Articles

Orthometalation of Primary Amines. 4.[1] Orthopalladation of Primary Benzylamines and (2-Phenylethyl)amine[†]

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By the refluxing of an acetonitrile solution of $[Pd(OAc)_2]_3$ and primary amines 4-$XC_6H_4CH_2NH_2$ (F, Cl, NO_2, OMe), 3,5-$X_2C_6H_3CH_2NH_2$ (X = OMe), or $PhCH_2CH_2NH_2$ (Pd:amine = 1:1) and subsequent addition of excess NaBr, the corresponding orthometalated complexes $[Pd\{C_6H_3(CH_2NH_2)\text{-}2,X\text{-}5\}(\mu\text{-}Br)]_2$, $[Pd\{C_6H_3(CH_2NH_2)\text{-}2,(OMe)_2\text{-}4,6\}(\mu\text{-}Br)]_2$, or $[Pd\{C_6H_3(CH_2NH_2)\text{-}2\}(\mu\text{-}Br)]_2$ are obtained. Alternatively, the hydrochloride of 4-$XC_6H_4CH_2NH_2$ (X = F, NO_2) can also be used to prepare the corresponding $[Pd\{C_6H_3(CH_2NH_2)\text{-}2,X\text{-}5\}(\mu\text{-}Cl)]_2$ complexes. These results show that primary benzylamines can be orthometalated even if the substituents are electron-withdrawing groups and that 2-(phenyl)ethylamine can be orthometalated in spite of the six-membered ring that it forms. These reactions occur *via* intermediate complexes $[Pd(OAc)_2L_2]$, which react with $[Pd(OAc)_2]_3$ to give the dimeric species $[Pd(OAc)(\mu\text{-}OAc)L]_2$ (L = amine), from which in turn the orthometalated complexes are formed. Each of these steps has been studied, and both types of intermediates have been isolated for all the amines. PPh_3 reacts with the orthometalated complexes to give the corresponding products of the bridge splitting. The crystal structures of $[Pd(OAc)(\mu\text{-}OAc)L]_2$ (L = 4-$O_2NC_6H_4CH_2NH_2$) and $[Pd\{C_6H_4(CH_2CH_2NH_2)\text{-}2\}Br(PPh_3)]$ have been determined by X-ray diffraction.

Introduction

The early work of Cope and Friedrich on cyclopalladation of benzylamine[2] derivatives has served notice to other authors to assume three requirements that the amine must meet.[3] The first established that the amine must be tertiary. Thus, orthopalladation using lithium tetrachloropalladate(II) was observed with *N*,*N*-dimethylbenzylamine or some of its aryl-substituted derivatives containing electron-releasing groups (2-methoxy, 3,5-dimethoxy). However, it does not occur with benzylamine or some N-monosubstituted derivatives (methyl, benzyl, phenyl) or even with the highly activated *N*-phenyl-(3,5-dimethoxybenzyl)amine. The second requirement is that the aryl group must not be deactivated as in 4-nitro-*N*,*N*-dimethylbenzylamine. Finally, the Pd−C−N ring formed after metalation must be a planar five-membered ring. The unsuccessful orthopalladation of the potential precursors of six- and seven-membered rings, *N*,*N*-dimethyl-2-phenyl-1-ethylamine and *N*,*N*-dimethyl-3-phenyl-1-propylamine, was the proof of this requirement. When these conditions are not met the complex $[PdCl_2(amine)_2]$ is isolated instead.[2] Since this pioneering work, some violations of these rules have been observed on varying the nature of the amine or the palladium complex.[4] Thus, Lewis *et al.*[3] and later Dunina *et al.*[4c] found that, contrary to the first rule, substitution at the α-benzyl position with a phenyl or methyl group allows the orthopalladation of the primary amine (triphenylmethyl)amine and of the secondary amines *N*-methyl(triphenylmethyl)amine or *N*-methyl-(α-methylbenzyl)amine. Finally, the substi-

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(2) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

(3) Cockburn, B. N.; Howe, D. V.; Keating, T.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 404.

(4) (a) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (b) Omae, I. *Coord. Chem. Rev.* **1988**, *83*, 137. (c) Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Russ. Chem. Rev.* **1988**, *57*, 250 and references therein.

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tution of the usual starting chloro complex of palladium by $[Pd(acac)_2]$[5] or $[Pd(OAc)_2]_3$[6] or by reacting $[PdI_2(amine)_2]$ with $AgBF_4$[7] allowed the orthopalladation of benzylamine. Using these two last methods we have also orthometalated (4-nitro-α-methylbenzyl)amine, which infringes the second rule,[2b] and (α-methylbenzyl)amine.[2a] In this paper we report a general and facile way to prepare orthometalated non-α-substituted primary amines that contain either an electron-withdrawing substituent on the aryl ring or lead to a six-membered metallacycle, transgressing against the above-mentioned three rules. Most of these results were communicated in national and international conferences.[8] The generalization of orthopalladation reactions to primary amines can expand the use of these types of complexes in organic synthesis.[9]

Experimental Section

General Procedures. Infrared spectra were recorded on Perkin-Elmer 1430 and 16F-PC-FT spectrometers. The C, H, and N analyses, conductance measurements in acetone, and melting point determinations were carried out as described elsewhere.[1] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ in a Varian Unity 300. Chemical shifts are referenced to TMS [^{1}H and $^{13}C\{^1H\}$], H_3PO_4 [$^{31}P\{^1H\}$], or $CFCl_3$ (^{19}F). Benzylamine, (4-Nitrobenzyl)amine hydrochloride, (4-fluorobenzyl)amine hydrochloride, (4-chlorobenzyl)amine, (4-methoxybenzyl)amine, (3,5-dimethoxybenzyl)amine, and 2-(phenyl)ethylamine were purchased from Aldrich and $[Pd(OAc)_2]_3$ was purchased from Johnson Matthey and used as received. (4-Nitrobenzyl)amine and (4-fluorobenzyl)amine were prepared by reacting the corresponding hydrochloride with NaOH. All those complexes soluble in acetone show molar conductivities in the range 0−4 Ω^{-1} cm^2 mol^{-1}.

Synthesis of Complexes 1a,b,e−g. To a suspension of $[Pd(OAc)_2]_3$ (547 mg, 0.81 mmol) in acetone (20 mL) was added the amine (4.87 mmol) to form an immediate yellow precipitate, which was stirred for 2 h, filtered out, washed with ether, and air-dried.

Synthesis of Complexes 1c,d. To a suspension of the hydrochloride (1.59 mmol) in dichloromethane (10 mL) was added aqueous NaOH (1.6 mL of 1 M solution, 1.6 mmol). After 10 min a clear solution formed. The layers were separated, and the aqueous layer was washed with dichloromethane (3 × 8 mL). $[Pd(OAc)_2]_3$ (180 mg, 0.267 mmol) was added to the organic layer, and an immediate yellow precipitate formed. The suspension was stirred at room temperature for 2 h and then filtered; the solid was washed with dichloromethane and air-dried.

$[Pd(OAc)_2(PhCH_2NH_2)_2]$ (1a). Yield: 83%. Mp: 140 °C dec. NMR (δ): ^{1}H, 1.85 (s, 3 H, Me), 3.74 (m, 2 H, CH_2), 4.24 (m, 2 H, NH_2), 7.27−7.41 (m, 5 H, Ph); $^{13}C\{^1H\}$, 23.5 (s, Me), 47.8 (s, CH_2), 128.1 (s, *p*-CH, Ph), 128.3, 128.9 (s, CH, Ph), 137.9 (s, C, Ph), 180.2 (s, CO). Anal. Calcd for $C_{18}H_{24}N_2O_4Pd$: C, 49.27; H, 5.51; N, 6.38. Found: C, 49.29; H, 5.51; N, 6.36.

$[Pd(OAc)_2(4\text{-}ClC_6H_4CH_2NH_2)_2]$ (1b). Yield: 87%. Mp: 172−174 °C dec. Anal. Calcd for $C_{18}H_{22}Cl_2N_2O_4Pd$: C, 42.58; H, 4.37; N, 5.52. Found: C, 42.92; H, 4.35; N, 5.63.

$[Pd(OAc)_2(4\text{-}NO_2C_6H_4CH_2NH_2)_2]\cdot 2H_2O$ (1c·2H$_2$O). Yield: 88%. Decomposition point: 149 °C. Anal. Calcd for $C_{18}H_{26}N_4O_{10}Pd$: C, 38.28; H, 4.64; N, 9.92. Found: C, 38.20; H, 4.55; N, 9.62.

$[Pd(OAc)_2(4\text{-}FC_6H_4CH_2NH_2)_2]$ (1d). Yield: 90%. Decomposition point: 158 °C. Anal. Calcd for $C_{18}H_{22}F_2N_2O_4Pd$: C, 45.54; H, 4.67; N, 5.90. Found: C, 45.71; H, 4.70; N, 5.86.

$[Pd(OAc)_2(4\text{-}MeOC_6H_4CH_2NH_2)_2]$ (1e). Yield: 75%. Mp: 158−159 °C dec. NMR (δ): ^{1}H, 1.87 (s, 3 H, Me), 3.67 (m, 2 H, CH_2), 3.78 (s, 3 H, OMe), 4.09 (m, 2 H, NH_2), 6.87 and 7.27 (AB, 4 H, C_6H_4, $^3J_{AB}$ = 8.4 Hz); $^{13}C\{^1H\}$, 23.6 (s, Me), 47.3 (s, CH_2), 55.3 (s, OMe), 114.3, 129.6 (s, CH, C_6H_4), 130.1, 159.4 (s, C, C_6H_4), 180.2 (s, CO). Anal. Calcd for $C_{20}H_{28}N_2O_6Pd$: C, 48.15; H, 5.66; N, 5.62. Found: C, 48.42; H, 5.80; N, 5.71.

$[Pd(OAc)_2\{3,5\text{-}(MeO)_2C_6H_3CH_2NH_2\}_2]\cdot 2H_2O$ (1f·2H$_2$O). Yield: 74%. Mp: 133 °C. Anal. Calcd for $C_{22}H_{36}N_2O_{10}Pd$: C, 44.42; H, 6.10; N, 4.71. Found: C, 44.19; H, 6.13; N, 4.82.

$[Pd(OAc)_2(PhCH_2CH_2NH_2)_2]$ (1g). Yield: 77%. Mp: 129 °C. NMR (δ): ^{1}H, 1.85 (s, 3 H, Me), 2.81 (m, 2 H, CH_2), 3.03 (m, 2 H, CH_2), 3.79 (m, 2 H, NH_2), 7.20−7.33 (m, 5 H, Ph); $^{13}C\{^1H\}$, 23.4 (s, Me), 36.2 (s, CH_2), 44.6 (s, CH_2), 126.7 (s, *p*-CH, Ph), 128.6, 128.7 (s, CH, Ph), 137.6 (s, C, Ph), 179.8 (s, CO). Anal. Calcd for $C_{20}H_{28}N_2O_4Pd$: C, 51.46; H, 6.05; N, 6.00. Found: C, 50.30; H, 5.92; N, 5.93.

Synthesis of Complexes 2a−g. To a suspension of the corresponding $[Pd(OAc)_2(amine)_2]$ (0.531 mmol) in dichloromethane (15 mL) was added $[Pd(OAc)_2]_3$ (119 mg, 0.177 mmol). The mixture was stirred at room temperature for 18 h, during which time a red solution formed. The solution was filtered through $MgSO_4$ and reduced in volume to *ca.* 2 mL, and *n*-hexane (diethyl ether in the case of **2c**) was added to precipitate the product as an orange solid. The complex was filtered out, washed with diethyl ether, and air-dried to give **2a−g** as an orange solid.

$[Pd(OAc)(\mu\text{-}OAc)(PhCH_2NH_2)]_2$ (2a). Yield: 81%. Mp: 85 °C. NMR (δ): ^{1}H, 1.88 (s, 3 H, Me), 1.89 (s, 3 H, Me), 3.54 (m, 1 H, CH_2), 3.68 (m, 1 H, CH_2), 4.22 (m, 1 H, NH), 5.35 (m, 1 H, NH), 7.34−7.52 (m, 5 H, Ph); $^3C\{^1H\}$, 23.0, 23.2 (s, Me), 47.9 (s, CH_2), 128.3 (s, *p*-CH, Ph), 128.4, 129.1 (s, CH, Ph), 137.6 (s, C, Ph), 180.0, 185.8 (s, CO). Anal. Calcd for $C_{22}H_{30}N_2O_8Pd_2$: C, 39.84.70; H, 4.56; N, 4.22. Found: C, 39.73; H, 4.57; N, 4.27.

$[Pd(OAc)(\mu\text{-}OAc)(4\text{-}ClC_6H_4CH_2NH_2)]_2$ (2b). Yield: 79%. Mp: 69−70 °C. NMR (δ): ^{1}H, 1.88, 1.89 (s, 3 H, Me), 3.61 (m, 2 H, CH_2), 4.25 (m, 1 H, NH), 5.44 (m, 1 H, NH), 7.34 y 7.50 (AB, 4 H, C_6H_4, $^3J_{AB}$ = 7.8 Hz); $^{13}C\{^1H\}$, 23.0, 23.2 (s, Me), 47.1 (s, CH_2), 129.2 (s, CH, C_6H_4), 130.0 (s, CH, C_6H_4), 134.3, 135.4 (s, C, C_6H_4), 180.0, 185.9 (s, CO). Anal. Calcd for $C_{22}H_{28}Cl_2N_2O_8Pd_2$: C, 36.09; H, 3.85; N, 3.83. Found: C, 36.37; H, 3.84; N, 4.05.

$[Pd(OAc)(\mu\text{-}OAc)(4\text{-}NO_2C_6H_4CH_2NH_2)]_2$ (2c). Yield: 94%. Mp: 219−220 °C. NMR (δ): ^{1}H, 1.89, 1.91 (s, 3 H, Me), 3.75 (m, 2 H, CH_2), 4.26 (m, 1 H, NH), 5.69 (m, 1 H, NH), 7.79 and 8.30 (AB, 4 H, C_6H_4, $^3J_{AB}$ = 8.4 Hz); $^{13}C\{^1H\}$ [$(CD_3)_2CO$, δ], 24.0, 24.2 (s, Me), 48.2 (s, CH_2), 125.4, 130.8 (s, CH, C_6H_4), 145.6, 149.2 (s, C, C_6H_4), 181.2, 187.2 (s, CO). Anal. Calcd for $C_{22}H_{28}N_4O_{12}Pd_2$: C, 35.08; H, 3.75; N, 7.44. Found: C, 34.72; H, 3.82; N, 7,56.

$[Pd(OAc)(\mu\text{-}OAc)(4\text{-}FC_6H_4CH_2NH_2)]_2$ (2d). Yield: 90%. Mp: 75−76 °C. NMR (δ): ^{1}H, 1.89, 1.90 (s, 3 H, Me), 3.61 (m, 2 H, CH_2), 4.24 (m, 1 H, NH), 5.42 (m, 1 H, NH), 7.09 (apparent triplet, 2 H, C_6H_4, $^3J_{HH} = {}^3J_{FH}$ = 8.7 Hz), 7.54 (dd, 2 H, C_6H_4, $^4J_{FH}$ = 5.25); $^{13}C\{^1H\}$, 22.9, 23.1 (s, Me), 47.0 (s, CH_2), 115.9 (d, CH, C_6H_4, $^2J_{FC}$ = 21.6 Hz), 130.3 (d, CH, C_6H_4, $^3J_{FC}$ = 8.6 Hz), 132.7 (d, C, C_6H_4, $^4J_{FC}$ = 3.5 Hz), 162.6 (s, C, C_6H_4, $^1J_{FC}$

(5) Baba, S.; Kawaguchi, S. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 415.
(6) Fuchita, Y.; Tsuchiya, H.; Miyafuji, A. *Inorg. Chim. Acta* **1995**, *233*, 91.
(7) Avshu, A.; O'Sullivan, R. D.; Parkins, A. W.; Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1619.
(8) Presented at the XIth FECHEM Conference on Organometallic Chemistry, Sept 10−15, 1995 (p 114 of the book of Abstracts), Parma, Italy. Presented at the XV Reunión del G.E.Q.O. September, 20−22, 1995 (Poster 67) Sevilla, Spain.
(9) Ryabov, A. D. *Synthesis*, **1985**, 233. Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335. Camargo, M.; Dani, P.; Dupont, J.; de Souza, R. F.; Pfeffer, M.; Tkatchenko, I. *J. Mol. Catal. A* **1996,** *109*, 127. Brisdon, Nair, P.; B. J.; Dyke, S. F. *Tetrahedron* **1981**, *37*, 173. Ryabov, A. D.; Sakodinskaya, I. K.; Dvoryantsev, S. N.; Eliseev, A. V.; Yatsimirsky, A. K.; Kuz'mina, L. G.; Struchkov, Yu. T. *Tetrahedron Lett.* **1986**, *27*, 2169. Clark, P. W.; Dyke, H. J.; Dyke, S. F.; Perry, G. *J. Organomet. Chem.* **1983**, *253*, 399. Pfeffer, M.; Sutter, J.-P.; DeCian, A.; Fischer, J. *Inorg. Chim. Acta* **1994**, *220*, 115.

= 247 Hz), 179.8, 185.7 (s, CO); ^{19}F, −113.7 (m). Anal. Calcd for $C_{22}H_{28}F_2N_2O_8Pd_2$: C, 37.79; H, 4.04; N, 4.01. Found: C, 38.04; H, 4.20; N, 3.80.

[Pd(OAc)(μ-OAc)(4-MeOC$_6$H$_4$CH$_2$NH$_2$)]$_2$ (2e). Yield: 73%. Mp: 58−60 °C. NMR (δ): ^{1}H, 1.89, 1.90 (s, 3 H, Me), 3.56 (m, 2 H, CH_2), 3.81 (s, 3 H, OMe), 4.20 (m, 1 H, NH), 5.27 (m, 1 H, NH), 6.92 and 7.44 (AB, 4 H, C_6H_4, $^3J_{AB}$ = 8.7 Hz); ^{13}C{^{1}H}, 23.0, 23.2 (s, Me), 47.2 (s, CH_2), 55.3 (s, OMe), 114.3 (s, CH, C_6H_4), 129.2 (s, C, C_6H_4), 129.8 (s, CH, C_6H_4), 159.5 (s, C, C_6H_4), 179.9, 185.6 (s, CO). Anal. Calcd for $C_{24}H_{34}N_2O_{10}Pd_2$: C, 39.85; H, 4.74; N, 3.87. Found: C, 40.41; H, 4.84; N, 3.94.

[Pd(OAc)(μ-OAc)(3,5-(MeO)$_2$C$_6$H$_3$CH$_2$NH$_2$)]$_2$ (2f). Yield: 87%. Mp: 67 °C. NMR (δ): ^{1}H, 1.89, 1.92 (s, 3 H, Me), 3.56 (m, 2 H, CH_2), 3.81 (s, 6 H, OMe), 4.20 (m, 1 H, NH), 5.37 (m, 1 H, NH), 6.42 (t, 1 H, C_6H_3, J = 2.1 Hz), 6.66 (d, 2 H, C_6H_3). Anal. Calcd for $C_{26}H_{38}N_2O_{12}Pd_2$: C, 39.86; H, 4.89; N, 3.58. Found: C, 39.87; H, 4.86; N, 3.53.

[Pd(OAc)(μ-OAc)(PhCH$_2$CH$_2$NH$_2$)]$_2$ (2g). Yield: 84%. Mp: 64 °C. NMR (δ): ^{1}H, 1.88 (s, 6 H, Me), 2.55 (m, 1 H, CH_2), 2.71 (m, 1 H, CH_2), 3.25 (m, 2 H, CH_2), 3.76 (m, 1 H, NH), 5.14 (m, 1 H, NH), 7.25−7.39 (m, 5 H, Ph); ^{13}C{^{1}H}, 22.9, 23.1 (s, Me), 36.3 (s, CH_2), 44.6 (s, CH_2), 126.8 (s, *p*-CH, Ph), 128.7, 128.9 (s, CH, Ph), 137.6 (s, C, Ph), 179.7, 185.6 (s, CO). Anal. Calcd for $C_{24}H_{34}N_2O_8Pd_2$: C, 41.70; H, 4.96; N, 4.05. Found: C, 40.76; H, 4.82; N, 3.98.

Synthesis of Complexes 3. Method a. The amine (1.22 mmol) and $[Pd(OAc)_2]_3$ (273 mg, 0.407 mmol) were refluxed in acetonitrile (20 mL) for 4 h. The resulting suspension was filtered through a plug of $MgSO_4$, the solvent removed, and acetone (25 mL) added. Solid NaBr (200 mg, 1.94 mmol) was added and the suspension stirred for 4 h. The solvent was removed, and the residue was collected with CH_2Cl_2, washed with water (3 × 15 mL) and diethyl ether (3 × 15 mL) and air-dried to afford complex **3** as a yellow (**3b**,**e**), orange (**3c**,**d**,**g**) or white solid (**3f**).

Method b. The corresponding complex **2** (0.546 mmol) was refluxed in acetonitrile (10 mL) for 4 h. The resulting mixture was filtered through a plug of $MgSO_4$, the solvent removed, and acetone (30 mL) added. Solid NaBr (230 mg, 2.24 mmol) was added and the resulting suspension stirred for 4 h. Solvent was removed, and the residue was collected with CH_2Cl_2, washed with water (3 × 15 mL) and diethyl ether (3 × 15 mL), and air-dried to afford complex **3**.

Method c. The amine·HCl (4.94 mmol) and $[Pd(OAc)_2]_3$ (1.11 g, 1.647 mmol) were refluxed in acetonitrile (50 mL) for 4 h. Solid NaBr (1.50 g, 14.58 mmol) was added to the suspension and the resulting mixture stirred for 8 h. Solvent was removed, and the residue was collected with CH_2Cl_2, washed with water (3 × 15 mL) and diethyl ether (3 × 15 mL), and air-dried to afford complex **3**.

Method d. Complex **2** (205 mg, 0.262 mmol) was dissolved in CH_2Cl_2 and solvent removed. The flask was kept in the oven at 80 °C for 2 h. Acetone (20 mL) and NaBr (200 mg, 1.94 mmol) were added, and the resulting mixture stirred for 4 h. A white solid precipitated. Solvent was removed, and the residue was collected with CH_2Cl_2, washed with water (3 × 15 mL) and diethyl ether (3 × 15 mL), and air-dried to afford complex **3**.

[Pd{C$_6$H$_4$(CH$_2$NH$_2$)-2}(μ-AcO)]$_2$ (3a). The amine (1.22 mmol) and $[Pd(OAc)_2]_3$ (273 mg, 0.407 mmol) were refluxed in acetonitrile (20 mL) for 4 h. The resulting suspension was filtered through a plug of $MgSO_4$ and the solvent removed, and the residue was collected with acetone, washed with diethyl ether (3 × 15 mL), and air-dried to afford complex **3a** as a yellow solid. Yield: 44%. Complex **3a** can also be prepared by refluxing complex **2a** (0.546 mmol) in acetonitrile (20 mL) for 2 h. Yield: 49%. The spectroscopic data of **3a** are identical to those reported in the literature.[6]

[Pd{C$_6$H$_3$(CH$_2$NH$_2$)-2,Cl-5}(μ-Br)]$_2$ (3b). Methods a (yield: 51%) and b (yield: 68%) were used. Mp: 234 °C dec. Anal. Calcd for $C_{14}H_{14}Br_2Cl_2N_2Pd_2$: C, 25.72; H, 2.16; N, 4.28. Found: C, 25.68; H, 2.11; N, 4.10.

[Pd{C$_6$H$_3$(CH$_2$NH$_2$)-2,NO$_2$-5}(μ-Br)]$_2$ (3c). Method c was used. Yield: 66%. Decomposition point: 205 °C. NMR [$(CD_3)_2SO$, δ]: ^{1}H, 4.07 (m, 2 H, CH_2), 5.76 (m, 2 H, NH_2), 7.30 (m, 1 H, H3), 7.87 (m, 1 H, H4), 8.76 (s, b, 1 H, H6). Anal Calcd for $C_{14}H_{14}Br_2N_4O_4Pd_2$: C, 24.92; H, 2.09; N, 8.30. Found: C, 25.66; H, 2.16; N, 8.15.

[Pd{C$_6$H$_3$(CH$_2$NH$_2$)-2,NO$_2$-5}(μ-Cl)]$_2$ (3c′). Method c was used but with acetone as the reaction solvent and a reaction time of 7 h. Yield: 69%. No satisfactory elemental analysis could be obtained due to the insolubility of **3c′**, but it can be used as starting material to prepare **3c** or **4c′**.

[Pd{C$_6$H$_3$(CH$_2$NH$_2$)-2,F-5}(μ-Br)]$_2$ (3d). Method c was used. The complex was recrystallized from acetone/CH_2Cl_2. Yield: 69%. Decomposition point: 215 °C. NMR [$(CD_3)_2CO$, δ]: ^{1}H, 4.14 (t, 2 H, CH_2, $^3J_{HH}$ = 5.7 Hz), 4.97 (m, 2 H, NH_2), 6.52 (m, 1 H, H3), 6.81 (apparent triplet, 1 H, H4, $^3J_{HH} = {}^3J_{FH}$ = 7.8 Hz), 7.55 (s, b, 1 H, H6). ^{19}F, −119.6 (s, b). Anal. Calcd for $C_{14}H_{14}Br_2F_2N_2Pd_2$: C, 27.08; H, 2.27; N, 4.51. Found: C, 26.70; H, 2.06; N, 4.51.

[Pd{C$_6$H$_3$(CH$_2$NH$_2$)-2,F-5}(μ-Cl)]$_2$ (3d′). Complex **3d′** was prepared in a similar manner to **3c′**. Yield: 48%. Decomposition point: 198 °C. NMR [$(CD_3)_2SO$, δ]: ^{1}H, 3.92 (t, 2 H, CH_2, $^3J_{HH}$ = 5.7 Hz), 5.58 (m, 2 H, NH_2), 6.77 (dt, 1 H, H4, $^3J_{HH} = {}^3J_{FH}$ = 8.7, $^4J_{FH}$ = 2.4 Hz), 7.00 (dd, 1 H, H3, $^3J_{HH}$= 8.1, $^4J_{FH}$ = 6 Hz), 7.54 (dd, 1 H, H6, $^3J_{FH}$ = 10.2, $^4J_{HH}$ = 2.7 Hz). Anal. Calcd for $C_{14}H_{14}Cl_2F_2N_2Pd_2$: C, 31.61; H, 2.65; N, 5.27. Found: C, 31.53; H, 2.60; N, 4.99.

[Pd{C$_6$H$_3$(CH$_2$NH$_2$)-2,(OMe)-5}(μ-Br)]$_2$ (3e). Methods a (yield: 51%) and b (yield: 48%) were used. Mp: 185−186 °C dec. NMR [$(CD_3)_2SO$, δ]: ^{1}H, 3.63 (s, 3 H, OMe), 3.89 (t, 2 H, CH_2, $^3J_{HH}$ = 5.7 Hz), 5.46 (m, 2 H, NH), 6.55 (d, 1 H, H4, C_6H_3, $^3J_{HH}$ = 7.8 Hz), 6.57 (d, 1 H, H3, C_6H_3), 7.39 (s, 1 H, H6, C_6H_3). Anal. Calcd for $C_{16}H_{20}Br_2N_2O_2Pd_2$: C, 29.80; H, 3.13; N, 4.36. Found: C, 30.33; H, 3.00; N, 4.16.

[Pd{C$_6$H$_2$(CH$_2$NH$_2$)-2,(OMe)$_2$-4,6}(μ-Br)]$_2$ (3f). Methods a (yield: 41%), b (yield: 43%), and d (yield: 79%) were used. No satisfactory analysis could be obtained due to the insolubility of this complex, but it can be used as starting material to prepare **4f**.

[Pd{C$_6$H$_4$(CH$_2$CH$_2$NH$_2$)-2}(μ-Br)]$_2$ (3g). Methods a (yield: 30%) and b (yield: 37%). Decomposition point: 175 °C. NMR [$(CD_3)_2CO$, δ]: ^{1}H, 3.51 (m, 2 H, CH_2), 3.96 (m, 2 H, CH_2), 4.37 (m, 2 H, NH_2), 6.69 (m, 1 H, C_6H_4), 6.83 (m, 2 H, C_6H_4), 7.36 (s, 1 H, C_6H_4). Anal. Calcd for $C_{16}H_{20}Br_2N_2Pd_2$: C, 31.35; H, 3.29; N, 4.57. Found: C, 31.18; H, 3.18; N, 4.59.

Synthesis of Complexes 4. To a suspension of the corresponding complex **3** (0.089 mmol) in dichloromethane (12 mL) was added PPh_3 (47 mg, 0.179 mmol). After the mixture was stirred for 2 h, a colorless solution formed, which was filtered through $MgSO_4$ and concentrated to ca. 3 mL. Diethyl ether (15 mL) was added to precipitate complex **4** as an off-white (**4a**,**c**,**c′**,**d′**), pale yellow (**4b**,**d**,**e**,**f**), or tan (**4g**) solid which was filtered out, washed with diethyl ether, and air-dried.

[Pd{C$_6$H$_4$(CH$_2$NH$_2$)-2}(OAc)(PPh$_3$)] (4a). Yield: 75%. Decomposition point: 235 °C. NMR (δ): ^{1}H, 1.41 (s, 3 H, Me), 4.26 (m, 2 H, CH_2), 4.73 (m, 2 H, NH_2), 6.38 (m, 2 H, C_6H_4), 6.82 (apparent triplet, 1 H, C_6H_4, J_{HH} = 7.2), 6.94 (d, 1 H, C_6H_4, J = 7.5 Hz), 7.26−7.44 (m, 9 H), 7.64−7.73 (m, 6 H, Ph); ^{13}C{^{1}H}, 24.0 (s, CH_3), 52.2 (d, CH_2, $^3J_{PC}$ = 2.2 Hz), 121.5 (s, CH, C_6H_4), 124.0 (s, CH, C_6H_4), 125.0 (d, CH, C_6H_4, J_{PC} = 5.0 Hz), 128.2 (d, *o*-CH, PPh_3, $^2J_{PC}$ = 11.0 Hz), 130.6 (d, *i*-CH, PPh_3, $^1J_{PC}$ = 47.8 Hz), 130.7 (d, *p*-C, PPh_3, $^4J_{PC}$ = 2.5 Hz), 135.8 (d, *m*-CH, PPh_3, $^3J_{PC}$ = 12.1 Hz), 139.2 (d, CH, C_6H_4, J_{PC} = 10.5 Hz), 145.9 (d, C, C_6H_4, J_{PC} = 2.5 Hz), 154.3 (s, C, C_6H_4),

178.5 (s, CO); $^{31}P\{^1H\}$, 41.2 (s). Anal. Calcd for $C_{27}H_{26}NO_2PPd$: C, 60.74; H, 4.91; N, 2.62. Found: C, 60.70; H, 4.98; N, 2.65.

[Pd{$C_6H_3(CH_2NH_2)$-2,Cl-5}Br(PPh_3)] (4b). Yield: 76%. Mp: 258 °C dec. NMR (δ): ^1H, 3.84 (m, 2 H, NH_2), 4.32 (m, 2 H, CH_2), 6.82 (dd, 1 H, H3, $^3J_{HH} = 8.1$, $^6J_{PH} = 2.1$ Hz), 6.93 (d, 1 H, H6, $^4J_{PH} = 8.1$ Hz), 7.34−7.63 (m, 10 H, H4 + Ph), 7.68−7.74 (m, 6 H, Ph); $^{31}P\{^1H\}$, 38.6 (s). Anal. Calcd for $C_{25}H_{22}BrClNPPd$: C, 50.96; H, 3.76; N, 2.38. Found: C, 50.53; H, 3.58; N, 2.34.

[Pd{$C_6H_3(CH_2NH_2)$-2,NO_2-5}Br(PPh_3)] (4c). Yield: 66%. Mp: 242 °C dec. NMR [$(Me)_2SO$, δ]: 4.19 (m, 2 H, NH_2), 5.47 (m, 2 H, CH_2), 7.09 (dd, 1 H, H3, $^3J_{HH} = 5.7$ Hz, $^5J_{HP} = 2.4$ Hz), 7.23 (d, 1 H, H6, $^4J_{HP} = 8.1$ Hz), 7.41−7.52 (m, 9 H, Ph), 7.61−7.69 (m, 7 H, H4 + Ph); $^{31}P\{^1H\}$, 39.5 (s). Anal. Calcd for $C_{25}H_{22}BrN_2O_2PPd$: C, 50.07; H, 3.70; N, 4.67. Found: C, 50.37; H, 3.70; N, 4.21.

[Pd{$C_6H_3(CH_2NH_2)$-2,NO_2-5}Cl(PPh_3)] (4c′). Yield: 78%. Mp 210 °C dec. NMR (δ): ^1H, 4.20 (m, 2 H, NH_2), 4.26 (m, 2 H, CH_2), 7.01 (d, 1 H, H3, $^3J_{HH} = 8.4$ Hz), 7.21 (dd, 1 H, H4, $^6J_{PH} = 2.1$), 7.26−7.47 (m, 10 H), 7.65−7.74 (m, 6 H, Ph); $^{31}P\{^1H\}$, 39.7 (s). Anal. Calcd for $C_{25}H_{22}ClN_2O_2PPd$: C, 54.08; H, 3.99; N, 5.04. Found: C, 53.94; H, 3.94; N, 5.03.

[Pd{$C_6H_3(CH_2NH_2)$-2,F-5}Br(PPh_3)] (4d). Yield: 84%. Decomposition point: 225 °C. NMR (δ): ^1H, 3.90 (m, 2 H, NH_2), 4.29 (m, 2 H, CH_2), 5.99 (ddd, 1 H, H3, $^3J_{HH} = 8.7$, $^4J_{FH} = 6.3$, $^5J_{PH} = 2.7$ Hz), 6.53 (dt, 1 H, H4, $^3J_{FH} = {}^3J_{HH} = 8.7$, $^6J_{PH} = 2.4$ Hz), 6.95 (dd, 1 H, H6, $^3J_{FH} = 8.4$, $^4J_{PH} = 5.7$ Hz), 7.35−7.47 (m, 9 H), 7.62−7.74 (m, 6 H, Ph); $^{13}C\{^1H\}$, 53.5 (s, CH_2), 110.7 (d, CH, C_6H_3, $^2J_{FC} = 22.2$ Hz), 122.1 (d, CH, C_6H_3, $^3J_{FC} = 7.5$ Hz), 124.1 (dd, CH, C_6H_3, $^2J_{FC} = 19.7$ Hz, $^3J_{PC} = 10.1$ Hz), 128.2 (d, *o*-CH, PPh_3, $^2J_{PC} = 10.6$ Hz), 130.2 (d, *i*-C, PPh_3, $^1J_{PC} = 50.3$ Hz), 130.8 (s, *p*-CH, PPh_3), 135.2 (d, *m*-CH, PPh_3, $^3J_{PC} = 11.6$ Hz), 148.5 (s, C, C_6H_3), 151.5 (d, C, C_6H_3, $^2J_{PC} = 2.5$), 159.3 (d, C, C_6H_3, $^1J_{FC} = 247$ Hz); $^{31}P\{^1H\}$, 42.1 (s); ^{19}F, −117.0 (m). Anal. Calcd for $C_{25}H_{22}BrFNPPd$: C, 52.43; H, 3.87; N, 2.45. Found: C, 52.86; H, 3.96; N, 2.46.

[Pd{$C_6H_3(CH_2NH_2)$-2,F-5}Cl(PPh_3)] (4d′). Yield: 77%. Mp: 194 °C dec. NMR (δ): ^1H, 3.93 (m, 2 H, NH_2), 4.26 (m, 2 H, CH_2), 5.98 (ddd, 1 H, H3, $^3J_{HH} = 8.7$, $^4J_{FH} = 6$, $^5J_{PH} = 2.7$ Hz), 6.53 (dt, 1 H, H4, $^3J_{FH} = {}^3J_{HH} = 8.4$, $^6J_{PH} = 2.4$ Hz), 6.92 (dd, 1 H, H6, $^3J_{FH} = 8.4$, $^4J_{PH} = 5.7$ Hz), 7.32−7.84 (m, 9 H), 7.66−7.73 (m, 6 H, Ph); $^{13}C\{^1H\}$, 52.7 (s, CH_2), 110.6 (d, CH, C_6H_3, $^2J_{FC} = 22.2$ Hz), 122.1 (d, CH, C_6H_3, $^3J_{FC} = 7.5$ Hz), 124.1 (dd, CH, C_6H_3, $^2J_{FC} = 19.7$ Hz, $^3J_{PC} = 10.1$ Hz), 128.2 (d, *o*-CH, PPh_3, $^2J_{PC} = 10.6$ Hz), 130.2 (d, *i*-C, PPh_3, $^1J_{PC} = 50.3$ Hz), 130.8 (s, *p*-CH, PPh_3), 135.2 (d, *m*-CH, PPh_3, $^3J_{PC} = 11.6$ Hz), 148.5 (s, C, C_6H_3), 151.5 (d, C, C_6H_3, $J_{PC} = 2.5$), 159.4 (d, C, C_6H_3, $^1J_{FC} = 242.4$ Hz); $^{31}P\{^1H\}$, 40.9 (s); ^{19}F, −117.0 (m). Anal. Calcd for $C_{25}H_{22}ClFNPPd$: C, 56.84; H, 4.20; N, 2.65. Found: C, 57.05; H, 4.51; N, 2.55.

[Pd{$C_6H_3(CH_2NH_2)$-2,OMe-5}Br(PPh_3)] (4e). Yield: 66%. Mp: 225 °C dec. NMR (δ): ^1H, 2.93 (s, 3 H, OMe), 3.87 (m, 2 H, NH_2), 4.26 (m, 2 H, CH_2), 5.96 (dd, 1 H, H3, $J_{HH} = 6.3$, $J_{PH} = 2.1$ Hz), 6.42 (dd, 1 H, H4, $J_{HH} = 8.1$, $J_{PH} = 2.1$ Hz), 6.91 (d, 1 H, H6, $J_{PH} = 8.1$ Hz), 7.32−7.45 (m, 9 H), 7.70−7.76 (m, 6 H, Ph); $^{13}C\{^1H\}$, 53.6 (d, CH_2, $^3J_{PC} = 2.0$ Hz), 58.9 (s, OMe), 111.6 (s, CH, C_6H_3), 121.9 (s, CH, C_6H_3), 122.2 (d, CH, C_6H_3, $^3J_{PC} = 11.6$ Hz), 128.2 (d, *o*-CH, PPh_3, $^2J_{PC} = 11.1$ Hz), 130.8 (d, *p*-C, PPh_3, $^4J_{PC} = 2.6$ Hz), 131.3 (d, *i*-CH, PPh_3, $^1J_{PC} = 49.8$ Hz), 135.3 (d, *m*-CH, PPh_3, $^3J_{PC} = 12.1$ Hz), 144.7 (s, C, C_6H_3), 152.7 (s, C, C_6H_3), 155.9 (d, C, C_6H_3, $J_{PC} = 6.0$ Hz); $^{31}P\{^1H\}$, 43.2 (s). Anal. Calcd for $C_{26}H_{25}BrNOPPd$: C, 53.40; H, 4.31; N, 2.40. Found: C, 53.07; H, 4.30; N, 2.41.

[Pd{$C_6H_2(CH_2NH_2)$-2,$(OMe)_2$-4,6}Br(PPh_3)] (4f). Yield: 61%. Mp: 149 °C dec. NMR (δ): ^1H, 2.38 (s, 3 H, OMe), 3.70 (s, 5 H, NH_2 and OMe), 4.38 (m, 2 H, CH_2), 5.60 (d, 1 H, H3, $J_{PH} = 1.8$ Hz), 6.33 (d, 1 H, H4, $J_{PH} = 2.4$ Hz), 7.26−7.36 (m, 9 H, PPh_3), 7.68−7.74 (m, 6 H, PPh_3); $^{31}P\{^1H\}$, 37.0 (s). Anal. Calcd for $C_{27}H_{27}BrNO_2PPd$: C, 52.75; H, 4.43; N, 2.28. Found: C, 52.87; H, 4.80; N, 2.08.

[Pd{$C_6H_4(CH_2CH_2NH_2)$-2}Br(PPh_3)] (4g). Yield: 56%. Decomposition point: 205 °C. NMR (δ): ^1H, 2.79 (m, 2 H, CH_2), 3.18 (m, 2 H, CH_2), 3.38 (m, 2 H, NH_2), 6.34 (dt, 1 H, H4, $J_{HH} = 7.5$, $J_{PH} = 1.2$ Hz), 6.51 (dd, 1 H, H3, $J_{HH} = 6.9$, $J_{PH} = 4.3$ Hz), 6.77 (dt, 1 H, H5, $J_{HH} = 7.2$, $J_{PH} = 1.2$ Hz), 6.87 (dd, 1 H, H6, $J_{HH} = 6.9$ Hz, $J_{PH} = 1.8$ Hz), 7.25−7.40 (m, 9 H, Ph), 7.50−7.60 (m, 6 H, Ph); $^{13}C\{^1H\}$, 37.8 (d, CH_2, $^3J_{PC} = 2.5$ Hz), 43.1 (s, CH_2), 123.9 (s, CH, C_6H_4), 125.0 (s, CH, C_6H_4), 125.1 (s, CH, C_6H_4), 126.1 (s, CH, C_6H_4), 127.9 (d, *o*-CH, PPh_3, $^2J_{PC} = 11.1$ Hz), 130.2 (d, *p*-C, PPh_3, $J_{PC} = 2.5$ Hz), 131.4 (d, *i*-CH, PPh_3, $J_{PC} = 50.4$ Hz), 134.8 (d, *m*-CH, PPh_3, $^3J_{PC} = 11.6$ Hz), 136.2 (d, C, C_6H_4, $^2J_{PC} = 10.5$ Hz), 138.9 (s, C, C_6H_4). $^{31}P\{^1H\}$, 34.1 (s). Anal. Calcd for $C_{26}H_{25}BrNPPd$: C, 54.90; H, 4.43; N, 2.46. Found: C, 54.57; H, 4.45; N, 2.43.

Table 1. Crystal Data for Compounds $2c{\cdot}CH_3COCH_3$ and 4g

molecular formula	$C_{25}H_{34}N_4O_{13}Pd_2$	$C_{26}H_{25}BrNPPd$
M_r	811.36	568.75
source	liquid diffusion CH_2Cl_2/Et_2O	liquid diffusion CH_2Cl_2/n-hexane
description	lath	tablet
color	yellow	dark orange
cryst system	monoclinic	orthorhombic
a, Å	32.212(10)	10.626(1)
b, Å	8.493(3)	16.483(1)
c, Å	25.251(7)	26.284(2)
β, deg	112.795(10)	
V, Å^3	6369(4)	4603(1)
Z	8	8
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, K	173(2)	298(2)
monochromator	graphite	graphite
space group	*C*2/*c*	*Pbca*
cryst size, mm	0.65 × 0.15 × 0.05	0.32 × 0.32 × 0.10
μ, mm^{-1}	1.197	2.625
abs corr	ψ scans	ψ scans
max transm, %	0.96	1.00
min transm, %	0.74	0.69
diffractometer type	Siemens P4	Siemens P4
data collcn method	ω scans	ω scans
2θ range, min−max	6.1−50.0	6.2−50.0
hkl limits	$-5 < h < 38$	$-1 < h < 12$
	$-10 < k < 4$	$-1 < k < 19$
	$-30 < h < 27$	$-31 < l < 31$
reflcns measd	8416	9478
indepdt reflcns	5577	4047
R_{int}	0.064	0.052
R1 ($I > 2\sigma(I)$), w*R*2[a]	0.0529, 0.1248	0.0306, 0.0550

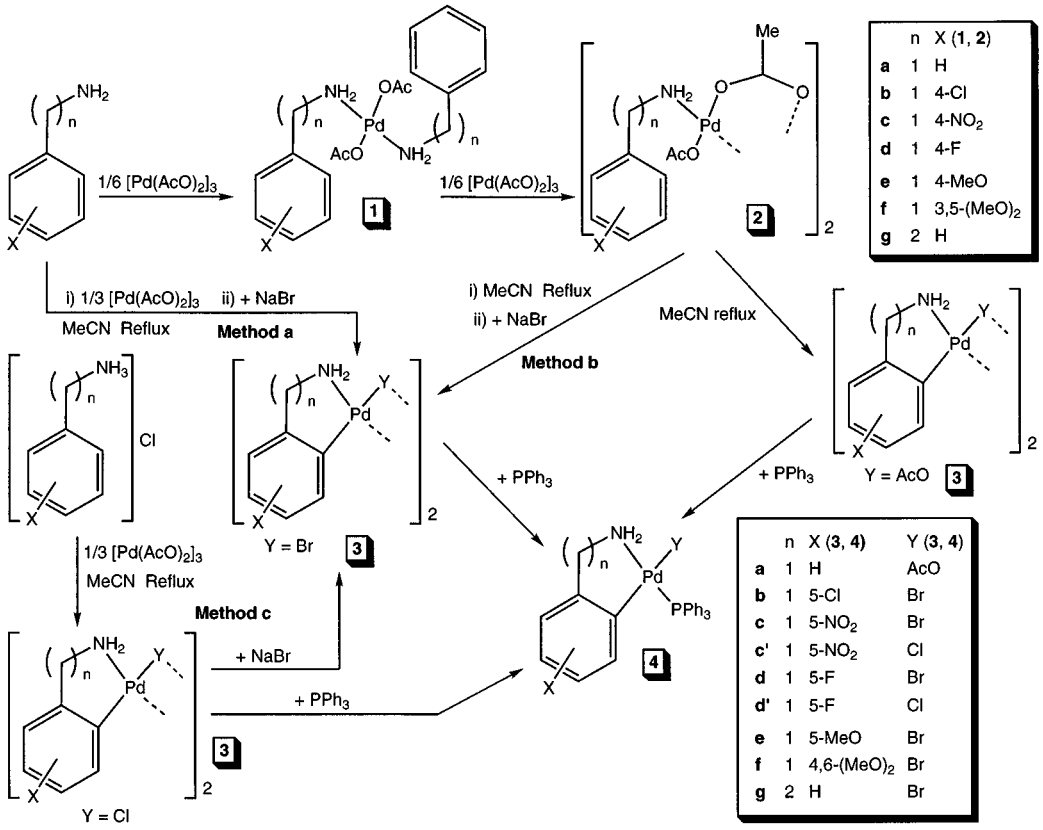
[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

Crystal Structures. A crystal of **2c** was mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. Unit cell parameters were determined from a least-squares fit of 53 accurately centered reflections ($8.0 < 2\theta < 22.9$). The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL 93).[10] Hydrogen atoms were included using a riding model or as rigid methyl groups. The final *R*(*F*) was 0.0529, for 390 parameters and 390 restraints. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and *a* and *b* are constants adjusted by the program. Maximum $\Delta/\sigma = 0.002$; maximum $\Delta\rho = 1.32$ e/Å^3.

A crystal of **4g** was mounted on a glass fiber and transferred to the diffractometer (Siemens P4) as summarized in Table 1. Unit cell parameters were determined from a least-squares fit of 42 accurately centered reflections ($6.1 < 2\theta < 24.7$). The structure was solved by direct methods and refined anisotro-

(10) Sheldrick, G. M. SHELXL 93, University of Göttingen, 1993.

Scheme 1



pically on F^2 (program SHELXTL).[11] Hydrogen atoms were included using a riding model. The final $R(F)$ was 0.0306, for 271 parameters and 230 restraints. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. Maximum $\Delta/\sigma = 0.001$; maximum $\Delta\rho = 0.28$ e/Å^3.

The programs use the neutral atom scattering factors $\Delta f'$ and $\Delta f''$ and absorption coefficients from ref 12.

Results and Discussion

Synthesis of Intermediates. When $C_6H_5CH_2NH_2$ or 4-$ClC_6H_4CH_2NH_2$ was reacted with $[Pd(OAc)_2]_3$ in molar ratio amine:Pd = 1 in acetone, an orange solution was obtained, in which a yellow solid gradually formed. This suspension led to another orange solution if stirred for several hours. When isolated, the intermediate yellow solid proved to be $[Pd(OAc)_2L_2]$ [L = $C_6H_5CH_2NH_2$ (**1a**), 4-$ClC_6H_4CH_2NH_2$ (**1b**)] in both cases. From the final orange solution the dimeric complex $[Pd(OAc)(\mu\text{-}OAc)L]_2$ [L = $C_6H_5CH_2NH_2$ (**2a**), 4-$ClC_6H_4CH_2NH_2$ (**2b**)] was obtained (see Scheme 1). The same process occurred more quickly in chloroform or dichloromethane. Thus, the reaction between $C_6H_5CH_2NH_2$ and $[Pd(OAc)_2]_3$ to give $[Pd(OAc)(\mu\text{-}OAc)L]_2$ lasted 8 h in acetone, but it was complete after 1.5 h in dichloromethane, probably because the intermediate $[Pd(OAc)_2L_2]$ is soluble in this solvent. These observations allowed the design of the best way to prepare other $[Pd(OAc)_2L_2]$ and $[Pd(OAc)(\mu\text{-}OAc)L]_2$ complexes. Thus, by using acetone as solvent, $[Pd(OAc)_2]_3$ reacted with different amines (amine:Pd = 2) to precipitate complexes $[Pd(OAc)_2L_2]$ [L = 4-$XC_6H_4CH_2NH_2$, X = H (**1a**), Cl (**1b**), NO_2 (**1c**), F (**1d**), OMe (**1e**); L = or 3,5-$X_2C_6H_3CH_2NH_2$, X = OMe (**1f**); L = $PhCH_2CH_2NH_2$ (**1g**)]. Dichloromethane was instead selected as solvent to prepare the corresponding complexes $[Pd(OAc)(\mu\text{-}OAc)L]_2$ (**2a**−**g**) by reacting the free amine with $[Pd(OAc)_2]_3$ (amine:Pd = 1). However, the synthesis of complexes **2a**−**g** was better achieved by reacting **1a**−**g** with $[Pd(OAc)_2]_3$ in molar ratio **1**:Pd = 1 in dichloromethane. To prove that complexes $[Pd(OAc)_2L_2]$ are intermediates in the synthesis of $[Pd(OAc)(\mu\text{-}OAc)L]_2$ from $[Pd(OAc)_2]_3$ and the amines not only in acetone but also in acetonitrile and in chlorinated solvents, the reaction between $[Pd(OAc)_2]_3$ and benzylamine (amine:Pd = 1) was monitored by ^{1}H NMR at room temperature. Initially, signals corresponding to the amine, complex **1a**, and unreacted $[Pd(OAc)_2]_3$ are present. After 5 min, **2a** started to form as shown by the presence of two multiplets corresponding to the CH_2 protons of this compound. With time, signals corresponding to complex **1a** decreased in intensity while the signal corresponding to complex **2a** became stronger. After 1.5 h, the reaction was complete and only complex **2a** was present in solution of $CDCl_3$. In acetonitrile, where most of the orthometalation reactions were carried out, the only difference is that the reaction is not completed after 2 h.

Orthometalation Reactions. By the refluxing of acetonitrile solutions of complexes **2a**−**g**, acetic acid is formed. The acetato complex **3a** can be isolated from this reaction, but in the other cases, the products are difficult to isolate as solids or to purify (see Scheme 1). In these cases, treatment of the resulting product with NaBr led to the orthometalated complexes [Pd{C_6H_3-

(11) SHELXTL, Version 5, Siemens Analytical X-Ray Instruments, Madison, WI, 1994.

(12) *International Tables for Crystallography*; Volume C (1992), Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502), 4.2.6.8 (pp 219−222), and 4.2.4.2 (pp 193−199).

(CH_2NH_2)-2,X-5}$(\mu$-Br)$]_2$ [X = Cl (**3b**), NO_2 (**3c**), F (**3d**), OMe (**3e**)], [Pd{$C_6H_2(CH_2NH_2)$-2,$(OMe)_2$-4,6}$(\mu$-Br)$]_2$ (**3f**), or [Pd{$C_6H_4(CH_2CH_2NH_2)$-2}$(\mu$-Br)$]_2$ (**3g**) (method a; see Scheme 1). Alternatively, one-pot synthesis of **3b**−**g** was achieved by refluxing a mixture of $[Pd(OAc)_2]_3$ and the amine (amine:palladium = 1) in acetonitrile for 4 h and then by addition of NaBr (method b; see Scheme 1). All these orthometalation reactions occur with some decomposition to metallic palladium. The best yields were obtained when the mixture was heated in acetonitrile slightly below its boiling point (78 °C). The orthometalation did not occur when a 2:1 amine:palladium molar ratio was used, but $[Pd(OAc)_2(L)_2]$ was formed instead.

A third method of orthometalation is applicable to the hydrochlorides of 4-$XC_6H_4CH_2NH_2$ (X = F, NO_2) (method c, see Scheme 1). Refluxing for 4 h acetonitrile solutions of $[Pd(OAc)_2]_3$ with these hydrochlorides (amine:Pd = 1) and then addition of NaBr led to **3c,d**. This one-pot synthesis is the best way to prepare these complexes. The chloro-bridging intermediates [Pd{$C_6H_3(CH_2NH_2)$-2,X-5}$(\mu$-Cl)$]_2$ [X = NO_2 (**3c′**), F (**3d′**)] in these reactions have been isolated. They can also be used to prepare **3c,d**. Orthometalation also occurs in the solid state for complexes **2e**,**f**, as shown by the smell of acetic acid. On heating complex **2f** at 80 °C in an oven, acetic acid formed and a black residue was obtained. When this residue was taken up in acetone and treated with an excess of NaBr, complex **3f** was isolated (65% yield). This observation points to the possibility that the C−H breaking takes place by an intramolecular interaction with the acetato ligand (see below).

Other solvents have also been tested as reaction media. Methods a and b have been tried with 4-$XC_6H_4CH_2NH_2$ (X = H, OMe, Cl) and with $PhCH_2CH_2NH_2$ using acetone or chloroform as solvent. Only in the case of benzylamine and acetone does the reaction works, even at room temperature. Method c also works in acetone, and this is the best way to prepare complexes **3c′**,**d′**.

Triphenylphosphine splits the halide bridge in complexes **3a**−**g**,**c′**,**d′** to give monomeric complexes **4a**−**g**,**c′**,**d′**, respectively.

Reaction Pathway. According to the above experimental data we can assume that reactions between $[Pd(OAc)_2]_3$ and amines give first the monomeric complexes **1**, which react with $[Pd(OAc)_2]_3$ to give the dimeric **2** (see Scheme 1). When an amine hydrochloride is used, its reaction with $[Pd(OAc)_2]_3$ could give acetic acid and mixed $[Pd(Cl)(AcO)L]_2$ complexes that, according to our data, give **3c′**,**d′** and acetic acid.

The only kinetic investigation on cyclopalladation of benzylamines, carried out by Ryabov, used *excess* amine (*N*,*N*-dimethylbenzylamine).[13] This circumstance prevents us from using his results because the precursor for Ryabov's orthometalation is $[Pd(OAc)_2(amine)_2]$, the amine is tertiary, and the reaction conditions are different. However, it is interesting to point out that, from the precursor $[Pd(OAc)_2(amine)_2]$, orthometalation requires[13] dissociation of one of the two coordinated amines to give "$Pd(OAc)_2L$" complexes. Therefore, also in this case, the immediate precursors of the orthometalated complexes are species related to our complexes **2**. We and other authors have also postulated the necessity of formation of complexes "$PdX_2(L)$" as precursors for orthometalation.[1,14] In our case, whether these monomeric T-shaped species lead to dimeric complexes like **2** and these are the immediate precursors for orthometalation or *vice versa*, it is difficult to ascertain. Although ^1H and ^{13}C NMR spectra of solutions in acetonitrile of **2a**,**b**,**e** are almost identical to those in $CDCl_3$, rapid equilibriums of these complexes with acetonitrile complexes could exist. In this case, these acetonitrile complexes could also be intermediates in the orthometalation reactions.

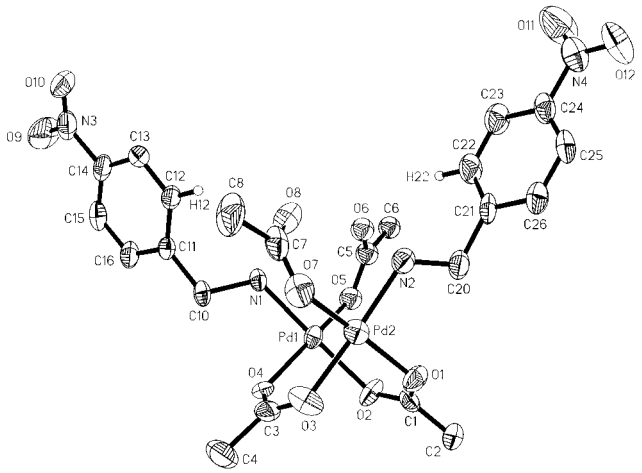


Figure 1. ORTEP plot of **2c** with the labeling scheme.

The crystal structure of complex **2c** (see Figure 1) reveals a distance of 2.429 Å between the oxygen atom O(6) of the monocoordinated acetate ligand bonded to Pd(1) and the *ortho* hydrogen atom H(22) of the amine coordinated to Pd(2), which is shorter than the sum of van der Waals radii of O and H (2.7 Å). A similar distance is observed between O(8) and H(12), 2.540 Å. These data suggest that the orthometalation reactions leading to **3e**,**f** by heating the dimers **2e**,**f** in the solid state could occur through an intramolecular process involving the above mentioned pairs of oxygen and hydrogen atoms. A similar proposal has been made by Ryabov for the orthometalation of *N*,*N*-dimethylbenzylamine in solution.[13] However, as mentioned above, he assumes a mononuclear intermediate "$Pd(OAc)_2L$" and, therefore, the interaction must occurs among ligands coordinated to the same palladium atom.

The reason given for the lack of orthometalation of primary amines is that the dissociative process $[Pd(OAc)_2(amine)_2] \rightarrow$ "$Pd(OAc)_2L$" + L is impossible for primary ones because they are bound more strongly to the metal.[13] Therefore, the problem can simply be overcome by starting from complexes $[Pd(OAc)(\mu$-$OAc)L]_2$ or by reacting $[Pd(OAc)_2]_3$ with the amine using a molar ratio Pd:amine = 1, as we did. The same ratio was used in all previous reactions that succeeded in

(13) (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403 and references therein. (b) Ryabov, A. D.; Sakodinskaya, I. N.; Yatsimirski, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629.

(14) Deeming, A. J.; Rothwell, I. P. *Pure Appl. Chem.* **1980**, *53*, 649. Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117. Nielson, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 205. Beller, M.; Riermeier, T. H.; Haber, S.; Kleiner, H.-J.; Herrmann, W. A. *Chem. Ber.* **1996**, *129*, 1259. Albert, J.; Granell, J.; Luque, A.; Mínguez, J.; Moragas, R.; Font-Bardía, M.; Soláns, X. *J. Organomet. Chem.* **1996**, *522*, 87.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 2c

Lengths			
Pd(1)−O(5)	1.953(10)	Pd(1)−O(4)	2.017(6)
Pd(1)−N(1)	2.021(6)	Pd(1)−O(2)	2.039(5)
Pd(2)−O(7)	1.985(6)	Pd(2)−O(3)	1.999(6)
Pd(2)−N(2)	2.008(7)	Pd(2)−O(1)	2.030(5)
O(1)−C(1)	1.251(8)	O(2)−C(1)	1.266(8)
O(3)−C(3)	1.255(10)	O(4)−C(3)	1.240(10)
O(7)−C(7)	1.273(12)	C(5)−O(5)	1.271(15)
N(1)−C(10)	1.509(9)	N(2)−C(20)	1.464(10)
Angles			
O(5)−Pd(1)−O(4)	163.5(3)	O(5)−Pd(1)−N(1)	88.9(4)
O(4)−Pd(1)−N(1)	91.6(2)	O(5)−Pd(1)−O(2)	86.7(3)
O(4)−Pd(1)−O(2)	92.2(2)	N(1)−Pd(1)−O(2)	175.4(2)
O(7)−Pd(2)−O(3)	86.0(3)	O(7)−Pd(2)−N(2)	90.0(3)
O(3)−Pd(2)−N(2)	176.0(3)	O(7)−Pd(2)−O(1)	170.3(3)
O(3)−Pd(2)−O(1)	90.9(3)	N(2)−Pd(2)−O(1)	92.9(3)
C(1)− O(1)−Pd(2)	127.0(5)	C(1)−O(2)−Pd(1)	124.8(5)
C(3)−O(3)−Pd(2)	124.0(6)	C(3)−O(4)−Pd(1)	125.6(6)
O(1)−C(1)−O(2)	125.3(8)	O(4)−C(3)−O(3)	127.2(9)

orthometalating benzylamine.[5−7] However, the attempt to orthometalate 2-(phenyl)ethylamine using [Pd(acac)$_2$] (1:1) was unsuccessful.[5] Our achievement is to have realized that formation of [Pd(OAc)(μ-OAc)L]$_2$ is the key to orthometalation of primary benzylamines and also for the synthesis of six-membered ring orthometalated primary amines as well as the use of acetonitrile as solvent.

Structure of Complexes. Complexes **1b**−**f** are insoluble in common organic solvents, but complexes **1a,e,g** dissolved easily in $CDCl_3$. Their ^{1}H NMR and ^{13}C NMR clearly indicated that only the *cis*- or *trans*-isomer was obtained, because only one set of signals was observed. We assumed a *trans*- geometry because it must be the thermodynamically most stable form, as proved for bis(amine)dihalogenopalladium(II) complexes.[15]

^{1}H NMR and ^{13}C{^{1}H} NMR for complexes **2a**−**g** showed only two signals for the acetate methyl groups: one for the bridging acetate methyl groups and another for the terminal acetate methyl groups. Thus, both ligands must have the same chemical enviroment and must adopt a *trans* disposition. This is proved by the crystal structure of complex **2c**, which has been determined by X-ray diffraction (Figure 1). Crystallographic data are listed in Table 1, and significant bond distances and bond angles are in Table 2. The structure of complex **2a** contains discrete dimeric molecules. Each palladium atom is bonded to four atoms in a square-planar coordination. The nitrogen of the amine and the oxygen atom from a terminal acetate group are mutually *cis*. The other two *cis* positions are occupied by two oxygen atoms from bridging acetates. The molecule only has a (noncrystallographic) C_2 axis, and so it is chiral. As far as we are aware, this is the first intermediate of this type isolated and characterized by X-ray diffraction.

It has been shown by IR[16] and X-ray diffraction studies[17] that complexes such as **3** have a dimeric *trans* geometry. We have determined the crystal structure of complex **4g** by X-ray diffraction (see Figure 2 and Tables 1 and 3), demonstrating the well-established

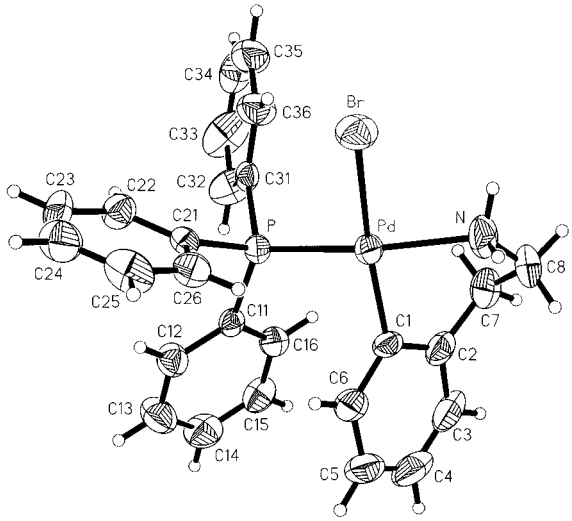


Figure 2. ORTEP plot of **4g** with the labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 4g

Lengths			
Pd−C(1)	2.004(4)	Pd−N	2.132(3)
Pd−P	2.2658(10)	Pd−Br	2.5682(5)
N−C(8)	1.464(5)	C(1)−C(6)	1.375(5)
C(1)−C(2)	1.399(5)	C(2)−C(3)	1.398(6)
C(2)−C(7)	1.498(5)	C(3)−C(4)	1.361(6)
C(4)−C(5)	1.360(6)	C(5)−C(6)	1.384(5)
C(7)−C(8)	1.518(5)		
Angles			
C(1)−Pd−N	87.97(14)	C(1)−Pd−P	91.70(11)
N−Pd−P	164.61(10)	C(1)−Pd−Br	166.47(11)
N−Pd−Br	85.95(9)	P−Pd−Br	97.36(3)
C(8)−N−Pd	119.5(2)	C(1)−C(2)−C(7)	120.1(4)
C(2)−C(7)−C(8)	110.6(4)	N−C(8)−C(7)	112.4(3)

tendency of PPh_3 and aryl ligands not to be *trans* each other when coordinated to class b metal atoms,[1b,18] according to the antisymbiotic effect.[18a] Compared to the structure of (*R*)-[Pd{$C_6H_3(CH_2(Me)NH_2)$-2}Br(PPh_3)][1a] (**A**), there are significant differences. Thus, whereas the Pd−C bond distances are similar [2.004(4) Å (**4g**) and 2.019(3) Å (**A**)], the Pd−N [2.132(3) Å], Pd−P [2.2658(10) Å], and Pd−Br [2.5682(5) Å] bond lengths in **4g** are longer than those in **A** [2.092(3), 2.244(1), 2.519(1) Å, respectively]. In addition, the palladium atom in **4g** has a very distorted square-planar coordination geometry: the angle between the planes Br−Pd−P and N−Pd−C(1) is 18.6°. Recent examples of this distortion have been described.[19] The Pd−N and Pd−C bonds form the basis of a six-membered chelate ring with an open-book shape. The angle between the Pd−C(1)−C(2)−C(7) and C(7)−C(8)−N−Pd planes is 58.5°.

(15) Coe, J. S.; Lyons, R. J. *Inorg. Chem.* **1970**, *9*, 1775.
(16) Dehand, J.; Pfeffer, M.; Shamir, J. *Spectrochim. Acta* **1977**, *33A*, 1101.
(17) Elder, R. C.; Cruea, R. D. P.; Morrison, R. F. *Inorg. Chem.* **1976**, *15*, 1623.
(18) (a) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712. (b) Dehand, J.; Jordanov, J.; Pfeffer, M.; Zinsius, M. *C. R. Acad. Sci., Ser. C* **1975**, *281*, 651. (c) Pfeffer, M.; Grandjean, D.; Le Borgne, G. *Inorg. Chem.* **1981**, *20*, 4426. (d) Arlen, C.; Pfeffer, M.; Bars, O.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1986**, 359. (e) Vicente, J.; Bermudez, M. D.; Carrion, F. J.; Jones, P. G. *J. Organomet. Chem.* **1996**, 508, 53. (f) Vicente, J.; Abad, J. A.; Fernandez-de-Bobadilla, R.; Jones, P. G.; Ramirez de Arellano, M. C. *Organometallics* **1996**, *15*, 24. (g) Vicente, J.; Bermudez, M. D.; Carrion, F. J. *Inorg. Chim. Acta* **1994**, *220*, 1. (h) Vicente, J.; Bermudez, M. D.; Carrillo M. P.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1992**, 1975. (i) Vicente, J.; Arcas, A; Bautista, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *New J. Chem.* **1996**, *20*, 345.
(19) (a) García-Ruano, J. L.; López-Solera, I.; Masaguer, J. R.; Navarro-Ranninger, C.; Martínez-Carrera, S. *Organometallics*, **1992**, *11*, 3013. (b) Minghetti, G.; Cinellu, M. A.; Ghelucci, G.; Gladiali, S.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107. (c) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (d) Newkome, G. R; Puckett, W. E.; Grupta, V. K.; Kieffer, G. E. *Chem. Rev* **1986**, *86*, 451.

Conclusions. We have shown, for the first time and contrary to previous hypotheses, that non-α-substituted primary benzylamines can be orthometalated even if the substituents are electron-withdrawing groups and that 2-(phenyl)ethylamine can be orthometalated in spite of the six-membered ring that is formed. Some probable intermediates of these orthometalation reactions have been isolated. If they are not, we have proved that can be used as starting materials for the orthopalladation. The crystal structure of one of these intermediates suggests the possibility that C−H activation is an intramolecular process.

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Supporting Information Available: Listings of X-ray parameters, all refined and calculated atomic coordinates, all isotropic and anisotropic thermal parameters, and complete bond lengths and angles for compounds **2c**·Me_2CO and **4g** (11 pages). Ordering information is given on any current masthead page.

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