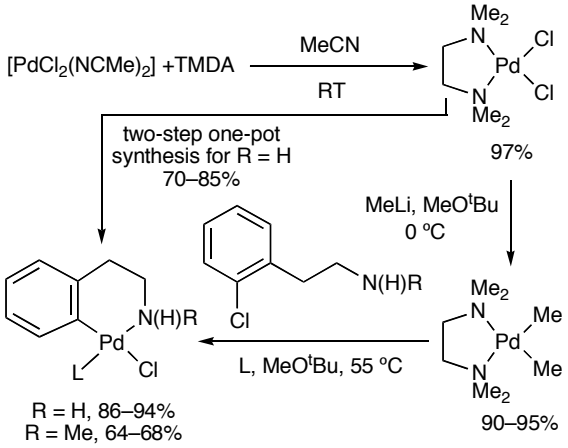
INTRODUCTION.

Buchwald et al. have shown that ortho-palladated derivatives of primary and secondary amines containing biarylmonophosphines are excellent precatalysts for C–C[1] and C–N cross-coupling reactions.[2,3] These precatalysts are particularly useful for substrates unstable at elevated reaction temperatures. They are prepared via a two-step one- or two-pot synthesis (Scheme 1) from [$PdCl_2$(TMEDA)] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), MeLi, the free phosphine and the corresponding 2-chlorophenethylamine or 2-(2-chlorophenyl)-*N*-methylethanamine in moderate to good yields (61–85%).[2] However, the reaction conditions are not straightforward: (1) an argon atmosphere is required; (2) the intermediate [$PdMe_2$(TMEDA)] can be isolated (in some cases it is required because it is used as starting material) but it has to be stored inside a nitrogen-filled glovebox or in a freezer under argon; moreover, this complex shows exothermic decomposition between 115–130 ºC; (3) if the 2-haloarylalkyl amine is not commercially available it has to be otherwise prepared, as it happens with the 2-(2-chlorophenyl)-*N*-methylethanamine;[2] and (4) the nature of the halo ligand is determined by that of the aryl halide, although it could be changed by metathesis, adding a new step to the process.

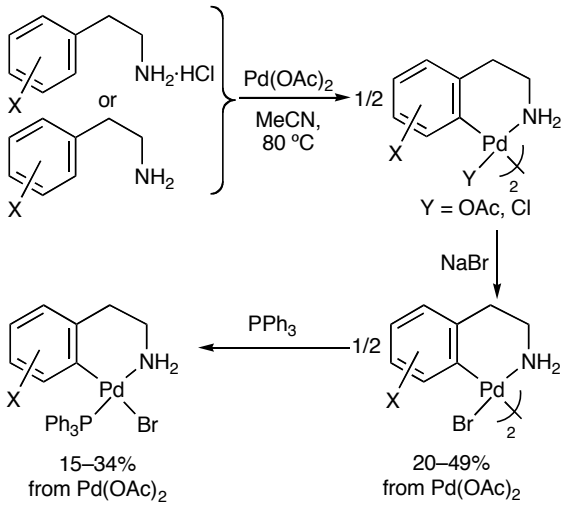
Back in 1997, we reported a general method to ortho-palladate primary arylalkylamines, which allowed the synthesis of five- and six-membered palladacycles (the synthesis of phenethylamine derivatives is illustrated in Scheme 2), even when the aryl ring contained electron-withdrawing substituents.[4-7] The reaction involved equimolecular amounts of the free amine or its hydrochloride and palladium acetate in acetonitrile at 80 ºC, affording the corresponding dimeric ortho-palladated acetato- or chloro-complex. Metathesis reaction of this complex with NaBr rendered the corresponding bromo derivative, which subsequently reacted with PPh_3 (molar ratio 1:2) to give the mononuclear phosphino adduct. This method presented some advantages over Buchwald's method. Thus, the reactions were

carried out without precautions against air or moisture, no other organometallic compound was used, the reagents are quite inexpensive, the intermediates were easily isolable and stable, and the method offered a great versatility to modify the nature of the ligands in the Buchwald-type precatalyst. However, the phosphino cyclopalladated complexes were obtained in poor yields (15–34%, based on $Pd(OAc)_2$).

Scheme 1. Buchwald's Synthesis of Palladacycles Containing Ortho-Metalated Phenethylamines

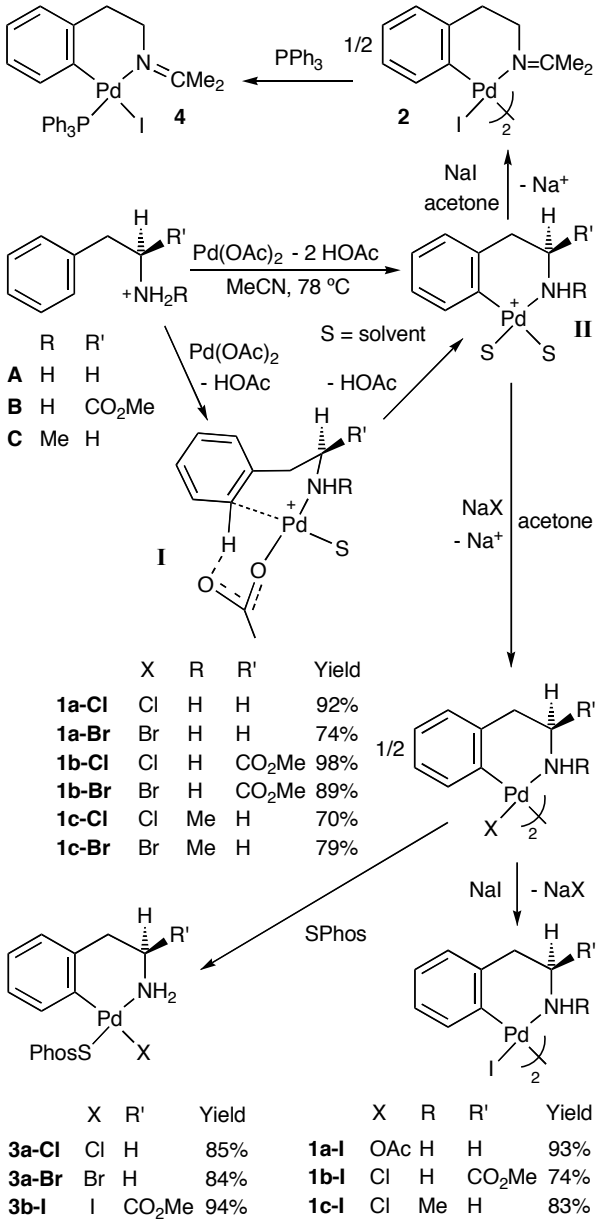


Scheme 2. Synthesis of Ortho-Palladated Phenethylamine Derivatives Using the Free Amine or Their Corresponding Hydrochlorides



Here, we report a new method of synthesis of a variety of halo-complexes of Pd(II) containing ortho-metalated primary or secondary phenethylamines, which adds to the advantages of our previously reported one, the good yields of the cyclopalladated complexes and the phosphino derivatives.[9]

Scheme 3. Improved Synthesis of Palladacycles Containing Ortho-Metalated Phenethylamines[a]



[a] The anion of the cationic species is TfO^-

RESULTS AND DISCUSSION

Synthesis. The ammonium triflate derived from phenethylamine ($PhCH_2CH_2NH_3$)OTf (**A**), L-phenylalanine methyl ester (*S*)-($PhCH_2CH(CO_2Me)NH_3$)OTf (**B**), or *N*-methyl-phenethylamine ($PhCH_2CH_2NH_2Me$)OTf (**C**) reacted with $Pd(OAc)_2$ in a 1:1 molar ratio, in acetonitrile at 75–78 ºC, to

give HOAc and, likely, intermediate **I**, which underwent an ortho metalation reaction to afford the solvento-complex **II** (Scheme 3),[10,11] which further reacted with NaX (X = Cl, Br) to render the halo-bridged cyclopalladated complex $[Pd_2(C,N\text{-}C_6H_4CH_2CHR'NHR\text{-}2)_2(\mu\text{-}X)_2]$ (R = R' = H, X = Cl (**1a-Cl**), Br (**1a-Br**); R = H, R' = CO_2Me, X = Cl (**1b-Cl**), Br (**1b-Br**); R = Me, R' = H, X = Cl (**1c-Cl**), Br (**1c-Br**)). The two steps of the global reaction are carried out in the same pot, replacing acetonitrile by acetone before adding the sodium salt. The yields of complexes **1** are in the range 70 – 98%, which contrats with those obtained using the free amine or its hydrochloride (see below). The different yields can be explained based on the different electrophilicity of the precursor of **II** (i.e., **I** when the ammonium triflate is used). Thus, the free amine or its hydrochloride would afford a *neutral* intermediate resulting from replacing the solvent ligand (S) in **I** by an acetato or chloro ligand. However, using the ammonium triflate, the weak donor triflato ligand does not replace S affording **I**, which *cationic* nature enhances the electrophilicity of palladium(II) and facilitates the ortho metalation process. In mechanistic studies on orthopalladation of arylalkylamines, an intermediate as **I** has been postulated.[10] A solvento-complex similar to **II** has been postulated as intermediate in the ortho metalation of α-methylbenzylamine starting from $[PdCl_2\{NH_2CH(Me)Ph\}_2]$ and $AgClO_4$ (1:2 molar ratio) and using acetone as solvent.[12] The synthesis of complexes **1a-Br**, **1b-Cl**, **1b-Br** and **1c-Br** had been previously reported by us, following a similar method to that described in Scheme 2, although **1b-Cl** was not isolated in a pure form and **1a-Br**, **1b-Br** and **1c-Br** were obtained in lower yields (**1a-Br**: 30%; **1b-Br**: 49%; **1c-Br**, 65%).[7,13]

When trying to use an analogous procedure to prepare the iodo-bridged complexes derived from the ammonium triflates **B** and **C**, intractable mixtures were obtained. Similar results were achieved when the addition of NaI was carried out in acetonitrile, instead of acetone. It is likely that a very unstable cationic iodo-derivative, $[Pd(C,N\text{-}C_6H_4CH_2CHR'NH_2\text{-}2)I(solvent)]^+$, formed during the reaction, which decomposed to give unidentified products. The enhanced electrophilicity of the palladium center in cationic or iodine-containing cyclopalladated complexes and their increased facility to undergo

reductive elimination is well documented.[14] However, the reaction of **A**, $Pd(OAc)_2$ and NaI in the same conditions used to prepare **1a-Cl** or **1a-Br** rendered the dimeric iodo-bridged ortho-palladated complex $[Pd_2(C,N\text{-}C_6H_4CH_2CH_2N{=}CMe_2\text{-}2)_2(\mu\text{-}I)_2]$ (**2**), that contained the imine arising from the condensation of phenethylamine and acetone (Scheme 3). Following an alternative method, the iodo-bridged ortho-metalated complexes $[Pd_2(C,N\text{-}C_6H_4CH_2CHR'NHR\text{-}2)_2(\mu\text{-}I)_2]$ (R = R' = H, X = I (**1a-I**); R = H, R' = CO_2Me, X = I (**1b-I**); R = Me, R' = H, X = I (**1c-I**)) were easily prepared in good yields by metathesis reaction of complexes **1a-OAc**, **1b-Cl** and **1c-Cl** with an excess of NaI in acetone (Scheme 3). We reported previously the synthesis of **1a-OAc** by palladation of phenethylamine.[17]

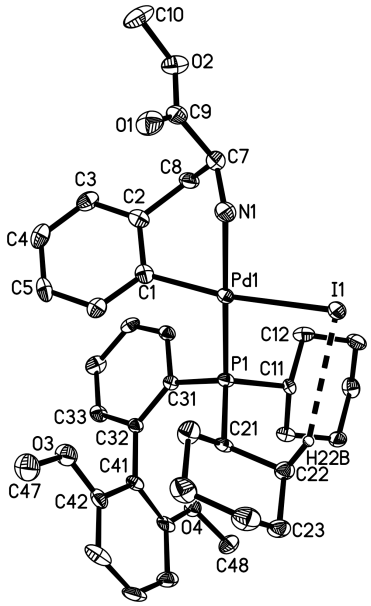


Figure 1. X-ray thermal ellipsoid plot (50% probability) of complex **3b-I**·$CHCl_3$ showing the labeling scheme (the solvent molecule and all the hydrogen atoms, excluding that involved in the hydrogen bond, have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–C(1) = 2.032(5), Pd(1)–N(1) = 2.126(4), Pd(1)–I(1) = 2.7060(5), Pd(1)–P(1) = 2.2848(12); C(1)–Pd(1)–N(1) = 84.32(17), N(1)–Pd(1)–I(1) = 86.60(12), I(1)–Pd(1)–P(1) = 93.82(3), P(1)–Pd(1)–C(1) = 95.29(13).

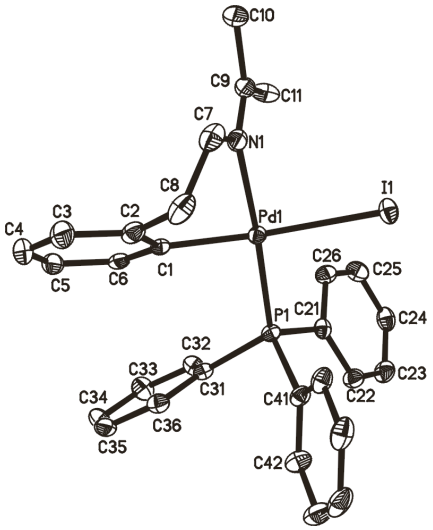


Figure 2. X-ray thermal ellipsoid plot (50% probability) of complex **4** showing the labeling scheme (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–C(1) = 2.009(2), Pd(1)–N(1) = 2.109(2), Pd(1)–I(1) = 2.7279(3), Pd(1)–P(1) = 2.2630(6), N(1)–C(9) = 1.282 (3); C(1)–Pd(1)–N(1) = 82.90(8), N(1)–Pd(1)–I(1) = 89.39(5), I(1)–Pd(1)–P(1) = 94.081(17), P(1)–Pd(1)–C(1) = 93.56(7).

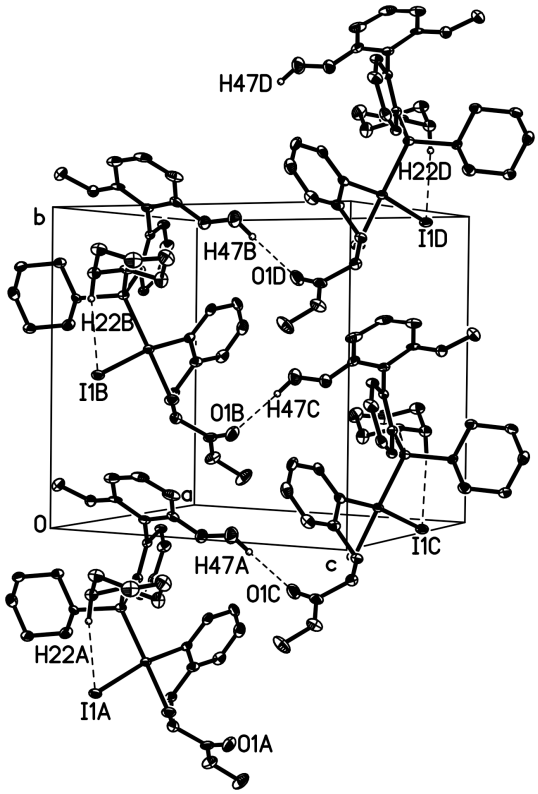


Figure 3. View of the hydrogen bond interactions in complex **3b-I**·$CHCl_3$. Only atoms involved in the

H bonding are labeled.

It is well known that the halo-bridges in dimeric ortho-palladated complexes containing primary arylalkylamines are easily split by various neutral ligands, including phosphines, pyridines or isocyanides.[4,5,11,15] Thus, the reaction of complex **1a-Cl**, **1a-Br** or **1b-I** with two equivalents of 2-dicyclohexylphosphino-2',6'-dimethoxyphenyl (SPhos) allowed the synthesis of the mononuclear phosphino-derivative **3a-Cl**, **3a-Br** or **3b-I**. Similarly, the imino-complex **2** reacted with PPh_3 (in a 1:2 molar ratio) to give compound **4**. Given the great stability of complexes **1**, it seems that any study on the catalytic properties of complexes **3** would gain flexibility if different phosphines can be tested using complexes **1** as starting materials. Complex **3a-Cl** has been previously prepared by Buchwald et al. via his two-step one-pot synthesis (Scheme 1) in an 85% yield. Although the overall yield for the synthesis of complex **3a-Cl** using our method is slightly lower (78%), the advantages are evident: 1) the starting materials ($Pd(OAc)_2$, phenethylamine, NaCl) are easily available and all but the common SPhos are much cheaper than those required for Buchwald's method; (2) the reactions are carried out without special precautions against air or moisture; (3) the dinuclear halo-bridged ortho-metalated complexes are extraordinarily stable in solid state and can be stored for very long periods of time; (4) these dinuclear complexes are very versatile, as different neutral ligands can split the halo-bridges to give mononuclear derivatives, such as other P-donor (other bulky phosphines or chiral ones) or N-donor (amines, pyridines) ligands; and (5) our method allows to change in a facile way the cyclometalated phenethylamine fragment as well as the halo ligand coordinated to Pd(II), thus modifying the chemical and physical properties of the palladacycle.[16]

NMR Spectra. The ^1H and ^{13}C NMR spectra of complexes **1a-Br**, **1b-Br**, **1c-Br** and **3a-Cl** are in agreement with the reported data.[2,4,7,13] For all the new compounds, their spectroscopic data correspond with the proposed structures. Thus, the halide-bridged orthometalated complexes exhibit in the aromatic region of their ^1H NMR spectra (DMSO-d_6) a set of two signal corresponding to the four remaning

protons of the cyclopalladated ring: a doublet (**1a-Cl**, **1a-I**, **1b-Cl**, **1c-Cl**, **2**) or a broad singlet (**1b-I**, **1c-I**) assigned to H6 (δ: 7.43–7.51 ppm; see Chart 1 for the numbering scheme), and a multiplet assigned to H3 + H4 + H5 (δ: 6.70–7.10 ppm). In the ^{13}C NMR spectra of these complexes, the resonances due to the carbon atoms bonded to Pd, when observed, are deshielded with respect to that of the corresponding triflate ($\Delta\delta$ = 18–20 ppm), as it occurs in other cyclopalladated complexes.[17] The protons of the NH_2 or CH_2 groups resonate as one broad signal in the complexes containing phenethylamine, while they become diastereotopic for (L)-phenylalanine methyl ester and *N*-methyl-phenethylamine derivatives. The ^{31}P NMR spectrum of complexes **3a-Cl**, **3a-Cl** and **3b-I** show a very broad singlet, suggesting dissociation of the phosphine favoured by its steric requirement.

Crystal Structures. The crystal structures of complexes **3b-I**·$CHCl_3$ (Figure 1) and **4** (Figure 2) have been determined by X-ray diffraction studies and they show the palladium atom in a slightly-distorted (**3b-I**·$CHCl_3$) or distorted (**4**) square-planar environment (mean deviation from the plane: 0.0224 Å, **3b-I**·$CHCl_3$; 0.0877 Å, **4**) with dihedral angles of 2.1º (**3b-I**·$CHCl_3$) and 9.6º (**4**) between the N(1)–Pd(1)–C(1) and P(1)–Pd(1)–I(1) planes. In both complexes, the chelated amino (**3I-b**·$CHCl_3$) or imino ligand (**4**) forms a six-membered metallacycle with a boat conformation. The features of complex **3b-I**·$CHCl_3$ and **4** are similar to those of analogous phosphino-complexes containing primary ortho-metalated phenethylamines,[2,4,5] or related imino-ligands.[18] The X-ray crystallographic study reveals the (*S*) absolute configuration of the α-carbon stereocenter in complex **3I-b**·$CHCl_3$. This complex exhibits an intramolecular non-classical hydrogen bond between the iodine atom and one hydrogen of the cyclohexyl group; besides, each molecule is connected to other two through hydrogen bonds between the oxygen atom of the carbonyl group and one of the hydrogen atoms of the OMe substituent on the biaryl group, giving rise to zigzag chains along the *b*-axis (Figure 3).

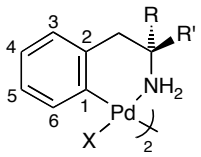
EXPERIMENTAL SECTION

General procedures. Infrared spectra were recorded on a Perkin Elmer 16F-PC-FT spectrometer. C, H,

N and S analyses, conductance measurements, and melting point determinations were carried out as described elsewhere.[13] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ in Bruker Avance 300 or 400 spectrometers. Chemical shifts are referenced to TMS [^{1}H and ^{13}C{^{1}H}]. Signals in the ^{1}H and ^{13}C NMR spectra of all complexes were assigned with the help of HMQC and HMBC techniques. Reactions were carried out at room temperature without special precautions against moisture.

Trifluoromethanesulfonic acid (triflic acid), 2-(phenyl)ethylamine (phenethylamine), L-phenylalanine methyl ester, *N*-methyl-phenethylamine, 2-dicyclohexylphosphino-2',6'-dimethoxyphenyl (SPhos; Aldrich), PPh_3 (Fluka), NaCl (J. T. Baker), NaBr, NaI (Scharlau), and $Pd(OAc)_2$ (Johnson Matthey) were used as received. Chart 1 gives the numbering scheme for the palladacycles.

Chart 1. Numbering Scheme for Ortho-Metalated Palladacycles



Synthesis of [$C_6H_5CH_2CH_2NH_3$]OTf (A). Triflic acid (2.5 mL of a solution that contains 11.3 mmol/L, 28.25 mmol) was slowly added to a solution of phenethylamine (3 mL, 23.89 mmol) in Et_2O (50 mL), and the resulting white suspension was vigorously stirred for 20 min. The mixture was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give compound **A** as a white solid. Yield: 5.46 g, 20.13 mmol, 84%. Mp: 204 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 125 (7.4 x 10^{-4} M). Anal. Calcd for $C_9H_{12}F_3NO_3S$ (271.257): C, 39.85; H, 4.46; N, 5.16; S, 11.82. Found: C, 39.81; H, 4.41; N, 5.18; S, 11.79. IR (cm^{-1}): ν(NH) 3177 vs. ^{1}H NMR (400.91 MHz, DMSO-d_6): δ 2.84 (m, 2 H, CH_2Ar), 3.04 (m, 2 H, CH_2N), 7.22–7.27 (m, 3 H, *p*-H and *o*- or *m*-H, C_6H_5), 7.30–7.35 (m, 2 H, *o*- or *m*-H, C_6H_5), 7.73 (br s, 3 H, NH_3). ^{13}C NMR (100.81 MHz): δ 33.1 (s, CH_2Ar), 40.0 (s, CH_2N), 126.8 (s, *p*-CH, C_6H_5), 128.6 (s, *o*- or *m*-CH, C_6H_5), 128.7 (s, *o*- or *m*-CH, C_6H_5), 137.2 (s, *i*-C, C_6H_5).

Synthesis of (*S*)-[$C_6H_5CH_2CH(CO_2Me)NH_3$]OTf (B). Na_2CO_3 (600 mg, 5.66 mmol) was added to a solution of L-phenylalanine methyl ester hydrochloride (1.00 g, 4.64 mmol) in water (15 mL) and the

resulting solution was stirred for 15 min. The reaction mixture was extracted with CH_2Cl_2 (3 x 15 mL), and the combined organic layers were dried over $MgSO_4$. The suspension was filtered, the filtrate was concentrated to ca. 5 mL, triflic acid (0.5 mL of a solution that contains 11.3 mmol/L, 5.65 mmol) was slowly added, and the resulting white suspension was vigorously stirred for 10 min. The mixture was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of compound B as a white solid (1.10 g). The filtrate was concentrated to ca. 3 mL and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a second crop of compound **B** as a white solid (300 mg). Yield: 1.40 g, 4.25 mmol, 92%. Mp: 151 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 126 (5.2 x 10^{-4} M). Anal. Calcd for $C_{11}H_{14}F_3NO_5S$ (329.293): C, 40.12; H, 4.29; N, 4.25; S, 9.74. Found: C, 39.90; H, 4.40; N, 4.23, S, 9.57. IR (cm^{-1}): ν(NH) 3224 vs; ν(CO) 1741 vs. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 3.06 (m, 2 H, CH_2), 3.69 (m, 2 H, Me), 4.33 (t, 1 H, CH, $^3J_{HH}$ = 6.6 Hz), 7.18–7.23 (m, 3 H, *o*-H, C_6H_5), 7.25–7.37 (m, 3 H, *m*-H and *p*-H, C_6H_5), 8.37 (br s, 3 H, NH_3). ^{13}C NMR (75.45 MHz, DMSO-d_6): δ 36.0 (s, CH_2), 52.7 (s, Me), 53.2 (s, CH), 120.7 (q, CF_3, $^1J_{CF}$ = 322.2 Hz), 127.4 (s, *p*-CH, C_6H_5), 128.7 (s, *m*-CH, C_6H_5), 129.4 (s, *o*-CH, C_6H_5), 134.4 (s, *i*-C, C_6H_5), 169.5 (s, CO).

Synthesis of [$C_6H_5CH_2CH_2NH_2Me$]OTf (C). Triflic acid (1.5 mL of a solution that contains 11.3 mmol/L, 16.95 mmol) was slowly added to a solution of *N*-methyl-phenethylamine (2.5 mL, 17.19 mmol) in Et_2O (40 mL), and the resulting white suspension was vigorously stirred for 15 min. The mixture was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give compound **C** as a white solid. Yield: 4560 mg, 15.98 mmol, 94%. Mp: 124 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 116 (7.43 x 10^{-4} M). Anal. Calcd for $C_{10}H_{14}F_3NO_3S$ (285.283): C, 42.10; H, 4.95; N, 4.91; S, 11.24. Found: C, 42.35; H, 4.75; N, 5.03; S, 11.27. IR (cm^{-1}): ν(NH) 3219 s, 3030 s. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 2.59 (s, 3 H, Me), 2.88 (m, 2 H, CH_2Ar), 3.14 (m, 2 H, CH_2N), 7.22–7.28 (m, 3 H, *o*- and *p*-H, C_6H_5), 7.31–7.37 (m, 2 H, *m*-H, C_6H_5), 8.32 (br s, 2 H, NH_2). ^{13}C NMR (75.45 MHz, DMSO-d_6): δ 31.5 (s, CH_2Ar), 32.6 (s, Me), 49.1 (s, CH_2N), 126.8 (s, *p*-CH, C_6H_5), 128.7 (s, *o*-CH and *p*-CH, C_6H_5), 137.0 (s, *i*-C, C_6H_5).

Synthesis of [Pd_2(*C*,*N*-$C_6H_4CH_2CH_2NH_2$-2)$_2$(μ-OAc)$_2$] (1a-OAc). Phenethylamine (0.5 mL, 3.982 mmol) was added to a suspension of $Pd(OAc)_2$ (894 mg, 3.982 mmol) in acetonitrile (55 mL), and the resulting mixture was heated at 60 ºC for 2 h and then at 78 ºC for 6 h. Decomposition to metallic palladium was observed. The mixture was filtered through a plug of Celite/Na_2CO_3, the solvent was removed from the filtrate, and CH_2Cl_2 (2 mL) and Et_2O (30 mL) were added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **1a-OAc** as a yellow solid. Yield: 815 mg, 1.427 mmol, 72%. Dec pt: 148 °C. Anal. Calcd for $C_{20}H_{26}N_2O_4Pd_2$ (571.238): C, 42.05; H, 4.59; N, 4.90. Found: C, 41.57; H, 4.57; N, 4.73. IR (cm^{-1}): ν(NH) 3319 m, 3301 s, 3193 s, 3112 s; ν(CO) 1594 vs, 1550 vs. ^{1}H NMR (300.10 MHz, DMSO-d_6): δ 1.77 (s, 3 H, Me), 2.35 (br s, 2 H, CH_2N), 2.90 (m, 2 H, CH_2Ar), 5.68 (br s, 2 H, NH_2), 6.85–6.97 (m, 3 H, H3 + H4 + H5), 7.42 (d, 1 H, H6, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR (100.81 MHz, DMSO-d_6): δ 29.9 (s, Me), 36.4 (s, CH_2N), 42.9 (s, CH_2Ar), 124.4 (s, CH, C4 + C5), 125.9 (s, CH, C3), 134.0 (s, CH, C6), 140.1 (s, C2), 143.7 (s, C1, C–Pd), 177.1 (br s, CO). The synthesis of **1a-OAc** was previously reported by us, although without experimental details and spectroscopical data.[17]

Synthesis of [Pd_2(*C*,*N*-$C_6H_4CH_2CH_2NH_2$-2)$_2$(μ-Cl)$_2$] (1a-Cl). The ammonium triflate **A** (1000 mg, 3.686 mmol) was added to a suspension of $Pd(OAc)_2$ (827.6 mg, 3.686 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 ºC for 2 h and then at 78 ºC for 4 h. The mixture was filtered through a plug of Celite/Na_2CO_3, the solvent was removed from the filtrate, acetone (30 ml) and NaCl (2000 mg, 34.22 mmol) were added, and the suspension was stirred for 12 h. The mixture was filtered, the solvent was removed from the filtrate, and CH_2Cl_2 (40 mL) was added. The suspension was filtered through a plug of Celite, solvent was removed from the filtrate, and the residue was vigorously stirred in Et_2O (15 mL) for 15 min. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **1a-Cl** as a pale orange solid. Yield: 886 mg, 1.691 mmol, 92%. Dec pt: 163 °C. Anal. Calcd for $C_{16}H_{20}Cl_2N_2Pd_2$ (524.056): C, 36.67; H, 3.85; N, 5.35. Found: C, 36.43; H, 3.87; N, 5.26. IR (cm^{-1}): ν(NH) 3300 s, 3228 m. ^{1}H NMR (300.10 MHz, DMSO-d_6): δ 2.33 (br s, 2 H, CH_2N),

2.83 (m, 2 H, CH_2Ar), 4.75 (br s, 2 H, NH_2), 6.85–6.97 (m, 3 H, H3 + H4 + H5), 7.46 (d, 1 H, H6, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR (100.81 MHz, DMSO-d_6): δ 37.3 (s, CH_2N), 42.7 (s, CH_2Ar), 124.5 (s, CH, C4 + C5), 125.9 (s, CH, C3), 133.9 (s, CH, C6), 140.0 (s, C2), 147.4 (s, C1, C–Pd).

Synthesis of [Pd$_2$(*C*,*N*-C$_6$H$_4$CH$_2$CH$_2$NH$_2$-2)$_2$(μ-Br)$_2$] (1a-Br). The ammonium triflate **A** (1000 mg, 3.686 mmol) was added to a suspension of $Pd(OAc)_2$ (828 mg, 3.688 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 ºC for 2 h and then at 78 ºC for 3.5 h. The mixture was filtered through a plug of Celite/Na_2CO_3, the solvent was removed from the filtrate, acetone (30 ml) and NaBr (2000 mg, 19.44 mmol) were added, and the suspension was stirred for 18 h. Solvent was removed and the residue was vigorously stirred in Et_2O (25 mL) for 15 min. The suspension was filtered, and the solid was washed with H_2O (3 x 10 mL) and Et_2O (3 x 5 mL) and air-dried to give complex **1a-Br** as a yellow solid. Yield: 840 mg, 1.37 mmol, 74%. Dec pt: 158 °C. Anal. Calcd for $C_{16}H_{20}Br_2N_2Pd_2$ (612.992): C, 31.35; H, 3.29; N, 4.57. Found: C, 31.36; H, 3.18; N, 4.54. IR (cm^{-1}): ν(NH) 3265 s, 3218 w. ^{1}H NMR (400.91 MHz, DMSO-d_6): δ 2.35 (m, 2 H, CH_2N), 2.85 ("t", 2 H, CH_2Ar, $^3J_{HH}$ = 5.6 Hz), 4.75 (br s, 2 H, NH_2), 6.85–6.96 (m, 3 H, H3 + H4 + H5), 7.46 (d, 1 H, H6, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR (100.81 MHz, DMSO-d_6): δ 37.3 (s, CH_2N), 42.5 (s, CH_2Ar), 124.6 (br s, CH, C4 + C5), 126.0 (s, CH, C3), 133.4 (s, CH, C6), 139.7 (s, C2), 149.1 (br s, C1, C–Pd). Spectroscopic data are in accordance with the data reported in the literature.[4]

Synthesis of [Pd$_2$(*C*,*N*-C$_6$H$_4$CH$_2$CH$_2$NH$_2$-2)$_2$(μ-I)$_2$] (1a-I). NaI (525 mg, 3.50 mmol) was added to solution of **1a-OAc** (200 mg, 0.350 mmol) in acetone (50 mL) and the suspension was stirred for 16 h. Solvent was removed, CH_2Cl_2 (40 mL) was added, and the resulting suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex 1a-I as a dark orange solid (120 mg). The filtrate was concentrated to ca. 4 mL and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a second crop of complex **1a-I** as a dark orange solid (110 mg). Yield: 230 mg, 0.325 mmol, 93%. Mp:

158 °C. Anal. Calcd for $C_{16}H_{20}I_2N_2Pd_2$ (706.992): C, 27.18; H, 2.85; N, 3.96. Found: C, 27.08; H, 2.67; N, 3.86. IR (cm^{-1}): ν(NH) 3180 m, 3282 m. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 2.37 (m, 2 H, CH_2N), 2.87 ("t", 2 H, CH_2Ar, $^3J_{HH}$ = 5.4 Hz), 4.74 (br s, 2 H, NH_2), 6.70–7.07 (m, 3 H, H3 + H4 + H5), 7.50 (d, 1 H, H6, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR (75.45 MHz, DMSO-d_6): δ 37.2 (s, CH_2N), 42.3 (s, CH_2Ar), 124.3 (br s, CH, C4 + C5), 126.1 (s, CH, C3), 128.5 (s, CH, C6), 139.7 (s, C2). The ^{13}C resonance corresponding to C1 (C–Pd) was not observed.

Synthesis of (*S*,*S*)-[Pd$_2${*C*,*N*-C$_6$H$_4$CH$_2$CH(CO$_2$Me)NH$_2$-2}$_2$(μ-Cl)$_2$] (1b-Cl). The ammonium triflate **B** (1200 mg, 3.645 mmol) was added to a suspension of $Pd(OAc)_2$ (820 mg, 3.653 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 ºC for 2 h and then at 79 ºC for 4 h. The mixture was filtered through a plug of Celite/Na_2CO_3, the solvent was removed from the filtrate, acetone (40 ml) and NaCl (3000 mg, 51.33 mmol) were added, and the suspension was stirred for 12 h. The solvent was removed, and CH_2Cl_2 (40 ml) was added. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (30 ml) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of the complex **1b-Cl** as an orange solid (700 mg, 1.093 mmol). The filtrate was concentrated to ca. 4 mL and *n*-hexane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-hexane (2 x 5 mL) and air-dried to give a second crop of the complex **1b-Cl** as an orange solid (450 mg, 0.703 mmol). Yield: 1150 mg, 2.796 mmol, 98%. Mp: 142 °C dec. Anal. Calcd for $C_{20}H_{24}Cl_2N_2O_4Pd_2$ (640.128): C, 37.52; H, 3.79; N, 4.37. Found: C, 37.57; H, 3.89; N, 4.49. IR (cm^{-1}): ν(NH) 3284 m, 3232 m; ν(CO) 1735 s. ^{1}H NMR (400.91 MHz, DMSO-d_6): 3.10 (dd, 1 H, CH_2, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 9.6 Hz), 3.20 (dd, 1 H, CH_2, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.6 Hz), 3.27–3.35 (m, partially obscured by the signal of H_2O of the deuterated solvent, 1 H, CH), 4.46 (br s, 1 H, NH_2), 5.49 (m, 1 H, NH_2), 6.92–7.00 (m, 3 H, H3 + H4 + H5), 7.45 (d, 1 H, H6, $^3J_{HH}$ = 7.6 Hz). ^{13}C NMR (100.81 MHz, DMSO-d_6): δ 45.5 (s, CH_2), 50.2 (s, CH), 52.8 (s, Me), 124.7 (s, CH, C4), 125.3 (s, CH, C5), 126.6 (s, CH, C3), 133.4 (s, CH, C6), 137.7 (s, C2), 147.6 (s, C1, C–Pd), 172.2 (s, CO).

Synthesis of (*S*,*S*)-[Pd$_2${*C*,*N*-C$_6$H$_4$CH$_2$CH(CO$_2$Me)NH$_2$-2}$_2$(μ-Br)$_2$] (1b-Br). The ammonium triflate **B** (1500 mg, 4.57 mmol) was added to a suspension of $Pd(OAc)_2$ (1028 mg, 4.58 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 65 ºC for 2 h and then at 78 ºC for 4 h. The mixture was filtered through a plug of Celite and Na_2CO_3, the solvent was removed form the filtrate, acetone (30 ml) and NaBr (3000 mg, 29.16 mmol) were added, and the suspension was stirred for 12 h. The solvent was removed, and CH_2Cl_2 (40 ml) was added. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 ml, and Et_2O (40 ml) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of the complex 1b-Br as a pale orange solid (972 mg, 1.33 mmol). The filtrate was concentrated to ca. 5 mL and *n*-pentane (30 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a second crop of the complex **1b-Br** as a pale orange solid (510 mg, 0.70 mmol). Yield: 1.482 g, 2.03 mmol, 89%. Anal. Calcd for $C_{20}H_{24}Br_2N_2O_4Pd_2$ (729.064): C, 32.95; H, 3.32; N, 3.84. Found: C, 32.79; H, 3.04; N, 3.85. IR (cm^{-1}): ν(NH) 3278 w, 3233 w; ν(CO) 1733 s. Spectroscopic data are in accordance with the data reported in the literature.[7]

Synthesis of (*S*,*S*)-[Pd$_2${*C*,*N*-C$_6$H$_4$CH$_2$CH(CO$_2$Me)NH$_2$-2}$_2$(μ-I)$_2$] (1b-I). NaI (470 mg, 3.13 mmol) was added to solution of **1b-Cl** (200 mg, 0.312 mmol) in acetone (50 mL) and the suspension was stirred for 16 h. Solvent was removed, CH_2Cl_2 (40 mL) was added, and the resulting suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **1a-I** as a dark orange solid (190 mg). Yield: 230 mg, 0.231 mmol, 74%. Mp: 179 °C dec. Anal. Calcd for $C_{20}H_{24}I_2N_2O_4Pd_2$ (823.07): C, 29.19; H, 2.94; N, 3.40. Found: C, 28.90; H, 2.81; N, 3.10. IR (cm^{-1}): ν(NH) 3241 w, 3172 w; ν(CO) 1724 vs. ^{1}H NMR (400.91 MHz, DMSO-d_6): 3.11 (br m, 1 H, CH_2), 3.20 (dd, 1 H, CH_2, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.6 Hz), 3.34–3.41 (br m, partially obscured by the signal of H_2O of the deuterated solvent, 1 H, CH), 3.70 (s. 3 H, Me), 4.57 (br s, 1 H, NH_2), 5.38 (br s, 1 H, NH_2), 6.70–7.05 (m, 3 H, H3 + H4 + H5), 7.51 (br s, 1 H, H6). ^{13}C NMR (100.81 MHz, DMSO-d_6): δ

45.3 (br s, CH_2), 50.1 (s, CH), 52.8 (s, Me), 125.0 (br s, CH), 126.7 (s, CH), 137.3 (s, C2), 172.3 (s, CO). The ^{13}C resonance corresponding to C1 (C–Pd) was not observed.

Synthesis of [Pd_2(*C*,*N*-$C_6H_4CH_2CH_2NHMe$-2)$_2$(μ-Cl)$_2$] (1c-Cl). The ammonium triflate C (800 mg, 2.804 mmol) was added to a suspension of $Pd(OAc)_2$ (629.5 mg, 2.804 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 ºC for 2 h and then at 78 ºC for 2 h. The mixture was filtered through a plug of Celite/Na_2CO_3, the solvent was removed from the filtrate, acetone (30 ml) and NaCl (2000 mg, 34.22 mmol) were added, and the suspension was stirred for 18 h. The solvent was removed, and CH_2Cl_2 (40 mL) was added. The suspension was filtered through a plug of Celite, solvent was removed from the filtrate, and the residue was vigorously stirred in Et_2O (15 mL) for 30 min. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **1c-Cl** as a pale orange solid. Yield: 510 mg, 0.924 mmol, 66%. Mp: 142 °C. Anal. Calcd for $C_{18}H_{24}Cl_2N_2Pd_2$ (552.142): C, 39.16; H, 4.38; N, 5.07. Found: C, 38.81; H, 4.58; N, 5.36. IR (cm^{-1}): ν(NH) 3226 s. ^1H NMR (400.91 MHz, DMSO-d_6): δ 1.68 (m, 1 H, CH_2N), 2.32 (d, 3 H, Me, $^3J_{HH}$ = 5.2 Hz), 2.83 (m, 1 H, CH_2Ar), 2.94 (m, 1 H, CH_2Ar), 3.03 (m, 1 H, CH_2N), 5.55 (br s, 1 H, NH), 6.84–7.10 (m, 3 H, H3 + H4+ H5), 7.43 (d, 1 H, H6, $^3J_{HH}$ = 7.6 Hz). ^{13}C NMR (100.81 MHz, DMSO-d_6): δ 40.5 (s, CH_2Ar), 42.3 (s, Me), 49.6 (s, CH_2N), 124.6 (s, CH, C4 or C5), 124.7 (s, CH, C4 or C5), 126.0 (s, CH, C3), 133.7 (s, CH, C6), 140.3 (s, C2), 148.3 (br s, C1, C–Pd).

Synthesis of [Pd_2(*C*,*N*-$C_6H_4CH_2CH_2NHMe$-2)$_2$(μ-Br)$_2$] (1c-Br). The ammonium triflate C (800 mg, 2.804 mmol) was added to a suspension of $Pd(OAc)_2$ (629.5 mg, 2.804 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 ºC for 2 h and then at 70 ºC for 3 h. The mixture was filtered through a plug of Celite/Na_2CO_3, the solvent was removed from the filtrate, acetone (30 ml) and NaBr (1500 mg, 14.58 mmol) were added, and the suspension was stirred for 18 h. The solvent was removed, and CH_2Cl_2 (40 mL) was added. The suspension was filtered through a plug of Celite, solvent was removed from the filtrate, and the residue was vigorously stirred in Et_2O (15 mL) for 30 min. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give crude

complex **1c-Br** as an orange solid. Yield: 714 mg, 1.114 mmol, 79%. Crude **1c-Br** was recrystallized from CH_2Cl_2/Et_2O to give an spectroscopically pure sample (recrystallization yield. 76%). IR (cm^{-1}): ν(NH) 3229. ^{1}H NMR (300.10 MHz): δ 1.99 (m, 1 H, CH_2N), 2.68 (d, 3 H, Me, $^3J_{HH}$ = 6.0 Hz), 2.98 (m, 2 H, 1 H of CH_2Ar + 1 H of CH_2N), 3.20 (m, 1 H, CH_2Ar), 3.82 (br s, 1 H, NH), 6.78–6.86 (m, 2 H, H3 + H5), 6.93 (t, 1 H, H4, $^3J_{HH}$ = 6.9 Hz), 7.39 (br d, 1 H, H6, $^3J_{HH}$ = 6.0 Hz). Spectroscopic data are in accordance with the data reported in the literature.[13]

Synthesis of [Pd$_2$(*C*,*N*-C$_6$H$_4$CH$_2$CH$_2$NHMe-2)$_2$(μ-I)$_2$] (1c-I). NaI (382 mg, 2.544 mmol) was added to solution of **1c-Cl** (140 mg, 0.254 mmol) in acetone (50 mL) and the suspension was stirred for 16 h. Solvent was removed, CH_2Cl_2 (40 mL) was added, and the resulting suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **1a-I** as a dark orange solid. Yield: 153 mg, 0.208 mmol, 83%. Mp: 155 °C dec. Calcd for $C_{18}H_{24}I_2N_2Pd_2$ (735.052): C, 29.41; H, 3.29; N, 3.81. Found: C, 29.53; H, 2.84; N, 3.74. IR (cm^{-1}): ν(NH) 3484 m, 3434 m, 3236 m. ^{1}H NMR (400.91 MHz, DMSO-d_6): δ 1.71 (br s, 1 H, CH_2N), 2.26 (d, 3 H, Me, $^3J_{HH}$ = 5.6 Hz), 2.85 (br m, 1 H, CH_2Ar), 2.91–3.20 (m, 2 H, 1 H of CH_2Ar + 1 H of CH_2N), 5.43 (br s, 1 H, NH), 6.70–7.05 (m, 3 H, H3 + H4 + H5), 7.43 (br s, 1 H, H6). ^{13}C NMR (100.81 MHz, DMSO-d_6): δ 40.4 (s, CH_2Ar), 42.8 (br s, Me), 49.4 (s, CH_2N), 124.2 (br s, CH), 126.0 (s, CH), 139.7 (br s, C2). The ^{13}C resonance corresponding to C1 (C–Pd) was not observed.

Synthesis of [Pd$_2$(*C*,*N*-C$_6$H$_4$CH$_2$CH$_2$N=CMe$_2$-2)$_2$(μ-I)$_2$] (2). The ammonium triflate A (1000 mg, 3.686 mmol) was added to a suspension of $Pd(OAc)_2$ (828 mg, 3.688 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 78 ºC for 4 h. The mixture was filtered through a plug of Celite/Na_2CO_3, the solvent was removed from the filtrate, acetone (30 ml) and NaI (2000 mg, 13.34 mmol) were added, and the suspension was stirred for 18 h. The solvent was removed, and the residue was stirred in Et_2O (30 mL) for 15 min. The suspension was filtered, and the solid was washed with H_2O (3 x 10 mL), acetone (2 x 5 mL) and Et_2O (2 x 5 mL), and air-dried to give complex **2** as a bright yellow

solid. Yield: 952 mg, 1.209 mmol, 66%. Dec pt: 198 °C. Anal. Calcd for $C_{22}H_{28}I_2N_2Pd_2$ (787.088): C, 33.57; H, 3.58; N, 3.55. Found: C, 33.27; H, 3.51; N, 3.52. IR (cm^{-1}): ν(C=N) 1644 m, 1629 m. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 1.97 (s, 3 H, Me), 2.51 (s, 3 H, Me), 2.97 (m, 2 H, 1 H of CH_2Ar + 1 H of CH_2N), 3.20 (m, 1 H, CH_2), 3.83 (br s, 1 H, CH_2), 6.70–6.90 (m, 3 H, H3 + H4 + H5), 7.29 (d, 1 H, H6, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR (75.45 MHz, DMSO-d_6): δ 22.2 (s, Me), 38.2 (br s, CH_2Ar), 49.1 (s, CH_2N), 124.1 (br s, CH, C_6H_4), 124.8 (br s, CH, C_6H_4), 125.7 (s, CH, C_6H_4), 139.7 (s, C, C_6H_4), 179.4 (s, C=N).

Synthesis of [Pd(*C*,*N*-$C_6H_4CH_2CH_2NH_2$-2)Cl(SPhos)] (3a-Cl). SPhos (188 mg, 0.458 mmol) was added to a suspension of complex **1a-Cl** (120 mg, 0.229 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of $MgSO_4$, solvent was removed from the filtrate, and the residue was vigorously stirred in *n*-pentane (15 mL). The suspension was filtered, and the solid was washed with *n*-pentane (2 x 1 mL) and air-dried to give complex **3a-Cl** as a pale yellow solid. Yield: 260 mg, 0.387 mmol, 85%. Mp: 176 °C dec. Anal. Calcd for $C_{34}H_{45}ClNO_2PPd$ (672.566): C, 60.72; H, 6.74; N, 2.08. Found: C, 60.43; H, 7.10; N, 2.17. IR (cm^{-1}): ν(NH) 3323 m, 3245 m, 3214 m, 3137 m. ^{1}H NMR (400.91 MHz, CD_2Cl_2): δ 0.94 (br m, 2 H), 1.09 (br m, 4 H), 1.42 (br s, 2 H), 1.56 (br m, 4 H), 1.72 (br s, 2 H), 1.89 (br s, 2 H), 2.03 (br s, 2 H), 2.20 (br m, 2 H), 2.71 (br s, 2 H), 3.13 (br m, 2 H), 3.17 (br s, 2 H), 3.69 (s, 6 H, Me), 6.40 ("t", 1 H, $^3J_{HH}$ = 7.0 Hz), 6.66 (d, 2 H, $^3J_{HH}$ = 8.4 Hz), 6.69–6.77 (m, 2 H), 6.83 (dd, 2 H, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.6 Hz), 6.88 (br d, 1 H, $^3J_{HH}$ = 6.8 Hz), 7.15–7.25 (m, 2 H), 7.37 (t, 1 H, $^3J_{HH}$ = 8.4 Hz). ^{31}P NMR (CD_2Cl_2, 162.29 MHz): δ 55.0 (br s). Spectroscopic data are in accordance with the data reported in the literature.[2]

Synthesis of [Pd(*C*,*N*-$C_6H_4CH_2CH_2NH_2$-2)Br(SPhos)]·H_2O (3a-Br·H_2O). SPhos (160 mg, 0.390 mmol) was added to a suspension of complex **1a-Br** (120 mg, 0.196 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of $MgSO_4$, solvent was removed from the filtrate, and the residue was vigorously stirred in *n*-pentane (15 mL). The suspension was filtered, and the solid was washed with *n*-pentane (2 x 1 mL) and air-dried to give

complex **3a-Br·H_2O** as a pale yellow solid. Yield: 240 mg, 0.326 mmol, 84%. Dec pt: 214 °C. Anal. Calcd for $C_{34}H_{45}BrNO_2PPd·H_2O$ (735.037): C, 55.56; H, 6.44; N, 1.91. Found: C, 55.57; H, 6.65; N, 2.12. IR (cm^{-1}): ν(NH) 3307 m, 3230 m, 3145 w. ^{1}H NMR (400.91 MHz, CD_2Cl_2): δ 0.95 (br m, 2 H), 1.09 (br m, 4 H), 1.41 (br s, 2 H), 1.56 (br m, 4 H), 1,56 (s, 2 H, H_2O), 1.72 (br s, 2 H), 1.87 (br s, 2 H), 2.03 (br s, 2 H), 2.24 (br m, 2 H), 2.73 (br s, 2 H), 3.15 (br m, 4 H), 3.70 (s, 6 H, Me), 6.42 (br t, 1 H, $^3J_{HH}$ = 6.8 Hz), 6.67 (d, 2 H, $^3J_{HH}$ = 8.4 Hz), 6.67–6.74 (m, 2 H), 6.82–6.88 (m, 2 H), 7.14–7.24 (m 2 H), 7.39 (br t, 1 H, $^3J_{HH}$ = 8.4 Hz). ^{31}P NMR (CD_2Cl_2, 162.29 MHz): δ 55.1 (br s).

Synthesis of (*S*)-[Pd{*C*,*N*-$C_6H_4CH_2CH(CO_2Me)NH_2$-2}I(SPhos)] (3b-I). SPhos (120 mg, 0.292 mmol) was added to a solution of complex **1b-I** (120 mg, 0.146 mmol) in CH_2Cl_2 (20 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of $MgSO_4$, solvent was removed from the filtrate, and the residue was vigorously stirred in *n*-pentane (15 mL). The suspension was filtered, and the solid was washed with *n*-pentane (2 x 3 mL) and air-dried to give complex **3b-I** as an orange solid. Yield: 226 mg, 0.276 mmol, 94%. Mp: 169 °C. Anal. Calcd for $C_{36}H_{45}INO_4PPd$ (820.057): C, 52.73; H, 5.53; N, 1.71. Found: C, 52.50; H, 5.89; N, 1.75. IR (cm^{-1}): ν(NH) 3322 m, 3266 m; ν(CO) 1739 s. ^{1}H NMR (400.91 MHz): δ 1.01 (br m, 4 H), 1.45–1.8 (br m, 11 H), 1.90 (br s, 2 H), 2.26 (br s, 3 H), 3.21 (d, 1 H, $^2J_{HH}$ = 12.8 Hz), 3.67 (s, 3 H, Me), 3.69 (s, 3 H, Me), 3.70 (s, 3 H, Me), 3.80 (br s, 2 H), 3.91 (br s, 2 H), 6.45 (br m, 1 H), 6.65 (t, 2 H, $^3J_{HH}$ = 7.6 Hz), 6.70 (m, 3 H), 6.85 (br s, 1 H), 6.93 (m, 1 H), 7.13 (br s, 1 H), 7.19 (br m, 1 H), 7.37 (t, 1 H, $^3J_{HH}$ = 8.4 Hz). ^{31}P NMR (162.29 MHz): δ 57.8 (v br s). Single crystals of **3b-I·$CHCl_3$** suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **3b-I** in $CHCl_3$.

Synthesis of [Pd(*C*,*N*-$C_6H_4CH_2CH_2N{=}CMe_2$-2)I(PPh_3)] (4). PPh_3 (67 mg, 0.255 mmol) was added to a suspension of complex 2 (100 mg, 0.127 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 1 h. The mixture was filtered through a plug of $MgSO_4$, solvent was removed from the filtrate, and the residue was vigorously stirred in Et_2O (15 mL) for 15 min. The suspension was filtered, and the solid was washed with Et_2O (2 x 1 mL) and air-dried to give complex **4** as a pale orange solid.

Yield: 147 mg, 0.224 mmol, 88%. Mp: 207 °C dec. Anal. Calcd for $C_{29}H_{29}INPPd$ (655.836): C, 53.11; H, 4.46; N, 2.14. Found: C, 53.14; H, 4.69; N, 2.21. IR (cm^{-1}): ν(C=N) 1659 m. ^{1}H NMR (400.91 MHz): δ 1.92 (s, 3 H, Me), 2.55 (br s, 3 H, Me), 2.99 (dd, 1 H, CH_2Ar, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 4.0 Hz), 3.08 (m, 1 H, CH_2N), 3.80 (m, 1 H, CH_2N), 4.27 (td, $^2J_{HH}$ = $^3J_{HH}$ = 13.4, $^3J_{HH}$ = 6.4 Hz), 6.27–6.32 (m, 2 H, H4 + H6), 6.71 (td, 1 H, H5, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 2.0 Hz), 6.81 (d, 1 H, H3, $^3J_{HH}$ = 7.6 Hz), 7.25–7.30 (m, 6 H, *m*-H, PPh_3), 7.33–7.38 (m, 3 H, *p*-H, PPh_3), 7.53–7.58 (m, 6 H, *o*-H, PPh_3). ^{13}C NMR (100.81 MHz): δ 22.2 (d, Me, $^4J_{CP}$ = 5 Hz), 34.3 (s, Me), 39.1 (s, CH_2Ar), 49.7 (s, CH_2N), 123.3 (s, CH5, C_6H_4), 125.3 (s, CH3 + CH6, C_6H_4), 127.8 (d, *m*-CH, PPh_3, $^3J_{CP}$ = 10.5 Hz), 130.0 (d, *p*-CH, PPh_3, $^4J_{CP}$ = 1.9 Hz), 132.0 (d, *i*-C, PPh_3, $^1J_{CP}$ = 50.1 Hz), 134.9 (d, *o*-CH, PPh_3, $^2J_{CP}$ = 11.3 Hz), 134.9 (s, CH4, C_6H_4), 140.1 (s, C2, C_6H_4), 155.6 (s, C1, C–Pd), 176.7 (s, C=N). ^{31}P NMR (162.29 MHz): δ 33.9 (s). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **4** in CH_2Cl_2.

Single-Crystal X-ray Structure Determinations. Relevant crystallographic data and details of the refinements for the structures of compounds **3b-I**·$CHCl_3$ and **4** are summarized in Table 1. Data Collection: Crystals suitable for X-ray diffraction were mounted in inert oil on a glass fiber and transferred to a Bruker SMART APEX diffractometer. Data were recorded at 100(2)K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and *ω*-scan mode. Multiscan absorption corrections were applied. Solution and Refinements: Crystal structures were solved by direct (**3b-I**·$CHCl_3$) or Patterson method (**4**) and all nonhydrogen atoms refined anisotropically on *F*2 using the program SHELXL-97.[19] Hydrogen atoms were refined as follows: Complex **3b-I**·$CHCl_3$: NH_2, free; methyl, rigid group; all others, riding. Complex **4**: methyl, rigid group; all others, riding. Special features: Complex **3b-I**·$CHCl_3$: absolute structure (Flack) parameter[20] -0.009(17); the chloroform is disordered over two positions with a ca. 60:40 occupancy distribution.

CONCLUSION

In summary, we report a new, useful, simple, atom efficient, flexible and inexpensive synthesis of chloro-, bromo- and iodo-complexes of Pd(II) containing ortho-metalated primary or secondary phenethylamines, which react with phosphines to render easily and economically Buchwald-type palladacycles.

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Supporting Information.

CIF files of the structures of **3b-I**·$CHCl_3$ and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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