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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 $[\text{Pd}(\text{OAc})_2]_3$ (3.2:1) in acetone, the orthometalated complex $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}(\mu\text{-OAc})_2]$ (**1**) is obtained. Metathetical reaction of **1** with NaBr affords the corresponding bromo-bridging dimer $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}(\mu\text{-Br})_2]$ (**2**). Neutral ligands split the bromo bridge to give monomeric complexes $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{Br}(\text{L})]$ [$\text{L} = \text{PPh}_3$, (**3a**), $\text{NH}(\text{CH}_2\text{Ph})_2$ (**3b**)]. Complexes $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}(\text{acac})]$ (**4**) or $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{L}_2]\text{ClO}_4$ [$\text{L} = \text{py}$ (**5a**), $\text{L}_2 = 1,5\text{-cyclooctadiene}$ (**5b**)] can be obtained by reacting complex **2** with $[\text{Ti}(\text{acac})]$ or with AgClO_4 and the free ligand. Complex **2** reacts with $\text{RC}\equiv\text{CR}$ ($\text{R} = \text{Me}$, Et, Ph) to give $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})-\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{Br}]$ [$\text{R} = \text{Me}$ (**6a**), Et (**6b**), Ph (**6c**)] through a double insertion of the alkyne into the Pd–C bond. Complex **6a** reacts with $\text{Ti}(\text{OTf})$ ($\text{OTf} = \text{CF}_3\text{SO}_3$) and neutral ligands to give $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{L}]\text{OTf}$ [$\text{R} = \text{Me}$, $\text{L} = \text{py}$ (**7**), phen (**8**)]. Complexes **6** insert CO or isocyanides $\text{R}'\text{NC}$ into the C–Pd bond to give 10-membered palladacycles $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{E})\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{Br}]$ [$\text{E} = \text{O}$, $\text{R} = \text{Me}$ (**9a**), Et (**9b**), Ph (**9c**); $\text{E} = \text{NR}'$, $\text{R}' = \text{tBu}$, $\text{R} = \text{Me}$ (**10a**), Et (**10b**); $\text{R}' = \text{C}_6\text{H}_3\text{-Me}_{2-2,6}$, $\text{R} = \text{Me}$ (**11a**), Et (**11b**)]. Complex **9a** reacts with $\text{Ti}(\text{OTf})$ and neutral ligands to give $[\text{Pd}\{\text{C}(=\text{O})\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{L}]\text{OTf}$ [$\text{R} = \text{Me}$, $\text{L} = \text{py}$ (**12**), tBuNC (**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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(1) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557.

(2) Ryabov, A. D. *Synthesis* **1985**, 233.

(3) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567.

(4) Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335.

(5) Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214.

(6) O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1165.

(7) Tollari, S.; Demartin, F.; Cenini, S.; Palmisano, G.; Raimondi, P. *J. Organomet. Chem.* **1997**, *527*, 93.

(8) Ballester, P.; Capo, M.; Garcias, X.; Saa, J. M. *J. Org. Chem.* **1993**, *58*, 328.

(9) Camargo, M.; Dani, P.; Dupont, J.; Desouza, R. F.; Pfeffer, M.; Tkatchenko, I. *J. Mol. Catal. A* **1996**, *109*, 127.

(10) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743.

(11) Santra, P. K.; Saha, C. H. *J. Mol. Catal.* **1987**, *39*, 279.

(12) Bose, A.; Saha, C. H. *J. Mol. Catal.* **1989**, *49*, 271.

(13) Stark, M. A.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 5881.

(14) Grove, D. M.; van Koten, G.; Verschuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 169.

(15) Hollis, T. K.; Overman, L. E. *Tetrahedron Lett.* **1997**, *38*, 8837.

(16) Albert, J.; Cadena, J. M.; Granell, J. *Tetrahedron: Asymmetry* **1997**, *8*, 991.

(17) Chelucci, G.; Cabras, M. A.; Saba, A.; Sechi, A. *Tetrahedron: Asymmetry* **1996**, *7*, 1027.

(18) Pabel, M.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1996**, *35*, 1244.

(19) Leitch, J.; Salem, G.; Hockless, D. C. R. *J. Chem. Soc., Dalton Trans.* **1995**, 649.

(20) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743.

(21) Chooi, S. Y. M.; Leung, P. H.; Lim, C. C.; Mok, K. F.; Quek, G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529.

(22) Leung, P. H.; Loh, S. K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 591.

(23) Dunina, V. V.; Golovan, E. B.; Gulyukina, N. S.; Buyevich, A. V. *Tetrahedron: Asymmetry* **1995**, *6*, 2731.

(24) Dunina, V. V.; Golovan, E. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2747.

(25) Wild, S. B. *Coord. Chem. Rev.* **1997**, *166*, 291.

(26) Albert, J.; Granell, J.; Minguez, J.; Muller, G.; Sainz, D.; Valerga, P. *Organometallics* **1997**, *16*, 3561.

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 $[\text{PdCl}_2\text{L}_2]$. 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 the reactivity 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 $[\text{PdCl}_2(\text{PPh}_3)_2]$ 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.

- (27) Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876.
- (28) Navarro-Ranninger, C.; López-Solera, I.; Pérez, J. M.; Masaguer, J. R.; Alonso, C. *Appl. Organomet. Chem.* **1993**, *7*, 57.
- (29) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215.
- (30) Beley, M.; Chodorowski-Kimmes, S.; Collin, J. P.; Sauvage, J. P. *Tetrahedron Lett.* **1993**, *34*, 2932.
- (31) Agnus, Y.; Gross, M.; Labarelle, M.; Louis, R.; Metz, B. *J. Chem. Soc., Chem. Commun.* **1994**, 939.
- (32) Loeb, S. J.; Shimizu, G. K. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1395.
- (33) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
- (34) Fuchita, Y.; Tsuchiya, H.; Miyafuji, A. *Inorg. Chim. Acta* **1995**, *233*, 91.
- (35) Clark, P. W.; Dyke, S. F. *J. Organomet. Chem.* **1985**, *281*, 389.
- (36) Cockburn, B. N.; Howe, D. V.; Keating, T.; Johnson, B. F. G.; Lewis, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 404.
- (37) Baba, S.; Kawaguchi, S. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 415.
- (38) Avshu, A.; O'Sullivan, R. D.; Parkins, A. W.; Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1619.
- (39) Fuchita, Y.; Yoshinaga, K.; Ikeda, Y.; Kinoshita-Kawashima, J. *J. Chem. Soc., Dalton Trans.* **1997**, 2495.
- (40) Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3619.
- (41) Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2535.
- (42) Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 826.
- (43) Dunina, V. V.; Zalevskaya, O. A.; Palii, S. P.; Zagorevskii, D. V.; Nekrasov, Y. S. *Russ. Chem. Bull.* **1996**, *45*, 694.
- (44) Fuchita, Y.; Tsuchiya, H. *Polyhedron* **1993**, *12*, 2079.
- (45) Selvakumar, K.; Vancheesan, S. *Polyhedron* **1997**, *16*, 2405.
- (46) Dunina, V. V.; Kuzmina, L. G.; Kazakova, M. Y.; Grishin, Y. K.; Veits, Y. A.; Kazakova, E. I. *Tetrahedron: Asymmetry* **1997**, *8*, 2537.
- (47) Pfeffer, M.; Rottevel, M. A.; Sutter, J.-P.; De Cían, A.; Fischer, J. *J. Organomet. Chem.* **1989**, *371*, C21.
- (48) Sutter, J. P.; Pfeffer, M.; Decian, A.; Fischer, J. *Organometallics* **1992**, *11*, 386.
- (49) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S.-E.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547.
- (50) Pfeffer, M.; Sutter, J. P.; Decian, A.; Fischer, J. *Organometallics* **1993**, *12*, 1167.
- (51) Ryabov, A. D.; Vaneldik, R.; Leborgne, G.; Pfeffer, M. *Organometallics* **1993**, *12*, 1386.
- (52) Lopez, C.; Solans, X.; Tramuns, D. *J. Organomet. Chem.* **1994**, *471*, 265.
- (53) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.
- (54) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941.
- (55) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029.
- (56) Pfeffer, M.; Sutter, J. P.; Rottevel, M. A.; Decian, A.; Fischer, J. *Tetrahedron* **1992**, *48*, 2427.
- (57) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550.
- (58) Vicente, J.; Saura-Llamas, I.; Ramírez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529.

- (59) Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G. *Inorg. Chim. Acta* **1994**, *222*, 1.
- (60) Dupont, J.; Pfeffer, M.; Theurel, L.; Rottevel, M. A.; Decian, A.; Fischer, J. *New J. Chem.* **1991**, *15*, 551.
- (61) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *J. Organomet. Chem.* **1992**, *436*, C9.
- (62) Catellani, M.; Marmiroli, B.; Fagnola, M. C.; Acquotti, D. *J. Organomet. Chem.* **1996**, *507*, 157.
- (63) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922.
- (64) Pfeffer, M.; Rottevel, M. A.; Leborgne, G.; Fischer, J. *J. Org. Chem.* **1992**, *57*, 2147.
- (65) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1996**, *118*, 6305.
- (66) Dupont, J.; Pfeffer, M. *J. Organomet. Chem.* **1987**, *321*, C13.
- (67) Spencer, J.; Pfeffer, M.; Decian, A.; Fischer, J. *J. Org. Chem.* **1995**, *60*, 1005.
- (68) Maassarani, F.; Pfeffer, M.; Spencer, J.; Wehman, E. *J. Organomet. Chem.* **1994**, *466*, 265.
- (69) Spencer, J.; Pfeffer, M. *Tetrahedron: Asymmetry* **1995**, *6*, 419.
- (70) Beydoun, N.; Pfeffer, M. *Synthesis* **1990**, 729.
- (71) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2043.
- (72) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 2386.
- (73) Beydoun, N.; Pfeffer, M.; Decian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3693.
- (74) Park, S. S.; Choi, J. K.; Yum, E. K.; Ha, D. C. *Tetrahedron Lett.* **1998**, *39*, 627.
- (75) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698.
- (76) Fancelli, D.; Fagnola, M. C.; Severino, D.; Bedeschi, A. *Tetrahedron Lett.* **1997**, *38*, 2311.
- (77) Fagnola, M. C.; Candiani, I.; Visentin, G.; Cabri, W.; Zarini, F.; Mongelli, N.; Bedeschi, A. *Tetrahedron Lett.* **1997**, *38*, 2307.
- (78) Zhang, H. C.; Brumfield, K. K.; Maryanoff, B. E. *Tetrahedron Lett.* **1997**, *38*, 2439.
- (79) Wensbo, D.; Eriksson, A.; Jeschke, T.; Annby, U.; Gronowitz, S.; Cohen, L. A. *Tetrahedron Lett.* **1993**, *34*, 2823.
- (80) Yamada, H.; Aoyagi, S.; Kibayashi, C. *Tetrahedron Lett.* **1997**, *38*, 3027.
- (81) Larock, R. C.; Doty, M. J.; Cacchi, S. J. *J. Org. Chem.* **1995**, *60*, 3270.
- (82) Coperet, C.; Sugihara, T.; Wu, G. Z.; Shimoyama, I.; Negishi, E. *J. Am. Chem. Soc.* **1995**, *117*, 3422.
- (83) Liao, H. Y.; Cheng, C. H. *J. Org. Chem.* **1995**, *60*, 3711.
- (84) Larock, R. C.; Yum, E. K. *J. Am. Chem. Soc.* **1991**, *113*, 6689.
- (85) Larock, R. C.; Tian, Q. P. *J. Org. Chem.* **1998**, *63*, 2002.

Chemical shifts are referred to TMS [^1H and $^{13}\text{C}\{^1\text{H}\}$] or H_3PO_4 [$^{31}\text{P}\{^1\text{H}\}$]. 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 $[\text{Pd}(\text{OAc})_2]_3$ (Johnson Matthey) were used as received.

Synthesis of $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})\text{-2}\}(\mu\text{-OAc})_2]$ (1**).** Dibenzylamine (2 mL, 10.40 mmol) and $[\text{Pd}(\text{OAc})_2]_3$ (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 $\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_4\text{Pd}_2$ (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}): $\nu(\text{NH}) = 3166$.

Synthesis of $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})\text{-2}\}(\mu\text{-Br})_2]$ (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. $\Lambda_M = 2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.23 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{Br}_2\text{N}_2\text{Pd}_2$ (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}): $\nu(\text{NH}) = 3200$. ^1H NMR ($[\text{D}_6]\text{acetone}$): $\delta = 3.95$ (d, 2H, CH_2 , $^3J_{\text{HH}} = 6.0$ Hz), 4.10 (dd, 1H, CH_2 , $^2J_{\text{HH}} = 13.5$ Hz, $^3J_{\text{HH}} = 10.0$ Hz), 4.56 (dd, 1H, CH_2 , $^3J_{\text{HH}} = 3.0$ Hz), 5.86 (s, b, 1H, NH), 6.73–6.91 (m, 3H, C_6H_4 and Ph), 7.29–7.44 (m, 4H, C_6H_4 and Ph), 7.60–7.63 (d, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{acetone}$): $\delta = 58.5$ (s, CH_2), 60.1 (s, CH_2), 122.2 (s, CH, C_6H_4), 125.1 (s, CH, C_6H_4), 125.6 (s, CH, C_6H_4), 125.5 (s, CH, C_6H_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_6H_4), 136.7 (s, *i*-C, Ph), 146.0 (s, C, C_6H_4), 149.8 (s, C, C_6H_4).

Synthesis of $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})\text{-2}\}\text{Br}(\text{PPh}_3)]$ (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). $\Lambda_M = 0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($6.53 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{BrNPPd}$ (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}): $\nu(\text{NH}) = 3280$. ^1H NMR (CDCl_3): $\delta = 3.80$ (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_6H_4 , $^3J_{\text{HH}} = 7.2$ Hz), 6.43 (t, 1H, H4 or H5, C_6H_4), 6.86 (t, 1H, H6, C_6H_4 , $^3J_{\text{HH}} = ^4J_{\text{HP}} = 7.2$ Hz), 7.04 (d, 1H, H3), 7.25–7.46 (m, 9H, Ph), 7.70–7.77 (m, 6H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 54.0$ (d, CH_2 , $J_{\text{PC}} = 2.0$ Hz), 57.3 (d, CH_2 , $J_{\text{PC}} = 3.0$ Hz), 122.9 (s, CH, C_6H_4), 124.1 (s, CH, C_6H_4), 125.0 (d, CH, C_6H_4 , $J_{\text{PC}} = 5.1$ Hz), 128.0 (d, *o*-CH, PPh_3 , $J_{\text{PC}} = 11.1$ Hz), 128.1 (s, CH, C_6H_5), 128.9 (s, CH, C_6H_5), 129.5 (s, CH, C_6H_5), 130.6 (d, *p*-CH, PPh_3 , $J_{\text{PC}} = 2.6$ Hz), 131.5 (d, *i*-CH, PPh_3 , $J_{\text{PC}} = 49.3$ Hz), 135.2 (d, *m*-CH, PPh_3 , $J_{\text{PC}} = 11.6$ Hz), 136.3 (s, C, C_6H_5), 137.5 (d, CH, C_6H_4 , $J_{\text{PC}} = 10.6$ Hz), 150.2 (d, C, C_6H_4 , $J_{\text{PC}} = 1.1$ Hz), 153.0 (s, C, C_6H_4). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 42.1$ (s).

Synthesis of $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})\text{-2}\}\text{Br}\{(\text{NH}(\text{CH}_2\text{Ph})_2\}_2]$ (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. $\Lambda_M = 0$

$\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.50 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{BrN}_2\text{Pd}$ (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}): $\nu(\text{NH}) = 3240$. ^1H NMR (CDCl_3): $\delta = 3.20$ (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_6H_4 , $^3J_{\text{HH}} = 7.2$ Hz), 6.77–6.93 (m, 3H, C_6H_4), 7.31–7.73 (m, 15H, C_6H_5).

Synthesis of $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})\text{-2}\}(\text{acac})]$ (4**).** To a solution of complex **2** (350 mg, 0.457 mmol) in CH_2Cl_2 (50 mL) was added solid $[\text{Ti}(\text{acac})]$ (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. $\Lambda_M = 0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($1.02 \times 10^{-3} \text{ mol L}^{-1}$). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{Pd}$ (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}): $\nu(\text{NH}) = 3175$. ^1H NMR (CDCl_3): $\delta = 1.95$ (s, 3H, Me), 2.06 (s, 3H, Me), 3.74 and 3.95 (AB part of an ABX system, 2H, CH_2 , $^2J_{\text{AB}} = 14$ Hz, $^3J_{\text{AX}} = 12$ Hz, $^3J_{\text{BX}} = 3$ Hz), 3.99 (dd, 1H, CH_2 , $^2J_{\text{HH}} = 13.5$ Hz, $^3J_{\text{HH}} = 10.5$ Hz), 4.26 (m, 1H, NH), 4.52 (dd, 1H, CH_2 , $^3J_{\text{HH}} = 3$ Hz), 5.34 (s, 1H, CH), 6.78 (m, 1H, C_6H_4), 6.96 (m, 2H, C_6H_4), 7.31–7.44 (m, 1H of C_6H_4 and 5H of Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 27.8$, 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_6H_4 or Ph), 129.1 (s, CH, Ph), 129.4 (s, CH, Ph), 130.8 (s, CH, C_6H_4 or Ph), 135.6, 145.6, 147.5 (s, C, Ph or C_6H_4), 186.7, 187.9 (s, CO).

Synthesis of $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})\text{-2}\}(\text{py})_2]\text{ClO}_4$ (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. $\Lambda_M = 107 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.71 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{ClN}_3\text{O}_4\text{Pd}$ (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}): $\nu(\text{NH}) = 3220$. ^1H NMR (CDCl_3): $\delta = 3.81$ (dd, 1H, CH_2 , $^2J_{\text{HH}} = 11.7$ Hz, $^3J_{\text{HH}} = 9.6$ Hz), 4.00 (m, 2H, CH_2), 4.85 (dd, 1H, CH_2 , $^2J_{\text{HH}} = 14.7$ Hz, $^3J_{\text{HH}} = 4.8$ Hz), 5.48 (s, b, 1H, NH), 6.03 (d, 1H, C_6H_4 , $^3J_{\text{HH}} = 6.9$ Hz), 6.78 (m, 1H, C_6H_4), 7.01 (m, 2H, C_6H_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). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 58.4$ (s, CH_2), 62.3 (s, CH_2), 122.7 (s, CH, C_6H_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_6H_4), 136.4 (s, C, Ph), 137.9 (s, CH, C_6H_4), 139.1 (s, CH, C_6H_4), 147.1 (s, C, C_6H_4), 149.4 (s, C, C_6H_4), 149.7, 151.9 (s, *o*-py).

Synthesis of $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})\text{-2}\}(\text{COD})]\text{ClO}_4$ (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 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 **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. $\Lambda_M = 91 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($1.00 \times 10^{-3} \text{ mol L}^{-1}$). Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{ClNO}_4\text{Pd}$ (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. ^1H 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 , $^2J_{\text{HH}}$ = 12 Hz, $^3J_{\text{HH}}$ = 10 Hz), 4.01 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 15 Hz, $^3J_{\text{HH}}$ = 1.0 Hz), 4.21 (m, 1H of CH_2 and NH), 4.86 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 15 Hz, $^3J_{\text{HH}}$ = 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NH}-\text{CH}_2\text{Ph})-2\}\text{Br}]$ [$\text{R} = \text{Me}$ (6a**)].** To a suspension of complex **2** (400 mg, 0.523 mmol) in CH_2Cl_2 (20 mL) was added $\text{MeC}\equiv\text{CMe}$ (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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($7.80 \times 10^{-4} \text{mol L}^{-1}$). Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{BrNPd}$ (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}): $\nu(\text{NH}) = 3202$. ^1H 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 , $^2J_{\text{HH}}$ = 13.8 Hz, $^3J_{\text{HH}}$ = 12.3 Hz), 3.40 (m, 1H, NH), 3.47 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.0 Hz, $^3J_{\text{HH}}$ = 2 Hz), 4.04 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.5 Hz, $^3J_{\text{HH}}$ = 2 Hz), 4.18 (dd, 1H, CH_2 , $^3J_{\text{HH}}$ = 3 Hz), 7.10–7.45 (m, 9H, C_6H_4 and Ph).

Synthesis of $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NH}-\text{CH}_2\text{Ph})-2\}\text{Br}]$ [$\text{R} = \text{Et}$ (6b**)].** To a suspension of complex **2** (200 mg, 0.261 mmol) in CH_2Cl_2 (20 mL) was added $\text{EtC}\equiv\text{CEt}$ (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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($6.90 \times 10^{-4} \text{mol L}^{-1}$). Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{BrNPd}$ (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}): $\nu(\text{NH}) = 3245$. ^1H NMR (CDCl_3): δ = 1.01 (t, 3H, Me, $^3J_{\text{HH}}$ = 7.5 Hz), 1.07 (t, 3H, Me, $^3J_{\text{HH}}$ = 7.5 Hz), 1.17 (t, 3H, Me, $^3J_{\text{HH}}$ = 7.5 Hz), 1.34 (t, 3H, Me, $^3J_{\text{HH}}$ = 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 , $^2J_{\text{HH}}$ = $^3J_{\text{HH}}$ = 13.0 Hz), 3.38 (m, 1H, NH), 3.38 (d, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.0 Hz), 4.07 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.5 Hz, $^3J_{\text{HH}}$ = 1.5 Hz), 4.14 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.5 Hz, $^3J_{\text{HH}}$ = 3.0 Hz), 7.07–7.46 (m, 9H, C_6H_4 and Ph).

Synthesis of $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NH}-\text{CH}_2\text{Ph})-2\}\text{Br}]$ [$\text{R} = \text{Ph}$ (6c**)].** To a suspension of complex **2** (100 mg, 0.131 mmol) in CH_2Cl_2 (25 mL) was added $\text{PhC}\equiv\text{CPh}$ (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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($5.68 \times 10^{-4} \text{mol L}^{-1}$). Anal. Calcd for $\text{C}_{42}\text{H}_{34}\text{BrNPd}$ (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}): $\nu(\text{NH}) = 3215$. ^1H NMR (CDCl_3): δ = 2.70 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.5 Hz, $^3J_{\text{HH}}$ = 3 Hz), 3.22 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.5 Hz, $^3J_{\text{HH}}$ = 2 Hz), 3.35 (t, 1H, CH_2 , $^2J_{\text{HH}}$ = $^3J_{\text{HH}}$ = 12.9 Hz), 3.55 (m, 1H, NH), 4.45 (d, 1H, CH_2 , $^2J_{\text{HH}}$ = 12.9 Hz), 6.70–7.70 (m, 29H, C_6H_4 and Ph).

Synthesis of $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NH}-\text{CH}_2\text{Ph})-2\}(\text{py})\text{OTf}]$ [$\text{R} = \text{Me}$ (7**)].** To a solution of complex **6a** (100 mg, 0.204 mmol) in acetone (15 mL) was added $\text{Ti}(\text{OTf})_3$ ($\text{OTf} = \text{CF}_3\text{SO}_3$) (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. $\Lambda_{\text{M}} = 118 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($5 \times 10^{-4} \text{mol L}^{-1}$). Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{F}_3\text{N}_2\text{O}_3\text{PdS}$ (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}): $\nu(\text{NH}) = 3221$. ^1H 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, $^3J_{\text{HH}}$ = 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 $[\text{Pd}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NH}-\text{CH}_2\text{Ph})-2\}(\text{phen})\text{OTf}]$ [$\text{R} = \text{Me}$ (8**)].** To a solution of complex **6a** (115 mg, 0.234 mmol) in acetone (15 mL) was added $\text{Ti}(\text{OTf})_3$ (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. $\Lambda_{\text{M}} = 122 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($5.9 \times 10^{-4} \text{mol L}^{-1}$). Anal. Calcd for $\text{C}_{35}\text{H}_{34}\text{F}_3\text{N}_3\text{O}_3\text{PdS}$ (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}): $\nu(\text{NH}) = 3245$. ^1H 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 , $^2J_{\text{HH}}$ = 12.3 Hz, $^3J_{\text{HH}}$ = 5.4 Hz), 4.48 and 4.67 (AB part of ABX system, 2H, CH_2 , $^2J_{\text{AB}}$ = 12 Hz, $^3J_{\text{AX}}$ = 17 Hz, $^3J_{\text{BX}}$ = 10 Hz), 4.74 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 12.3 Hz, $^3J_{\text{HH}}$ = 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, $^3J_{\text{HH}}$ = 4.8 Hz, $^3J_{\text{HH}}$ = 8.1 Hz), 8.11 (s, 2H, H5, phen), 8.42 (dd, 1H, H3, phen, $^3J_{\text{HH}}$ = 4.8 Hz, $^3J_{\text{HH}}$ = 8.1 Hz), 8.55 (dd, 1H, H2, phen, $^4J_{\text{HH}}$ = 1.2 Hz, $^3J_{\text{HH}}$ = 5.4 Hz), 8.67 (dd, 1H, H4, phen, $^4J_{\text{HH}}$ = 1.2 Hz, $^3J_{\text{HH}}$ = 8.4 Hz), 8.71 (dd, 1H, H4, phen, $^4J_{\text{HH}}$ = 1.2 Hz, $^3J_{\text{HH}}$ = 8.4 Hz), 9.59 (dd, 1H, H2, phen, $^4J_{\text{HH}}$ = 1.2 Hz, $^3J_{\text{HH}}$ = 4.8 Hz).

Synthesis of $[\text{Pd}\{\text{C}(=\text{O})\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{Br}]$ [$\text{R} = \text{Me}$ (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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($6.20 \times 10^{-4} \text{mol L}^{-1}$). Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{BrNOPd}$ (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}): $\nu(\text{NH}) = 3225$, $\nu(\text{CO}) = 1675$. ^1H 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 , $^2J_{\text{HH}}$ = $^3J_{\text{HH}}$ = 13.0 Hz), 3.52 (d, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.0 Hz), 3.66 (m, 1H, NH), 4.03 (d, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.0 Hz), 4.31 (dd, 1H, CH_2 , $^2J_{\text{HH}}$ = 13.0 Hz, $^3J_{\text{HH}}$ = 3 Hz), 7.07–7.46 (m, 9H, C_6H_4 and Ph).

Synthesis of $[\text{Pd}\{\text{C}(=\text{O})\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{C}_6\text{H}_4(\text{CH}_2\text{NHCH}_2\text{Ph})-2\}\text{Br}]$ [$\text{R} = \text{Et}$ (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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($5.56 \times 10^{-4} \text{mol L}^{-1}$). Anal. Calcd for $\text{C}_{27}\text{H}_{34}\text{BrNOPd}$ (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}): $\nu(\text{NH}) = 3215$, $\nu(\text{CO}) = 1680$. ^1H NMR (CDCl_3): δ = 1.06 (t, 3H, Me, $^3J_{\text{HH}}$ = 7.5 Hz), 1.08 (t, 3H, Me, $^3J_{\text{HH}}$ = 7.5 Hz), 1.26 (t, 3H, Me, $^3J_{\text{HH}}$ = 7.5 Hz), 1.49

(t, 3H, Me, $^3J_{\text{HH}} = 7.5$ 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 CH₂), 3.35 (m, 1H, NH), 3.44 (d, 1H, CH₂, $^2J_{\text{HH}} = 13.0$ Hz), 3.97 (d, 1H, CH₂, $^2J_{\text{HH}} = 13.0$ Hz), 4.23 (dd, 1H, CH₂, $^2J_{\text{HH}} = 13.0$ Hz, $^3J_{\text{HH}} = 3.6$ Hz), 7.13–7.47 (m, 9H, C₆H₄ and Ph).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C₆H₄-(CH₂NHCH₂Ph)-2}Br] [R = Ph (9c)]. CO was bubbled through a solution of complex **6c** (111 mg, 0.150 mmol) in CH₂Cl₂ (30 mL) for 1.5 h. After 8 h of stirring, the solution was filtered through a plug of MgSO₄. 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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.20 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₄₃H₃₄BrNOPd (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): $\nu(\text{NH}) = 3205$, $\nu(\text{CO}) = 1700$. ¹H NMR (CDCl₃): $\delta = 2.70$ (dd, 1H, CH₂, $^2J_{\text{HH}} = 14.1$ Hz, $^3J_{\text{HH}} = 2.7$ Hz), 3.23 (dd, 1H, CH₂, $^2J_{\text{HH}} = 14.1$ Hz, $^3J_{\text{HH}} = 2$ Hz), 3.35 (t, 1H, CH₂, $^2J_{\text{HH}} = ^3J_{\text{HH}} = 13.5$ Hz), 3.55 (m, 1H, NH), 4.45 (d, 1H, CH₂, $^2J_{\text{HH}} = 13.5$ Hz), 6.70–7.70 (m, 29H, C₆H₄ and Ph).

Synthesis of [Pd{C(=N^tBu)C(R)=C(R)C(R)=C(R)C₆H₄-(CH₂NHCH₂Ph)-2}Br] [R = Me (10a)]. To a solution of complex **6a** (154 mg, 0.314 mmol) in CH₂Cl₂ (15 mL) was added ^tBuNC (36 μL , 0.319 mmol). After 12 h, a yellow solution was formed, which was filtered through a plug of MgSO₄. 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. $\Lambda_{\text{M}} = 2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.57 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₂₇H₃₅BrN₂Pd (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): $\nu(\text{NH}) = 3245$, $\nu(\text{CN}) = 1662$, 1633. ¹H NMR (CDCl₃): $\delta = 1.69$ (s, 3H, Me), 1.73 (s, 9H, Me of ^tBu), 1.84 (s, 3H, Me), 1.97 (s, 3H, Me), 2.00 (s, 3H, Me), 2.73 (m, 1H, CH₂), 2.98 (m, 1H, CH₂), 3.60 (d, 1H, CH₂, $^2J_{\text{HH}} = 12.5$ Hz), 4.03 (m, 1H, NH), 4.27 (dd, 1H, CH₂, $^2J_{\text{HH}} = 12.5$ Hz, $^3J_{\text{HH}} = 3$ Hz), 7.08 (m, 1H, C₆H₄), 7.16 (m, 1H, C₆H₄), 7.23–7.46 (m, 7H, C₆H₄ and Ph).

Synthesis of [Pd{C(=N^tBu)C(R)=C(R)C(R)=C(R)C₆H₄-(CH₂NHCH₂Ph)-2}Br] [R = Et (10b)]. To a solution of complex **6b** (120 mg, 0.216 mmol) in CH₂Cl₂ (15 mL) was added ^tBuNC (25 μL , 0.216 mmol). After 12 h, a yellow solution was formed, which was filtered through a plug of MgSO₄. 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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.0 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₃₁H₄₃BrN₂Pd (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): $\nu(\text{NH}) = 3240$, $\nu(\text{CN}) = 1652$, 1626. ¹H NMR (CDCl₃): $\delta = 0.90$ (t, 3H, Me, $^3J_{\text{HH}} = 7.5$ Hz), 1.04 (t, 3H, Me, $^3J_{\text{HH}} = 7.5$ Hz), 1.20 (t, 3H, Me, $^3J_{\text{HH}} = 7.5$ Hz), 1.51 (m, 3H, Me), 1.76 (s, 9H, Me of ^tBu), 1.88 (m, 2H, Et), 2.19 (m, 4H, Et), 2.36 (m, 4H, Et), 2.65 (m, 2H of Et and 1H of CH₂), 3.02 (m, 1H, CH₂), 3.55 (d, 1H, CH₂, $^2J_{\text{HH}} = 13.0$ Hz), 4.02 (m, 1H, NH), 4.26 (dd, 1H, CH₂, $^2J_{\text{HH}} = 13.0$ Hz, $^3J_{\text{HH}} = 3.3$ Hz), 7.14–7.42 (m, 9H, C₆H₄ and Ph).

Synthesis of [Pd{C(=NC₆H₃Me₂,2,6)C(R)=C(R)C(R)=C(R)C₆H₄-(CH₂NHCH₂Ph)-2}Br] [R = Me (11a)]. To a solution of complex **6a** (155 mg, 0.316 mmol) in CH₂Cl₂ (15 mL) was added 2,6-Me₂C₆H₃NC (41 mg, 0.316 mmol). After 11 h, a dark yellow solution was formed, which was filtered through a plug of MgSO₄. 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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.14 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₃₁H₃₅BrN₂Pd (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): $\nu(\text{NH}) = 3249$. ¹H NMR (CDCl₃, -60 °C): $\delta = 1.74$ (s, 3H, Me), 2.04 (s,

3H, Me), 2.12 (s, 3H, Me), 2.16 (s, 3H, Me), 2.26 (s, 3H, MeC₆H₃), 2.68 (s, 3H, MeC₆H₃), 2.70 (d, 1H, CH₂, $^2J_{\text{HH}} = 13.2$ Hz), 3.29 (m, 1H, NH), 3.47 (d, 1H, CH₂, $^2J_{\text{HH}} = 12.3$ Hz), 3.88 (d, 1H, CH₂, $^2J_{\text{HH}} = 13.2$ Hz), 4.10 (d, 1H, CH₂, $^2J_{\text{HH}} = 12$ Hz), 7.09–7.53 (m, 12H, C₆H₃, C₆H₄ and Ph).

Synthesis of [Pd{C(=NC₆H₃Me₂,2,6)C(R)=C(R)C(R)=C(R)C₆H₄-(CH₂NHCH₂Ph)-2}Br] [R = Et (11b)]. To a solution of complex **6b** (100 mg, 0.183 mmol) in CH₂Cl₂ (15 mL) was added 2,6-Me₂C₆H₃NC (24 mg, 0.183 mmol). After 9 h, a yellow solution was formed, which was filtered through a plug of MgSO₄. 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. $\Lambda_{\text{M}} = 0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.69 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₃₅H₄₃BrN₂Pd (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): $\nu(\text{NH}) = 3240$. ¹H NMR (CDCl₃, -60 °C): $\delta = 0.76$ (t, 3H, Me, $^3J_{\text{HH}} = 6.9$ Hz), 1.11 (t, 3H, Me, $^3J_{\text{HH}} = 6.9$ Hz), 1.37 (t, 3H, Me, $^3J_{\text{HH}} = 7.2$ Hz), 1.57 (t, 3H, Me, $^3J_{\text{HH}} = 6.9$ Hz), 1.81 (m, 2H, CH₂), 2.08 (m, 2H, CH₂), 2.26 (s, 5H, MeC₆H₃ and CH₂), 2.68 (s, 6H, MeC₆H₃, Et, and 1H of CH₂), 3.21 (m, 1H, NH), 3.46 (d, 1H, CH₂, $^2J_{\text{HH}} = 12.3$ Hz), 3.85 (d, 1H, CH₂, $^2J_{\text{HH}} = 13.2$ Hz), 4.13 (d, 1H, CH₂, $^2J_{\text{HH}} = 12.3$ Hz), 7.08–7.47 (m, 12H, C₆H₃, C₆H₄ and Ph).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C₆H₄-(CH₂NHCH₂Ph)-2}(py)]OTf [R = Me (12)]. To a solution of complex **9a** (315 mg, 0.607 mmol) in CH₂Cl₂ (15 mL) was added Tf(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 CH₂Cl₂ (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 MgSO₄. 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. $\Lambda_{\text{M}} = 91 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($4.5 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₂₉H₃₁F₃N₂O₄PdS (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): $\nu(\text{NH}) = 3230$, $\nu(\text{CO}) = 1698$. ¹H NMR (CDCl₃): $\delta = 1.70$ (s, 3H, Me), 1.71 (s, 3H, Me), 2.20 (s, 3H, Me), 2.29 (s, 3H, Me), 2.99 (dd, 1H, CH₂, $^2J_{\text{HH}} = 13.2$ Hz, $^3J_{\text{HH}} = 9.9$ Hz), 3.49 (m, 1H, CH₂), 3.71 (apparent d, 1H, CH₂), 3.97 (m, 1H, NH), 4.52 (apparent d, 1H, CH₂), 7.07–7.50 (m, 12H, C₆H₄ 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)C₆H₄-(CH₂NHCH₂Ph)-2}(CN^tBu)]OTf [R = Me (13)]. To a solution of complex **9a** (110 mg, 0.212 mmol) in CH₂Cl₂ (15 mL), was added Tf(OTf) (75 mg, 0.21 mmol), and the mixture was stirred for 1 h and then filtered through Celite. ^tBuNC (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. $\Lambda_{\text{M}} = 145 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($4.8 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₂₉H₃₅F₃N₂O₄PdS (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): $\nu(\text{NH}) = 3196$, $\nu(\text{CN}) = 2195$, $\nu(\text{CO}) = 1688$. ¹H NMR (CDCl₃): $\delta = 1.39$ (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, CH₂), 3.38 (dd, 1H, CH₂, $^2J_{\text{HH}} = 12.0$ Hz, $^3J_{\text{HH}} = 4.8$ Hz), 4.03 (apparent d, 1H, CH₂), 4.53 (apparent d, 1H, CH₂), 5.33 (m, 1H, NH), 7.06–7.49 (m, 9H, C₆H₄ and Ph).

Synthesis of [Pd{C(=O)C(R)=C(R)C(R)=C(R)C₆H₄-(CH₂NHCH₂Ph)-2}(phen)]OTf [R = Me (14)]. To a solution of complex **9a** (128 mg, 0.247 mmol) in CH₂Cl₂ (15 mL) was added Tf(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**·CH₂Cl₂, **7**, **9a**, and **13**

	2 ·CH ₂ Cl ₂	7	9a	13
formula	C ₂₉ H ₃₀ Br ₂ Cl ₂ N ₂ Pd ₂	C ₂₈ H ₃₁ F ₃ N ₂ O ₃ PdS	C ₂₃ H ₂₆ BrNOPd	C ₂₉ H ₃₅ F ₃ N ₂ O ₄ PdS
<i>M_r</i>	850.07	639.01	518.76	671.05
source	CH ₂ Cl ₂ slow	Et ₂ O/CH ₂ Cl ₂	Et ₂ O/CH ₂ Cl ₂	<i>n</i> -hexane/CH ₂ Cl ₂
cryst habit	yellow needle	colorless prism	yellow tablet	colorless plate
cryst system	monoclinic	monoclinic	orthorhombic	monoclinic
<i>a</i> (Å)	7.9861(6)	10.595(2)	10.935(2)	9.5021(14)
<i>b</i> (Å)	22.350(2)	16.958(2)	17.524(3)	27.997(4)
<i>c</i> (Å)	16.949(2)	15.978(2)	22.241(4)	11.2982(14)
β (deg)	90.960(7)	103.21(1)		102.433(12)
<i>V</i> (Å ³)	3024.9(4)	2794.8(7)	4261.9(12)	2935.2(7)
<i>Z</i>	4	4	8	4
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
<i>T</i> (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	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>
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
<i>hkl</i> limits	– <i>h</i> , ± <i>k</i> , ± <i>l</i>	– <i>h</i> , + <i>k</i> , ± <i>l</i>	± <i>h</i> , + <i>k</i> , ± <i>l</i>	+ <i>h</i> , – <i>k</i> , ± <i>l</i>
no. rflns measd	7223	5199	14 234	9546
no. indep rflns	3377	4918	3747	5173
<i>R</i> _{int}	0.1465	0.0219	0.0411	0.0322
<i>R</i> 1 ^a	0.0542	0.0292	0.0220	0.0348
<i>wR</i> 2 ^b	0.1174	0.0527	0.0340	0.0561

^a *R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$ for reflections with $I > 2\sigma(I)$. ^b *wR*2 = $[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]^{0.5}$ 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 MgSO₄. 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. $\Lambda_M = 81 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($3.6 \times 10^{-4} \text{ mol L}^{-1}$). Anal. Calcd for C₃₆H₃₄F₃N₃O₄PdS (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. ¹H NMR ([D₆]-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, CH₂), 3.42 (m, 1H, NH), 3.67 (apparent d, 1H, CH₂), 4.96 (dd, 1H, CH₂, *J*_{HH} = 13.2, *J*_{HH} = 3.6 Hz), 6.63 (d, 1H, C₆H₄, ³*J*_{HH} = 7.5 Hz), 6.91 (t, 1H, C₆H₄, ³*J*_{HH} = 7.5 Hz), 7.07 (t, 1H, C₆H₄, ³*J*_{HH} = 7.5 Hz), 7.34–7.58 (m, 6H, C₆H₄ and C₆H₅), 7.73 (dd, 1H, H₃, phen, ³*J*_{HH} = 4.8 Hz, ³*J*_{HH} = 8.1 Hz), 8.14 (dd, 1H, H₃, phen, ³*J*_{HH} = 4.5 Hz, ³*J*_{HH} = 7.8 Hz), 8.25 (d, 1H, H₅, phen, ³*J*_{HH} = 9.0 Hz), 8.31 (d, 1H, H₅, phen, ³*J*_{HH} = 9.0 Hz), 8.73 (d, 1H, H₄, phen, ³*J*_{HH} = 8.1 Hz), 8.81 (s, b, 1H, H₂), 8.88 (dd, 1H, H₄, phen, ³*J*_{HH} = 8.1 Hz), 9.82 (d, 1H, H₂, phen, ³*J*_{HH} = 3.6 Hz).

X-ray Structure Determinations. Crystals of **2**·CH₂Cl₂, **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**·CH₂Cl₂ 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**·CH₂Cl₂ 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* > 2σ(*I*)] was 0.0542, for 327 parameters and 301 restraints.

Maximum Δ/σ = 0.001, and maximum Δρ = 1.78 e⁻ Å⁻³. For compound **7** the final *R*(*F*) [*I* > 2σ(*I*)] was 0.0292, for 351 parameters and 11 restraints. Maximum Δ/σ = 0.001, and maximum Δρ = 0.35 e⁻ Å⁻³. For compound **9a** the final *R*(*F*) [*I* > 2σ(*I*)] was 0.0220, for 248 parameters and 225 restraints. Maximum Δ/σ = 0.001, and maximum Δρ = 0.34 e⁻ Å⁻³. For compound **13** the final *R*(*F*) [*I* > 2σ(*I*)] was 0.0348, for 372 parameters and 11 restraints. Maximum Δ/σ = 0.002, and maximum Δρ = 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, Δ*f*' and Δ*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{C₆H₄(CH₂NHCH₂Ph)-2}(μ-OAc)₂] (**1**) precipitated as a deep yellow solid which was isolated in high yield (90%) (Scheme 1). The bromo complex [Pd{C₆H₄(CH₂NHCH₂Ph)-2}(μ-Br)₂] (**2**), obtained by reacting **1** with NaBr, reacts with neutral ligands *L* to give complexes [Pd{C₆H₄(CH₂NHCH₂Ph)-2}Br(*L*)] [*L* = PPh₃, (**3a**), NH(CH₂Ph)₂ (**3b**)], with Tl(acac) to give [Pd{C₆H₄(CH₂NHCH₂Ph)-2}(acac)] (**4**), and with AgClO₄ and pyridine (py) or 1,5-cyclooctadiene (COD) to give cationic complexes [Pd{C₆H₄(CH₂NHCH₂Ph)-2}L₂] [*L* = py, (**5a**), L₂ = 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**·CH₂Cl₂^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**

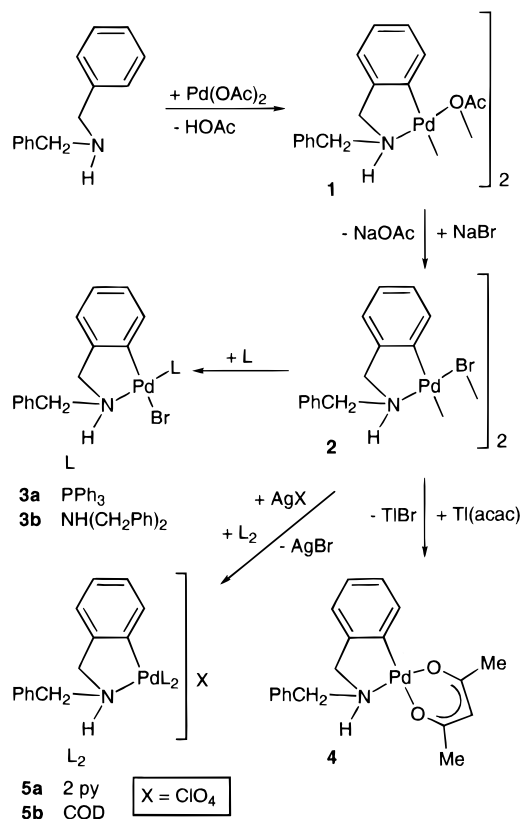
Pd–C(1)	1.980(2)	Pd–N	2.201(2)
Pd–C(4)	2.168(2)	Pd–Br	2.5197(4)
Pd–C(5)	2.204(2)		
O–C(1)	1.207(3)	C(1)–Pd–C(4)	80.45(10)
C(1)–C(2)	1.472(4)	C(1)–Pd–C(5)	94.20(10)
C(2)–C(3)	1.333(3)	C(4)–Pd–C(5)	37.69(9)
C(3)–C(4)	1.500(3)	N–Pd–C(5)	90.77(8)
C(4)–C(5)	1.412(3)	C(1)–Pd–Br	90.85(7)

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)

heating of complex **1** in acetonitrile or chlorobenzene, no reaction took place. By reaction of complex **1** with AgClO₄ in acetone, a substitution of the acetato ligand by acetone occurred, as shown by ¹H NMR spectroscopy. Reaction of **4** with PPh₃ or pyridine gave mixtures of [Pd{C₆H₄(CH₂NHCH₂Ph)-2}(C-acac)(L)] (L = PPh₃, 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)-C₆H₄(CH₂NHCH₂Ph)-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 Ti(OTf) (OTf = CF₃SO₃) and neutral ligands L to give [Pd{C(R)=C(R)C(R)=C(R)-C₆H₄(CH₂NHCH₂Ph)-2}L]OTf [R = Me, L = py (**7**), phen (**8**)] (Scheme 2). Complexes **6a,b** insert CO or isocyanides RNC into the C–Pd bond to give 10-membered palladacycles [Pd{C(E)C(R)=C(R)C(R)=C(R)-C₆H₄(CH₂NHCH₂-

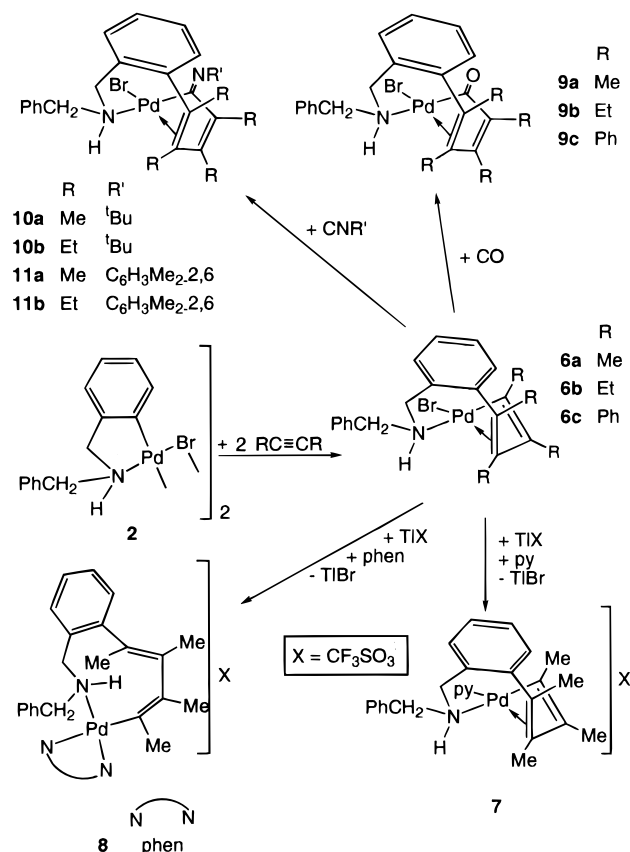
Scheme 1

Ph)-2}Br] [E = O, R = Me (**9a**), Et (**9b**); E = NR', R' = ^tBu, R = Me (**10a**), Et (**10b**); R' = C₆H₃Me₂-2,6, 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 ^tBuNC 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.

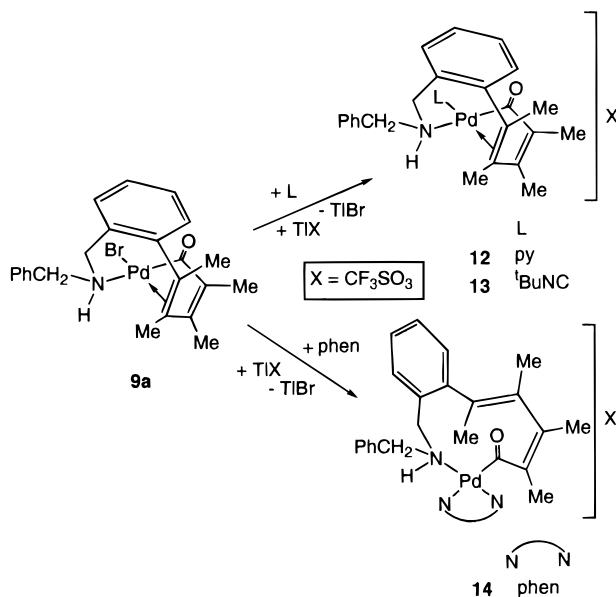
Complex **9a** reacts with Ti(OTf) and neutral ligands L to give [Pd{C(R)=C(R)C(R)=C(R)-C₆H₄(CH₂NHCH₂Ph)-2}L]OTf [R = Me, L = py (**12**), ^tBuNC (**13**), phen (**14**)] (Scheme 3).

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 PPh₃ or py, but although decomposition took place, no organic products were isolated. When these complexes were reacted with Zn, NaBH₄, or LiAlH₄, 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 (Cl₂-IPh, H₂O₂), 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

h⁴² or in acetone 8 h⁸⁹ and the yield was poor (40–44%). The difficulty (but not impossibility) of cyclo-metalating 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 PPh₃ (**3a**) or NH(CH₂Ph)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 AgClO₄ 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 PPh₃ or pyridine, also failed. We expected that the C-acac ligand in the resulting complex [Pd{C₆H₄(CH₂NHCH₂Ph)-2}(C-acac)(L)] (L = PPh₃, 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)C₆H₄(CH₂NHCH₂Ph)-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 primary⁵⁸ 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*-arylvinyllpalladium 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)-C₆H₄(CH₂NHCH₂Ph)-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

(89) Vicente, J. Unpublished results.

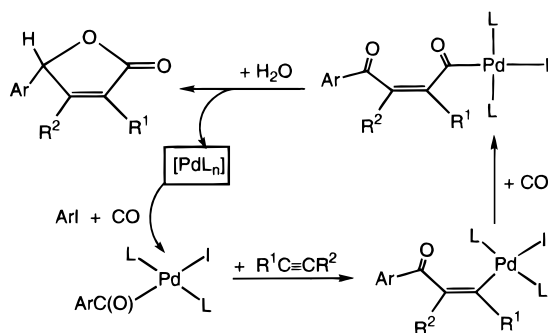
(90) Maassarani, F.; Pfeffer, M.; Borgne, G. L. *Organometallics* **1990**, *9*, 3003.

(91) Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169.

(92) Dupont, J.; Pfeffer, M.; Daran, J.-C.; Gouteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421.

(93) Vicente, J.; Abad, J. A.; Fernández-de-Bobadilla, R.; Jones, P. G.; Ramirez de Arellano, M. C. *Organometallics* **1996**, *15*, 24.

Scheme 4



CO to give the corresponding complex **9c**, but its reaction with ^tBuNC 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 Et₃N and catalytic amounts of [PdCl₂(PPh₃)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

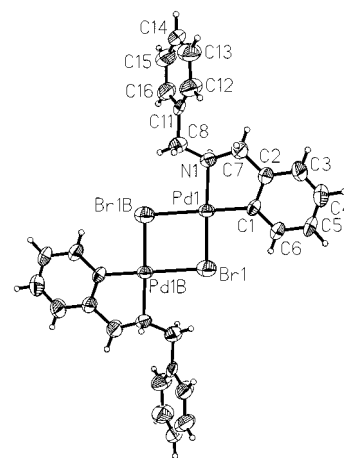


Figure 1. Ellipsoid representation (50% probability), showing the labeling scheme of one of the centrosymmetric dimers of complex **2**·CH₂Cl₂.

prepare PhCH₂C₆H₄C(Me)=C(Me)C(Me)=C(Me)CO₂-Me-**2** by reacting **9a** with Et₃N in MeOH following a similar reported reaction of cyclopalladated complexes with CO and Et₃N.⁷ However, although reaction takes place (as shown by extensive decomposition to Pd metal) even after removal of the metal, Et₃NHBr, and some starting material, we could not separate the mixture of organic products.

Complex **9a** reacts with Tl(OTf) and neutral ligands to give cationic complexes [Pd{C(=O)C(R)=C(R)C(R)=C(R)C₆H₄(CH₂NHCH₂Ph)-2}L]OTf [R = Me, L = py (**12**), ^tBuNC (**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(C₆H₄CHMeNH₂-2)(*μ*-Br)₂],⁴⁰ the NMR data of **2** could be those of [Pd{C₆H₄(CH₂NHCH₂Ph)-2}(Br)(acetone-*d*₆)].

The crystal structure of **2**·CH₂Cl₂ 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**·CH₂Cl₂ there are two independent centrosymmetric pal-

- (94) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramirez de Arellano, M. C. *Chem. Commun.* **1997**, 959.
 (95) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.
 (96) Yamamoto, A. *J. Organomet. Chem.* **1995**, *500*, 337.
 (97) Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433.
 (98) Delis, J. G. P.; Rep, M.; Rülke, R. E.; van Leeuwen, P.; Vrieze, K.; Fraanje, J.; Goubitz, K. *Inorg. Chim. Acta* **1996**, *250*, 87.
 (99) Green, M. J.; Britovsek, G. J. P.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1996**, 1563.
 (100) Ankersmit, H. A.; Loken, B. H.; Kooijman, H.; Spek, A. L.; Vrieze, K.; van Koten, G. *Inorg. Chim. Acta* **1996**, *252*, 141.
 (101) Dekker, G.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; Vanleeuwen, P.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937.
 (102) Jin, H.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1995**, 2159.
 (103) Reger, D. L.; Garza, D. G. *Organometallics* **1993**, *12*, 554.
 (104) Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263.
 (105) Wehman, P.; Rülke, R. E.; Kaasjager, V. E.; Kamer, P. C. J.; Kooijman, H.; Spek, A. L.; Elsevier, C. J.; Vrieze, K.; Vanleeuwen, P. *J. Chem. Soc., Chem. Commun.* **1995**, 331.
 (106) Toth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388.
 (107) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469.
 (108) Kim, Y. J.; Song, S. W.; Lee, S. C.; Lee, S. W.; Osakada, K.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **1998**, 1775.
 (109) Campora, J.; Graiff, C.; Palma, P.; Carmona, E.; Tiripicchio, A. *Inorg. Chim. Acta* **1998**, *269*, 191.
 (110) Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917.
 (111) Gutierrez, E.; Nicasio, M. C.; Paneque, M.; Ruiz, C.; Salazar, V. *J. Organomet. Chem.* **1997**, *549*, 167.
 (112) Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; Vanleeuwen, P.; Veldman, N.; Spek, A. L.; Vaneer, F. J. R. *Organometallics* **1997**, *16*, 2948.
 (113) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193.
 (114) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.
 (115) Veya, P.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.
 (116) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531.
 (117) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. *Organometallics* **1994**, *13*, 3862.
 (118) Yamamoto, Y.; Tanase, T.; Yanai, T.; Asano, T.; Kobayashi, K. *J. Organomet. Chem.* **1993**, *456*, 287.

- (119) Omae, I. *Organometallic Intramolecular-Coordination Compounds*; Elsevier: Amsterdam, The Netherlands, 1986.
 (120) Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Russ. Chem. Rev.* **1988**, *57*, 250.
 (121) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
 (122) Barro, J.; Granell, J.; Sainz, D.; Sales, J.; Fontbardia, M.; Solans, X. *J. Organomet. Chem.* **1993**, *456*, 147.
 (123) Vila, J. M.; Gayoso, M.; Pereira, M. T.; Ortigueira, J. M.; Fernández, A.; Bailey, N. A.; Adams, H. *Polyhedron* **1993**, *12*, 171.
 (124) Crispini, A.; Ghedini, M.; Neve, F. *J. Organomet. Chem.* **1993**, *448*, 241.
 (125) Vila, J. M.; Gayoso, M.; Pereira, M. T.; Romar, A.; Fernández, J. J.; Thornton-Pett, M. *J. Organomet. Chem.* **1991**, *401*, 385.

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* positions¹²⁸ (*transphobia*).^{94,129} The proposed geometry of the dibenzylamine adduct **3b** is based on that of the related complex [Pd{C₆H₄{CH(Me)NH₂}-2}Br{NH₂CH(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 $\nu(\text{NH})$ band in the range 3166–3280 cm^{-1} . Those resulting after CO insertion show a $\nu(\text{CO})$ 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 $\nu(\text{CN})$. Similarly, complexes **11a,b** show three bands in the range of 1660–1580 cm^{-1} , one of which should also be assigned to $\nu(\text{CN})$. In complex **13**, $\nu(\text{CN})$ 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(R¹)=C(R²)C(R³)=C(R⁴)-Ar}X] [Ar = (Cp)FeC₅H₃CH₂NMe₂-2, X = Cl, R¹ = R² = R³ = R⁴ = Ph,⁴⁷ Et;^{48,57} Ar = C₆H₄CH₂N=CH(C₆H₃Cl₂-2,6)-2, X = Br, R¹ = R² = R³ = R⁴ = Ph;¹³¹ X = Cl, R¹ = R² = R³ = R⁴ = Ph, Ar = (Cp)FeC₅H₃CH=NR⁵-2, R⁵ = CH₂Ph,⁵² CHMeC₆H₁₁, CH₂C₉H₁₅;¹³² Ar = C₆H₄CH₂-NMe₂, X = Br, R¹ = R³ = Me, R² = R⁴ = Ph, R¹ = R⁴ =

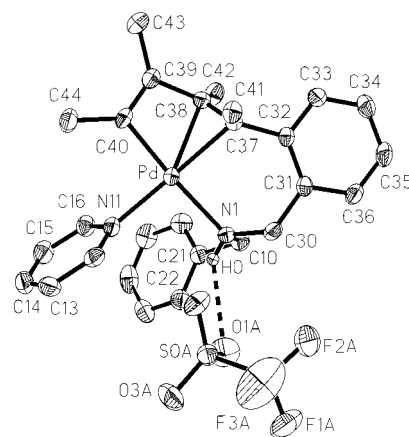


Figure 2. Ellipsoid representation (50% probability), showing the labeling scheme of complex **7** and the triflate anion and the cation interaction. H atoms (except N–H) are omitted for clarity.

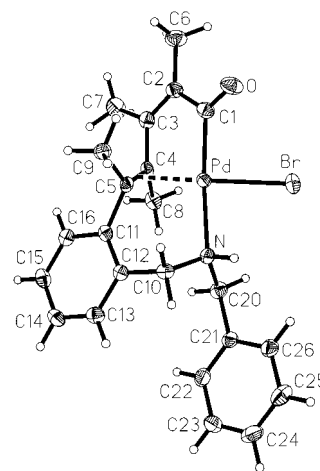


Figure 3. Ellipsoid representation (50% probability), showing the labeling scheme of complex **9a**.

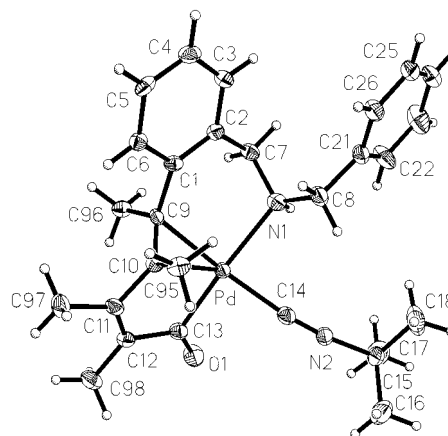


Figure 4. Ellipsoid representation (50% probability), showing the labeling scheme of the cation of complex **13**.

Me, R² = R³ = Ph;⁴⁹ Ar = C₆H₄CH₂NMe₂, X = Cl, R¹ = Ph, R² = Me, R³ = R⁴ = CO₂Me;⁵¹ Ar = C₆H₄N=C(Me)-NHPh, X = Cl, R¹ = R³ = Ph, R² = R⁴ = CO₂Et].⁹² There is no crystal structure of any complex related to complexes **9a** and **13**.

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

(126) Vila, J. M.; Gayoso, M.; Pereira, M. T.; Rodriguez, M. C.; Ortigueira, J. M.; Thornton-Pett, M. *J. Organomet. Chem.* **1992**, 426, 267.

(127) Aullon, G.; Ujaque, G.; Lledos, A.; Alvarez, S.; Alemany, P. *Inorg. Chem.* **1998**, 37, 804.

(128) Pearson, R. G. *Inorg. Chem.* **1973**, 12, 712.

(129) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, 16, 2127.

(130) Albert, J.; Granell, J.; Luque, A.; Minguez, J.; Moragas, R.; Fontbardia, M.; Solans, X. *J. Organomet. Chem.* **1996**, 522, 87.

(131) Albert, J.; Granell, J.; Sales, J.; Solans, X. *J. Organomet. Chem.* **1989**, 379, 177.

(132) Zhao, G.; Wang, Q. G.; Mak, T. C. W. *Tetrahedron: Asymmetry* **1998**, 9, 2253.

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;

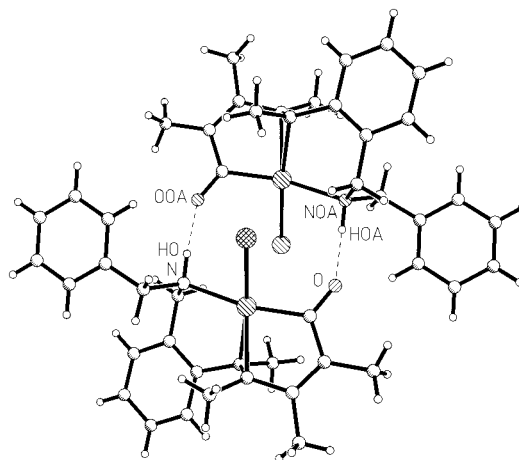


Figure 5. View of the dimers formed in **9a** through hydrogen bonds.

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].

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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>.

OM990143Y

(133) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, T. J. *Chem. Soc., Dalton Trans.* **1989**, S1.