Palladium-Assisted Formation of Carbon−Carbon Bonds. 8.[1] Synthesis and Reactivity toward Internal Alkynes, Carbon Monoxide, and Isocyanides of Orthopalladated Dibenzylamine Complexes

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By refluxing of dibenzylamine and $[Pd(OAc)_2]_3$ (3.2:1) in acetone, the orthometalated complex $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}(\mu\text{-}OAc)]_2$ (**1**) is obtained. Metathetical reaction of **1** with NaBr affords the corresponding bromo-bridging dimer $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}(\mu\text{-}Br)]_2$ (**2**). Neutral ligands split the bromo bridge to give monomeric complexes $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}Br(L)]$ [L = PPh_3, (**3a**), $NH(CH_2Ph)_2$ (**3b**)]. Complexes $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}(acac)]$ (**4**) or $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}L_2]ClO_4$ [L = py (**5a**), L_2 = 1,5-cyclooctadiene (**5b**)] can be obtained by reacting complex **2** with [Tl(acac)] or with $AgClO_4$ and the free ligand. Complex **2** reacts with RC≡CR (R = Me, Et, Ph) to give $[Pd\{C(R)=C(R)C(R)=C(R)\text{-}C_6H_4(CH_2NHCH_2Ph)\text{-}2\}Br]$ [R = Me (**6a**), Et (**6b**), Ph (**6c**)] through a double insertion of the alkyne into the Pd−C bond. Complex **6a** reacts with Tl(OTf) (OTf = CF_3SO_3) and neutral ligands to give $[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4(CH_2NHCH_2Ph)\text{-}2\}L]OTf$ [R = Me, L = py (**7**), phen (**8**)]. Complexes **6** insert CO or isocyanides R′NC into the C−Pd bond to give 10-membered palladacycles $[Pd\{C(R)=C(R)C(R)=C(R)C(E)C_6H_4(CH_2NHCH_2Ph)\text{-}2\}Br]$ [E = O, R = Me (**9a**), Et (**9b**), Ph (**9c**); E = NR′, R′ = ^{t}Bu, R = Me (**10a**), Et (**10b**); R′ = $C_6H_3Me_2$-2,6, R = Me (**11a**), Et (**11b**)]. Complex **9a** reacts with Tl(OTf) and neutral ligands to give $[Pd\{C(=O)C(R)=C(R)C(R)=C(R)C_6H_4(CH_2NHCH_2Ph)\text{-}2\}L]OTf$ [R = Me, L = py (**12**), ^{t}BuNC (**13**), phen (**14**)]. The crystal structures of **2**·CH_2Cl_2, **7**, **9a**, and **13** have been solved.

Introduction

Interest in orthometalated complexes arises from their potential application in organic synthesis,[2−8] in catalysis,[9−15] as chiral resolving agents,[16−27] as drugs,[28] and as new materials.[29−32]

The orthopalladation of aliphatic amines was initially reported to fail for primary and secondary amines.[33]

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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) but did not occur, for example, with L = benzylamine, dibenzylamine, and *N*-methyl- or *N*-phenylbenzylamine; these reactions led to the adducts $[PdCl_2L_2]$. However, using different palladium reagents and/or experimental reaction conditions, it has been demonstrated that benzylamine, and some of its secondary amine derivatives, can be orthometalated.[34−46] In this paper, we describe for the first time the orthopalladation of dibenzylamine and the synthesis of some derivatives of the resulting product.

Insertion reactions of alkynes into the metal−carbon bond of orthopalladated complexes and, in particular, those derived from tertiary benzylamines have been widely studied (mainly by Pfeffer).[2−5,47−57] We have reported the only study devoted to reactions of alkynes with an orthopalladated primary benzylamine.[58] As far as we are aware, Heck has reported the only known example of a reaction between an orthopalladated secondary amine and one acetylene.[57] In this paper, we give account of the first study of a cyclopalladated secondary amine (dibenzylamine) with various alkynes.

The insertion reactions of alkynes into the palladium−carbon bond are interesting processes that have been used, after depalladation,[2−4] to prepare spirocyclic compounds,[59,60] indenols, indenones,[61] carbocycles,[47,54,56,57,60,62,63] and oxygen,[50,64,65] sulfur,[5,66,67] and nitrogen heterocycles.[49,50,55,63,64,68−73] In some cases, the palladation reaction and the insertion of the alkyne form part of a catalytic cycle yielding interesting organic compounds.[57,74−85] Recently, Negishi has reported the reaction of 4-octyne with PhI and CO (10−40 atm) in the presence of Et_3N and catalytic amounts of $[PdCl_2(PPh_3)_2]$ at 100−140 °C to give 2-butenolides.[82] These compounds are formed through a sequential insertion of carbon monoxide−alkyne−carbon monoxide. In this paper we report the isolation of products resulting from the sequential insertion of alkyne and carbon monoxide at atmospheric pressure and temperature into the aryl−Pd bond. As far as we are aware, the only precedent for such reaction is that between CO and the diinserted product of the reaction of orthopalladated dimethylbenzylamine with 3-hexyne, although it was performed at 50 °C and 25 psi.[57]

Experimental Section

General Procedures. Unless otherwise stated, NMR spectra were recorded on $CDCl_3$ in a Varian Unity 300.

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Chemical shifts are referred to TMS [^{1}H and ^{13}C{^{1}H}] or H_3PO_4 [^{31}P{^{1}H}]. Reactions were carried out at room temperature without special precautions against moisture. **Warning:** *Perchlorate salts may be explosive!*

Solvents and reagents were purified as follows: acetone, distilled from $KMnO_4$; ether, distilled from Na/benzophenone; CH_2Cl_2, distilled from P_2O_5 and then from Na_2CO_3; *n*-hexane, distilled from $CaCl_2$. Dibenzylamine, 3-hexyne (Aldrich), 2-butyne, diphenylacetylene, and triphenylphosphine (Fluka) and $[Pd(OAc)_2]_3$ (Johnson Matthey) were used as received.

Synthesis of [Pd{C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}(μ-OAc)]$_2$ (1). Dibenzylamine (2 mL, 10.40 mmol) and $[Pd(OAc)_2]_3$ (2.2 g, 3.27 mmol) were refluxed in acetone (20 mL) for 2 h. Complex **1** precipitated as a dark yellow solid, which was collected, washed with diethyl ether (3 × 15 mL), and air-dried. Yield: 3.2 g, 4.42 mmol, 90%. Mp: 160−161 °C. Anal. Calcd for $C_{32}H_{34}N_2O_4Pd_2$ (723.4): C, 53.13; H, 4.74; N, 3.87. Found: C, 53.19; H, 4.80; N, 4.01. IR (Nujol, cm^{-1}): ν(NH) = 3166.

Synthesis of [Pd{C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}(μ-Br)]$_2$ (2). To a suspension of complex **1** (1010 mg, 1.397 mmol) in acetone (40 mL) was added solid NaBr (1000 mg, 9.718 mmol) and the resulting mixture stirred for 6 h. The solvent was removed, and the residue was taken up in CH_2Cl_2 (100 mL); the solution was filtered through a plug of $MgSO_4$ and concentrated to ca. 5 mL. Complex **2** precipitated as a bright yellow solid, which was collected and air-dried. Yield: 840 mg, 1.10 mmol, 78%. Mp: 113−114 °C. Λ_M = 2 Ω^{-1} cm^2 mol^{-1} (5.23 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{28}H_{28}Br_2N_2Pd_2$ (765.2): C, 43.95; H, 3.69; N, 3.66. Found: C, 44.07; H, 3.71; N, 3.63. IR (Nujol, cm^{-1}): ν(NH) = 3200. ^{1}H NMR ([D$_6$]acetone): δ = 3.95 (d, 2H, CH$_2$, $^3J_{HH}$ = 6.0 Hz), 4.10 (dd, 1H, CH$_2$, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 10.0 Hz), 4.56 (dd, 1H, CH$_2$, $^3J_{HH}$ = 3.0 Hz), 5.86 (s, b, 1H, NH), 6.73−6.91 (m, 3H, C$_6$H$_4$ and Ph), 7.29−7.44 (m, 4H, C$_6$H$_4$ and Ph), 7.60−7.63 (d, 2H, Ph). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 58.5 (s, CH$_2$), 60.1 (s, CH$_2$), 122.2 (s, CH, C$_6$H$_4$), 125.1 (s, CH, C$_6$H$_4$), 125.6 (s, CH, C$_6$H$_4$), 125.5 (s, CH, C$_6$H$_4$), 129.0 (s, *p*-CH, Ph), 129.5 (s, *o*-CH or *m*-CH, Ph), 130.4 (s, *o*-CH or *m*-CH, Ph), 135.6 (s, CH, C$_6$H$_4$), 136.7 (s, *i*-C, Ph), 146.0 (s, C, C$_6$H$_4$), 149.8 (s, C, C$_6$H$_4$).

Synthesis of [Pd{C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}Br(PPh$_3$)] (3a). To a suspension of complex **2** (41 mg, 0.053 mmol) in acetone (25 mL) was added solid PPh_3 (29 mg, 0.11 mmol). The resulting solution was stirred for 1 h and then filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether (25 mL) was added to precipitate complex **3a** as a pale yellow solid, which was collected and air-dried. Yield: 42 mg, 0.065 mmol, 61%. Mp: 214−215 °C (dec). Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (6.53 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{32}H_{29}BrNPPd$ (644.9): C, 59.60; H, 4.53; N, 2.17. Found: C, 59.69; H, 4.55; N, 2.19. IR (Nujol, cm^{-1}): ν(NH) = 3280. ^{1}H NMR ($CDCl_3$): δ = 3.80 (m, 3H, CH$_2$), 4.61 (m, 3H, NH and CH$_2$), 4.13 (m, 1H, NH), 6.34 (t, 1H, H4 or H5, C$_6$H$_4$, $^3J_{HH}$ = 7.2 Hz), 6.43 (t, 1H, H4 or H5, C$_6$H$_4$), 6.86 (t, 1H, H6, C$_6$H$_4$, $^3J_{HH}$ = $^4J_{HP}$ = 7.2 Hz), 7.04 (d, 1H, H3), 7.25−7.46 (m, 9H, Ph), 7.70−7.77 (m, 6H, Ph). ^{13}C{^{1}H}NMR ($CDCl_3$): δ = 54.0 (d, CH$_2$, J_{PC} = 2.0 Hz), 57.3 (d, CH$_2$, J_{PC} = 3.0 Hz), 122.9 (s, CH, C$_6$H$_4$), 124.1 (s, CH, C$_6$H$_4$), 125.0 (d, CH, C$_6$H$_4$, J_{PC} = 5.1 Hz), 128.0 (d, *o*-CH, PPh$_3$, J_{PC} = 11.1 Hz), 128.1 (s, CH, C$_6$H$_5$), 128.9 (s, CH, C$_6$H$_5$), 129.5 (s, CH, C$_6$H$_5$), 130.6 (d, *p*-CH, PPh$_3$, J_{PC} = 2.6 Hz), 131.5 (d, *i*-CH, PPh$_3$, J_{PC} = 49.3 Hz), 135.2 (d, *m*-CH, PPh$_3$, J_{PC} = 11.6 Hz), 136.3 (s, C, C$_6$H$_5$), 137.5 (d, CH, C$_6$H$_4$, J_{PC} = 10.6 Hz), 150.2 (d, C, C$_6$H$_4$, J_{PC} = 1.1 Hz), 153.0 (s, C, C$_6$H$_4$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 42.1 (s).

Synthesis of [Pd{C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}Br{(NH(CH$_2$Ph)$_2$}] (3b). To a suspension of complex **2** (123 mg, 0.161 mmol) in CH_2Cl_2 (20 mL) was added benzylamine (60 μL, 0.32 mmol). The resulting solution was stirred for 4 h and then filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and *n*-hexane (25 mL) was added to precipitate complex **3b** as a yellow solid, which was collected and air-dried. Yield: 142 mg, 0.245 mmol, 76%. Mp: 124−125 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5.50 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{28}H_{29}BrN_2Pd$ (579.9): C, 58.00; H, 5.04; N, 4.83. Found: C, 57.48; H, 4.83; N, 4.82. IR (Nujol, cm^{-1}): ν(NH) = 3240. ^{1}H NMR ($CDCl_3$): δ = 3.20 (m, 1H, NH), 3.48 (m, 2H, CH$_2$), 3.90−4.16 (m, 5H, CH$_2$ and NH), 4.62 (m, 2H, CH$_2$), 6.21 (d, 1H, C$_6$H$_4$, $^3J_{HH}$ = 7.2 Hz), 6.77−6.93 (m, 3H, C$_6$H$_4$), 7.31−7.73 (m, 15H, C$_6$H$_5$).

Synthesis of [Pd{C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}(acac)] (4). To a solution of complex **2** (350 mg, 0.457 mmol) in CH_2Cl_2 (50 mL) was added solid [Tl(acac)] (278 mg, 0.915 mmol), with stirring for 8 h. The resulting precipitate was removed by filtration through a plug of Celite. The solvent was removed to ca. 2 mL, and diethyl ether was added (25 mL) to obtain complex **4** as a white solid which was collected, washed with diethyl ether, and air-dried. Yield: 293 mg, 0.729 mmol, 80%. Mp: 209−211 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (1.02 × 10^{-3} mol L^{-1}). Anal. Calcd for $C_{19}H_{21}NO_2Pd$ (401.8): C, 56.80; H, 5.27; N, 3.49. Found: C, 56.88; H, 5.20; N, 3.48. IR (Nujol, cm^{-1}): ν(NH) = 3175. ^{1}H NMR ($CDCl_3$): δ = 1.95 (s, 3H, Me), 2.06 (s, 3H, Me), 3.74 and 3.95 (AB part of an ABX system, 2H, CH$_2$, $^2J_{AB}$ = 14 Hz, $^3J_{AX}$ = 12 Hz, $^3J_{BX}$ = 3 Hz), 3.99 (dd, 1H, CH$_2$, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 10.5 Hz), 4.26 (m, 1H, NH), 4.52 (dd, 1H, CH$_2$, $^3J_{HH}$ = 3 Hz), 5.34 (s, 1H, CH), 6.78 (m, 1H, C$_6$H$_4$), 6.96 (m, 2H, C$_6$H$_4$), 7.31−7.44 (m, 1H of C$_6$H$_4$ and 5H of Ph). ^{13}C{^{1}H}NMR: δ = 27.8, 28.2 (s, Me), 56.6, 60.2 (s, CH$_2$), 100.2 (s, CH), 120.6, 124.4, 124.9, 128.5 (s, CH, C$_6$H$_4$ or Ph), 129.1 (s, CH, Ph), 129.4 (s, CH, Ph), 130.8 (s, CH, C$_6$H$_4$ or Ph), 135.6, 145.6, 147.5 (s, C, Ph or C$_6$H$_4$), 186.7, 187.9 (s, CO).

Synthesis of [Pd{C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}(py)$_2$]ClO$_4$ (5a). To a solution of complex **2** (115 mg, 0.150 mmol) in acetone (20 mL) was added solid $AgClO_4$ (70 mg, 0.30 mmol), and the mixture was left to stand for 30 min. The resulting precipitate of silver chloride was then removed by filtration through a plug of $MgSO_4$; pyridine (0.05 mL, 0.5 mmol) was added, and the resulting colorless solution was stirred for 6 h and then filtered again through $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether was added (25 mL) to precipitate complex **5a** as a white solid, which was collected, washed with diethyl ether, and air-dried. Yield: 109 mg, 0.195 mmol, 65%. Mp: 190−191. °C. Λ_M = 107 Ω^{-1} cm^2 mol^{-1} (5.71 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{24}H_{24}ClN_3O_4Pd$ (560.4): C, 51.45; H, 4.32; N, 7.50. Found: C, 51.75; H, 4.35; N, 7.65. IR (Nujol, cm^{-1}): ν(NH) = 3220. ^{1}H NMR ($CDCl_3$): δ = 3.81 (dd, 1H, CH$_2$, $^2J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 9.6 Hz), 4.00 (m, 2H, CH$_2$), 4.85 (dd, 1H, CH$_2$, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 4.8 Hz), 5.48 (s, b, 1H, NH), 6.03 (d, 1H, C$_6$H$_4$, $^3J_{HH}$ = 6.9 Hz), 6.78 (m, 1H, C$_6$H$_4$), 7.01 (m, 2H, C$_6$H$_4$), 7.19−7.30 (m, 5H, Ph), 7.19−7.45 (m, 4H, *m*-py), 7.60 (m, 1H, *p*-py), 7.89 (m, 1H, *p*-py), 8.08 (m, 2H, *o*-py), 8.72 (m, 2H, *o*-py). ^{13}C{^{1}H}NMR: δ = 58.4 (s, CH$_2$), 62.3 (s, CH$_2$), 122.7 (s, CH, C$_6$H$_4$), 125.3, 125.6 (s, *m*-py), 126.5 (s, CH, Ph), 128.6 (s, CH, Ph), 129.0 (s, CH, Ph), 129.9 (s, *p*-py), 132.5 (s, CH, C$_6$H$_4$), 136.4 (s, C, Ph), 137.9 (s, CH, C$_6$H$_4$), 139.1 (s, CH, C$_6$H$_4$), 147.1 (s, C, C$_6$H$_4$), 149.4 (s, C, C$_6$H$_4$), 149.7, 151.9 (s, *o*-py).

Synthesis of [Pd{C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}(COD)]ClO$_4$ (5b). To a solution of complex **2** (95 mg, 0.12 mmol) in acetone (30 mL) was added solid $AgClO_4$ (51 mg, 0.25 mmol), and the mixture was left to stand for 30 min. The resulting precipitate of silver chloride was then removed by filtration through a plug of $MgSO_4$; COD (0.05 mL, 0.3 mmol) was added, and the resulting colorless solution was stirred for 6h and then filtered again through $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether was added (25 mL) to precipitate complex **5b** as a white solid, which was collected, washed with diethyl ether, and air-dried. Yield: 105 mg, 0.206 mmol, 86%. Mp: 186−188 °C. Λ_M = 91 Ω^{-1} cm^2 mol^{-1} (1.00 × 10^{-3} mol L^{-1}). Anal. Calcd for $C_{22}H_{26}ClNO_4Pd$ (510.3): C, 51.78; H, 5.14; N, 2.74. Found: C, 51.78; H, 5.30; N, 2.76. IR (Nujol, cm^{-1}): ν-

(NH) = 3185. ^{1}H NMR ($CDCl_3$): δ = 1.82 (m, 1H, CH_2, COD), 2.28 (m, 1H, CH_2, COD), 2.68 (m, 6H, CH_2, COD), 3.85 (dd, 1H, CH_2, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 10 Hz), 4.01 (dd, 1H, CH_2, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 1.0 Hz), 4.21 (m, 1H of CH_2 and NH), 4.86 (dd, 1H, CH_2, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 4.8 Hz), 5.79 (m, 2H, CH, COD), 6.29 (m, 1H, CH, COD), 6.41 (m, 1H, CH, COD), 6.76 (d, 1H, C_6H_4), 7.05 (m, 2H, C_6H_4), 7.12−7.20 (m, 2H, C_6H_4), 7.42−7.50 (m, 3H, Ph). 7.59−7.63 (m, 2H, Ph). ^{13}C{^{1}H}NMR: δ = 27.5, 28.7, 29.3, 30.0 (s, CH_2, COD), 58.5, 61.6 (s, CH_2), 109.4, 111.2 (s, CH, COD), 120.9 (s, CH, C_6H_4), 124.3, 124.9 (s, CH, COD), 126.8, 127.4, 129.3 (s, CH, C_6H_4 or Ph), 129.5, 130.0 (s, CH, Ph), 131.1 (s, CH, C_6H_4 or Ph), 136.0 (s, C, Ph), 149.8, 150.1 (s, C, C_6H_4).

Synthesis of [Pd{C(R)=C(R)C(R)=C(R)C$_6$H$_4$(CH$_2$NH-CH$_2$Ph)-2}Br] [R = Me (6a)]. To a suspension of complex **2** (400 mg, 0.523 mmol) in CH_2Cl_2 (20 mL) was added MeC≡CMe (300 μL, 3.82 mmol). After 8 h, a dark yellow solution was formed, which was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and *n*-pentane (25 mL) was added to precipitate complex **6a** as a yellow solid, which was collected and air-dried. Yield: 306 mg, 0.624 mmol, 60%. Mp: 154−156 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (7.80 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{22}H_{26}BrNPd$ (490.7): C, 53.84; H, 5.34; N, 2.85. Found: C, 53.69; H, 5.38; N, 2.75. IR (Nujol, cm^{-1}): ν(NH) = 3202. ^{1}H NMR ($CDCl_3$): δ = 1.81 (s, 3H, Me), 1.85 (s, 3H, Me), 2.10 (s, 3H, Me), 2.12 (s, 3H, Me), 2.87 (dd, 1H, CH_2, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 12.3 Hz), 3.40 (m, 1H, NH), 3.47 (dd, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 2 Hz), 4.04 (dd, 1H, CH_2, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 2 Hz), 4.18 (dd, 1H, CH_2, $^3J_{HH}$ = 3 Hz), 7.10−7.45 (m, 9H, C_6H_4 and Ph).

Synthesis of [Pd{C(R)=C(R)C(R)=C(R)C$_6$H$_4$(CH$_2$NH-CH$_2$Ph)-2}Br] [R = Et (6b)]. To a suspension of complex **2** (200 mg, 0.261 mmol) in CH_2Cl_2 (20 mL) was added EtC≡CEt (180 μL, 1.57 mmol). After 6 h, a dark yellow solution was formed, which was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and *n*-hexane (25 mL) was added to precipitate complex **6b** as a yellow solid, which was collected and air-dried. Yield: 165 mg, 0.302 mmol, 58%. Mp: 145 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (6.90 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{26}H_{34}BrNPd$ (546.9): C, 57.10; H, 6.27; N, 2.56. Found: C, 59.92; H, 6.34; N, 2.61. IR (Nujol, cm^{-1}): ν(NH) = 3245. ^{1}H NMR ($CDCl_3$): δ = 1.01 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.07 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.17 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.34 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.91 (m, 2H, Et), 2.14 (m, 1H, Et), 2.39 (m, 4H, Et), 2.60 (m, 1H, Et), 2.77 (apparent t, 1H, CH_2, $^2J_{HH}$ = $^3J_{HH}$ = 13.0 Hz), 3.38 (m, 1H, NH), 3.38 (d, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz), 4.07 (dd, 1H, CH_2, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 1.5 Hz), 4.14 (dd, 1H, CH_2, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 3.0 Hz), 7.07−7.46 (m, 9H, C_6H_4 and Ph).

Synthesis of [Pd{C(R)=C(R)C(R)=C(R)C$_6$H$_4$(CH$_2$NH-CH$_2$Ph)-2}Br] [R = Ph (6c)]. To a suspension of complex **2** (100 mg, 0.131 mmol) in CH_2Cl_2 (25 mL) was added PhC≡CPh (187 mg, 1.04 mmol). After 12 h, a yellow solution was formed, which was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether (25 mL) was added to precipitate complex **6c** as a bright yellow solid, which was collected and air-dried. Yield: 130 mg, 0.176 mmol, 67%. Mp: 175−176 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5.68 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{42}H_{34}BrNPd$ (739.0): C, 68.25; H, 4.64; N, 1.89. Found: C, 67.97; H, 4.53; N, 2.02. IR (Nujol, cm^{-1}): ν(NH) = 3215. ^{1}H NMR ($CDCl_3$): δ = 2.70 (dd, 1H, CH_2, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 3 Hz), 3.22 (dd, 1H, CH_2, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 2 Hz), 3.35 (t, 1H, CH_2, $^2J_{HH}$ = $^3J_{HH}$ = 12.9 Hz), 3.55 (m, 1H, NH), 4.45 (d, 1H, CH_2, $^2J_{HH}$ = 12.9 Hz), 6.70−7.70 (m, 29H, C_6H_4 and Ph).

Synthesis of [Pd{C(R)=C(R)C(R)=C(R)C$_6$H$_4$(CH$_2$NH-CH$_2$Ph)-2}(py)]OTf [R = Me (7)]. To a solution of complex **6a** (100 mg, 0.204 mmol) in acetone (15 mL) was added Tl(OTf) (OTf = CF_3SO_3) (73 mg, 0.20 mmol), and the mixture was stirred for 20 min. Pyridine (0.1 mL, 1.00 mmol) was added, and the resulting yellow suspension was stirred for 6 h and then filtered through $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether (25 mL) was added to precipitate complex **7** as a pale yellow solid, which was collected and air-dried. Yield: 77 mg, 0.12 mmol, 60%. Mp: 174−176 °C. Λ_M = 118 Ω^{-1} cm^2 mol^{-1} (5 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{28}H_{31}F_3N_2O_3PdS$ (639.0): C, 52.63; H, 4.89; N, 4.38; S, 5.02. Found: C, 52.32; H, 5.04; N, 4.45; S, 4.80. IR (Nujol, cm^{-1}): ν(NH) = 3221. ^{1}H NMR ($CDCl_3$, −60 °C): δ = 1.09 (s, 3H, Me), 1.81 (s, 3H, Me), 2.16 (s, 3H, Me), 2.17 (s, 3H, Me), 2.81 (apparent triplet, 1H, NH), 3.53 (apparent doublet, 1H, CH_2), 4.11 (apparent doublet, 1H, CH_2), 4.27 (apparent doublet, 1H, CH_2), 4.72 (apparent doublet, 1H, CH_2), 6.68 (d, 1H, *o*-py, $^3J_{HH}$ = 5.1 Hz), 6.89 (apparent triplet, 1H, *m*-py), 7.12−7.54 (m, 10H, C_6H_4 and Ph and *p*-py), 7.71 (apparent triplet, 1H, *m*-py), 8.83 (d, 1H, *o*-py, J_{HH} = 5.1 Hz).

Synthesis of [Pd{C(R)=C(R)C(R)=C(R)C$_6$H$_4$(CH$_2$NH-CH$_2$Ph)-2}(phen)]OTf [R = Me (8)]. To a solution of complex **6a** (115 mg, 0.234 mmol) in acetone (15 mL) was added Tl(OTf) (85 mg, 0.24 mmol), and the mixture was stirred for 20 min; 1,10-phenanthroline monohydrate (47 mg, 0.24 mmol) was added, and the resulting yellow suspension was stirred for 1 h and then filtered through $MgSO_4$. The solvent was removed to ca. 1 mL, and diethyl ether (25 mL) was added to precipitate complex **8** as a bright yellow solid, which was collected and air-dried. Yield: 130 mg, 0.176 mmol, 75%. Mp: 164−166 °C. Λ_M = 122 Ω^{-1} cm^2 mol^{-1} (5.9 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{35}H_{34}F_3N_3O_3PdS$ (739.7): C, 56.78; H, 4.63; N, 5.68; S, 4.33. Found: C, 56.61; H, 4.68; N, 5.78; S, 4.33. IR (Nujol, cm^{-1}): ν(NH) = 3245. ^{1}H NMR ($CDCl_3$): δ = 1.03 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 2.83 (m, 1H, NH), 4.43 (dd, 1H, CH_2, $^2J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 5.4 Hz), 4.48 and 4.67 (AB part of ABX system, 2H, CH_2, $^2J_{AB}$ = 12 Hz, $^3J_{AX}$ = 17 Hz, $^3J_{BX}$ = 10 Hz), 4.74 (dd, 1H, CH_2, $^2J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 4 Hz), 7.05 (m, 2H, C_6H_4), 7.19 (m, 1H, C_6H_4), 7.27−7.41 (m, 6H, C_6H_4 and C_6H_5), 7.90 (dd, 1H, H3, phen, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 8.1 Hz), 8.11 (s, 2H, H5, phen), 8.42 (dd, 1H, H3, phen, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 8.1 Hz), 8.55 (dd, 1H, H2, phen, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 5.4 Hz), 8.67 (dd, 1H, H4, phen, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 8.4 Hz), 8.71 (dd, 1H, H4, phen, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 8.4 Hz), 9.59 (dd, 1H, H2, phen, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 4.8 Hz).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}Br] [R = Me (9a)]. CO was bubbled through a solution of complex **6a** (250 mg, 0.509 mmol) in CH_2Cl_2 (30 mL) for 1.5 h. After 8 h of stirring, the solution was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether (25 mL) was added to precipitate complex **9a** as a yellow solid, which was collected and air-dried. Yield: 190 mg, 0.366 mmol, 72%. Mp: 187−188 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (6.20 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{23}H_{26}BrNOPd$ (518.8): C, 53.25; H, 5.05; N, 2.70. Found: C, 53.14; H, 4.95; N, 2.68. IR (Nujol, cm^{-1}): ν(NH) = 3225, ν(CO) = 1675. ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 3H, Me), 1.76 (s, 3H, Me), 2.11 (s, 3H, Me), 2.15 (s, 3H, Me), 2.73 (apparent t, 1H, CH_2, $^2J_{HH}$ = $^3J_{HH}$ = 13.0 Hz), 3.52 (d, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz), 3.66 (m, 1H, NH), 4.03 (d, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz), 4.31 (dd, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 3 Hz), 7.07−7.46 (m, 9H, C_6H_4 and Ph).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}Br] [R = Et (9b)]. CO was bubbled through a solution of complex **6b** (160 mg, 0.293 mmol) in CH_2Cl_2 (30 mL) for 1.5 h. After 8 h of stirring, the solution was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether (25 mL) was added to precipitate complex **9b** as a yellow solid, which was collected and air-dried. Yield: 160 mg, 0.278 mmol, 95%. Mp: 178−180 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5.56 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{27}H_{34}BrNOPd$ (574.9): C, 56.41; H, 5.96; N, 2.44. Found: C, 56.46; H, 6.09; N, 2.45. IR (Nujol, cm^{-1}): ν(NH) = 3215, ν(CO) = 1680. ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.08 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.26 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.49

(t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.77 (m, 2H, Et), 2.16 (m, 3H, Et), 2.43 (m, 2H, Et), 2.72 (m, 1H of Et and 1H of CH_2), 3.35 (m, 1H, NH), 3.44 (d, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz), 3.97 (d, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz), 4.23 (dd, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 3.6 Hz), 7.13−7.47 (m, 9H, C_6H_4 and Ph).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}Br] [R = Ph (9c)]. CO was bubbled through a solution of complex **6c** (111 mg, 0.150 mmol) in CH_2Cl_2 (30 mL) for 1.5 h. After 8 h of stirring, the solution was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and a mixture of diethyl ether/*n*-hexane (1:1, 25 mL) was added to precipitate complex **9c** as a yellow solid, which was collected and air-dried. Yield: 80 mg, 0.104 mmol 70%. Mp: 205 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5.20 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{43}H_{34}BrNOPd$ (567.1): C, 67.33; H, 1.82; N, 4.47. Found: C, 67.68; H, 1.89; N, 4.51. IR (Nujol, cm^{-1}): ν(NH) = 3205, ν(CO) = 1700. ^{1}H NMR ($CDCl_3$): δ = 2.70 (dd, 1H, CH_2, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 2.7 Hz), 3.23 (dd, 1H, CH_2, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 2 Hz), 3.35 (t, 1H, CH_2, $^2J_{HH}$ = $^3J_{HH}$ = 13.5 Hz), 3.55 (m, 1H, NH), 4.45 (d, 1H, CH_2, $^2J_{HH}$ = 13.5 Hz), 6.70−7.70 (m, 29H, C_6H_4 and Ph).

Synthesis of [Pd{C(=N^{t}Bu)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}Br] [R = Me (10a)]. To a solution of complex **6a** (154 mg, 0.314 mmol) in CH_2Cl_2 (15 mL) was added ^{t}BuNC (36 μL, 0.319 mmol). After 12 h, a yellow solution was formed, which was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether (25 mL) was added to precipitate complex **10a** as a yellow solid, which was collected, washed with diethyl ether, and air-dried. Yield: 120 mg, 0.209 mmol, 67%. Mp: 165−166 °C. Λ_M = 2 Ω^{-1} cm^2 mol^{-1} (5.57 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{27}H_{35}BrN_2Pd$ (573.9): C, 56.51; H, 6.14; N, 4.88. Found: C, 56.56; H, 6.18; N, 4.78. IR (Nujol, cm^{-1}): ν(NH) = 3245, ν(CN) = 1662, 1633. ^{1}H NMR ($CDCl_3$): δ = 1.69 (s, 3H, Me), 1.73 (s, 9H, Me of ^{t}Bu), 1.84 (s, 3H, Me), 1.97 (s, 3H, Me), 2.00 (s, 3H, Me), 2.73 (m, 1H, CH_2), 2.98 (m, 1H, CH_2), 3.60 (d, 1H, CH_2, $^2J_{HH}$ = 12.5 Hz), 4.03 (m, 1H, NH), 4.27 (dd, 1H, CH_2, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 3 Hz), 7.08 (m, 1H, C_6H_4), 7.16 (m, 1H, C_6H_4), 7.23−7.46 (m, 7H, C_6H_4 and Ph).

Synthesis of [Pd{C(=N^{t}Bu)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}Br] [R = Et (10b)]. To a solution of complex **6b** (120 mg, 0.216 mmol) in CH_2Cl_2 (15 mL) was added ^{t}BuNC (25 μL, 0.216 mmol). After 12 h, a yellow solution was formed, which was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and diethyl ether (25 mL) was added to precipitate complex **10b** as a yellow solid, which was collected, washed with diethyl ether, and air-dried. Yield: 110 mg, 0.175 mmol, 81%. Mp: 166−168 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5.0 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{31}H_{43}BrN_2Pd$ (630.0): C, 59.10; H, 6.87; N, 4.45. Found: C, 59.04; H, 6.95; N, 4.38. IR (Nujol, cm^{-1}): ν(NH) = 3240, ν(CN) = 1652, 1626. ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.04 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.20 (t, 3H, Me, $^3J_{HH}$ = 7.5 Hz), 1.51 (m, 3H, Me), 1.76 (s, 9H, Me of ^{t}Bu), 1.88 (m, 2H, Et), 2.19 (m, 4H, Et), 2.36 (m, 4H, Et), 2.65 (m, 2H of Et and 1H of CH_2), 3.02 (m, 1H, CH_2), 3.55 (d, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz), 4.02 (m, 1H, NH), 4.26 (dd, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 3.3 Hz), 7.14−7.42 (m, 9H, C_6H_4 and Ph).

Synthesis of [Pd{C(=NC$_6$H$_3$Me$_2$-2,6)C(R)=C(R)C(R)=C(R)C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}Br] [R = Me (11a)]. To a solution of complex **6a** (155 mg, 0.316 mmol) in CH_2Cl_2 (15 mL) was added 2,6-$Me_2C_6H_3NC$ (41 mg, 0.316 mmol). After 11 h, a dark yellow solution was formed, which was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and *n*-hexane (25 mL) was added to precipitate complex **11a** as a yellow solid, which was collected, washed with *n*-hexane, and air-dried. Yield: 157 mg, 0.257 mmol, 81%. Mp: 188−190 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5.14 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{31}H_{35}BrN_2Pd$ (621.9): C, 59.86; H, 5.67; N, 4.50. Found: C, 59.55; H, 5.70; N, 4.43. IR (Nujol, cm^{-1}): ν(NH) = 3249. ^{1}H NMR ($CDCl_3$, −60 °C): δ = 1.74 (s, 3H, Me), 2.04 (s, 3H, Me), 2.12 (s, 3H, Me), 2.16 (s, 3H, Me), 2.26 (s, 3H, MeC_6H_3), 2.68 (s, 3H, MeC_6H_3), 2.70 (d, 1H, CH_2, $^2J_{HH}$ = 13.2 Hz), 3.29 (m, 1H, NH), 3.47 (d, 1H, CH_2, $^2J_{HH}$ = 12.3 Hz), 3.88 (d, 1H, CH_2, $^2J_{HH}$ = 13.2 Hz), 4.10 (d, 1H, CH_2, $^2J_{HH}$ = 12 Hz), 7.09−7.53 (m, 12H, C_6H_3, C_6H_4 and Ph).

Synthesis of [Pd{C(=NC$_6$H$_3$Me$_2$-2,6)C(R)=C(R)C(R)=C(R)C$_6$H$_4$(CH$_2$NHCH$_2$Ph)-2}Br] [R = Et (11b)]. To a solution of complex **6b** (100 mg, 0.183 mmol) in CH_2Cl_2 (15 mL) was added 2,6-$Me_2C_6H_3NC$ (24 mg, 0.183 mmol). After 9 h, a yellow solution was formed, which was filtered through a plug of $MgSO_4$. The solvent was removed to ca. 2 mL, and *n*-hexane (25 mL) was added to precipitate complex **11b** as a yellow solid, which was collected, washed with *n*-hexane, and air-dried. Yield: 100 mg, 0.147 mmol, 81%. Mp: 160−162 °C. Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5.69 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{35}H_{43}BrN_2Pd$ (678.1): C, 61.99; H, 6.39; N, 4.13. Found: C, 61.55; H, 6.10; N, 4.10. IR (Nujol, cm^{-1}): ν(NH) = 3240. ^{1}H NMR ($CDCl_3$, −60 °C): δ = 0.76 (t, 3H, Me, $^3J_{HH}$ = 6.9 Hz), 1.11 (t, 3H, Me, $^3J_{HH}$ = 6.9 Hz), 1.37 (t, 3H, Me, $^3J_{HH}$ = 7.2 Hz), 1.57 (t, 3H, Me, $^3J_{HH}$ = 6.9 Hz), 1.81 (m, 2H, CH_2), 2.08 (m, 2H, CH_2), 2.26 (s, 5H, MeC_6H_3 and CH_2), 2.68 (s, 6H, *Me*C_6H_3, *Et*, and 1H of CH_2), 3.21 (m, 1H, NH), 3.46 (d, 1H, CH_2, $^2J_{HH}$ = 12.3 Hz), 3.85 (d, 1H, CH_2, $^2J_{HH}$ = 13.2 Hz), 4.13 (d, 1H, CH_2, $^2J_{HH}$ = 12.3 Hz), 7.08−7.47 (m, 12H, C_6H_3, C_6H_4 and Ph).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}(py)]OTf [R = Me (12)]. To a solution of complex **9a** (315 mg, 0.607 mmol) in CH_2Cl_2 (15 mL) was added Tl(OTf) (215 mg, 0.607 mmol), and the mixture was stirred for 5 h and then filtered through Celite. The solvent was removed to ca. 1 mL, and a mixture of diethyl ether/*n*-hexane (25 mL, 1:1) was added to precipitate a pale yellow solid, which was taken up in CH_2Cl_2 (15 mL). Pyridine (0.2 mL, 2.0 mmol) was added, and the resulting pale yellow solution was stirred for 22 h and filtered through $MgSO_4$. The solvent was removed to ca. 1 mL, and diethyl ether was added to precipitate complex **12** as a pale yellow solid, which was collected and air-dried. Yield: 236 mg, 0.354 mmol, 58%. Mp: 202 °C. Λ_M = 91 Ω^{-1} cm^2 mol^{-1} (4.5 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{29}H_{31}F_3N_2O_4PdS$ (667.1): C, 52.21; H, 4.68; N, 4.20; S, 4.80. Found: C, 52.08; H, 4.83; N, 3.50; S, 5.09. IR (Nujol, cm^{-1}): ν(NH) = 3230, ν(CO) = 1698. ^{1}H NMR ($CDCl_3$): δ = 1.70 (s, 3H, Me), 1.71 (s, 3H, Me), 2.20 (s, 3H, Me), 2.29 (s, 3H, Me), 2.99 (dd, 1H, CH_2, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 9.9 Hz), 3.49 (m, 1H, CH_2), 3.71 (apparent d, 1H, CH_2), 3.97 (m, 1H, NH), 4.52 (apparent d, 1H, CH_2), 7.07−7.50 (m, 12H, C_6H_4 and Ph and py), 7.73 (m, 1 H, py), 8.46 (d, 1H, py).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}(CN^{t}Bu)]OTf [R = Me (13)]. To a solution of complex **9a** (110 mg, 0.212 mmol) in CH_2Cl_2 (15 mL), was added Tl(OTf) (75 mg, 0.21 mmol), and the mixture was stirred for 1 h and then filtered through Celite. ^{t}BuNC (25 μL, 0.22 mmol) was added, and the resulting solution was stirred for 23 h and filtered through Celite. The solvent was removed to ca. 1 mL, and *n*-hexane (25 mL) was added to precipitate complex **13** as a pale yellow solid, which was collected and air-dried. Yield: 115 mg, 0.171 mmol, 81%. Mp: 135 °C. Λ_M = 145 Ω^{-1} cm^2 mol^{-1} (4.8 × 10^{-4} mol L^{-1}). Anal. Calcd for $C_{29}H_{35}F_3N_2O_4PdS$ (671.1): C, 51.90; H, 5.26; N, 4.17; S, 4.78. Found: C, 51.93; H, 5.40; N, 4.20; S, 4.73. IR (Nujol, cm^{-1}): ν(NH) = 3196, ν(CN) = 2195, ν(CO) = 1688. ^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 9H, CMe), 1,73 (s, 3H, Me), 1.79 (s, 3H, Me), 2.18 (s, 3H, Me), 2.32 (s, 3H, Me), 2.95 (apparent t, 1H, CH_2), 3.38 (dd, 1H, CH_2, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 4.8 Hz), 4.03 (apparent d, 1H, CH_2), 4.53 (apparent d, 1H, CH_2), 5.33 (m, 1H, NH), 7.06−7.49 (m, 9H, C_6H_4 and Ph).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C$_6$H$_4$-(CH$_2$NHCH$_2$Ph)-2}(phen)]OTf [R = Me (14)]. To a solution of complex **9a** (128 mg, 0.247 mmol) in CH_2Cl_2 (15 mL) was added Tl(OTf)(87 mg, 0.65 mmol), and the mixture was stirred for 1 h and then filtered through Celite. 1,10-Phenanthroline (52 mg, 0.26 mmol) was added, and the resulting solution was

Table 1. Crystal Data for Complexes 2·CH_2Cl_2, 7, 9a, and 13

	2·CH_2Cl_2	7	9a	13
formula	$C_{29}H_{30}Br_2Cl_2N_2Pd_2$	$C_{28}H_{31}F_3N_2O_3PdS$	$C_{23}H_{26}BrNOPd$	$C_{29}H_{35}F_3N_2O_4PdS$
M_r	850.07	639.01	518.76	671.05
source	CH_2Cl_2 slow evaporation	Et_2O/CH_2Cl_2 liquid diffusion	Et_2O/CH_2Cl_2 liquid diffusion	*n*-hexane/CH_2Cl_2 liquid diffusion
cryst habit	yellow needle	colorless prism	yellow tablet	colorless plate
cryst system	monoclinic	monoclinic	orthorhombic	monoclinic
a (Å)	7.9861(6)	10.595(2)	10.935(2)	9.5021(14)
b (Å)	22.350(2)	16.958(2)	17.524(3)	27.997(4)
c (Å)	16.949(2)	15.978(2)	22.241(4)	11.2982(14)
β (deg)	90.960(7)	103.21(1)		102.433(12)
V (Å^3)	3024.9(4)	2794.8(7)	4261.9(12)	2935.2(7)
Z	4	4	8	4
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	293(2)	173(2)	183(2)	173(2)
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite	graphite
space group	$P2_1/n$	$P2_1/c$	*Pbca*	$P2_1/n$
cryst size (mm)	0.72 × 0.06 × 0.06	0.35 × 0.25 × 0.20	0.48 × 0.44 × 0.16	0.50 × 0.35 × 0.06
μ (mm^{-1})	4.029	0.791	2.758	0.759
abs corr	ψ scans	ψ scans	ψ scans	ψ scans
transms	0.857/0.678	0.802/0.774	0.979/0.468	0.847/0.748
diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P4
scan method	ω scans	ω scans	ω scans	ω scans
2θ range (deg)	6−50	6−50	6−50	6−50
hkl limits	$-h,\pm k,\pm l$	$-h,+k,\pm l$	$\pm h,+k,\pm l$	$+h,-k,\pm l$
no. rflns measd	7223	5199	14 234	9546
no. indep rflns	3377	4918	3747	5173
R_{int}	0.1465	0.0219	0.0411	0.0322
$R1^a$	0.0542	0.0292	0.0220	0.0348
w$R2^b$	0.1174	0.0527	0.0340	0.0561

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

stirred for 5 h and filtered through $MgSO_4$. The solvent was removed to ca. 1 mL, and diethyl ether (25 mL) was added to precipitate complex **14** as a pale yellow solid, which was collected and air-dried. Yield: 148 mg, 0.193 mmol, 78%. Mp: 174 °C. $\Lambda_M = 81\ \Omega^{-1}\ cm^2\ mol^{-1}$ (3.6×10^{-4} mol L^{-1}). Anal. Calcd for $C_{36}H_{34}F_3N_3O_4PdS$ (768.2): C, 56.29; H, 4.46; N, 5.47; S, 4.17. Found: C, 55.63; H, 4.73; N, 5.06; S, 3.43. IR (Nujol, cm^{-1}): ν(NH) = 3269, 3230; ν(CO) = 1688. ^{1}H NMR ([D_6]-acetone): δ = 1.43 (s, 3H, Me), 1.95 (s, 3H, Me), 2.26 (s, 3H, Me), 2.34 (s, 3H, Me), 3.28 (m, 2H, CH_2), 3.42 (m, 1H, NH), 3.67 (apparent d, 1H, CH_2), 4.96 (dd, 1H, CH_2, J_{HH} = 13.2, J_{HH} = 3.6 Hz), 6.63 (d, 1H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 6.91 (t, 1H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.07 (t, 1H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.34−7.58 (m, 6H, C_6H_4 and C_6H_5), 7.73 (dd, 1H, H3, phen, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 8.1 Hz), 8.14 (dd, 1H, H3, phen, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 7.8 Hz), 8.25 (d, 1H, H5, phen, $^3J_{HH}$ = 9.0 Hz), 8.31 (d, 1H, H5, phen, $^3J_{HH}$ = 9.0 Hz), 8.73 (d, 1H, H4, phen, $^3J_{HH}$ = 8.1 Hz), 8.81 (s, b, 1H, H2), 8.88 (dd, 1H, H4, phen, $^3J_{HH}$ = 8.1 Hz), 9.82 (d, 1H, H2, phen, $^3J_{HH}$ = 3.6 Hz).

X-ray Structure Determinations. Crystals of **2**·CH_2Cl_2, **7**, **9a**, and **13** were mounted on glass fibers and transferred to the diffractometer (Siemens P4) as summarized in Table 1. Cell constants were refined from ca. 60 reflections in the 2θ range 10−25°. The structure of **9a** was solved by direct methods, and the others were solved by the heavy-atom method; all structures were subjected to anisotropic full-matrix least-squares refinement. Programs used were SHELXL-97 (**7** and **13**)[86] and SHELXL-93 (**2**·CH_2Cl_2 and **9a**).[87] Hydrogen atoms bonded to nitrogen were refined freely; others were included using rigid methyl groups or a riding model. For compound **2**·CH_2Cl_2 the dichloromethane molecule is disordered over two sites (68 and 32% occupancy) and the maximum difference peak is at ca. 1 Å of the Pd(1) atom. The final $R(F)$ [$I > 2\sigma(I)$] was 0.0542, for 327 parameters and 301 restraints. Maximum $\Delta/\sigma = 0.001$, and maximum $\Delta\rho = 1.78$ e$^-$ Å^{-3}. For compound **7** the final $R(F)$ [$I > 2\sigma(I)$] was 0.0292, for 351 parameters and 11 restraints. Maximum $\Delta/\sigma = 0.001$, and maximum $\Delta\rho = 0.35$ e$^-$ Å^3. For compound **9a** the final $R(F)$ [$I > 2\sigma(I)$] was 0.0220, for 248 parameters and 225 restraints. Maximum $\Delta/\sigma = 0.001$, and maximum $\Delta\rho = 0.34$ e$^-$ Å^{-3}. For compound **13** the final $R(F)$ [$I > 2\sigma(I)$] was 0.0348, for 372 parameters and 11 restraints. Maximum $\Delta/\sigma = 0.002$, and maximum $\Delta\rho = 0.38$ e$^-$ Å^{-3}. Restraints were applied to local ring symmetry and *U* components of neighboring light atoms. The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$, and absorption coefficients from the International Tables for Crystallography.[88] Selected bond lengths and angles for the compounds are found in Tables 2−5.

Results

By the refluxing in acetone of a mixture of dibenzylamine and $[Pd(OAc)_2]_3$ (3.2:1 molar ratio), the complex $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}(\mu\text{-}OAc)]_2$ (**1**) precipitated as a deep yellow solid which was isolated in high yield (90%) (Scheme 1). The bromo complex $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}(\mu\text{-}Br)]_2$ (**2**), obtained by reacting **1** with NaBr, reacts with neutral ligands L to give complexes $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}Br(L)]$ [L = PPh_3, (**3a**), $NH(CH_2Ph)_2$ (**3b**)], with Tl(acac) to give $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}(acac)]$ (**4**), and with $AgClO_4$ and pyridine (py) or 1,5-cyclooctadiene (COD) to give cationic complexes $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}L_2]$ [L = py, (**5a**), L_2 = COD (**5b**)].

We attempted a double orthometalation of dibenzylamine using different reaction conditions. Thus, by the

(86) Sheldrick, G. M. *SHELXL 97*; University of Göttingen: Göttingen, Germany, 1997.
(87) Sheldrick, G. M. *SHELXL 93*; University of Göttingen: Göttingen, Germany, 1993.
(88) *International Tables for Crystallography*; 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).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 2·CH_2Cl_2[a]

Pd(1)−C(1)	1.962(14)	Pd(1)−N(1)	2.092(9)
Pd(1)−Br(1)	2.430(2)	Pd(1)−Br(1)#1	2.580(2)
Pd(1A)−C(1A)	1.983(13)	Pd(1A)−N(1A)	2.069(11)
Pd(1A)−Br(1A)#2	2.436(2)	Pd(1A)−Br(1A)	2.585(2)
C(1)−Pd(1)−N(1)	83.4(5)	C(1)−Pd(1)−Br(1)	94.8(4)
N(1)−Pd(1)−Br(1)#1	96.3(3)	Br(1)−Pd(1)−Br(1)#1	85.59(7)
C(1A)−Pd(1A)−N(1A)	82.8(5)	C(1A)−Pd(1A)−Br(1A)#2	95.2(4)
N(1A)−Pd(1A)−Br(1A)	96.4(3)	Br(1A)#2−Pd(1A)−Br(1A)	85.71(7)

[a] Symmetry transformations: #1, $-x, -y, -z + 2$; #2, $-x - 1, -y, -z + 2$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 7

Pd−C(40)	2.007(3)	Pd−N(11)	2.088(2)
Pd−C(38)	2.226(3)	Pd−N(1)	2.189(2)
Pd−C(37)	2.229(3)		
C(40)−Pd−N(11)	91.40(11)	N(11)−Pd−C(37)	170.31(10)
C(40)−Pd−N(1)	175.88(11)	N(1)−Pd−C(37)	89.83(10)
N(11)−Pd−N(1)	92.65(9)	C(38)−Pd−C(37)	36.22(10)
C(40)−Pd−C(38)	64.48(11)	C(10)−N(1)−C(30)	110.1(2)
C(40)−Pd−C(37)	86.05(11)	N(1)−C(30)−C(31)	112.8(2)

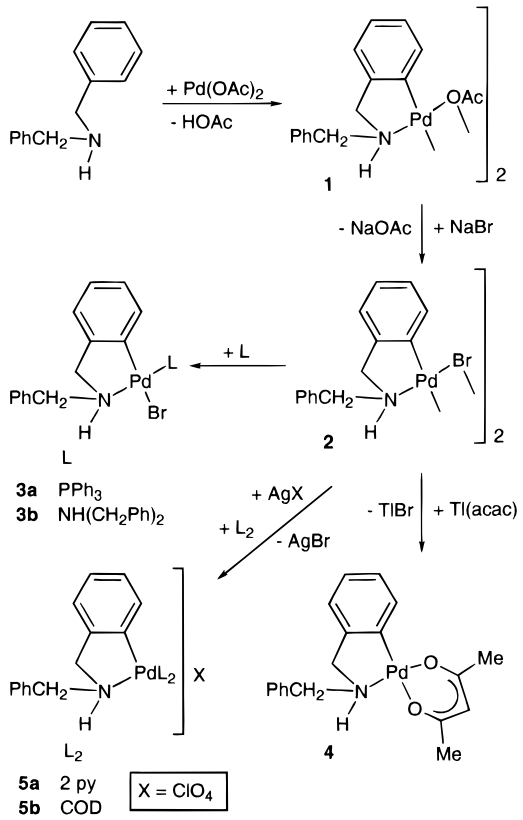
Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 9a

Pd−C(1)	1.980(2)	Pd−N	2.201(2)
Pd−C(4)	2.168(2)	Pd−Br	2.5197(4)
Pd−C(5)	2.204(2)		
O−C(1)	1.207(3)	C(1)−Pd−C(4)	80.45(10)
C(1)−C(2)	1.472(4)	C(1)−Pd−C(5)	94.20(10)
C(2)−C(3)	1.333(3)	C(4)−Pd−C(5)	37.69(9)
C(3)−C(4)	1.500(3)	N−Pd−C(5)	90.77(8)
C(4)−C(5)	1.412(3)	C(1)−Pd−Br	90.85(7)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex 13

Pd−C(13)	2.020(3)	O(1)−C(13)	1.201(4)
Pd−C(14)	2.038(4)	C(9)−C(10)	1.398(5)
Pd−C(10)	2.202(3)	N(1)−C(8)	1.486(5)
Pd−C(9)	2.228(3)	N(1)−C(7)	1.491(4)
Pd−N(1)	2.233(3)	N(2)−C(14)	1.143(4)
N(2)−C(15)	1.474(5)		
C(13)−Pd−C(14)	88.29(14)	C(9)−Pd−N(1)	89.55(12)
C(13)−Pd−C(10)	79.47(13)	C(14)−N(2)−C(15)	173.1(4)
C(13)−Pd−C(9)	97.86(13)	O(1)−C(13)−C(12)	123.6(3)
C(10)−Pd−C(9)	36.78(12)	O(1)−C(13)−Pd	118.8(3)
C(14)−Pd−N(1)	86.71(13)	C(12)−C(13)−Pd	117.4(2)

Scheme 1



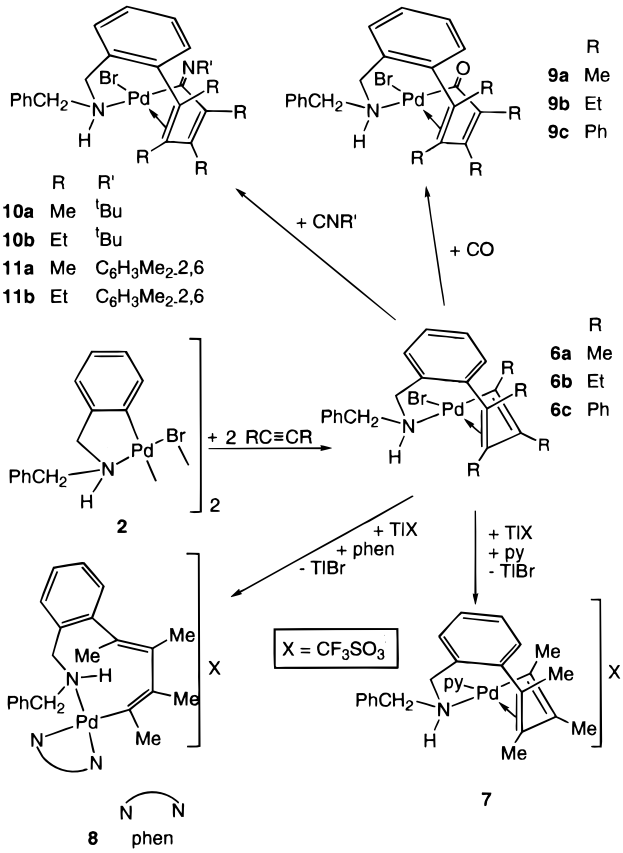
heating of complex **1** in acetonitrile or chlorobenzene, no reaction took place. By reaction of complex **1** with $AgClO_4$ in acetone, a substitution of the acetato ligand by acetone occurred, as shown by ^1H NMR spectroscopy. Reaction of **4** with PPh_3 or pyridine gave mixtures of [Pd{$C_6H_4(CH_2NHCH_2Ph)$-2}(C-acac)(L)] (L = PPh_3, py) and other products (by NMR spectroscopy). We also attempted to palladate two molecules of dibenzylamine by refluxing **3b** in acetonitrile for 5 h. However, it was recovered unchanged.

A suspension of **2** in dichloromethane reacts with an excess of alkyne RC≡CR (1:6−8 molar ratio) to give a solution from which complex [Pd{C(R)═C(R)C(R)═C(R)-$C_6H_4(CH_2NHCH_2Ph)$-2}Br] [R = Me (**6a**), Et (**6b**), Ph (**6c**)], resulting from a double insertion of the alkyne into the Pd−C bond, is obtained (Scheme 2). Complex **6a** reacts with Tl(OTf) (OTf = CF_3SO_3) and neutral ligands L to give [Pd{C(R)═C(R)C(R)═C(R)$C_6H_4(CH_2$-$NHCH_2Ph)$-2}L]OTf [R = Me, L = py (**7**), phen (**8**)] (Scheme 2). Complexes **6a**,**b** insert CO or isocyanides R′NC into the C−Pd bond to give 10-membered palladacycles [Pd{C(E)C(R)═C(R)C(R)═C(R)$C_6H_4(CH_2NHCH_2$-Ph)-2}Br] [E = O, R = Me (**9a**), Et (**9b**); E = NR′, R′ = ^{t}Bu, R = Me (**10a**), Et (**10b**); R′ = $C_6H_3Me_2$-2,6, R = Me (**11a**), Et (**11b**)] in good yields. When an excess of isocyanide is used, oily residues are obtained that cannot be isolated as solids. Complex **6c** reacted with CO to give complex **9c**, but reaction with ^{t}BuNC leads to a mixture of coordinated and inserted derivatives as shown by two bands in the IR spectrum, at 2192 and 1650 cm^{-1}. When the mixture was heated in chloroform, it was recovered unchanged.

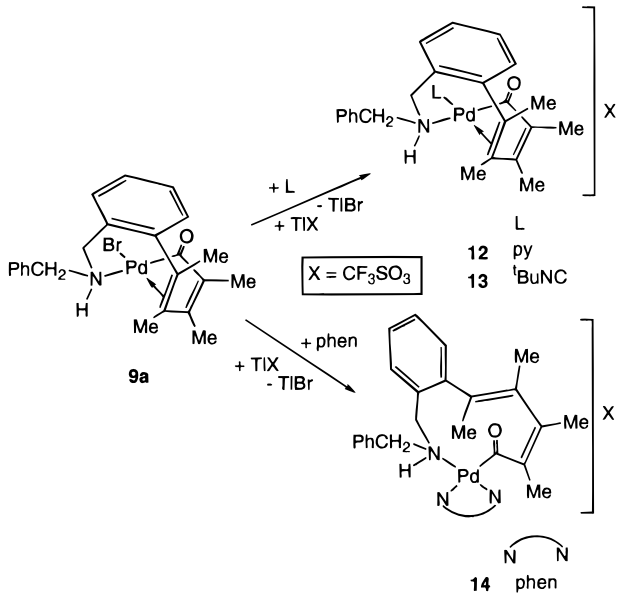
Complex **9a** reacts with Tl(OTf) and neutral ligands L to give [Pd{C(═O)C(R)═C(R)C(R)═C(R)$C_6H_4(CH_2$-$NHCH_2Ph)$-2}L]OTf [R = Me, L = py (**12**), ^{t}BuNC (**13**), phen (**14**)] (Scheme 3).

We have carried out a great number of different reactions in order to obtain organic derivatives. Thus, we attempted to eliminate the palladium atom by reduction of complexes **6a** and **9a** with PPh_3 or py, but although decomposition took place, no organic products were isolated. When these complexes were reacted with Zn, $NaBH_4$, or $LiAlH_4$, the starting materials were recovered. We tried to break the C−Pd bond of complex **6a** by using HX (X = Cl, Br) or oxidizing agents (Cl_2-IPh, H_2O_2), and again, in all cases reactions take place

Scheme 2



Scheme 3



but complicated mixtures were obtained from which no pure compounds could be isolated. Similar reactions with complex **9a** led to similar disappointing results.

Discussion

The cyclopalladation of dibenzylamine using $[Pd(OAc)_2]_3$ was very easily achieved by refluxing a mixture (3.2:1 molar ratio) of both reagents in acetone for 2 h giving a high yield (90%) of the complex **1**, whereas that of benzylamine required refluxing in acetonitrile for 4 h [42] or in acetone 8 h [89] and the yield was poor (40−44%). The difficulty (but not impossibility) of cyclometalating primary amines has been discussed widely.[34,37,38,40−42]

To have a more soluble starting material, we exchanged the acetato ligand for bromo by reacting complex **1** with NaBr to give complex **2**. From **2** we have prepared neutral and cationic complexes **3**−**5** resulting from the cleavage of the bromo bridge [using PPh_3 (**3a**) or $NH(CH_2Ph)_2$ (**3b**)] or by substitution of the bromo ligand by anionic [acetylacetonato (**4**)] or neutral [py (**5a**) or COD (**5a**)] ligands (see Scheme 1).

Attempts at double orthometalation of dibenzylamine by heating solutions of **1**, in acetonitrile or chlorobenzene, or by reacting **1** with $AgClO_4$ proved unsuccessful, although both methods have been applied for the palladation of primary amines.[38,40,42] A third potential route to double orthometalation, by reacting the acac complex **4** with PPh_3 or pyridine, also failed. We expected that the C-acac ligand in the resulting complex $[Pd\{C_6H_4(CH_2NHCH_2Ph)\text{-}2\}(C\text{-}acac)(L)]$ (L = PPh_3, py) (detected by NMR) could deprotonate the nonpalladated phenyl group. Benzylamine have been cyclopalladated using $[Pd(acac)_2]$.[37]

The reaction of **2** with excess of alkynes takes place by insertion of two molecules of the alkyne into the Pd−C bond to give complexes $[Pd\{C(R)=C(R)C(R)=C(R)C_6H_4(CH_2NHCH_2Ph)\text{-}2\}Br]$ [R = Me (**6a**), Et (**6b**), Ph (**6c**)] (see Scheme 2). This behavior is the same as that observed in reactions of different alkynes with cyclopalladated primary[58] and tertiary amines.[3,47−49,51,55,57,73,90] The only precedent for this insertion reaction with a cyclopalladated secondary amine is that reported by Heck between diphenylacetylene and orthopalladated *N*-methyl-3,4-dimethoxybenzylamine bromo dimer.[57] Although the insertion of one molecule of an alkyne into a [Pd]−aryl bond always leads to a *cis*-arylvinylpalladium complex,[3,5,51,53,55,60,66,67,71,73,91−93] the product resulting from a second insertion into the Pd−C bond usually displays a [Pd]-*cis*-C(R)=C(R)-*trans*-C(R)=C(R)-aryl geometry, which requires the isomerization of the first inserted alkyne. However, we have isolated and structurally characterized a diinserted product of this type with *cis*−*cis* geometry.[93] According to the crystal structure of some derivatives of **6a** (see below) we have proposed the usual [Pd]-*cis*-C(R)=C(R)-*trans*-C(R)=C(R)-aryl geometry, which is also in agreement with the proposal that this is the preferred arrangement when the starting compound is a cyclopalladated complex.[93]

Complex **6a** reacts with Tl(OTf) and neutral ligands to give cationic complexes $[Pd\{C(R)=C(R)C(R)=C(R)\text{-}C_6H_4(CH_2NHCH_2Ph)\text{-}2\}L]OTf$ [R = Me, L = py (**7**), phen (**8**)].

Whereas complexes **6a**,**b** insert CO or isocyanides into the C−Pd bond to give the corresponding 10-membered palladacycles **9**−**11** in good yields (Scheme 2), **6c** inserts

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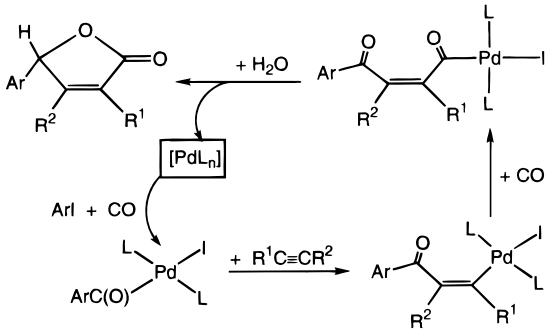
Scheme 4



CO to give the corresponding complex **9c**, but its reaction with ^{t}BuNC lead to a mixture of coordinated and inserted derivatives. Insertion of CO[6,94−111] and isocyanides[1,6,108−118] into the C−Pd bond of alkyl-, π-allyl-, and arylpalladium complexes are very well studied reactions, but those leading to complexes **9**−**11** have, as their only precedent, a CO insertion reported in the above-mentioned work by Heck.[57] However, in this case, the CO insertion took place at 50 °C and 25 psi. Recently, the reaction of 4-octyne with ArI (Ar = Ph, *p*-tolyl) and CO (10−40 atm) in the presence of Et_3N and catalytic amounts of $[PdCl_2(PPh_3)_2]$ at 100−140 °C to give 2-butenolides has been reported.[82] A sequential insertion of carbon monoxide−alkyne−carbon monoxide was postulated (Scheme 4). We have attempted to prepare $PhCH_2C_6H_4C(Me)=C(Me)C(Me)=C(Me)CO_2$-Me-2 by reacting **9a** with Et_3N in MeOH following a similar reported reaction of cyclopalladated complexes with CO and Et_3N.[7] However, although reaction takes place (as shown by extensive decomposition to Pd metal) even after removal of the metal, Et_3NHBr, and some starting material, we could not separate the mixture of organic products.

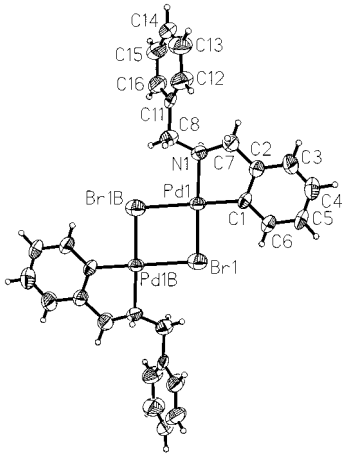


Figure 1. Ellipsoid representation (50% probability), showing the labeling scheme of one of the centrosymmetric dimers of complex **2**·CH_2Cl_2.

Complex **9a** reacts with Tl(OTf) and neutral ligands to give cationic complexes $[Pd\{C(=O)C(R)=C(R)C(R)=C(R)C_6H_4(CH_2NHCH_2Ph)-2\}L]OTf$ [R = Me, L = py (**12**), ^{t}BuNC (**13**), phen (**14**)] (Scheme 3). Complexes **7** and **12** contain only one molecule of pyridine even when an excess of this ligand is used.

Structure of Complexes. The insolubility of complex **1** in organic solvents prevents the recording of its NMR spectra. However, it has been formulated as a dimer by analogy to all reported complexes of this type,[119−121] including complex **2** whose crystal structure has been solved (see below). Both N atoms in complex **2** are chiral centers, and *cis*/*trans* isomerism at the two palladium atoms led up to six possible stereoisomers. The solid-state crystal structure of **2** is that of the *trans*-*RS* isomer (Figure 1), and NMR data in acetone-d_6 is in accordance with this structure. More likely, however, due to the similar behavior in acetone solution of **2** and *RS*-$[Pd(C_6H_4CHMeNH_2$-2$)(\mu$-Br$)_2]$,[40] the NMR data of **2** could be those of $[Pd\{C_6H_4(CH_2NHCH_2Ph)-2\}(Br)$(acetone-$d_6$)].

The crystal structure of **2**·CH_2Cl_2 is the first of a cyclopalladated secondary amine and also the first bromo-bridged cyclopalladated amine. The few reported bromo-bridged cyclopalladated complexes are derived from imines or azobenzene.[122−126] For complex **2**·CH_2Cl_2 there are two independent centrosymmetric pal-

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ladium dimers with coplanar coordination planes. With few exceptions, this disposition is normal in dimeric halo-bridging cyclometalated complexes of d^8 elements.[127] The Pd−Br bond distances in **2** [2.430(2)−2.436(2) Å (*trans* to N), 2.580−2.585(2) (*trans* to C) Å] are consistent with the greater *trans* influence of the aryl group than the amine. Similar values for these bond lengths and also for the C−Pd [1.962(14), 1.983(13) Å] and the N−Pd [2.069(11), 2.092(9) Å] bond distances have been found in bromo-bridged cyclopalladated imines and azobenzene [Pd−Br, 2.639(1)−2.548(4) Å (*trans* to C), 2.450(1)−2.439(3) Å (*trans* to N); C−Pd, 1.954(24)−2.021(7); N−Pd, 2.022(18)−2.050(5)].

The structure proposed for complex **3a** takes into account the inherent instability of Pd(II) complexes containing one C and one P donor ligands in mutually *trans* positions[128] (*transphobia*).[94,129] The proposed geometry of the dibenzylamine adduct **3b** is based on that of the related complex [Pd{C_6H_4{$CH(Me)NH_2$}-2}Br{$NH_2CH(Me)Ph$}].[130] The proposed structures for complexes **6**, **9b**,**c**, and **10**−**12** are based on the crystal structure of **7**, **9a**, and **13** and those of related complexes.[47−49,51,52,57,92,131,132] The structures proposed for **8** and **14** are based on the assumption that they are square-planar complexes. However, a pentacoordination involving an additional π-bond between the *trans*-vinyl group and the palladium atom cannot be discarded.

The IR spectra of all complexes show a ν(NH) band in the range 3166−3280 cm^{-1}. Those resulting after CO insertion show a ν(CO) band in the range of 1675−1700 cm^{-1}. Those complexes resulting after isocyanide insertion show one or two bands in the range of 1626−1662 cm^{-1}, one of which should be assigned to ν(CN). Similarly, complexes **11a,b** show three bands in the range of 1660−1580 cm^{-1}, one of which should also be assigned to ν(CN). In complex **13**, ν(CN) appears at 2195 cm^{-1} as expected for a coordinated isonitrile.

The structure of complex **7** (Figure 2) is similar to that of related complexes resulting from the insertion of alkynes into cyclopalladated complexes; i.e., it shows the first alkyne molecule inserted as a *trans*-vinyl group π-bonded to palladium, while the second one is *cis*, with the last carbon atom σ-bonded to palladium and coordinated *trans* to the amine N atom. However, **7** is the only cationic complex of this family of X-ray structurally characterized complexes; all the others are neutral complexes of the type [Pd{$C(R^1)$=$C(R^2)C(R^3)$=$C(R^4)$-Ar}X] [Ar = $(Cp)FeC_5H_3CH_2NMe_2$-2, X = Cl, $R^1 = R^2 = R^3 = R^4$ = Ph,[47] Et;[48,57] Ar = $C_6H_4CH_2N$=$CH(C_6H_3Cl_2$-2,6)-2, X = Br, $R^1 = R^2 = R^3 = R^4$ = Ph;[131] X = Cl, $R^1 = R^2 = R^3 = R^4$ = Ph, Ar = $(Cp)FeC_5H_3CH$=NR^5-2, R^5 = CH_2Ph,[52] $CHMeC_6H_{11}$, $CH_2C_9H_{15}$;[132] Ar = $C_6H_4CH_2$-NMe_2, X = Br, $R^1 = R^3$ = Me, $R^2 = R^4$ = Ph, $R^1 = R^4$ = Me, $R^2 = R^3$ = Ph;[49] Ar = $C_6H_4CH_2NMe_2$, X = Cl, R^1 = Ph, R^2 = Me, $R^3 = R^4 = CO_2Me$;[51] Ar = C_6H_4=C(Me)-NHPh, X = Cl, $R^1 = R^3$ = Ph, $R^2 = R^4 = CO_2Et$].[92] There is no crystal structure of any complex related to complexes **9a** and **13**.

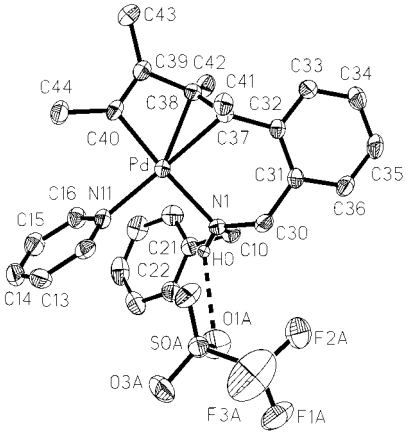

Figure 2. Ellipsoid representation (50% probability), showing the labeling scheme of complex **7** and the triflate anion and the cation interaction. H atoms (except N−H) are omitted for clarity.

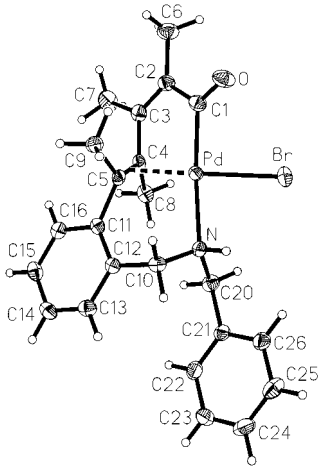

Figure 3. Ellipsoid representation (50% probability), showing the labeling scheme of complex **9a**.

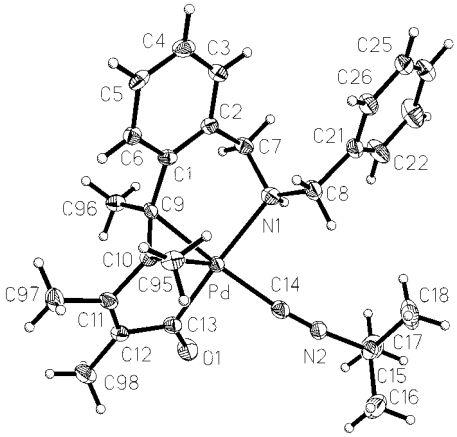

Figure 4. Ellipsoid representation (50% probability), showing the labeling scheme of the cation of complex **13**.

Because complexes **7**, **9a** (Figure 3), and **13** (Figure 4) present some common features, we will discuss their

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structures together. The Pd, the three atoms directly σ-coordinated to it, and the midpoint of the π-bonded C═C group display a very distorted square-planar coordination: the angles between the planes L−Pd−N [L = N(11) (**7**), Br (**9a**), C(14) (**13**)] and C(*n*)−Pd−X (*n* = 40 (**7**), 1 (**9a**), 13 (**13**); X = midpoint of C═C)] are 5.1° (**7**), 24.9° (**9a**), and 28.2° (**13**). The angles between the C═C segments and the mean coordination planes are 50.8° (**7**), 57.6° (**9a**), and 40.8° (**13**). The Pd−N_{amine} bond distances [2.189(2) (**7**), 2.201(2) (**9a**), 2.233(3) (**13**) Å] are significantly longer than the Pd−$N_{pyridine}$ bond distance in **7** [2.088(2) Å] and even longer than the Pd−N_{amine} bond distance in complex **2** [2.041(2) Å], as attributable to the *trans* influence of the ligands: σ-bonded C > π-bonded alkene > Br. The Pd−Br bond distance in **9a** [2.5197(4) Å] is intermediate between those in complex **2** [2.430(2) (*trans* to N), 2.580(2) (*trans* to C) Å] suggesting the series of trans influence: aryl > π-bonded alkene > N_{amine}. The Pd−C bond distances do not differ greatly, at around 2 Å [2.007(3) (**7**), 1.980(2) (**9a**), 2.020-(3) (**13**) Å]. The C═O bond distances are normal for acyl complexes [1.207(3) (**9a**), 1.201(4) (**13**) Å].[133] In complex **7**, the triflate anion is hydrogen bonded with the NH group [H···O, 2.51(3) Å; N···O, 3.178(4), Å; N−H···O, 145(2)°] (Figure 2). Complex **9a** forms dimers through a pair of hydrogen bonds between the oxygen atom of the carbonyl group and the NH group [H···O, 2.08 Å; N···O, 2.932(3), Å; N−H···O, 152°] (Figure 5). In complex **13**, the triflate anion bridges, intramolecularly, the NH group, via a hydrogen bond [H···O, 2.21(3) Å; N···O, 3.011(4) Å; N−H···O, 169(3)°], and the palladium atom via a weak Pd···O contact [Pd···O, 3.076 Å].

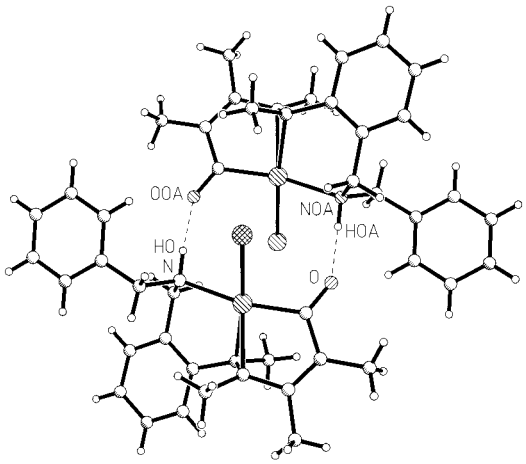

Figure 5. View of the dimers formed in **9a** through hydrogen bonds.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **2**, **7**, **9a**, and **13** (26 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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