

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

José Vicente,\* Isabel Saura-Llamas,\* María-José Oliva-Madrid, and José-Antonio García-López

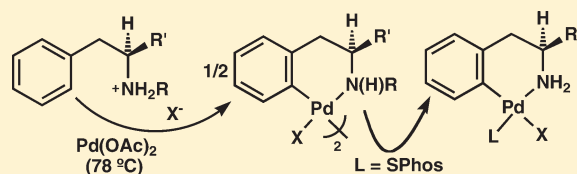
Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, E-30071 Murcia, Spain

Delia Bautista

SAI, Universidad de Murcia, Apartado 4021, E-30071 Murcia, Spain

**S** Supporting Information

**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  $[\text{Pd}(\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{R}')\text{NHR}-2)\text{X}(\text{phosphine})]$  that can be easily prepared by reaction of  $\text{Pd}(\text{OAc})_2$ , 1 equiv of the ammonium triflate  $[\text{PhCH}_2\text{CH}(\text{R}')\text{NH}_2\text{R}]\text{OTf}$ , and an excess of  $\text{NaX}$  and then treating the resulting complexes  $[\text{Pd}_2(\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{R}')\text{NHR}-2)_2(\mu\text{-X})_2]$  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<sup>1</sup> and C–N cross-coupling reactions.<sup>2,3</sup> 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  $[\text{PdCl}_2(\text{TMEDA})]$  (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%).<sup>2</sup> However, the reaction conditions are not straightforward: (1) an argon atmosphere is required; (2) the intermediate  $[\text{PdMe}_2(\text{TMEDA})]$  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 and 130 °C; (3) if the 2-haloarylalkylamine is not commercially available, it has to be otherwise prepared, as it happens with the 2-(2-chlorophenyl)-*N*-methylethanamine;<sup>2</sup> 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.<sup>4–7</sup> The reaction involved equimolecular amounts of the free amine or its hydrochloride and palladium acetate in acetonitrile at 80 °C, 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  $\text{PPh}_3$  (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 were 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.<sup>8</sup> However, the phosphino cyclopalladated complexes were obtained in poor yields (15–34%, based on  $\text{Pd}(\text{OAc})_2$ ).

Here, we report a new method of synthesis of a variety of halo complexes of Pd(II) containing ortho-metallated 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.<sup>9</sup>

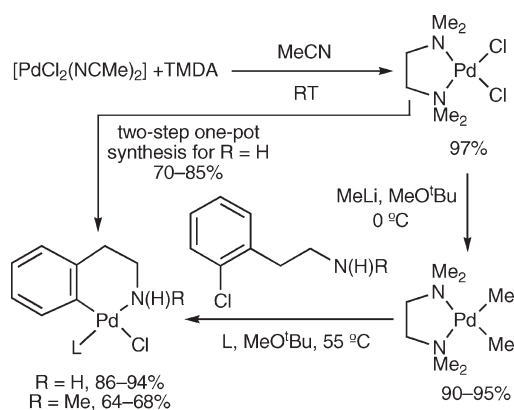
## RESULTS AND DISCUSSION

**Synthesis.** The ammonium triflate derived from phenethylamine ( $\text{PhCH}_2\text{CH}_2\text{NH}_3$ )OTf (A), *L*-phenylalanine methyl ester (*S*)-( $\text{PhCH}_2\text{CH}(\text{CO}_2\text{Me})\text{NH}_3$ )OTf (B), or *N*-methylphenethylamine ( $\text{PhCH}_2\text{CH}_2\text{NH}_2\text{Me}$ )OTf (C) reacted with  $\text{Pd}(\text{OAc})_2$  in a 1:1 molar ratio, in acetonitrile at 75–78 °C, to give HOAc and, likely, intermediate I, which underwent an ortho-metallation

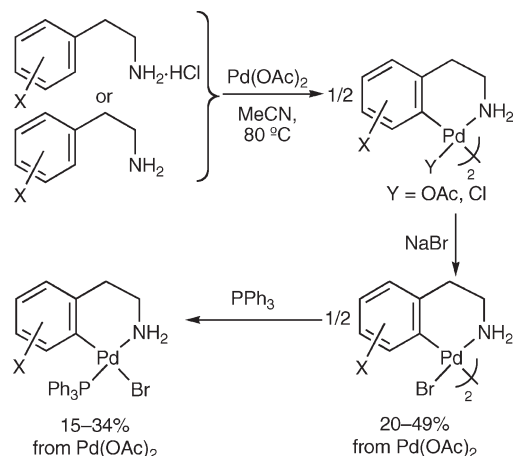
Received: May 30, 2011

Published: July 28, 2011

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

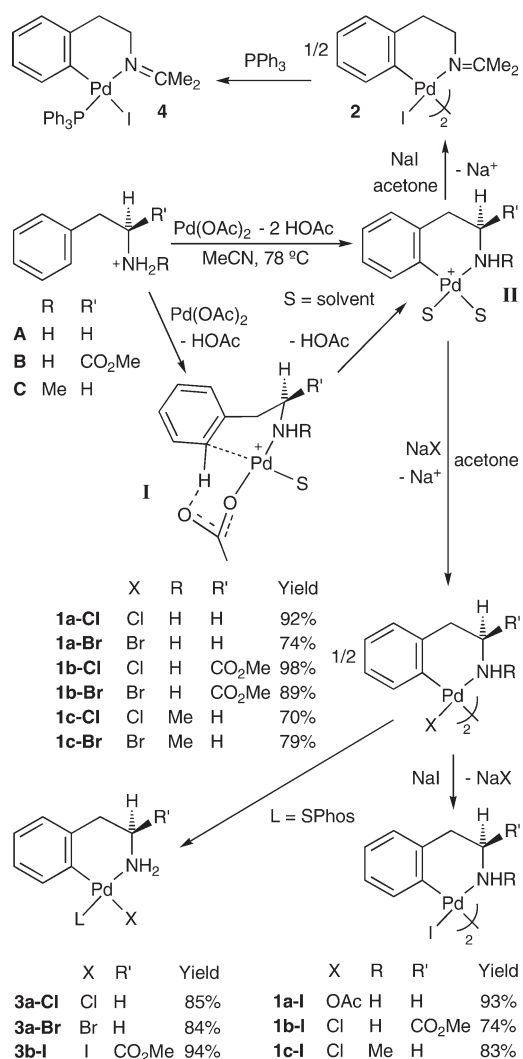


**Scheme 2.** Synthesis of Ortho-palladated Phenethylamine Derivatives Using the Free Amines or Their Corresponding Hydrochlorides



reaction to afford the solvento complex **II** (Scheme 3),<sup>10,11</sup> which further reacted with NaX (X = Cl, Br) to render the halo-bridged cyclopalladated complex  $[\text{Pd}_2(\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{R}')\text{NHR}-2)(\mu\text{-X})_2]$  (R = R' = H, X = Cl (**1a-Cl**), Br (**1a-Br**); R = H, R' = CO<sub>2</sub>Me, 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 **I** are in the range 70–98%, in contrast with those obtained using the free amine or its hydrochloride (see below). The different yields can be explained on the basis of 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 ligand triflate does not replace S, affording **I**, the *cationic* nature of which enhances the electrophilicity of palladium(II) and facilitates the ortho-metalation process. In mechanistic studies on ortho-palladation of arylalkylamines, an intermediate such as **I** has been postulated.<sup>12</sup> A solvento complex similar to **II** has been postulated as an intermediate in

**Scheme 3.** Improved Synthesis of Palladacycles Containing Ortho-metalated Phenethylamines<sup>a</sup>

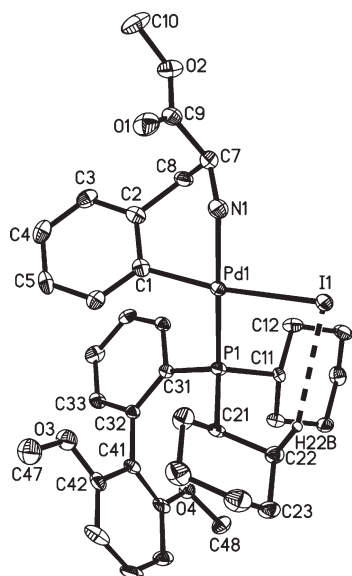
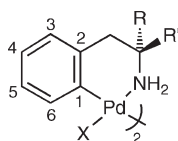


<sup>a</sup> The anion of the cationic species is TfO<sup>−</sup>.

the ortho-metalation of  $\alpha$ -methylbenzylamine starting from  $[\text{PdCl}_2\{\text{NH}_2\text{CH}(\text{Me})\text{Ph}\}_2]$  and AgClO<sub>4</sub> (1:2 molar ratio) and using acetone as solvent.<sup>13</sup> 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%).<sup>7,14</sup>

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,  $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{R}')\text{NH}_2)_2\text{I}(\text{solvent})]^+$ , 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.<sup>15</sup> However, the reaction of **A**, Pd(OAc)<sub>2</sub>, and NaI in the same conditions used to prepare **1a-Cl** or **1a-Br** rendered the

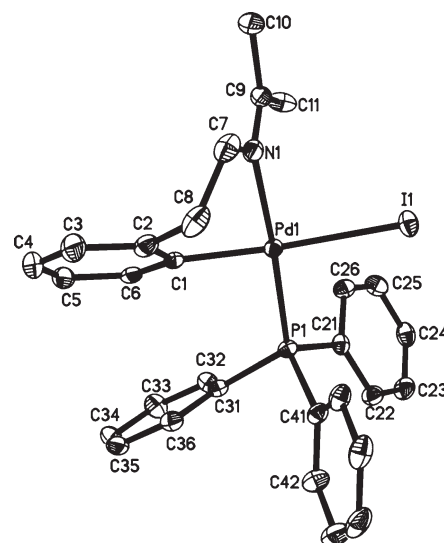
**Chart 1. Numbering Scheme for Ortho-metallated Palladacycles**



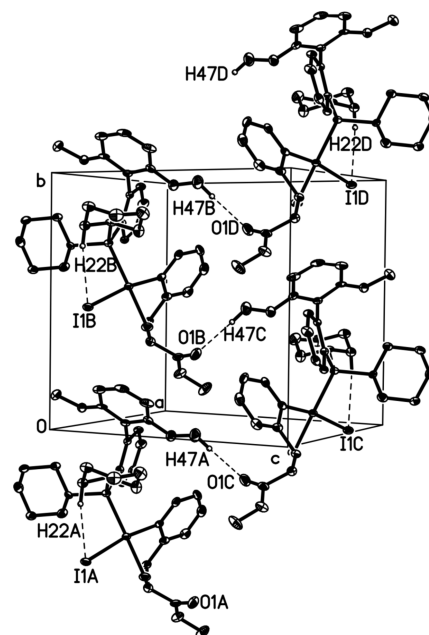
**Figure 1.** X-ray thermal ellipsoid plot (50% probability) of complex **3b-I**·CHCl<sub>3</sub> showing the labeling scheme (the solvent molecule and all the hydrogen atoms, excluding that involved in the hydrogen bond, have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–C(1) = 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).

dimeric iodo-bridged ortho-palladated complex [Pd<sub>2</sub>(C,N-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CH<sub>2</sub>N=CMe<sub>2</sub>-2)<sub>2</sub>(μ-I)<sub>2</sub>] (**2**), which contained the imine arising from the condensation of phenethylamine and acetone (Scheme 3). Following an alternative method, the iodo-bridged ortho-metallated complexes [Pd<sub>2</sub>(C,N-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH(R')NHR-2)<sub>2</sub>(μ-I)<sub>2</sub>] (R = R' = H, X = I (**1a-I**); R = H, R' = CO<sub>2</sub>Me, 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.<sup>16</sup>

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.<sup>4,5,11,17</sup> 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<sub>3</sub> (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 Buchwald-type complexes **3** would gain flexibility if different phosphines can be tested using complexes **1** as starting materials. Complex **3a-Cl** has



**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<sub>3</sub>. Only atoms involved in the hydrogen bonding are labeled.

been previously prepared by Buchwald et al. via his two-step one-pot synthesis (Scheme 1) in an 85% yield and used as precatalyst in coupling reactions.<sup>2</sup> Although the overall yield for the synthesis of complex **3a-Cl** using our method is slightly lower (78%), the advantages of our method are evident: (1) the starting materials (see Scheme 3) are easily available, and all but the common SPhos are much cheaper; (2) the reactions are carried out without special precautions against air or moisture; (3) the dinuclear halo-bridged ortho-metallated 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.<sup>18</sup>

**NMR Spectra.** The <sup>1</sup>H and <sup>13</sup>C NMR spectra of complexes **1a-Br**, **1b-Br**, **1c-Br**, and **3a-Cl** are in agreement with the reported data.<sup>2,4,7,14</sup> For all the new compounds, their spectroscopic data correspond with the proposed structures. Thus, the halo-bridged ortho-metalated complexes exhibit in the aromatic region of their <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>) a set of two signals 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 ( $\delta$  7.43–7.51 ppm; see Chart 1 for the numbering scheme) and a multiplet assigned to H3 + H4 + H5 ( $\delta$  6.70–7.10 ppm). In the <sup>13</sup>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.<sup>16</sup> The protons of the NH<sub>2</sub> or CH<sub>2</sub> groups resonate as one broad signal in the complexes containing phenethylamine, while they become diastereotopic for L-phenylalanine methyl ester and N-methylphenethylamine derivatives. The <sup>31</sup>P NMR spectra of complexes **3a-Cl**, **3a-Br**, and **3b-I** show a very broad singlet, suggesting dissociation of the phosphine favored by its steric requirement.

**Crystal Structures.** The crystal structures of complexes **3b-I**·CHCl<sub>3</sub> (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<sub>3</sub>) or distorted (**4**) square-planar environment (mean deviation from the plane: 0.0224 Å, **3b-I**·CHCl<sub>3</sub>; 0.0877 Å, **4**) with dihedral angles of 2.1° (**3b-I**·CHCl<sub>3</sub>) and 9.6° (**4**) between the N(1)–Pd(1)–C(1) and P(1)–Pd(1)–I(1) planes. In both complexes, the chelated amino (**3b-I**·CHCl<sub>3</sub>) or imino ligand (**4**) forms a six-membered metallacycle with a boat conformation. The features of complexes **3b-I**·CHCl<sub>3</sub> and **4** are similar to those of analogous phosphino complexes containing primary ortho-metalated phenethylamines<sup>2,4,5</sup> or related imino ligands.<sup>19</sup> The X-ray crystallographic study reveals the *S* absolute configuration of the  $\alpha$ -carbon stereocenter in complex **3b-I**·CHCl<sub>3</sub>. This complex exhibits an intramolecular nonclassical hydrogen bond between the iodine atom and one hydrogen of the cyclohexyl group; besides, each molecule is connected to another 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.<sup>14</sup> Unless otherwise stated, NMR spectra were recorded in CDCl<sub>3</sub> in Bruker Avance 300 or 400 spectrometers. Chemical shifts are referenced to TMS [<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}]. Signals in the <sup>1</sup>H and <sup>13</sup>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-methylphenethylamine, 2-dicyclohexylphosphino-2',6'-dimethoxyphenyl (SPhos; Aldrich), PPh<sub>3</sub> (Fluka), NaCl (J. T. Baker), NaBr, NaI (Scharlau), and Pd(OAc)<sub>2</sub> (Johnson Matthey) were used as received. Chart 1 gives the numbering scheme for the palladacycles.

**Synthesis of [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>]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<sub>2</sub>O (50 mL), and the resulting white suspension was vigorously stirred for 20 min. The mixture was filtered, and the solid was washed with Et<sub>2</sub>O (2 × 5 mL) and air-dried to give compound **A** as a white solid. Yield: 5.46 g, 20.13 mmol, 84%. Mp: 204 °C.  $\Lambda_M$  ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>): 125 ( $7.4 \times 10^{-4}$  M). Anal. Calcd for C<sub>9</sub>H<sub>12</sub>F<sub>3</sub>NO<sub>3</sub>S (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<sup>-1</sup>):  $\nu$ (NH) 3177 vs. <sup>1</sup>H NMR (400.91 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.84 (m, 2 H, CH<sub>2</sub>Ar), 3.04 (m, 2 H, CH<sub>2</sub>N), 7.22–7.27 (m, 3 H, *p*-H and *o*- or *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.30–7.35 (m, 2 H, *o*- or *m*-H, C<sub>6</sub>H<sub>5</sub>), 7.73 (br s, 3 H, NH<sub>3</sub>). <sup>13</sup>C NMR (100.81 MHz):  $\delta$  33.1 (s, CH<sub>2</sub>Ar), 40.0 (s, CH<sub>2</sub>N), 126.8 (s, *p*-CH, C<sub>6</sub>H<sub>5</sub>), 128.6 (s, *o*- or *m*-CH, C<sub>6</sub>H<sub>5</sub>), 128.7 (s, *o*- or *m*-CH, C<sub>6</sub>H<sub>5</sub>), 137.2 (s, *i*-C, C<sub>6</sub>H<sub>5</sub>).

**Synthesis of (S)-[C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH(CO<sub>2</sub>Me)NH<sub>3</sub>]OTf (B).** Na<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL), and the combined organic layers were dried over MgSO<sub>4</sub>. 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<sub>2</sub>O (2 × 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<sub>2</sub>O (20 mL) was added. The suspension was filtered, and the solid was washed with Et<sub>2</sub>O (2 × 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.  $\Lambda_M$  ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>): 126 ( $5.2 \times 10^{-4}$  M). Anal. Calcd for C<sub>11</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>3</sub>S (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<sup>-1</sup>):  $\nu$ (NH) 3224 vs;  $\nu$ (CO) 1741 vs. <sup>1</sup>H NMR (300.1 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  3.06 (m, 2 H, CH<sub>2</sub>), 3.69 (m, 2 H, Me), 4.33 (t, 1 H, CH, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz), 7.18–7.23 (m, 3 H, *o*-H, C<sub>6</sub>H<sub>5</sub>), 7.25–7.37 (m, 3 H, *m*-H and *p*-H, C<sub>6</sub>H<sub>5</sub>), 8.37 (br s, 3 H, NH<sub>3</sub>). <sup>13</sup>C NMR (75.45 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  36.0 (s, CH<sub>2</sub>), 52.7 (s, Me), 53.2 (s, CH), 120.7 (q, CF<sub>3</sub>, <sup>1</sup>*J*<sub>CF</sub> = 322.2 Hz), 127.4 (s, *p*-CH, C<sub>6</sub>H<sub>5</sub>), 128.7 (s, *m*-CH, C<sub>6</sub>H<sub>5</sub>), 129.4 (s, *o*-CH, C<sub>6</sub>H<sub>5</sub>), 134.4 (s, *i*-C, C<sub>6</sub>H<sub>5</sub>), 169.5 (s, CO).

**Synthesis of [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>Me]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-methylphenethylamine (2.5 mL, 17.19 mmol) in Et<sub>2</sub>O (40 mL), and the resulting white suspension was vigorously stirred for 15 min. The mixture was filtered, and the solid was washed with Et<sub>2</sub>O (2 × 5 mL) and air-dried to give compound **C** as a white solid. Yield: 4.56 g, 15.98 mmol, 94%. Mp: 124 °C.  $\Lambda_M$  ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>): 116 ( $7.43 \times 10^{-4}$  M). Anal. Calcd for C<sub>10</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>3</sub>S (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<sup>-1</sup>):  $\nu$ (NH) 3219 s, 3030 s. <sup>1</sup>H NMR (300.1 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.59 (s, 3 H, Me), 2.88 (m, 2 H, CH<sub>2</sub>Ar), 3.14 (m, 2 H, CH<sub>2</sub>N), 7.22–7.28 (m, 3 H, *o*- and *p*-H, C<sub>6</sub>H<sub>5</sub>), 7.31–7.37 (m, 2 H, *m*-H, C<sub>6</sub>H<sub>5</sub>), 8.32 (br s, 2 H, NH<sub>2</sub>). <sup>13</sup>C NMR (75.45 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  31.5 (s, CH<sub>2</sub>Ar), 32.6 (s, Me), 49.1 (s, CH<sub>2</sub>N), 126.8 (s, *p*-CH, C<sub>6</sub>H<sub>5</sub>), 128.7 (s, *o*-CH and *p*-CH, C<sub>6</sub>H<sub>5</sub>), 137.0 (s, *i*-C, C<sub>6</sub>H<sub>5</sub>).

**Synthesis of [Pd<sub>2</sub>(C,N-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>-2)<sub>2</sub>( $\mu$ -OAc)<sub>2</sub>] (1a-OAc).** Phenethylamine (0.5 mL, 3.982 mmol) was added to a suspension of Pd(OAc)<sub>2</sub> (894 mg, 3.982 mmol) in acetonitrile (55 mL), and the resulting mixture was heated at 60 °C for 2 h and then at 78 °C for 6 h.

Decomposition to metallic palladium was observed. The mixture was filtered through a plug of Celite/ $\text{Na}_2\text{CO}_3$ , the solvent was removed from the filtrate, and  $\text{CH}_2\text{Cl}_2$  (2 mL) and  $\text{Et}_2\text{O}$  (30 mL) were added. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  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  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_4\text{Pd}_2$  (571.238): C, 42.05; H, 4.59; N, 4.90. Found: C, 41.57; H, 4.57; N, 4.73. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3319 m, 3301 s, 3193 s, 3112 s;  $\nu(\text{CO})$  1594 vs, 1550 vs.  $^1\text{H}$  NMR (300.10 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  1.77 (s, 3 H, Me), 2.35 (br s, 2 H,  $\text{CH}_2\text{N}$ ), 2.90 (m, 2 H,  $\text{CH}_2\text{Ar}$ ), 5.68 (br s, 2 H,  $\text{NH}_2$ ), 6.85–6.97 (m, 3 H, H3 + H4 + H5), 7.42 (d, 1 H, H6,  $^3J_{\text{HH}} = 7.2$  Hz).  $^{13}\text{C}$  NMR (100.81 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  29.9 (s, Me), 36.4 (s,  $\text{CH}_2\text{N}$ ), 42.9 (s,  $\text{CH}_2\text{Ar}$ ), 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.<sup>16</sup>

**Synthesis of  $[\text{Pd}_2(\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2-2)_2(\mu\text{-Cl})_2]$  (**1a-Cl**).** The ammonium triflate **A** (1000 mg, 3.686 mmol) was added to a suspension of  $\text{Pd}(\text{OAc})_2$  (827.6 mg, 3.686 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 °C for 2 h and then at 78 °C for 4 h. The mixture was filtered through a plug of Celite/ $\text{Na}_2\text{CO}_3$ , 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  $\text{CH}_2\text{Cl}_2$  (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  $\text{Et}_2\text{O}$  (15 mL) for 15 min. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  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  $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pd}_2$  (524.056): C, 36.67; H, 3.85; N, 5.35. Found: C, 36.43; H, 3.87; N, 5.26. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3300 s, 3228 m.  $^1\text{H}$  NMR (300.10 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.33 (br s, 2 H,  $\text{CH}_2\text{N}$ ), 2.83 (m, 2 H,  $\text{CH}_2\text{Ar}$ ), 4.75 (br s, 2 H,  $\text{NH}_2$ ), 6.85–6.97 (m, 3 H, H3 + H4 + H5), 7.46 (d, 1 H, H6,  $^3J_{\text{HH}} = 7.5$  Hz).  $^{13}\text{C}$  NMR (100.81 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  37.3 (s,  $\text{CH}_2\text{N}$ ), 42.7 (s,  $\text{CH}_2\text{Ar}$ ), 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  $[\text{Pd}_2(\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2-2)_2(\mu\text{-Br})_2]$  (**1a-Br**).** The ammonium triflate **A** (1000 mg, 3.686 mmol) was added to a suspension of  $\text{Pd}(\text{OAc})_2$  (828 mg, 3.688 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 °C for 2 h and then at 78 °C for 3.5 h. The mixture was filtered through a plug of Celite/ $\text{Na}_2\text{CO}_3$ , 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  $\text{Et}_2\text{O}$  (25 mL) for 15 min. The suspension was filtered, and the solid was washed with  $\text{H}_2\text{O}$  ( $3 \times 10$  mL) and  $\text{Et}_2\text{O}$  ( $3 \times 5$  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  $\text{C}_{16}\text{H}_{20}\text{Br}_2\text{N}_2\text{Pd}_2$  (612.992): C, 31.35; H, 3.29; N, 4.57. Found: C, 31.36; H, 3.18; N, 4.54. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3265 s, 3218 w.  $^1\text{H}$  NMR (400.91 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.35 (m, 2 H,  $\text{CH}_2\text{N}$ ), 2.85 (“t”, 2 H,  $\text{CH}_2\text{Ar}$ ,  $^3J_{\text{HH}} = 5.6$  Hz), 4.75 (br s, 2 H,  $\text{NH}_2$ ), 6.85–6.96 (m, 3 H, H3 + H4 + H5), 7.46 (d, 1 H, H6,  $^3J_{\text{HH}} = 7.2$  Hz).  $^{13}\text{C}$  NMR (100.81 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  37.3 (s,  $\text{CH}_2\text{N}$ ), 42.5 (s,  $\text{CH}_2\text{Ar}$ ), 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.<sup>4</sup>

**Synthesis of  $[\text{Pd}_2(\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2-2)_2(\mu\text{-I})_2]$  (**1a-I**).** NaI (525 mg, 3.50 mmol) was added to a solution of **1a-OAc** (200 mg, 0.350 mmol) in acetone (50 mL), and the suspension was stirred for 16 h. Solvent was removed,  $\text{CH}_2\text{Cl}_2$  (40 mL) was added, and the resulting suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, and  $\text{Et}_2\text{O}$  (30 mL) was added. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  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 ( $2 \times 5$  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  $\text{C}_{16}\text{H}_{20}\text{I}_2\text{N}_2\text{Pd}_2$  (706.992): C, 27.18; H, 2.85; N, 3.96. Found: C, 27.08; H, 2.67; N, 3.86. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3180 m, 3282 m.  $^1\text{H}$  NMR (300.1 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.37 (m, 2 H,  $\text{CH}_2\text{N}$ ), 2.87 (“t”, 2 H,  $\text{CH}_2\text{Ar}$ ,  $^3J_{\text{HH}} = 5.4$  Hz), 4.74 (br s, 2 H,  $\text{NH}_2$ ), 6.70–7.07 (m, 3 H, H3 + H4 + H5), 7.50 (d, 1 H, H6,  $^3J_{\text{HH}} = 7.2$  Hz).  $^{13}\text{C}$  NMR (75.45 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  37.2 (s,  $\text{CH}_2\text{N}$ ), 42.3 (s,  $\text{CH}_2\text{Ar}$ ), 124.3 (br s, CH, C4 + C5), 126.1 (s, CH, C3), 128.5 (s, CH, C6), 139.7 (s, C2). The  $^{13}\text{C}$  resonance corresponding to C1 (C–Pd) was not observed.

**Synthesis of  $(S,S)\text{-}[\text{Pd}_2\{\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{CO}_2\text{Me})\text{NH}_2-2\}_2(\mu\text{-Cl})_2]$  (**1b-Cl**).** The ammonium triflate **B** (1200 mg, 3.645 mmol) was added to a suspension of  $\text{Pd}(\text{OAc})_2$  (820 mg, 3.653 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 °C for 2 h and then at 79 °C for 4 h. The mixture was filtered through a plug of Celite/ $\text{Na}_2\text{CO}_3$ , 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  $\text{CH}_2\text{Cl}_2$  (40 mL) was added. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and  $\text{Et}_2\text{O}$  (30 mL) was added. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  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 ( $2 \times 5$  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  $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{N}_2\text{O}_4\text{Pd}_2$  (640.128): C, 37.52; H, 3.79; N, 4.37. Found: C, 37.57; H, 3.89; N, 4.49. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3284 m, 3232 m;  $\nu(\text{CO})$  1735 s.  $^1\text{H}$  NMR (400.91 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  3.10 (dd, 1 H,  $\text{CH}_2$ ,  $^2J_{\text{HH}} = 13.2$ ,  $^3J_{\text{HH}} = 9.6$  Hz), 3.20 (dd, 1 H,  $\text{CH}_2$ ,  $^2J_{\text{HH}} = 13.2$ ,  $^3J_{\text{HH}} = 3.6$  Hz), 3.27–3.35 (m, partially obscured by the signal of  $\text{H}_2\text{O}$  of the deuterated solvent, 1 H, CH), 4.46 (br s, 1 H,  $\text{NH}_2$ ), 5.49 (m, 1 H,  $\text{NH}_2$ ), 6.92–7.00 (m, 3 H, H3 + H4 + H5), 7.45 (d, 1 H, H6,  $^3J_{\text{HH}} = 7.6$  Hz).  $^{13}\text{C}$  NMR (100.81 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  45.5 (s,  $\text{CH}_2$ ), 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  $(S,S)\text{-}[\text{Pd}_2\{\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{CO}_2\text{Me})\text{NH}_2-2\}_2(\mu\text{-Br})_2]$  (**1b-Br**).** The ammonium triflate **B** (1500 mg, 4.57 mmol) was added to a suspension of  $\text{Pd}(\text{OAc})_2$  (1028 mg, 4.58 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 65 °C for 2 h and then at 78 °C for 4 h. The mixture was filtered through a plug of Celite and  $\text{Na}_2\text{CO}_3$ , the solvent was removed from 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  $\text{CH}_2\text{Cl}_2$  (40 mL) was added. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and  $\text{Et}_2\text{O}$  (40 mL) was added. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  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 ( $2 \times 5$  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  $\text{C}_{20}\text{H}_{24}\text{Br}_2\text{N}_2\text{O}_4\text{Pd}_2$  (729.064): C, 32.95; H, 3.32; N, 3.84. Found: C, 32.79; H, 3.04; N, 3.85. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3278 w, 3233 w;  $\nu(\text{CO})$  1733 s. Spectroscopic data are in accordance with the data reported in the literature.<sup>7</sup>

**Synthesis of  $(S,S)\text{-}[\text{Pd}_2\{\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{CO}_2\text{Me})\text{NH}_2-2\}_2(\mu\text{-I})_2]$  (**1b-I**).** NaI (470 mg, 3.13 mmol) was added to a solution of **1b-Cl** (200 mg, 0.312 mmol) in acetone (50 mL), and the suspension



was stirred for 16 h. Solvent was removed,  $\text{CH}_2\text{Cl}_2$  (40 mL) was added, and the resulting suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, and  $\text{Et}_2\text{O}$  (30 mL) was added. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and air-dried to give complex **1b-I** as a dark orange solid (190 mg). Yield: 230 mg, 0.231 mmol, 74%. Mp: 179 °C dec. Anal. Calcd for  $\text{C}_{20}\text{H}_{24}\text{I}_2\text{N}_2\text{O}_4\text{Pd}_2$  (823.07): C, 29.19; H, 2.94; N, 3.40. Found: C, 28.90; H, 2.81; N, 3.10. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3241 w, 3172 w;  $\nu(\text{CO})$  1724 vs.  $^1\text{H}$  NMR (400.91 MHz,  $\text{DMSO}-d_6$ ): 3.11 (br m, 1 H,  $\text{CH}_2$ ), 3.20 (dd, 1 H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 13.2$ ,  $^3J_{\text{HH}} = 3.6$  Hz), 3.34–3.41 (br m, partially obscured by the signal of  $\text{H}_2\text{O}$  of the deuterated solvent, 1 H, CH), 3.70 (s, 3 H, Me), 4.57 (br s, 1 H,  $\text{NH}_2$ ), 5.38 (br s, 1 H,  $\text{NH}_2$ ), 6.70–7.05 (m, 3 H, H3 + H4 + H5), 7.51 (br s, 1 H, H6).  $^{13}\text{C}$  NMR (100.81 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  45.3 (br s,  $\text{CH}_2$ ), 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  $^{13}\text{C}$  resonance corresponding to C1 (C–Pd) was not observed.

**Synthesis of  $[\text{Pd}_2(\text{C},N\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NHMe-2})_2(\mu\text{-Cl})_2]$  (**1c-Cl**).** The ammonium triflate **C** (800 mg, 2.804 mmol) was added to a suspension of  $\text{Pd}(\text{OAc})_2$  (629.5 mg, 2.804 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 °C for 2 h and then at 78 °C for 2 h. The mixture was filtered through a plug of Celite/ $\text{Na}_2\text{CO}_3$ , 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  $\text{CH}_2\text{Cl}_2$  (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  $\text{Et}_2\text{O}$  (15 mL) for 30 min. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  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  $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pd}_2$  (552.142): C, 39.16; H, 4.38; N, 5.07. Found: C, 38.81; H, 4.58; N, 5.36. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3226 s.  $^1\text{H}$  NMR (400.91 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  1.68 (m, 1 H,  $\text{CH}_2\text{N}$ ), 2.32 (d, 3 H, Me,  $^3J_{\text{HH}} = 5.2$  Hz), 2.83 (m, 1 H,  $\text{CH}_2\text{Ar}$ ), 2.94 (m, 1 H,  $\text{CH}_2\text{Ar}$ ), 3.03 (m, 1 H,  $\text{CH}_2\text{N}$ ), 5.55 (br s, 1 H, NH), 6.84–7.10 (m, 3 H, H3 + H4 + H5), 7.43 (d, 1 H, H6,  $^3J_{\text{HH}} = 7.6$  Hz).  $^{13}\text{C}$  NMR (100.81 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  40.5 (s,  $\text{CH}_2\text{Ar}$ ), 42.3 (s, Me), 49.6 (s,  $\text{CH}_2\text{N}$ ), 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  $[\text{Pd}_2(\text{C},N\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NHMe-2})_2(\mu\text{-Br})_2]$  (**1c-Br**).** The ammonium triflate **C** (800 mg, 2.804 mmol) was added to a suspension of  $\text{Pd}(\text{OAc})_2$  (629.5 mg, 2.804 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 60 °C for 2 h and then at 70 °C for 3 h. The mixture was filtered through a plug of Celite/ $\text{Na}_2\text{CO}_3$ , 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  $\text{CH}_2\text{Cl}_2$  (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  $\text{Et}_2\text{O}$  (15 mL) for 30 min. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  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  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give a spectroscopically pure sample (recrystallization yield: 76%). IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3229.  $^1\text{H}$  NMR (300.10 MHz):  $\delta$  1.99 (m, 1 H,  $\text{CH}_2\text{N}$ ), 2.68 (d, 3 H, Me,  $^3J_{\text{HH}} = 6.0$  Hz), 2.98 (m, 2 H, 1 H of  $\text{CH}_2\text{Ar}$  + 1 H of  $\text{CH}_2\text{N}$ ), 3.20 (m, 1 H,  $\text{CH}_2\text{Ar}$ ), 3.82 (br s, 1 H, NH), 6.78–6.86 (m, 2 H, H3 + H5), 6.93 (t, 1 H, H4,  $^3J_{\text{HH}} = 6.9$  Hz), 7.39 (br d, 1 H, H6,  $^3J_{\text{HH}} = 6.0$  Hz). Spectroscopic data are in accordance with the data reported in the literature.<sup>14</sup>

**Synthesis of  $[\text{Pd}_2(\text{C},N\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NHMe-2})_2(\mu\text{-I})_2]$  (**1c-I**).** NaI (382 mg, 2.544 mmol) was added to a solution of **1c-Cl** (140 mg, 0.254 mmol) in acetone (50 mL), and the suspension was stirred for 16 h. Solvent was removed,  $\text{CH}_2\text{Cl}_2$  (40 mL) was added, and the resulting suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, and  $\text{Et}_2\text{O}$  (30 mL) was added. The suspension

was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and air-dried to give complex **1c-I** as a dark orange solid. Yield: 153 mg, 0.208 mmol, 83%. Mp: 155 °C dec. Calcd for  $\text{C}_{18}\text{H}_{24}\text{I}_2\text{N}_2\text{Pd}_2$  (735.052): C, 29.41; H, 3.29; N, 3.81. Found: C, 29.53; H, 2.84; N, 3.74. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3484 m, 3434 m, 3236 m.  $^1\text{H}$  NMR (400.91 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  1.71 (br s, 1 H,  $\text{CH}_2\text{N}$ ), 2.26 (d, 3 H, Me,  $^3J_{\text{HH}} = 5.6$  Hz), 2.85 (br m, 1 H,  $\text{CH}_2\text{Ar}$ ), 2.91–3.20 (m, 2 H, 1 H of  $\text{CH}_2\text{Ar}$  + 1 H of  $\text{CH}_2\text{N}$ ), 5.43 (br s, 1 H, NH), 6.70–7.05 (m, 3 H, H3 + H4 + H5), 7.43 (br s, 1 H, H6).  $^{13}\text{C}$  NMR (100.81 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  40.4 (s,  $\text{CH}_2\text{Ar}$ ), 42.8 (br s, Me), 49.4 (s,  $\text{CH}_2\text{N}$ ), 124.2 (br s, CH), 126.0 (s, CH), 139.7 (br s, C2). The  $^{13}\text{C}$  resonance corresponding to C1 (C–Pd) was not observed.

**Synthesis of  $[\text{Pd}_2(\text{C},N\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{N}=\text{CMe}_2\text{-2})_2(\mu\text{-I})_2]$  (**2**).** The ammonium triflate **A** (1000 mg, 3.686 mmol) was added to a suspension of  $\text{Pd}(\text{OAc})_2$  (828 mg, 3.688 mmol) in acetonitrile (50 mL), and the resulting solution was heated at 78 °C for 4 h. The mixture was filtered through a plug of Celite/ $\text{Na}_2\text{CO}_3$ , 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  $\text{Et}_2\text{O}$  (30 mL) for 15 min. The suspension was filtered, and the solid was washed with  $\text{H}_2\text{O}$  ( $3 \times 10$  mL), acetone ( $2 \times 5$  mL), and  $\text{Et}_2\text{O}$  ( $2 \times 5$  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  $\text{C}_{22}\text{H}_{28}\text{I}_2\text{N}_2\text{Pd}_2$  (787.088): C, 33.57; H, 3.58; N, 3.55. Found: C, 33.27; H, 3.51; N, 3.52. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$  1644 m, 1629 m.  $^1\text{H}$  NMR (300.1 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  1.97 (s, 3 H, Me), 2.51 (s, 3 H, Me), 2.97 (m, 2 H, 1 H of  $\text{CH}_2\text{Ar}$  + 1 H of  $\text{CH}_2\text{N}$ ), 3.20 (m, 1 H,  $\text{CH}_2$ ), 3.83 (br s, 1 H,  $\text{CH}_2$ ), 6.70–6.90 (m, 3 H, H3 + H4 + H5), 7.29 (d, 1 H, H6,  $^3J_{\text{HH}} = 7.5$  Hz).  $^{13}\text{C}$  NMR (75.45 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  22.2 (s, Me), 38.2 (br s,  $\text{CH}_2\text{Ar}$ ), 49.1 (s,  $\text{CH}_2\text{N}$ ), 124.1 (br s, CH,  $\text{C}_6\text{H}_4$ ), 124.8 (br s, CH,  $\text{C}_6\text{H}_4$ ), 125.7 (s, CH,  $\text{C}_6\text{H}_4$ ), 139.7 (s, C,  $\text{C}_6\text{H}_4$ ), 179.4 (s, C=N).

**Synthesis of  $[\text{Pd}(\text{C},N\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2\text{-2})\text{Cl}(\text{SPhos})]$  (**3a-Cl**).** SPhos (188 mg, 0.458 mmol) was added to a suspension of complex **1a-Cl** (120 mg, 0.229 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of  $\text{MgSO}_4$ , 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 ( $2 \times 1$  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  $\text{C}_{34}\text{H}_{45}\text{ClINO}_2\text{PPd}$  (672.566): C, 60.72; H, 6.74; N, 2.08. Found: C, 60.43; H, 7.10; N, 2.17. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3323 m, 3245 m, 3214 m, 3137 m.  $^1\text{H}$  NMR (400.91 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  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,  $^3J_{\text{HH}} = 7.0$  Hz), 6.66 (d, 2 H,  $^3J_{\text{HH}} = 8.4$  Hz), 6.69–6.77 (m, 2 H), 6.83 (dd, 2 H,  $^3J_{\text{HH}} = 7.2$ ,  $^4J_{\text{HH}} = 1.6$  Hz), 6.88 (br d, 1 H,  $^3J_{\text{HH}} = 6.8$  Hz), 7.15–7.25 (m, 2 H), 7.37 (t, 1 H,  $^3J_{\text{HH}} = 8.4$  Hz).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162.29 MHz):  $\delta$  55.0 (br s). Spectroscopic data are in accordance with the data reported in the literature.<sup>2</sup>

**Synthesis of  $[\text{Pd}(\text{C},N\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2\text{-2})\text{Br}(\text{SPhos})] \cdot \text{H}_2\text{O}$  (**3a-Br**  $\cdot \text{H}_2\text{O}$ ).** SPhos (160 mg, 0.390 mmol) was added to a suspension of complex **1a-Br** (120 mg, 0.196 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of  $\text{MgSO}_4$ , 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 ( $2 \times 1$  mL) and air-dried to give complex **3a-Br**  $\cdot \text{H}_2\text{O}$  as a pale yellow solid. Yield: 240 mg, 0.326 mmol, 84%. Dec pt: 214 °C. Anal. Calcd for  $\text{C}_{34}\text{H}_{45}\text{BrNO}_2\text{PPd} \cdot \text{H}_2\text{O}$  (735.037): C, 55.56; H, 6.44; N, 1.91. Found: C, 55.57; H, 6.65; N, 2.12. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3307 m, 3230 m, 3145 w.  $^1\text{H}$  NMR (400.91 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  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,  $\text{H}_2\text{O}$ ), 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,  $^3J_{\text{HH}} = 6.8$  Hz), 6.67 (d, 2 H,  $^3J_{\text{HH}} = 8.4$  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,  $^3J_{\text{HH}} = 8.4$  Hz).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162.29 MHz):  $\delta$  55.1 (br s).

**Synthesis of (S)-[Pd{C,N-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH(CO<sub>2</sub>Me)NH<sub>2</sub>-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  $\text{CH}_2\text{Cl}_2$  (20 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of  $\text{MgSO}_4$ , 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 ( $2 \times 3$  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  $\text{C}_{36}\text{H}_{45}\text{INO}_4\text{PPd}$  (820.057): C, 52.73; H, 5.53; N, 1.71. Found: C, 52.50; H, 5.89; N, 1.75. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  3322 m, 3266 m;  $\nu(\text{CO})$  1739 s.  $^1\text{H}$  NMR (400.91 MHz):  $\delta$  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,  $^2J_{\text{HH}} = 12.8$  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,  $^3J_{\text{HH}} = 7.6$  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,  $^3J_{\text{HH}} = 8.4$  Hz).  $^{31}\text{P}$  NMR (162.29 MHz):  $\delta$  57.8 (v br s). Single crystals of 3b-I·CHCl<sub>3</sub> suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of 3b-I in CHCl<sub>3</sub>.

**Synthesis of [Pd(C,N-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N=CMe<sub>2</sub>-2)I(PPh<sub>3</sub>)] (4).** PPh<sub>3</sub> (67 mg, 0.255 mmol) was added to a suspension of complex 2 (100 mg, 0.127 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), and the resulting solution was stirred for 1 h. The mixture was filtered through a plug of  $\text{MgSO}_4$ , solvent was removed from the filtrate, and the residue was vigorously stirred in  $\text{Et}_2\text{O}$  (15 mL) for 15 min. The suspension was filtered, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 1$  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  $\text{C}_{29}\text{H}_{29}\text{INPPd}$  (655.836): C, 53.11; H, 4.46; N, 2.14. Found: C, 53.14; H, 4.69; N, 2.21. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$  1659 m.  $^1\text{H}$  NMR (400.91 MHz):  $\delta$  1.92 (s, 3 H, Me), 2.55 (br s, 3 H, Me), 2.99 (dd, 1 H,  $\text{CH}_2\text{Ar}$ ,  $^2J_{\text{HH}} = 13.4$ ,  $^3J_{\text{HH}} = 4.0$  Hz), 3.08 (m, 1 H,  $\text{CH}_2\text{N}$ ), 3.80 (m, 1 H,  $\text{CH}_2\text{N}$ ), 4.27 (td,  $^2J_{\text{HH}} = ^3J_{\text{HH}} = 13.4$ ,  $^3J_{\text{HH}} = 6.4$  Hz), 6.27–6.32 (m, 2 H, H4 + H6), 6.71 (td, 1 H, H5,  $^3J_{\text{HH}} = 7.2$ ,  $^4J_{\text{HH}} = 2.0$  Hz), 6.81 (d, 1 H, H3,  $^3J_{\text{HH}} = 7.6$  Hz), 7.25–7.30 (m, 6 H, *m*-H, PPh<sub>3</sub>), 7.33–7.38 (m, 3 H, *p*-H, PPh<sub>3</sub>), 7.53–7.58 (m, 6 H, *o*-H, PPh<sub>3</sub>).  $^{13}\text{C}$  NMR (100.81 MHz):  $\delta$  22.2 (d, Me,  $^4J_{\text{CP}} = 5$  Hz), 34.3 (s, Me), 39.1 (s,  $\text{CH}_2\text{Ar}$ ), 49.7 (s,  $\text{CH}_2\text{N}$ ), 123.3 (s, CHS, C<sub>6</sub>H<sub>4</sub>), 125.3 (s, CH3 + CH6, C<sub>6</sub>H<sub>4</sub>), 127.8 (d, *m*-CH, PPh<sub>3</sub>,  $^3J_{\text{CP}} = 10.5$  Hz), 130.0 (d, *p*-CH, PPh<sub>3</sub>,  $^4J_{\text{CP}} = 1.9$  Hz), 132.0 (d, *i*-C, PPh<sub>3</sub>,  $^1J_{\text{CP}} = 50.1$  Hz), 134.9 (d, *o*-CH, PPh<sub>3</sub>,  $^2J_{\text{CP}} = 11.3$  Hz), 134.9 (s, CH4, C<sub>6</sub>H<sub>4</sub>), 140.1 (s, C2, C<sub>6</sub>H<sub>4</sub>), 155.6 (s, C1, C–Pd), 176.7 (s, C=N).  $^{31}\text{P}$  NMR (162.29 MHz):  $\delta$  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  $\text{CH}_2\text{Cl}_2$ .

**Single-Crystal X-ray Structure Determinations.** 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 K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and  $\omega$ -scan mode. Multiscan absorption corrections were applied. Solution and Refinements: Crystal structures were solved by direct (3b-I·CHCl<sub>3</sub>) or Patterson method (4), and all non-hydrogen atoms refined anisotropically on  $F^2$  using the program SHELXL-97.<sup>20</sup> Hydrogen atoms were refined as follows. Complex 3b-I·CHCl<sub>3</sub>: NH<sub>2</sub> free; methyl, rigid group; all others, riding. Complex 4: methyl, rigid group; all others, riding. Special features: Complex 3b-I·CHCl<sub>3</sub>: absolute structure (Flack) parameter<sup>21</sup> –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.

## ASSOCIATED CONTENT

**S Supporting Information.** CIF files of the structures of 3b-I·CHCl<sub>3</sub> and 4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [jvs1@um.es](mailto:jvs1@um.es) (J.V.); [ims@um.es](mailto:ims@um.es) (I.S.-L.).

## ACKNOWLEDGMENT

We thank the Ministerio de Educación y Ciencia (Spain), FEDER (CTQ2007-60808/BQU), and Fundación Séneca (04539/GERM/06) for financial support. J.-A.G.-L. and M.-J. O.-M. are grateful to the University of Murcia (Spain) and to the Ministerio de Educación y Ciencia (Spain), respectively, for their research grants.

## REFERENCES

- (1) Biscoe, M. R.; Buchwald, S. L. *Org. Lett.* **2009**, *11*, 1773.
- (2) Johansson, C. C. C.; Colacot, T. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 676.
- (3) Biscoe, M. R.; Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 6686.
- (4) Fors, B. P.; Watson, D. A.; Biscoe, M. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 13552.
- (5) Fors, B. P.; Davis, N. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, S766.
- (6) Maiti, D.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 17423.
- (7) Lee, B. K.; Biscoe, M. R.; Buchwald, S. L. *Tetrahedron Lett.* **2009**, *50*, 3672.
- (8) Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 15914.
- (9) Henderson, J. L.; Buchwald, S. L. *Org. Lett.* **2010**, *12*, 4442.
- (10) Hartman, R. L.; Naber, J. R.; Zaborenko, N.; Buchwald, S. L.; Jensen, K. F. *Org. Process Res. Dev.* **2010**, *14*, 1347.
- (11) Naber, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 9469.
- (12) Maiti, D.; Fors, B. P.; Henderson, J. L.; Nakamura, Y.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 57.
- (13) Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 826.
- (14) Vicente, J.; Saura-Llamas, I.; Cuadrado, J.; Ramírez de Arellano, M. C. *Organometallics* **2003**, *22*, 5513.
- (15) Vicente, J.; Saura-Llamas, I.; Bautista, D. *Organometallics* **2005**, *24*, 6001.
- (16) Vicente, J.; Saura-Llamas, I.; García-López, J. A.; Calmuschi-Cula, B.; Bautista, D. *Organometallics* **2007**, *26*, 2768.
- (17) For another generation of pre-catalysts, see Kinzel, T.; Zhang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14073.
- (18) A patent application for the method reported here has been submitted (P201031658).
- (19) Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Russ. Chem. Rev.* **1988**, *57*, 250.
- (20) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
- (21) Kurzev, S. A.; Kazankov, G. M.; Ryabov, A. D. *Inorg. Chim. Acta* **2002**, *340*, 192.
- (22) Lapointe, D.; Fagnou, K. *Chem. Lett.* **2010**, *39*, 1118.
- (23) Vicente, J.; Saura-Llamas, I. *Comments Inorg. Chem.* **2007**, *29*, 39.
- (24) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2969.
- (25) Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3619.
- (26) Vicente, J.; Saura-Llamas, I.; Turpin, J.; Bautista, D.; Ramírez de Arellano, C.; Jones, P. G. *Organometallics* **2009**, *28*, 4175.

- (15) Wu, G. Z.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *S*, 1922. Maassarani, F.; Pfeffer, M.; Le Borgne, G. *J. Chem. Soc., Chem. Commun.* **1987**, 565. Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029. Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2043. Dupont, J.; Pfeffer, M.; Daran, J.-C.; Gouteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421. Maassarani, F.; Pfeffer, M.; Spencer, J.; Wehman, E. *J. Organomet. Chem.* **1994**, 466, 265. Spencer, J.; Pfeffer, M.; De Cian, A.; Fischer, J. *J. Org. Chem.* **1995**, *60*, 1005.
- (16) Vicente, J.; Saura-Llamas, I.; García-López, J. A.; Bautista, D. *Organometallics* **2009**, *28*, 448.
- (17) Fuchita, Y.; Tsuchiya, H.; Miyafuji, A. *Inorg. Chim. Acta* **1995**, *233*, 91. Albert, J.; Granell, J.; Tavera, R. *Polyhedron* **2003**, *22*, 287.
- (18) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, 576, 23. Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. Díez, L.; Espinet, P.; Miguel, J. A. *J. Chem. Soc., Dalton Trans.* **2001**, 1189. Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, 689, 4055.
- (19) Albert, J.; Gomez, M.; Granell, J.; Sales, J.; Solans, X. *Organometallics* **1990**, *9*, 1405. Albert, J.; Cadena, J. M.; González, A.; Granell, J.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **2002**, 663, 277. Albert, J.; Cadena, J. M.; González, A.; Granell, J.; Solans, X.; Font-Bardia, M. *Chem. Commun.* **2003**, 528. Albert, J.; Cadena, J. M.; González, A.; Granell, J.; Solans, X.; Font-Bardia, M. *Chem.—Eur. J.* **2006**, *12*, 887.
- (20) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.
- (21) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

#### ■ NOTE ADDED AFTER ASAP PUBLICATION

Reference 8 has been changed from the version of this citation that was first posted on the web on July 28, 2011. The version of reference 8 that appears as of August 17, 2011, is correct.