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Synthesis and Reactivity of Ortho-Palladated Phenylacetamides. Intramolecular C−N vs C−O Reductive Coupling after CO or XyNC Insertion into the Pd−C Bond. Synthesis of Isoquinoline- and Isocoumarin-Based Heterocycles

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Aryl palladium complexes [Pd{$C_6H_4CH_2C(O)NRR'$-2}I(N^N)] (N^N = *N,N,N′,N′*-tetramethylethylenediamine = tmeda, NRR′ = NH_2 (**1a**), NHMe (**1b**), NMe_2 (**1c**); N^N = 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dbbpy), NRR′ = NHMe (**1b′**)) are prepared by oxidative addition of the corresponding 2-(2-iodophenyl)acetamide to "Pd(dba)$_2$" ([$Pd_2(dba)_3$]·dba; dba = dibenzylideneacetone) in the presence of the N^N chelating ligand. Cationic cyclometalated derivatives [Pd{κ^2*C,O*-$C_6H_4CH_2C(O)NRR'$-2}(N^N)]OTf (N^N = tmeda, NRR′ = NH_2 (**2a**), NHMe (**2b**), NMe_2 (**2c**); N^N = dbbpy, R = NHMe (**2b′**)) are obtained by reacting the appropriate complex **1** with AgOTf. The reaction of **2b′** with PPh_3 affords [Pd{$C_6H_4CH_2C(O)NHMe$-2}(dbbpy)(PPh_3)]OTf (**3b′**). Neutral amidate complexes of the type [Pd{κ^2*C,N*-$C_6H_4CH_2C(O)NR$-2}(N^N)] (N^N = tmeda, R = H (**4a**), Me (**4b**); N^N = dbbpy, R = Me (**4b′**)) are obtained upon deprotonation of the corresponding complex **1** with KO^{t}Bu. The complex [Pd{$C_6H_4CH_2C(O)NHMe$-2}{$CH(CN)_2$}(dbbpy)] (**5b′**) has been prepared by reacting **4b′** with malononitrile. Acyl derivatives [Pd{$C(O)C_6H_4CH_2C(O)NRR'$-2}I(N^N)] (N^N = tmeda, NRR′ = NH_2 (**6a**), NHMe (**6b**), NMe_2 (**6c**); N^N = dbbpy, NRR′ = NHMe (**6b′**)) have been prepared by reacting the corresponding complex **1** with CO at low temperature; when N^N = tmeda, prolonged reaction times and high temperatures lead to Pd(0) and isoquinoline-1,3(2*H*,4*H*)-dione (**7a**), a 1:2 mixture of 2-methylisoquinoline-1,3(2*H*,4*H*)-dione (**7b**) and 3-(dimethylamino)-1*H*-2-benzopyran-1-one (**8b**), or 3-(methylamino)-1*H*-2-benzopyran-1-one (**8c**), respectively. Similar results are obtained from the reactions of **2a−c** with CO under much milder conditions, while **2b′** reacts with CO in acetone to give the isochroman-1-one derivative *N*,3,3-trimethyl-1-oxo-3,4-dihydro-1*H*-2-benzopyrane-4-carboxamide (**9**). While the reaction of **1b′** with 1 equiv of XyNC (Xy = 2,6-dimethylphenyl) gives the iminoacyl complex [Pd{$C(=NXy)$-$C_6H_4CH_2C(O)NHMe$-2}I(dbbpy)] (**10b′**), the homologous products from the tmeda derivative **1a**, **1b**, or **1c** decompose, giving Pd(0) and 1-(2,6-dimethylphenylimino)-1,2-dihydroisoquinolin-3(4*H*)-one (**11a**), 1-(2,6-dimethylphenylimino)-2-methyl-1,2-dihydroisoquinolin-3(4*H*)-one (**11b**), or 1-(2,6-dimethylphenylimino)-3-(*N*,*N*-dimethylamino)-1*H*-2-benzopyrane (**12c**), respectively. The reaction of **1a** or **1b′** with 3 equiv of XyNC affords *trans*-[Pd{$C(=NXy)C_6H_4CH_2C(O)NHR$-2}I$(CNXy)_2$] (R = H (**13a**), Me (**13b**)); the protonation of **13b** with HOTf leads to [Pd{$C(=NHXy)C_6H_4CH_2C(O)NH_2$-2}I$(CNXy)_2$]OTf (**14a**). Complexes [Pd{$C(=NXy)C_6H_4${$C_6H_4CH_2C(O)NRR'$-2}-2}(CNXy)(N^N)]OTf (N^N = tmeda, NRR′ = NHMe (**15b**), NMe_2 (**15c**); N^N = dbbpy, NRR′ = NHMe (**15b′**)) are obtained by reacting the appropriate complex **2** with 2 equiv of XyNC.

Introduction

Amides are commonly employed as substrates or reagents in a variety of important palladium-mediated syntheses. Based on its ability to coordinate through the oxygen atom, the amide unit can act as a directing group in palladium-catalyzed C−H functionalization reactions,[1] which may lead to C−C[2] or C−O[3] coupling products. The palladium-catalyzed amidations of aryl halides[4−6] are among the most

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significant examples of the amide function participating directly in the bond formation process. These reactions have been shown to proceed through aryl(amidate)palladium complexes that undergo C−N reductive coupling.[6−8] In addition, a number of related Pd(II)-catalyzed amidations of C−H bonds have been reported, for which the participation of amidate complexes has also been proposed.[9]

Our research group is interested in the synthesis of orthofunctionalized aryl palladium complexes and the study of their reactivity toward unsaturated molecules, thereby seeking new routes for organic synthesis. In this article, we describe the synthesis of aryl palladium complexes bearing an ortho-acetamide group and of several cyclometalated derivatives, including neutral amidate complexes. We report also a systematic study of the reactions of these aryl complexes with CO and XyNC (Xy = 2,6-dimethylphenyl). This type of reactions have been widely studied, as they are involved in the synthesis of acyl[10−15] and iminoacyl[11,13−20] palladium complexes and also in many stoichiometric and catalytic syntheses of organic compounds.[13−15,20−22] We report in this work that, depending on the substituents on the amidic nitrogen, these insertion reactions lead to isoquinoline- or isocoumarin-based heterocycles resulting from intramolecular C−N or C−O couplings. Both types of heterocyclic structures are present in numerous natural products and biologically active molecules, and both the development of suitable synthetic strategies and the study of their pharmacological activity are the subjects of intensive research.[23]

Experimental Section

General Considerations, Materials, and Instrumentation. Unless otherwise noted, all preparations were carried out at room temperature under atmospheric conditions. Synthesis grade solvents were obtained from commercial sources. Toluene, CH_2Cl_2, and THF were degassed and dried using a Pure Solv MD-5 solvent purification system from Innovative Technology, Inc. The compounds $[Pd_2(dba)_3]\cdot dba$,[24] 2-(2-iodophenyl)-acetamide,[25] 2-(2-iodophenyl)-*N*-methylacetamide,[26] and 2-(2-iodophenyl)-*N,N*-dimethylacetamide[27] were prepared according to published procedures. All other reagents were obtained from

(2) Tang, S.; Peng, P.; Zhong, P.; Li, J.-H. *J. Org. Chem.* **2008**, *73*, 5476. Shabashov, D.; Daugulis, O. *Org. Lett.* **2006**, *8*, 4947. Tang, S.; Peng, P.; Pi, S.-F.; Liang, Y.; Wang, N.-X.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1179.
(3) Wang, G.-W.; Yuan, T.-T.; Wu, X.-L. *J. Org. Chem.* **2008**, *73*, 4717.
(4) Wolfe, J. P.; Rennels, R. A.; Buchwald, S. L. *Tetrahedron* **1996**, *52*, 7525. Yin, J. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 6043.
(5) Yin, J. J.; Buchwald, S. L. *Org. Lett.* **2000**, *2*, 1101.
(6) Ikawa, T.; Barder, T. E.; Biscoe, M. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 13001.
(7) Fujita, K.-I.; Yamashita, M.; Puschmann, F.; Álvarez-Falcón, M. M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 9044.
(8) Monteiro, A. L.; Davis, W. M. *J. Braz. Chem. Soc.* **2004**, *15*, 83.
(9) Tsang, W. C. P.; Zheng, N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 14560. Tsang, W. C. P.; Munday, R. H.; Brasche, G.; Zheng, N.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 7603. Thansandote, P.; Hulcoop, D. G.; Langer, M.; Lautens, M. *J. Org. Chem.* **2009**, *74*, 1673. Neumann, J. J.; Rakshit, S.; Droege, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6892.
(10) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem.—Eur. J.* **1999**, *5*, 3066.
(11) Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683.
(12) Yamamoto, A.; Tanase, T.; Yanai, T.; Asano, T.; Kobayashy, K. *J. Organomet. Chem.* **1993**, *456*, 287. Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Commun.* **1997**, 959. Kim, Y.-J.; Song, S.-W.; Lee, S.-C.; Lee, S.-W.; Osakada, K.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **1998**, 1775. Hoare, J. L.; Cavell, K. J.; Hecker, R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2197. Dupont, J.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3193.
(13) Vicente, J.; Saura-Llamas, I.; García-López, J.-A.; Bautista, D. *Organometallics* **2008**, *28*, 448.
(14) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Förtsch, W.; Jones, P. G. *Organometallics* **2004**, *23*, 4414.
(15) Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G.; Nájera, C.; Botella-Segura, L. *Organometallics* **2005**, *24*, 5044.
(16) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1980**, *41*, 229. Böhm, A.; Polborn, K.; Sünkel, K.; Beck, W. *Z. Naturforsch., B: Chem. Sci.* **1998**, *53*, 448. Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E. *J. Organomet. Chem.* **1983**, *254*, 371. Zografidis, A.; Polborn, K.; Beck, W.; Markies, B. A.; van Koten, G. *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 1494. Yamamoto, Y.; Yamazaki, H. *Synthesis* **1976**, 750. Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; Van Leeuwen, P.; Veldman, N.; Spek, A. L.; Van Neer, F. J. R. *Organometallics* **1997**, *16*, 2948. Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Jones, P. G.; Bautista, D. *Organometallics* **2008**, *27*, 3254. Dupont, J.; Pffefer, M.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 899. Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587. Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917. Kim, Y. J.; Chang, X. H.; Han, J. T.; Lim, M. S.; Lee, S. W. *Dalton Trans.* **2004**, 3699. Vicente, J.; Abad, J. A.; López-Serrano, J.; Clemente, R.; Ramírez de Arellano, M. C.; Jones, P. G.; Bautista, D. *Organometallics* **2003**, *22*, 4248. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454. Vicente, J.; Chicote, M. T.; Martinez-Martinez, A. J.; Bautista, D. *Organometallics* **2009**, *28*, 5915. Vicente, J.; Arcas, A.; Juliá-Hernández, F.; Bautista, D.; Jones, P. G. *Organometallics* **2010**, *29*, 3066.
(17) Vicente, J.; Abad, J. A.; Frankland, A. D.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272.
(18) Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Rink, B.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **2004**, *23*, 1292.
(19) Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fischer, A. K. *Organometallics* **2001**, *20*, 2704.
(20) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557.
(21) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley: Chinchester, U.K., 1995. Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985. Albinati, A.; Pregosin, P. S.; Rüedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046. Carbayo, A.; Cuevas, J. V.; Garcia Herbosa, G. *J. Organomet. Chem.* **2002**, *658*, 15. Vicente, J.; Abad, J. A.; Martķnez-Viviente, E.; Jones, P. G. *Organometallics* **2003**, *22*, 1967. Curran, D. P.; Du, W. *Org. Lett.* **2002**, *4*, 3215. Gehrig, K.; Klaus, A. J.; Rys, P. *Helv. Chim. Acta* **1983**, *66*, 2603. Vicente, J.; Saura-Llamas, I.; Garcķa-López, J.-A.; Calmuschi-Cula, B.; Bautista, D. *Organometallics* **2007**, *26*, 2768. Lin, Y.-S.; Yamamoto, A. *Organometallics* **1998**, *17*, 3466. Mori, M.; Chiba, K.; Ban, Y. *J. Org. Chem.* **1978**, *43*, 1684. Saluste, C. G.; Whitby, R. J.; Furber, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4156. Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433. Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1027.
(22) Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G. *Organometallics* **2004**, *23*, 4711.
(23) Roy, S.; Roy, S.; Neuenswander, B.; Hill, D.; Larock, R. C. *J. Comb. Chem.* **2009**, *11*, 1061. Chrzanowska, M.; Rozwadowska, M. D. *Chem. Rev.* **2004**, *104*, 3341. Billamboz, M.; Bailly, F.; Barreca, M. L.; De, L. L.; Mouscadet, J.-F.; Calmels, C.; Andreola, M.-L.; Witvrouw, M.; Christ, F.; Debyser, Z.; Cotelle, P. *J. Med. Chem.* **2008**, *51*, 7717. Louerat, F.; Fort, Y.; Mamane, V. *Tetrahedron Lett.* **2009**, *50*, 5716. Parthasarathy, K.; Cheng, C. H. *J. Org. Chem.* **2009**, *74*, 9359. Tsou, H.-R.; Liu, X.; Birnberg, G.; Kaplan, J.; Otteng, M.; Tran, T.; Kutterer, K.; Tang, Z.; Suayan, R.; Zask, A.; Ravi, M.; Bretz, A.; Grillo, M.; McGinnis, J. P.; Rabindran, S. K.; Ayral-Kaloustian, S.; Mansour, T. S. *J. Med. Chem.* **2009**, *52*, 2289. Tsou, H.-R.; Otteng, M.; Tran, T.; Floyd, M. B., Jr.; Reich, M.; Birnberg, G.; Kutterer, K.; Ayral-Kaloustian, S.; Ravi, M.; Nilakantan, R.; Grillo, M.; McGinnis, J. P.; Rabindran, S. K. *J. Med. Chem.* **2008**, *51*, 3507. Shahzad, S. A.; Venin, C.; Wirth, T. *Eur. J. Org. Chem.* **2010**, 3465. Roy, S.; Roy, S.; Neuenswander, B.; Hill, D.; Larock, R. C. *J. Comb. Chem.* **2009**, *11*, 1128.
(24) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.
(25) Hays, S. J.; Caprathe, B. W.; Gilmore, J. L.; Amin, N.; Emmerling, M. R.; Michael, W.; Nadimpalli, R.; Nath, R.; Raser, K. J.; Stafford, D.; Watson, D.; Wang, K.; Jaen, J. *J. Med. Chem.* **1998**, *41*, 1060.
(26) Yu, Y.; Stephenson, G. A.; Mitchell, D. *Tetrahedron Lett.* **2006**, *47*, 3811.
(27) Kenny, J. R.; Maggs, J. L.; Meng, X.; Sinnott, D.; Clarke, S. E.; Park, B. K.; Stachulski, A. V. *J. Med. Chem.* **2004**, *47*, 2816.

commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 200, 300, or 400 spectrometers usually at 298 K, unless otherwise indicated. Chemical shifts are referred to internal TMS (^{1}H and ^{13}C{^{1}H}) or external 85% H_3PO_4 (^{31}P{^{1}H}). The assignments of the ^{1}H and ^{13}C{^{1}H} NMR spectra were made with the help of HMBC and HMQC experiments. Inserted and coordinated XyNC are denoted by XyNC^i and XyNC^c, respectively, and the C_6H_4 aryl group is denoted as Ar. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets. High-resolution ESI mass spectra were recorded on an Agilent 6220 Accurate-Mass TOF LC/MS.

In the following, only representative procedures for the synthesis of each series of analogous Pd complexes are given. The synthesis and data for the rest of complexes are given in the Supporting Information.

Representative Procedure for the Syntheses of Complexes [Pd{$C_6H_4CH_2C(O)NRR'$-2}]I(N^N) (N^N = tmeda, NRR′ = NH_2 (1a), NHMe (1b), NMe_2 (1c); N^N = dbbpy, NRR′ = NHMe (1b′)). Synthesis of 1a. To a suspension of Pd(dba)$_2$ (641 mg, 1.11 mmol) in CH_2Cl_2 (20 mL) was added tmeda (0.25 mL, 1.67 mmol), and the mixture was stirred for 10 min under an N_2 atmosphere. 2-(2-Iodophenyl)acetamide (310 mg, 1.19 mmol) was then added, and the stirring was continued for 1 h. The resulting suspension was filtered through Celite, and the solution was concentrated (8 mL). Addition of Et_2O (25 mL) led to the precipitation of a pale orange solid, which was filtered off, washed with Et_2O (3 × 5 mL), and vacuum-dried to give **1a**. Yield: 339 mg, 63%. Anal. Calcd for $C_{14}H_{24}IN_3OPd$: C, 34.77; H, 5.00; N, 8.69. Found: C, 34.69; H, 5.09; N, 8.57. Mp: 170 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3372, 3175; ν(CO), 1672. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.30 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.06 (dd, $^4J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 6.90 (td, $^4J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 6.85 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 6.26 (br, 1 H, NH), 5.26 (br, 1 H, NH), 4.76, 3.77 (AB system, $^2J_{HH}$ = 14.4 Hz, 2 H, CH_2, acetamide), 2.89−2.83 (m, 1 H, CH_2, tmeda), 2.73 (s, 3 H, Me, tmeda), 2.70 (s, 3 H, Me, tmeda), 2.72−2.62 (m, 2 H, CH_2, tmeda), 2.58−2.50 (m, 1 H, CH_2, tmeda), 2.43 (s, 3 H, Me, tmeda), 2.18 (s, 3 H, CH_3, tmeda). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 175.6 (CO), 145.1 (C, Ar), 140.0 (C, Ar), 137.2 (CH, Ar), 128.1 (CH, Ar), 125.9 (CH, Ar), 124.1 (CH, Ar), 62.6 (CH_2, tmeda), 58.7 (CH_2, tmeda), 50.9 (Me, tmeda), 50.8 (Me, tmeda), 49.6 (Me, tmeda), 49.4 (Me, tmeda), 48.2 (CH_2, acetamide).

Representative Procedure for the Syntheses of Complexes [Pd{κ^2-*C,O*-$C_6H_4CH_2C(O)NRR'$-2}(N^N)]OTf (N^N = tmeda, NRR′ = NH_2 (2a), NHMe (2b), NMe_2 (2c); N^N = dbbpy, NRR′ = NHMe (2b′)). Synthesis of 2a. To a solution of **1a** (82 mg, 0.17 mmol) in acetone (20 mL) was added AgOTf (52 mg, 0.20 mmol). The resulting suspension was stirred for 1 h and filtered through Celite. Partial evaporation of the filtrate (1 mL) and addition of Et_2O (20 mL) led to the precipitation of a colorless solid, which was collected by filtration, washed with Et_2O (3 × 3 mL), and vacuum-dried to give **2a**. Yield: 74 mg, 86%. Anal. Calcd for $C_{15}H_{24}F_3N_3O_4PdS$: C, 35.62; H, 4.78; N, 8.31; S, 6.34. Found: C, 35.78; H, 4.73; N, 8.29; S, 6.01. Mp: 190−192 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3400, 3330, 3202; ν(CO), 1654. ^{1}H NMR (400.9 MHz, $(CD_3)_2CO$): δ 8.70 (br, 1 H, NH), 8.20 (br, 1 H, NH), 7.32 (m, 1 H, Ar), 7.01−6.93 (m, 3 H, Ar), 4.22 (s, 2 H, CH_2, acetamide), 3.10 (m, 2 H, CH_2, tmeda), 2.87 (m, 2 H, CH_2, tmeda), 2.84 (s, 6 H, Me, tmeda), 2.67 (s, 6 H, Me, tmeda). ^{13}C{^{1}H} NMR (75.5 MHz, $(CD_3)_2CO$): δ 181.6 (CO), 148.3 (C, Ar), 135.5 (C, Ar), 133.3 (CH, Ar), 127.2 (CH, Ar), 126.4 (CH, Ar), 125.4 (CH, Ar), 65.5 (CH_2, tmeda), 57.8 (CH_2, tmeda), 51.9 (Me, tmeda), 48.4 (CH_2, acetamide), 47.5 (Me, tmeda).

[Pd{$C_6H_4CH_2C(O)NHMe$-2}(dbbpy)(PPh_3)]OTf (3b′). To a solution of **2b′** (91 mg, 0.14 mmol) in CH_2Cl_2 (10 mL) was added PPh_3 (36 mg, 0.14 mmol). The resulting solution was stirred for 1 h, filtered through anhydrous $MgSO_4$, and concentrated (1 mL). *n*-Hexane (20 mL) was added to precipitate a white solid, which was collected by filtration, washed with *n*-hexane (3 × 3 mL), and vacuum-dried to give **3b′**. Yield: 88 mg, 69%. Anal. Calcd for $C_{46}H_{49}F_3N_3O_4PPdS$: C, 59.13; H, 5.29; N, 4.50; S, 3.43. Found: C, 58.82; H, 5.25; N, 4.38; S, 3.27. Mp: 156−159 °C. IR (Nujol, cm^{-1}): ν(NH), 3340; ν(CO), 1670. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.13 (br s, 2 H, H3, dbbpy), 7.56 (m, 6 H, *o*-H, Ph), 7.46 (m, 3 H, *p*-H, Ph), 7.36 (m, 6 H, *m*-H, Ph), 7.30 (m, 2 H, H5, dbbpy), 7.21 (d, $^3J_{HH}$ = 6.0 Hz, 1 H, H6, dbbpy), 7.18 (ddd, $^5J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 8 Hz, 1 H, Ar), 7.10 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, H6, dbbpy), 7.05 (br q, 1 H, NH), 6.92 (m, 2 H, Ar), 6.72 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 3.65, 3.01 (AB system, $^2J_{AB}$ = 14.8 Hz, 2 H, CH_2), 2.23 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, N*Me*), 1.38 (s, 9 H, ^{t}Bu), 1.37 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 171.1 (CO), 164.5, 164.3 (C4, dbbpy), 155.7, 155.6 (C2, dbbpy), 155.4 (d, $^2J_{CP}$ = 11.0 Hz, C-Pd), 150.3, 149.9 (C6, dbbpy), 138.7 (d, $^3J_{CP}$ = 2.6 Hz, C, Ar), 134.6 (d, $^2J_{CP}$ = 12.1 Hz, *o*-C, Ph), 133.3 (d, $^2J_{CP}$ = 5.0 Hz, CH, Ar), 132.3 (CH, Ar), 131.4 (d, $^4J_{CP}$ = 2.1 Hz, *p*-C, Ph), 129.0 (d, $^1J_{CP}$ = 51.9 Hz, *i*-C, Ph), 128.9 (d, $^3J_{CP}$ = 11.0 Hz, *m*-C, Ph), 126.1 (CH, Ar), 125.0 (CH, Ar), 123.4, 122.9 (C5, dbbpy), 119.9, 119.1 (C3, dbbpy), 46.5 (CH_2), 35.5, 35.4 (*C*Me$_3$), 30.2, 30.1 (C*Me*$_3$), 25.8 (N*Me*).

Representative Procedure for the Syntheses of Complexes [Pd{κ^2-*C,N*-$C_6H_4CH_2C(O)NR$-2}(N^N)] (N^N = tmeda, R = H (4a), Me (4b); N^N = dbbpy, R = Me (4b′)). Synthesis of 4a. To a solution of **1a** (107 mg, 0.22 mmol) in HO^{t}Bu (10 mL) were added KO^{t}Bu (50 mg, 0.45 mmol) and CH_2Cl_2 (2 mL), and the mixture was stirred for 2 h. The resulting suspension was filtered through Celite, and the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (20 mL) and filtered through Celite. Partial evaporation of the filtrate (1 mL) and slow addition of *n*-pentane (15 mL) led to the formation of a colorless precipitate, which was filtered off, washed with *n*-pentane (3 × 3 mL), and vacuum-dried to give **4a**·H_2O. Yield: 58 mg, 74%. Anal. Calcd for $C_{14}H_{25}N_3O_2Pd$: C, 44.99; H, 6.74; N, 11.24. Found: C, 44.95; H, 6.87; N, 11.17. Mp: 185−190 °C. IR (Nujol, cm^{-1}): ν(NH), 3385, 3269; ν(CO), 1577. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.23−7.19 (m, 1 H, Ar), 6.96−6.92 (m, 1 H, Ar), 6.92−6.86 (m, 2 H, Ar), 3.85 (br, 1 H, NH), 3.72 (s, 2 H, CH_2, acetamide), 2.79−2.74 (m, 2 H, CH_2, tmeda), 2.66 (s, 6 H, Me, tmeda), 2.60 (m, 2 H, CH_2, tmeda), 2.56 (s, 6 H, Me, tmeda), 1.83 (s, 2 H, H_2O). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 179.0 (CO), 148.5 (C, Ar), 143.2 (C, Ar), 132.2 (CH, Ar), 126.0 (CH, Ar), 124.3 (CH, Ar), 123.7 (CH, Ar), 63.1 (CH_2, tmeda), 58.0 (CH_2, tmeda), 50.5 (Me, tmeda), 50.2 (CH_2, acetamide), 48.0 (Me, tmeda).

[Pd{$C_6H_4CH_2C(O)NHMe$-2}{$CH(CN)_2$}(dbbpy)] (5b′). To a solution of **4b′** (95.6 mg, 0.183 mmol) in CH_2Cl_2 (10 mL) was added malononitrile (12.2 mg, 0.185 mmol), and the mixture was stirred for 1 h. The resulting colorless solution was concentrated (1 mL), and *n*-pentane (30 mL) was slowly added, whereupon a colorless solid precipitated, which was filtered off, washed with *n*-pentane (3 × 5 mL), and vacuum-dried to give **5b′**·0.25H_2O. Yield: 87 mg, 81%. Anal. Calcd for $C_{30}H_{35.5}N_5O_{1.25}Pd$: C, 60.81; H, 6.04; N, 11.82. Found: C, 60.67; H, 6.19; N, 11.93. Mp: 169−172 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3371; ν(CN), 2213, 2206; ν(CO), 1674. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.89 (d, $^3J_{HH}$ = 5.6 Hz, 1 H, H6, dbbpy), 8.03 (d, $^4J_{HH}$ = 1.6 Hz, 1 H, H3, dbbpy), 7.98 (d, $^4J_{HH}$ = 1.6 Hz, 1 H, H3, dbbpy), 7.68 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 5.6 Hz, 1 H, H5, dbbpy), 7.53 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.46 (d, $^3J_{HH}$ = 5.6 Hz, 1 H, H6, dbbpy), 7.27 (m, 1 H, H5, dbbpy), 7.23 (dd, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, Ar), 7.07 (m, 2 H, Ar), 5.96 (br q, $^3J_{HH}$ = 4.4 Hz, 1 H, NH), 4.03, 3.74 (AB system, $^2J_{AB}$ = 15.2 Hz, 2 H, CH_2), 2.71 (s, 1 H, $CH(CN)_2$), 2.55 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, NMe), 1.64 (s, 0.5 H, H_2O), 1.46 (s, 9 H, ^{t}Bu), 1.38 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 172.4 (CO), 164.2, 163.9 (C4, dbbpy), 155.9 (C, Ar), 155.3,

154.4 (C2, dbbpy), 150.5, 149.4 (C6, dbbpy), 139.2 (C, Ar), 135.4 (CH, Ar), 129.9 (CH, Ar), 126.3 (CH, Ar), 124.5 (CH, Ar), 124.3, 123.8 (C5, dbbpy), 121.1, 120.6 (CN), 118.5, 118.4 (C3, dbbpy), 47.1 (CH_2), 35.6, 35.5 (CMe_3), 30.3, 30.2 (CMe_3), 26.1 (NMe) ($CH(CN)_2$ not observed).

Representative Procedure for the Syntheses of [Pd{C(O)C_6H_4-CH_2C(O)NRR′-2}I(N^N)] (N^N = tmeda, NRR′ = NH_2 (6a), NHMe (6b), NMe_2 (6c); N^N = dbbpy, NRR′ = NHMe (6b′)). Synthesis of 6a. CO was bubbled through a stirred solution of **1a** (105 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) at −17 °C for 30 min, and the resulting solution was filtered through anhydrous $MgSO_4$. Partial evaporation of the filtrate (1 mL) and addition of Et_2O (20 mL) led to the precipitation of a yellow solid, which was collected by filtration, washed with Et_2O (3 × 3 mL), and vacuum-dried to give **6a**. Yield: 80 mg, 72%. Anal. Calcd for $C_{15}H_{24}IN_3O_2Pd$: C, 35.21; H, 4.73; N, 8.21. Found: C, 35.08; H, 4.73; N, 7.83. Mp: 165 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3396, 3187; ν(CO), 1671, 1635. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 9.14 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.51 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.38 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.23 (dd, $^4J_{HH}$ = 0.8 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H3, Ar), 6.34 (s, 1 H, NH), 5.19 (s, 1 H, NH), 3.76 (s, 2 H, CH_2, acetamide), 2.73 (m, 2 H, CH_2, tmeda), 2.60 (s, 3 H, Me, tmeda), 2.55 (m, 2 H, CH_2, tmeda), 2.47 (s, 3 H, Me, tmeda). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 173.3 (CO), 139.7 (CH, Ar), 138.4 (C, Ar), 131.4 (CH, Ar), 131.2 (CH, Ar), 130.7 (C, Ar), 127.0 (CH, Ar), 61.9 (CH_2, tmeda), 57.7 (CH_2, tmeda), 50.4 (Me, tmeda), 49.0 (Me, tmeda), 41.6 (CH_2) (Pd*C* not observed).

Isoquinoline-1,3(2*H*,4*H*)-dione (7a). A solution of **2a** (105 mg, 0.21 mmol) in acetone (15 mL) was stirred under a CO atmosphere (1.4 bar) at room temperature for 3 h. A black precipitate of Pd gradually formed. The solvent was evaporated under vacuum, the residue was extracted with CH_2Cl_2 (6 × 5 mL), and the extracts were filtered through anhydrous $MgSO_4$. The filtrate was evaporated to dryness; the yellow residue was stirred in water (15 mL), collected by filtration, and washed with water (5 × 3 mL). The crude product was recrystallized from ethanol to give **7a** as a pale yellow microcrystalline solid. Yield: 17 mg, 51%. Mp: 224−236 °C (lit. 217,[28] 233−235 °C[29]). The ^{1}H NMR data are in agreement with those reported in the literature.[28,29]

2-Methylisoquinoline-1,3(2*H*,4*H*)-dione (7b). A solution of **2b** (111 mg, 0.21 mmol) and NEt_3 (80 μL, 0.57 mmol) in acetone (15 mL) was stirred under a CO atmosphere (1.4 bar) at room temperature for 3 h. A black precipitate of Pd gradually formed. The solvent was evaporated under vacuum, the residue was extracted with CH_2Cl_2 (6 × 5 mL), and the extracts were filtered through anhydrous $MgSO_4$. The yellow filtrate was evaporated to dryness, the residue was extracted with *n*-hexane (20 + 6 × 5 mL), and the extracts were filtered through anhydrous $MgSO_4$. The solvent was then removed under reduced pressure to give **7b** as a colorless solid. Yield: 25 mg, 67%. Mp: 120−122 °C (lit.[30] 120−121 °C). The ^{1}H NMR data are in agreement with those reported in the literature.[30]

3-(Methylamino)-1*H*-2-benzopyran-1-one (8b). A solution of **2b** (81 mg, 0.16 mmol) in acetone (15 mL) was stirred under a CO atmosphere (1.4 bar) for 2.5 h. A black precipitate of Pd gradually formed. The solvent was evaporated under vacuum, the residue was extracted with Et_2O (6 × 5 mL), and the combined extracts were filtered through Celite. The filtrate was washed with a saturated aqueous solution of K_2CO_3 (3 × 5 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give **8b** as a bright yellow solid. Yield: 16 mg, 59%. Mp: 116−119 °C. IR (Nujol, cm^{-1}): ν(N−H), 3303; ν(COO), 1719, 1651. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{10}H_{10}NO_2$ $[M + H]^+$ requires 176.0706, found: 176.0711, error = 3.01 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.07 (ddd, $^5J_{HH}$ = 0.8 Hz, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 8.0 Hz, 1 H, H8), 7.51 (ddd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 8.0 Hz, 1 H, H6), 7.18 (br d, $^3J_{HH}$ = 8.0 Hz, 1 H, H5), 7.12 (ddd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 8.0 Hz, 1 H, H7), 5.19 (s, 1 H, H4), 4.24 (br s, 1 H, NH), 2.86 (d, $^3J_{HH}$ = 5.2 Hz, 3 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 161.9 (CO), 156.8 (C3), 141.8 (C4a), 134.9 (C6), 129.6 (C8), 123.4 (C5), 123.2 (C7), 115.4 (C8a), 76.0 (C4), 28.8 (Me).

3-(Dimethylamino)-1*H*-2-benzopyran-1-one (8c). A solution of **1c** (61 mg, 0.12 mmol) in $CHCl_3$ (20 mL) was stirred under a CO atmosphere (1.4 bar) at 50 °C for 3 days. A black precipitate of Pd gradually formed. The solvent was evaporated under vacuum, the residue was extracted with Et_2O (6 × 5 mL), and the extracts were filtered through Celite. Compound **8c** was obtained as a bright yellow solid after evaporation of the solvent under vacuum. Yield: 23 mg, 93%. Mp: 67−71 °C. IR (Nujol, cm^{-1}): ν(COO), 1752, 1734. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{11}H_{12}NO_2$ $[M + H]^+$ requires 190.0863, found 190.0874, error = 5.99 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.06 (m, 1 H, H8), 7.47 (ddd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 8.4 Hz, 1 H, H6), 7.14 (br d, $^3J_{HH}$ = 8.4 Hz, 1 H, H5), 7.08 (ddd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 8.4 Hz, 1 H, H7), 5.21 (s, 1 H, H4), 2.99 (s, 6 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 161.9 (CO), 157.0 (C3), 142.1 (C4a), 134.7 (C6), 129.6 (C8), 123.4 (C5), 122.9 (C7), 114.5 (C8a), 77.8 (C4), 37.7 (Me).

***N*,3,3-Trimethyl-1-oxo-3,4-dihydro-1*H*-2-benzopyrane-4-carboxamide (9).** A solution of **2b′** (103 mg, 0.15 mmol) in acetone (15 mL) was stirred under a CO atmosphere (1.4 bar) for 90 min. The resulting black suspension was filtered through Celite, and the filtrate was concentrated to dryness. The residue was dissolved in CH_2Cl_2 (15 mL), Et_3N (42 μL, 0.30 mmol) was added, and the solution was stirred for 1 h. Partial evaporation of the solvent (2 mL) and addition of Et_2O (20 mL) led to the precipitation of a colorless solid, which was filtered off, washed with Et_2O (3 × 3 mL), and vacuum-dried to give **9**. Yield: 24 mg, 67%. Mp: 243−244 °C. IR (Nujol, cm^{-1}): ν(NH), 3306; ν(CO), 1710, 1642. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{13}H_{16}NO_3$ $[M + H]^+$ requires 234.1125, found 234.1126, error = 0.54 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.17 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, H8), 7.61 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, H6), 7.48 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, H7), 7.33 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, H5), 5.56 (br s, 1 H, NH), 3.72 (s, 1 H, H4), 2.79 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, NMe), 1.60 (s, 3 H, Me_2C), 1.44 (s, 3 H, Me_2C). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 169.4 (CO, amide), 164.3 (C1), 136.9 (C4a), 134.5 (C6), 130.6 (C8), 128.8 (C7), 128.2 (C5), 124.2 (C8a), 81.5 (C3), 55.5 (C4), 28.0 (Me_2C), 26.7 (NMe), 25.8 (Me_2C).

[Pd{C(=NXy)$C_6H_4$$CH_2$C(O)NHMe-2}I(dbbpy)] (10b′). To a solution of **1b′** (114 mg, 0.18 mmol) in CH_2Cl_2 (7 mL) was added XyNC (23 mg, 0.18 mmol); the mixture was stirred for 1 h and concentrated under reduced pressure (2 mL). *n*-Pentane (30 mL) was then added to precipitate a yellow solid, which was collected by filtration, washed with *n*-pentane (3 × 3 mL), and vacuum-dried to give **10b′**·0.25CH_2Cl_2. Yield: 110 mg, 78%. Anal. Calcd for $C_{36.25}H_{43.5}Cl_{0.5}IN_4OPd$: C, 54.27; H, 5.47; N, 6.98. Found: C, 54.01; H, 5.18; N, 7.17. Mp: 155−158 °C. IR (Nujol, cm^{-1}): ν(C=N), 1567; ν(CO), 1665. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 9.34 (d, $^3J_{HH}$ = 6.0 Hz, 1 H, H6, dbbpy), 9.00 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.96 (d, $^3J_{HH}$ = 6.0 Hz, 1 H, H6, dbbpy), 7.93 (overlapped broad signal, 1 H, NH), 7.91 (d, $^4J_{HH}$ = 1.6 Hz, 1 H, H3, dbbpy), 7.87 (d, $^4J_{HH}$ = 1.6 Hz, 1 H, H3, dbbpy), 7.46 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.40 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 5.6 Hz, 1 H, H5, dbbpy), 7.31−7.38 (m, 3 H, H5 dbbpy + Ar), 6.99−6.90 (m, 3 H, Xy), 5.30 (s, 0.5 H, CH_2Cl_2), 4.00 (br, 2 H, CH_2), 2.60 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, NMe), 2.23 (s, 6 H, Me, Xy), 1.38, 1.37 (both s, 9 H each, ^{t}Bu). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 184.0 (C=N), 172.2 (CO), 163.6, 163.2 (C4, dbbpy), 155.4, 152.9 (C2, dbbpy),

(28) Huh, D. H.; Jeong, J. S.; Lee, H. B.; Ryu, H.; Kim, Y. G. *Tetrahedron* **2002**, *58*, 9925.
(29) Deady, L. W.; Quazi, N. H. *J. Heterocycl. Chem.* **1994**, *31*, 793.
(30) Malamas, M. S.; Hohman, T. C.; Millen, J. *J. Med. Chem.* **1994**, *37*, 2043.

152.9 (C6, dbbpy), 149.7 (*i*-C, Xy), 149.6 (C6, dbbpy), 140.0 (C, Ar), 136.7 (CH, Ar), 131.8 (C, Ar), 130.2 (CH, Ar), 128.5 (CH, Ar), 128.0 (CH, Xy), 126.5 (CH, Ar), 123.8, 123.5 (C5, dbbpy), 123.3 (CH, Xy), 118.6, 117.8 (C3, dbbpy), 41.7 (CH_2), 35.5, 35.4 (CMe_3), 30.3, 30.2 (CMe_3), 26.0 (N*Me*), 20.7 (Me, Xy) (*o*-C of Xy and CH_2Cl_2 not observed).

1-(2,6-Dimethylphenylimino)-1,2-dihydroisoquinolin-3(4*H*)-one (11a). To a solution of **1a** (183 mg, 0.38 mmol) in CH_2Cl_2 (25 mL) was added XyNC (49.6 mg, 0.38 mmol). The mixture was stirred for 30 min, concentrated under reduced pressure (10 mL), and then stirred for 24 h, whereupon a black suspension formed. The solvent was removed under vacuum, the residue was extracted with Et_2O (10 × 5 mL), and the combined extracts were filtered through anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure led to the precipitation of **11a** as a colorless solid. Yield: 59 mg, 58%. Mp: 149−151 °C. IR (Nujol, cm^{-1}): ν(N−H), 3360; ν(CO), 1694; ν(C═N), 1645. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{17}H_{17}N_2O$ $[M + H]^+$ requires 265.1335, found 265.1333, error = 0.75 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.52 (dd, $^4J_{HH}$ = 0.8 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H8), 7.63 (br, 1 H, NH), 7.55 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H6), 7.46 (br t, $^3J_{HH}$ = 7.6 Hz, 1 H, H7), 7.28 (br d, $^3J_{HH}$ = 7.6 Hz, 1 H, H5), 7.09 (br d, $^3J_{HH}$ = 7.6 Hz, 2 H, *m*-H, Xy), 6.97 (br t, $^3J_{HH}$ = 7.6 Hz, 1 H, *p*-H, Xy), 3.97 (s, 2 H, H4), 2.08 (s, 6 H, Me, Xy). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 168.4 (CO), 145.0 (C═N), 143.6 (*i*-C, Xy), 133.0 (C4a), 132.0 (C6), 128.6 (*m*-C, Xy), 127.7 (*o*-C, Xy), 127.65 (C5), 127.60 (C7), 127.1 (C8), 125.8 (C8a), 124.2 (*p*-C, Xy), 35.8 (C4), 17.9 (Me, Xy).

1-(2,6-Dimethylphenylimino)-2-methyl-1,2-dihydroisoquinolin-3(4*H*)-one (11b). To a solution of **1b** (198 mg, 0.40 mmol) in $CHCl_3$ (20 mL) was added XyNC (52 mg, 0.40 mmol); the mixture was refluxed for 3 h and then stirred at room temperature for 60 h. The resulting black suspension was worked up as described for **11a** to give **11b** as a pale yellow solid. Yield: 89 mg, 80%. Mp: 108−112 °C. IR (Nujol, cm^{-1}): ν(CO), 1697; ν(C═N), 1644. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{18}H_{19}NO_2$ $[M + H]^+$ requires 279.1492, found 279.1487, error = 1.79 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.35 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H6), 7.23 (br d, $^3J_{HH}$ = 7.6 Hz, 1 H, H5), 7.17 (br, 1 H, H8), 7.05 (br d, $^3J_{HH}$ = 7.6 Hz, 2 H, *m*-H, Xy), 6.99 (br t, $^3J_{HH}$ = 4.8 Hz, H7), 6.90 (br t, $^3J_{HH}$ = 7.6 Hz, 1 H, *p*-H, Xy), 3.93 (s, 2 H, H4), 3.50 (s, 3 H, NMe), 2.00 (s, 6 H, Me, Xy). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.0 (CO), 147.8 (C═N), 146.2 (*i*-C, Xy), 132.2 (C4a) 131.1 (C6), 128.4 (*m*-C, Xy), 127.7 (C5), 127.0 (C7), 126.7 (C8), 126.2 (br, C8a), 125.2 (*o*-C, Xy), 122.6 (*p*-C, Xy), 37.4 (C4), 29.6 (NMe), 18.2 (Me, Xy).

1-(2,6-Dimethylphenylimino)-3-(*N*,*N*-dimethylamino)-1*H*-2-benzopyran (12c). To a solution of **1c** (91 mg, 0.17 mmol) in $CHCl_3$ (15 mL) was added XyNC (23 mg, 0.17 mmol), and the mixture was stirred at 60 °C for 24 h. Gradual formation of colloidal Pd was observed. The solvent was removed under vacuum, the residue was extracted with Et_2O (6 × 5 mL), and the combined extracts were filtered through anhydrous $MgSO_4$. Compound **12c** was isolated as a yellow oil after evaporation of the solvent under reduced pressure. Yield: 51 mg, 98%. IR (Nujol, cm^{-1}): ν(C═N), 1673, 1623. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{19}H_{21}N_2O$ $[M + H]^+$ requires 293.1648, found 293.1652, error = 1.09 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.26 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, H8), 7.38 (ddd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H6), 7.10−7.06 (m, 2 H, H7 + H5), 7.03 (br d, $^3J_{HH}$ = 7.6 Hz, 2 H, *m*-H, Xy), 6.87 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, *p*-H, Xy), 4.94 (s, 1 H, H4), 2.60 (s, 6 H, NMe_2), 2.14 (s, 6 H, Me, Xy). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 155.6 (C3), 148.8 (C═N), 145.4 (*i*-C, Xy), 138.2 (C4a), 132.4 (C6), 128.1 (*o*-C, Xy), 127.4 (*m*-C, Xy), 127.3 (C8), 123.1 (C7), 122.9 (C5), 122.4 (*p*-C, Xy), 117.8 (C8a), 76.0 (C4), 37.1 (NMe_2), 18.2 (Me, Xy).

Representative Procedure for the Syntheses of Complexes *trans*-[Pd{C(═NXy)$C_6H_4CH_2$C(O)NRR′-2}I(CNXy)$_2$] (NRR′ = NH_2 (13a), NHMe (13b)). Synthesis of 13a. To a solution of **1a** (93 mg, 0.19 mmol) in CH_2Cl_2 (20 mL) was added XyNC (78 mg, 0.59 mmol). The mixture was stirred at room temperature for 30 min and concentrated under reduced pressure (3 mL). The addition of *n*-pentane (15 mL) led to the precipitation of a yellow solid, which was filtered off, washed with *n*-pentane (3 × 3 mL), and vacuum-dried to give **13a**·H_2O. Yield: 134 mg, 92%. Anal. Calcd for $C_{35}H_{37}IN_4O_2Pd$: C, 53.96; H, 4.79; N, 7.19. Found: C, 53.84; H, 4.59; N, 7.25. Mp: 122−127 °C (dec). IR (Nujol, cm^{-1}): ν(C≡N), 2180; ν(CO), 1687; ν(C═N), 1586. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.24 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, Ar), 7.72 (br, 1 H, NH), 7.46 (m, 2 H, Ar), 7.35 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.23 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, *p*-H, XyNC[c]), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 4 H, *m*-H, XyNC[c]), 6.96 (s, 3 H, XyNC[i]), 5.07 (br, 1 H, NH), 3.88 (s, 2 H, CH_2), 2.22 (s, 12 H, Me, XyNC[c]), 2.21 (s, 6 H, Me, XyNC[i]), 1.66 (br s, 2 H, H_2O). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 183.6 (*C*═N), 173.7 (CO), 149.3 (*i*-C, XyNC[i]), 144.6 (C, Ar), 135.7 (*o*-C, XyNC[c]), 132.7 (CH, Ar), 130.7 (CH, Ar), 130.2 (CH, XyNC[c]), 130.0 (C, Ar), 129.0 (CH, Ar), 128.4 (CH, XyNC[i]), 128.1 (CH, XyNC[c]), 127.3 (*o*-C, XyNC[i]), 127.1 (CH, Ar), 124.2 (CH, XyNC[i]), 41.6 (CH_2), 19.2 (Me, XyNC[i]), 18.7 (Me, XyNC[c]); *C*≡N and *i*-C of XyNC[c] not observed.

***trans*-[Pd{C(═NHXy)$C_6H_4CH_2$C(O)NH_2)-2}I(CNXy)$_2$]OTf (14a).** To a solution of **13a** (159.2 mg, 0.21 mmol) in CH_2Cl_2 (15 mL) was added HOTf (18.3 μL, 0.21 mmol), and the mixture was stirred for 1 h. The resulting solution was concentrated under reduced pressure (1 mL), and Et_2O (30 mL) was added to precipitate a yellow solid, which was filtered off, washed with Et_2O (3 × 3 mL), and vacuum-dried to give **14a**. Yield: 173.0 mg, 91%. Anal. Calcd for $C_{36}H_{36}F_3IN_4O_4PdS$: C, 47.46; H, 3.98; N, 6.15; S, 3.52. Found: C, 47.73; H, 3.82; N, 6.18; S, 3.48. Mp: 143−145 °C (dec). IR (Nujol, cm^{-1}): ν(C≡N), 2199; ν(CO), 1650; ν(C═N), 1588. ^1H NMR (400.9 MHz, $CDCl_3$): δ 16.36 (br, 1 H, NH, iminium), 9.03 (br, 1 H, NH, acetamide), 8.36 (dd, $^4J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.95 (dd, $^4J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.65 (m, 2 H, Ar), 7.31 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, *p*-H, Xy), 7.13 (d, $^3J_{HH}$ = 7.5 Hz, 6 H, *m*-H, Xy), 6.04 (br, NH, acetamide), 4.06 (s, 2 H, CH_2), 2.35 (s, 6 H, Me, Xy, iminium), 2.19 (s, 12 H, Me, XyNC[c]). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 176.5 (CO), 142.1 (C, Ar), 139.7 (*i*-C, Xy, iminium), 136.0 (*o*-C, XyNC[c]), 134.5 (CH, Ar), 133.9 (CH, Ar), 133.1 (CH, Ar), 132.8 (*o*-C, Xy, iminium), 131.3 (CH, XyNC[c]), 130.0 (C, Ar), 129.7 (CH, Ar), 129.4 (CH, Xy, iminium), 128.5 (CH, XyNC[c]), 39.2 (CH_2), 18.9 (Me, Xy, iminium), 18.6 (Me, XyNC[c]); *C*═N, *C*≡N, and *i*-C of XyNC[c] not observed.

Representative Procedure for the Syntheses of Complexes [Pd-{C(═NXy)$C_6H_4CH_2$C(O)NRR′-2}(CNXy)(N^N]OTf (N^N = tmeda, NRR′ = NHMe (15b), NMe_2 (15c); N^N = dbbpy, NRR′ = NHMe (15b′)). Synthesis of 15b. To a solution of **2b** (125 mg, 0.24 mmol) in CH_2Cl_2 (15 mL) was added XyNC (63 mg, 0.48 mmol), and the resulting yellow solution was stirred for 2.5 h, filtered through Celite, and concentrated under reduced pressure (2 mL). The addition of Et_2O (25 mL) led to the precipitation of a yellow solid, which was filtered off, washed with Et_2O (5 × 3 mL), and vacuum-dried to give **15b**·0.5H_2O. Yield: 126 mg, 66%. Anal. Calcd for $C_{34}H_{45}F_3N_5O_{4.5}PdS$: C, 51.61; H, 5.73; N, 8.85; S, 4.05. Found: C, 51.51; H, 5.76; N, 8.86; S, 3.85. Mp: 103−104 °C . IR (Nujol, cm^{-1}): ν(NH), 3327; ν(C≡N), 2182; ν(CO), 1662; ν(C═N), 1583. ^1H NMR (300.1 MHz, $CDCl_3$): δ 8.20 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, Ar), 7.59−7.39 (m, 4 H, Ar + NH), 7.32 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *p*-H, XyNC[c]), 7.14 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, *m*-H, XyNC[c]), 7.04−6.90 (m, 3 H, XyNC[i]), 3.81 (br, 2 H, CH_2, acetamide), 2.80 (br, 4 H, CH_2, tmeda), 2.59 (d, $^3J_{HH}$ = 4.5 Hz, 3 H, NMe, acetamide), 2.42 (br s, 12 H, Me, tmeda), 2.17 (br s, 12 H, Me, XyNC), 1.84 (br s, 1 H, H_2O). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 180.4 (C═N), 171.3 (CO), 149.5 (*i*-C, XyNC[i]), 138.2 (C, Ar), 135.3 (*o*-C, XyNC[c]), 132.2 (CH, Ar), 131.9 (C, Ar), 131.0 (CH, Ar), 130.9 (CH, XyNC[c]), 130.0 (CH, Ar), 128.5 (CH,

Table 1. Crystallographic Data for 1b′, 2b′·Me$_2$CO, 3b′, and 4b′·0.5CH$_2$Cl$_2$

	1b′	**2b′·Me$_2$CO**	**3b′**	**4b′·0.5CH$_2$Cl$_2$**
formula	$C_{27}H_{34}IN_3OPd$	$C_{31}H_{40}F_3N_3O_5PdS$	$C_{46}H_{49}F_3N_3O_4PPdS$	$C_{27.5}H_{34}ClN_3OPd$
fw	649.87	730.12	934.31	564.43
T (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	triclinic	triclinic	triclinic
space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.4414(6)	10.2621(5)	12.2756(5)	12.1373(5)
b (Å)	11.7373(5)	13.5328(7)	13.6966(5)	13.4080(6)
c (Å)	17.4652(8)	14.1804(7)	14.0469(5)	16.7547(7)
α (deg)	90	63.950(2)	70.198(4)	95.000(2)
β (deg)	90	71.051(2)	82.776(4)	99.522(2)
γ (deg)	90	72.364(2)	76.276(4)	105.510(2)
V (Å^3)	2755.4(2)	1643.30(14)	2156.00(14)	2566.23(19)
Z	4	2	2	4
ρ_{calcd} (Mg m^{-3})	1.567	1.476	1.439	1.461
μ (mm^{-1})	1.817	0.688	0.576	0.852
R1[a]	0.0203	0.0484	0.0291	0.0532
wR2[b]	0.0473	0.1189	0.0703	0.1082

[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.

Table 2. Crystallographic Data for 5b′, 6b′, 8b, 9, and 10b′

	5b′	**6b′**	**8b**	**9**	**10b′**
formula	$C_{30}H_{35}N_5OPd$	$C_{28}H_{34}IN_3O_2Pd$	$C_{10}H_9NO_2$	$C_{13}H_{15}NO_3$	$C_{36}H_{43}IN_4OPd$
fw	588.03	677.88	175.18	233.26	781.04
T (K)	100(2)	103(2)	110(2)	100(2)	100(2)
λ (Å)	0.71073	1.54184	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pn	$C2/c$
a (Å)	10.6664(2)	19.8663(6)	19.5562(5)	7.8580(2)	31.3723(16)
b (Å)	26.7297(3)	10.1395(3)	11.9837(3)	9.7895(2)	12.4240(6)
c (Å)	10.2585(2)	14.4269(5)	7.2383(2)	8.1530(2)	21.9332(11)
α (deg)	90	90	90	90	90
β (deg)	108.641(3)	109.676(4)	100.198(4)	108.008(3)	118.671(2)
γ (deg)	90	90	90	90	90
V (Å^3)	2771.36(8)	2736.39(15)	1669.55(8)	596.45(2)	7500.7(6)
Z	4	4	8	2	8
ρ_{calcd} (Mg m^{-3})	1.409	1.645	1.394	1.299	1.383
μ (mm^{-1})	0.701	14.554	0.098	0.093	1.348
R1[a]	0.0224	0.0342	0.0342	0.0266	0.0268
wR2[b]	0.0533	0.0921	0.0852	0.0711	0.0701

[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.

XyNC^{c+i}), 127.5 (CH, Ar), 124.5 (CH, XyNC^i), 60.9 (CH_2, tmeda), 49.5 (Me, tmeda), 41.4 (CH_2, acetamide), 26.1 (NMe, acetamide), 19.8 (Me, XyNC^i), 18.6 (Me, XyNC^c); *C*≡N and *i*-C of XyNC^c and *o*-C of XyNC^i not observed.

X-ray Structure Determinations. Crystals suitable for X-ray diffraction studies were obtained by liquid−liquid diffusion from CH_2Cl_2/*n*-hexane: **1b′**, **3b′**, **4b′**·0.5CH_2Cl_2; CH_2Cl_2/*n*-pentane: **6b′**, **10b′**, **13b**·CH_2Cl_2, **14a**; acetone/Et_2O: **2b′**·Me_2CO; $CDCl_3$/*n*-pentane: **5b′**; CH_2Cl_2/Et_2O: **9**, **15c**, or by sublimation at low pressure: **8b**, **11b**. Numerical details are presented in Tables 1−3. The data for **1b′**, **2b′**, **4b′**, **10b′**, **11b**, and **13b′** were collected on a Bruker Smart APEX CCD diffractometer using monochromated Mo Kα radiation in ω-scan mode. The data for **6b′** were collected on an Oxford Diffraction Nova O diffractometer using mirror-focused Cu Kα radiation in ω-scan mode. The data for **3b′**, **5b′**, **8b**, **9**, **14a**, and **15c** were collected on an Oxford Diffraction Xcalibur S diffractometer using monochromated Mo Kα radiation in ω-scan mode. The structures were solved by direct methods and refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen).[31] Restraints to local aromatic ring symmetry or light-atom displacement factor components were applied in some cases. Treatment of hydrogen atoms is as follows: NH free except for **1b′**, **2b′**, **6b′**, **10b′** (free with DFIX) and **14a** (free with SADI); ordered methyl groups, rigid; all others, riding. *Special features of refinement:* **1b′**: The Flack parameter is 0.001(14). One ^{t}Bu group is disordered over two positions. **2b′**: The triflate anion is disordered over two positions. An ill-defined region of residual electron density was tentatively interpreted as a disordered acetone. Its hydrogen atoms were not included in the refinement. **4b′**: One ^{t}Bu group is disordered over two positions. **9**: In the absence of significant anomalous scattering, Friedel opposite reflections were merged and the Flack parameter is thus meaningless. **10b′**: A region of residual electron density could not be interpreted in terms of realistic solvent molecules, even allowing for possible disorder. For this reason the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands) was employed to remove mathematically the effects of the solvent. Standard deviations of refined parameters should be interpreted with caution. The void volume per cell was 1021 Å^3, with a void electron count per cell of 240. This solvent was not taken into account when calculating derived parameters such as the formula weight, because the nature of the solvent was uncertain.

(31) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

Results and Discussion

Syntheses of Ortho-Palladated Phenylacetamides and Cyclometalated Derivatives. Aryl derivatives of the type [Pd{$C_6H_4CH_2C(O)NRR'$-2}]I(N^N)] (N^N = tmeda, NRR′ = NH_2

Table 3. Crystallographic Data for 11b, 13b·CH_2Cl_2, 14a, and 15c

	11b	13b·CH_2Cl_2	14a	15c
formula	$C_{18}H_{18}N_2O$	$C_{37}H_{39}Cl_2IN_4OPd$	$C_{36}H_{36}F_3IN_4O_4PdS$	$C_{35}H_{46}F_3N_5O_4PdS$
fw	278.34	859.92	911.05	796.23
T (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	13.0014(12)	19.2766(8)	8.3013(3)	10.6738(2)
b (Å)	7.8134(7)	8.5432(6)	14.7697(4)	14.8048(3)
c (Å)	15.2139(14)	23.3527(9)	16.4066(4)	22.7526(4)
α (deg)	90	90	87.250(3)	90
β (deg)	111.926(2)	110.859(2)	75.566(4)	92.482(3)
γ (deg)	90	90	76.134(4)	90
V (Å^3)	1433.7(2)	3593.8(3)	1891.16(10)	3592.07(12)
Z	4	4	2	4
ρ_{calcd} (Mg m^{-3})	1.290	1.589	1.600	1.472
μ (mm^{-1})	0.081	1.559	1.419	0.635
R1[a]	0.0599	0.0266	0.0278	0.0239
wR2[b]	0.1265	0.0633	0.0728	0.0454

[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.

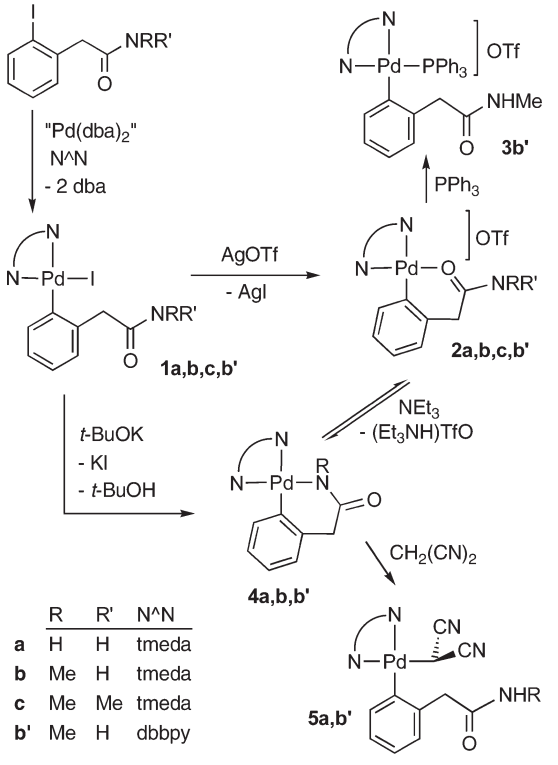
(**1a**), NHMe (**1b**), NMe_2 (**1c**); N^N = dbbpy, NRR′ = NHMe (**1b′**); Scheme 1) were synthesized by oxidative addition of the corresponding 2-(2-iodophenyl)acetamides to "Pd(dba)$_2$" ([$Pd_2(dba)_3$]·dba; dba = dibenzylideneacetone) in the presence of tmeda or dbbpy. The reactions took place at room temperature in toluene, THF, or CH_2Cl_2, and the products were isolated in yields over 60%.

The reactions of complexes **1** with 1 equiv of AgOTf led to the precipitation of AgI and the formation of the corresponding cationic cyclopalladated derivatives [Pd{κ^2C,O-$C_6H_4CH_2C$(O)NRR′-2}(N^N)]OTf (N^N = tmeda, NRR′ = NH_2 (**2a**), NHMe (**2b**), NMe_2 (**2c**); N^N = dbbpy, NRR′ = NHMe (**2b′**)), which were isolated in high yields. In these complexes, the amide function is coordinated to the metal through the oxygen atom, as revealed by the IR and NMR spectra and the crystal structure of **2b′** (see below). The reaction of **2b′** with 1 equiv of PPh_3 led to the splitting of the Pd−O bond to give the phosphino complex [Pd{$C_6H_4CH_2C$(O)NHMe-2}(dbbpy)(PPh_3)]OTf (**3b′**) in 69% yield.

Deprotonation of the amide function in complex **1a**, **1b**, or **1b′** with KO^{t}Bu in HO^{t}Bu led to the neutral cyclopalladated derivatives [Pd{κ^2C,N-$C_6H_4CH_2C$(O)NR-2}(N^N)] (N^N = tmeda, R = H (**4a**), Me (**4b**); N^N = dbbpy, R = Me (**4b′**)), which result from the displacement of the iodo ligand by the nitrogen of the anionic amidate group and were isolated in moderate to good yields. When NEt_3 was used instead, deprotonation of the amide occurred only to a small extent, as detected by NMR. A significantly higher amount of the amidate complexes **4** (around 33%) was detected by NMR after treatment of the cationic complexes **2a**, **2b**, or **2b′** with excess NEt_3 in acetone.

In order to explore their basic character and usefulness for the preparation of other derivatives, we studied the reactivity of **4a** and **4b′** toward the methylene-active compounds malononitrile, acetylacetone, methyl cyanoacetate, and dimethyl malonate. However, only the most acidic of these reagents, malononitrile,[32] reacted to give the expected derivatives [Pd{$C_6H_4CH_2C$(O)NHR-2}{$CH(CN)_2$}(N^N)] (N^N = tmeda, R = H (**5a**); N^N = dbbpy and R = Me (**5b′**)); whereas **5b′** was obtained using 1 equiv of malononitrile, the formation of **5a** required an excess of this reagent and the complex could not be isolated in pure form, probably because of the lower basicity of the C(O)NH group as compared to C(O)NMe.

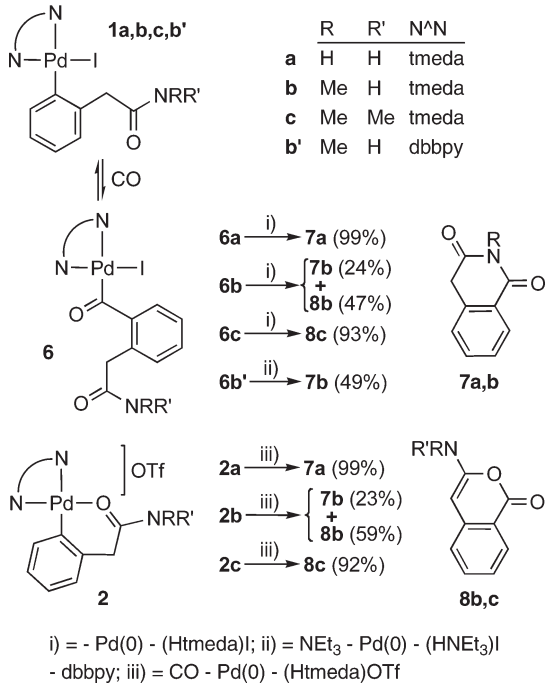
Scheme 1



Reactions with CO and Decomposition of the Resulting Acyl Complexes. The reactions of complexes **1** with CO in CH_2Cl_2 at −17 °C afforded the insertion products [Pd{C(O)C_6H_4-CH_2C(O)NRR′-2}I(N^N)] (N^N = tmeda, NRR′ = NH_2 (**6a**), NHMe (**6b**), NMe_2 (**6c**); N^N = dbbpy, NRR′ = NHMe (**6b′**)), which were isolated in high yields (Scheme 2). The isolation of these compounds in pure form required low temperature because they slowly lose CO in solution at room temperature to give the parent arylpalladium compounds. Moreover, the tmeda complexes **6a**−**c** gradually decomposed when kept in solution under CO at room or higher

(32) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

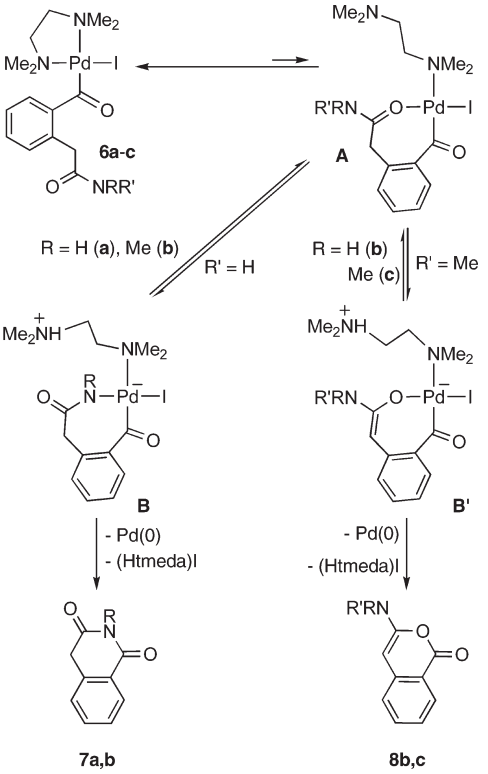
Scheme 2



temperatures (Scheme 2). Complete decomposition of **6a** was observed after 30 h of reaction of **1a** with CO (1.4 bar) at 50 °C in $CDCl_3$ to give quantitatively colloidal palladium, (tmedaH)I,[33] and isoquinoline-1,3(2*H*,4*H*)-dione (**7a**) (homophthalimide),[28,29,34] resulting from the reductive C−N coupling. Decomposition of **6b**, formed *in situ* from **1b** under CO, was considerably slower and reached only 71% after 3 days (1.4 bar, 50 °C), giving an approximately 1:2 mixture of 2-methylisoquinoline-1,3(2*H*,4*H*)-dione[30] (**7b**) and the new isocoumarin derivative 3-(methylamino)-1*H*-2-benzopyran-1-one (**8b**), resulting from C−N and C−O couplings, respectively. Complex **6c** also decomposed under CO (1.4 bar, 3 days, 50 °C), giving via a C−O coupling exclusively the new compound 3-(dimethylamino)-1*H*-2-benzopyran-1-one (**8c**), which was isolated in 93% yield.

A possible reaction pathway for the C−N and/or C−O coupling processes from the tmeda derivatives **6a**−**c** is outlined in Scheme 3. We assume that an equilibrium is established between **6** and the intermediate complex **A**, in which the tmeda ligand is monocoordinated and the acetamide group is *O*-coordinated, increasing the acidities of both the NH (if present) and CH_2 protons. The nonbonded tmeda nitrogen might reasonably be responsible for the deprotonation of the NH and/or CH_2 groups, either intra- or intermolecularly. The different nature of the proton involved determines in turn the nature of the corresponding deprotonated complex, an amidato **B**, similar to **4**, or an aminoenolato **B′**, which could then undergo a C−N or C−O reductive coupling, respectively. While for **6c** only the C−O coupling can take place, for **6a** and **6b** both the C−N and C−O coupling products are possible and the relative proportions in which they are obtained are expected to be determined by the relative concentrations of intermediates **B** and **B′**, largely dictated by the relative acidities of NH and CH_2 protons, as

Scheme 3



well as by the rates of the reductive coupling steps. According to literature data,[32,35] NH protons are somewhat more acidic than α-CH protons in amides, but in the case of the NHMe derivative the difference between the acidities of these two types of protons will be diminished because of the electron-donating methyl group. Therefore, in the case of **6a**, the deprotonation and coupling steps lead to **7a** because of the higher concentration of the corresponding amidate **B** and/or the more rapid C−N coupling compared to the C−O coupling. For **6b**, the deprotonation of the methylene group competes with that of the NHMe group, giving a 1:2 mixture of **7b** and **8b**, perhaps because the steric repulsion of the methyl substituent makes the C−N coupling slower than the C−O coupling. Correspondingly, the slower decomposition of **6b** than of **6a** (see above) can be caused by the slower C−N coupling in the amidate **B** corresponding to **6b** than that in the unsubstituted analogue **6a**. We note that a similar reasoning has been used to explain the general observation that palladium-catalyzed intermolecular amidations of aryl halides are much slower when acyclic secondary amides are used instead of primary amides.[5]

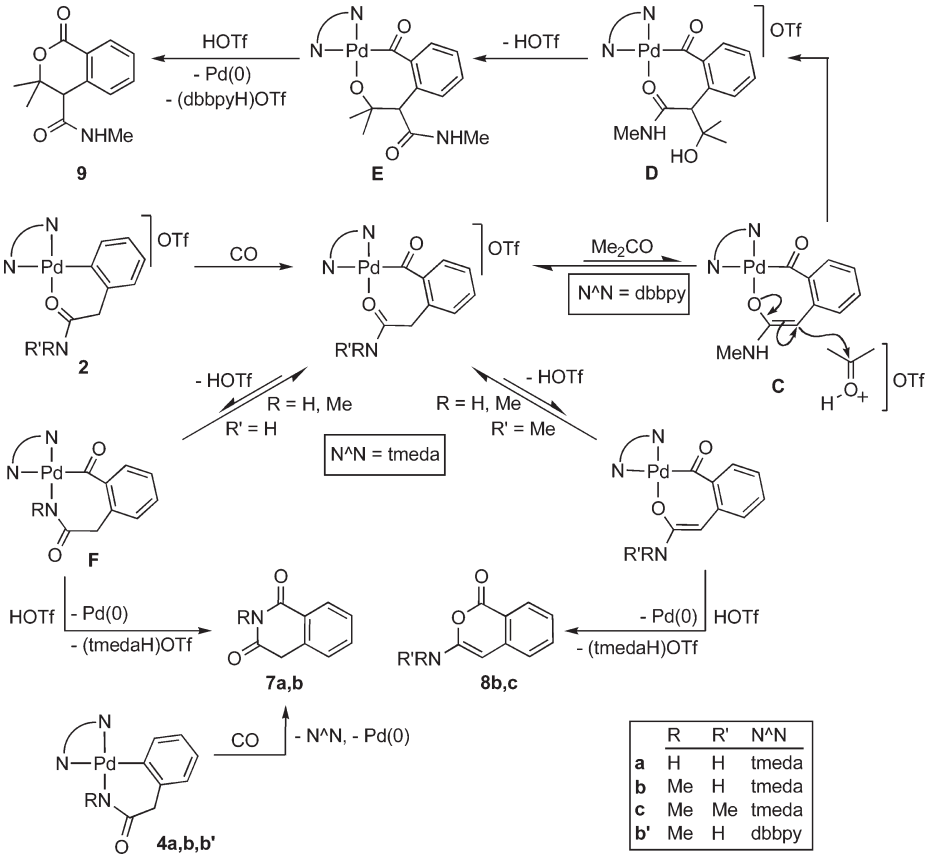
In contrast to the tmeda derivative **6b**, the dbbpy complex **6b′** gave only traces of **7b** and **8b** after 30 h under CO (1.4 bar) at 50 °C. The stability of **6b′** can be attributed to the better coordination ability and lower basicity of the dbbpy ligand, which hinders its participation as a base in the process. When the reaction of **1b′** with CO was carried out in the presence of NEt_3, the reductive coupling did take place to an appreciable extent, although it was rather slow (49% after 48 h at 50 °C) and gave exclusively the isoquinolinedione **7b**; as mentioned above, NEt_3 deprotonates complex **1b′** to give, to a small extent, only amidate complex **4b′**, which would react with CO to give solely the C−N coupling product.

(33) Chitsaz, S.; Breyhan, T.; Pauls, J.; Neumuller, B. *Z. Anorg. Allg. Chem.* **2002**, *628*, 956.

(34) Barnard, I. F.; Elvidge, J. A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1813.

(35) Bordwell, F. G.; Fried, H. E. *J. Org. Chem.* **1991**, *56*, 4218.

Scheme 4



	R	R'	N^N
a	H	H	tmeda
b	Me	H	tmeda
c	Me	Me	tmeda
b'	Me	H	dbbpy

The reaction of the cationic cyclometalated tmeda complex **2a**, **2b**, or **2c** with CO (1.4 bar, 3 h at room temperature in acetone) led to the formation of colloidal Pd and solutions containing **7a** (100% yield), **7b** + **8b** (82% total yield; 0.4:1 molar ratio), or **8c** (92% yield), respectively, at a much faster rate than their parent iodocomplexes **1a**−**c** (Scheme 4). This is a new example of a well-known behavior: the rates of migratory insertions or catalytic reactions involving some such processes are enhanced when they involve cationic species and a coordination position is easily accessible to the molecule to be inserted.[36] At a preparative scale, compound **7a** was isolated in 51% yield, while by extracting an Et_2O solution of the mixture of **7b** and **8b** with aqueous K_2CO_3, compound **8b** was isolated in 59% yield. In order to avoid the formation of **8b** and thus isolate **7b**, we carried out the reaction of **2b** with CO in the presence of NEt_3, which gave exclusively **7b** (67% yield); as previously noted for the reaction of **1b′** with CO, this result is explained by the formation of the amidate **4b**, which then reacts with CO to give the C−N coupling product. The formation of the organic products from the reactions of **2a**−**c** with CO must involve amidate and aminoenolate intermediates similar to those proposed for the reactions of the iodo complexes **1a**−**c** with CO. However, given the higher acidity of the acetamide protons in the cationic complexes **2a**−**c** and the strengthening of the Pd−N bonds relative to **1a**−**c**, it is likely that the deprotonation step does not involve the participation of the tmeda ligand and it is carried out by the acetone used as solvent (Scheme 4).

We have found that the dbbpy complex **2b′** shows a different behavior toward CO than do **2a**−**c**. Thus, **2b′** reacted with CO (1.4 bar) in acetone at room temperature to give the isochroman-1-one derivative *N*,3,3-trimethyl-1-oxo-3,4-dihydro-1*H*-2-benzopyrane-4-carboxamide (**9**), along with colloidal palladium and (dbbpyH)OTf, in a process that involves the participation of the solvent. A possible reaction pathway for the formation of **9** is outlined in Scheme 4. The better coordination ability of dbbpy relative to tmeda may stabilize the aminoenolate intermediate **C**, making the reductive C−O coupling more difficult and favoring the reaction with a protonated acetone molecule to give **D**. This step is related to the previously reported reactions of *N*,*N*-disubstituted 3-amino-1*H*-2-benzopyran-1-ones with aldehydes to give 3,4-dihydro-1*H*-2-benzopyrane-4-carboxamides analogous to **9**,[37] although these require more energetic conditions, such as refluxing of the reagents in acetic acid, ethanol, or acetonitrile. Next, the deprotonation of **D** would afford the alcoholato complex **E** and, finally, compound **9** would result from a C−O reductive coupling.

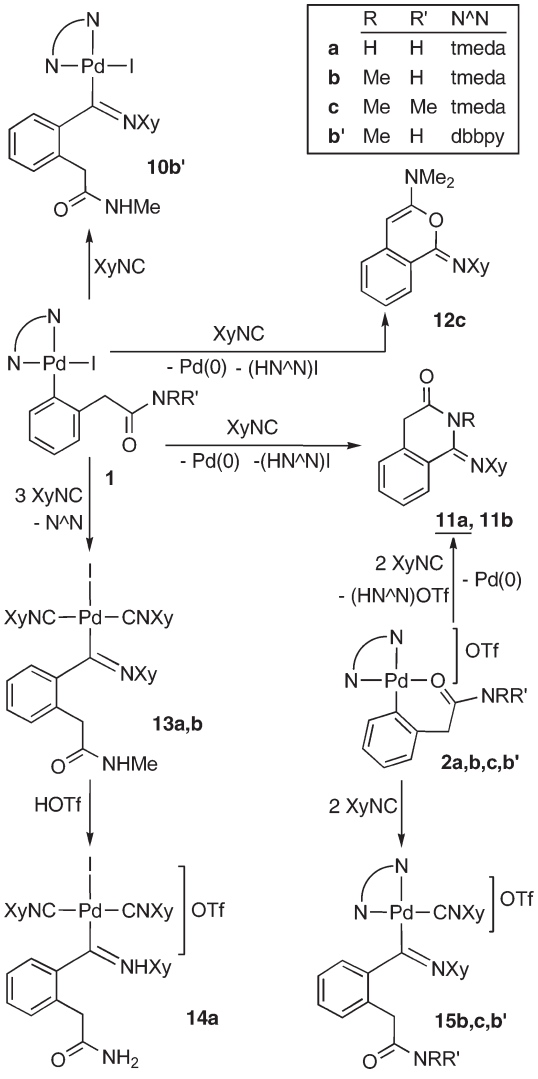
The neutral amidate complexes **4a** and **4b** or **4b′** also reacted rapidly with CO at room temperature in acetone to give Pd(0) and high yields of **7a** and **7b**, respectively, which result from a C−N coupling, probably occurring through an intermediate such as **F** (Scheme 4). This fact additionally

(36) Dekker, G.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598. Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469. Yamamoto, A. *J. Organomet. Chem.* **1995**, *500*, 337. Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. Kayaki, Y.; Tsukamoto, H.; Kaneko, M.; Shimizu, I.; Yamamoto, A.; Tachikawa, M.; Nakajima, T. *J. Organomet. Chem.* **2001**, *622*, 199.

(37) Boyd, G. V.; Monteil, R. L.; Lindley, P. F.; Mahmoud, M. M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1351.

suggests that, in solution, the amidates are not in equilibrium, at least to an appreciable extent, with their isomeric aminoenolates.

Scheme 5



Reactions with XyNC. The reaction of the dbbpy complex **1b′** with 1 equiv of XyNC (Xy = 2,6-dimethylphenyl) gave the insertion product [Pd{C(=NXy)$C_6H_4CH_2$C(O)NHMe-2}I(dbbpy)] (**10b′**) (Scheme 5). However, the analogous iminoacyl derivatives could not be isolated when starting from the tmeda derivatives **1a** and **1b** because they immediately started to decompose, even at low temperature, giving colloidal Pd, (tmedaH)I, and the C−N coupling products 1-(2,6-dimethylphenylimino)-1,2-dihydroisoquinolin-3(4*H*)-one (**11a**) or 1-(2,6-dimethylphenylimino)-2-methyl-1,2-dihydroisoquinolin-3(4*H*)-one (**11b**), respectively. As observed for the previous C−N couplings, the decomposition is much faster for the unsubstituted derivative **1a** (30 min at room temperature) than for its methyl-substituted analogue **1b**, the latter requiring harsher reaction conditions (3 h at 61 °C). Compounds **11** are new members of the small family of imino derivatives of isoquinoline-1,3(2*H*,4*H*)-dione.[34,38] The reaction of **1c** with 1 equiv of XyNC gave a mixture containing a new organometallic derivative, probably the expected insertion product, and unreacted starting material, which could not be separated. However, heating this mixture at 60 °C for 24 h led to its gradual decomposition to give colloidal Pd, (tmedaH)I, and an almost quantitative yield of the new iminoisocoumarin derivative 1-(2,6-dimethylphenylimino)-3-(*N*,*N*-dimethylamino)-1*H*-2-benzopyran (**12c**), resulting from a C−O coupling. Although the formation of these organic products probably takes place through reaction pathways analogous to that proposed for the reactions of **1a**−**c** with CO, the experimental data clearly show that, for **1a** and **1b**, the C−N couplings are much faster than in the reactions with CO, and also than the C−O couplings. This would explain the isolation of only one iminoacyl complex and the absence of C−O coupling products in these reactions with XyNC.

The reactions of **1a** or **1b′** with 3 equiv of XyNC gave *trans*-[Pd{C(=NXy)$C_6H_4CH_2$C(O)NHR-2}I$(CNXy)_2$] (R = H (**13a**), Me (**13b**)), which result from the displacement of the chelating ligands by two of the isocyanide molecules and the insertion of a third isocyanide into the Pd−C bond. The occupancy of both positions cis to the iminoacyl ligand prevents the coordination of the acetamide group and consequently rules out any coupling process such as that observed in the equimolecular reaction (see above and Scheme 5). The

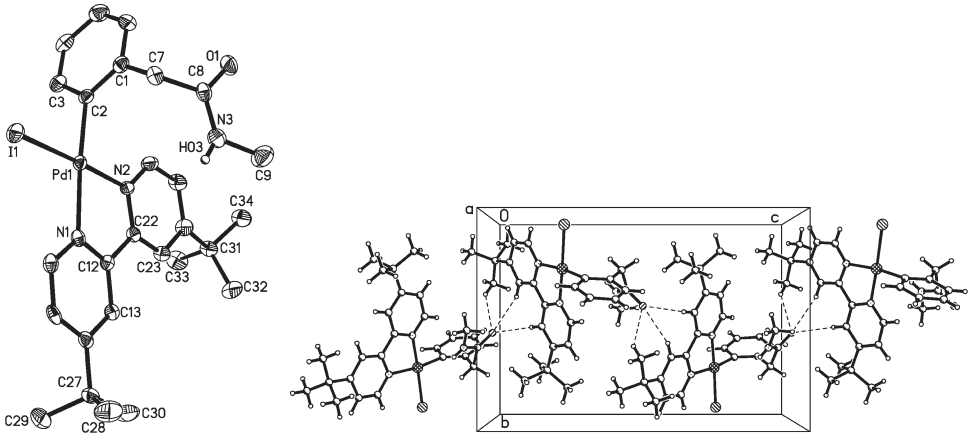


Figure 1. Thermal ellipsoid plot (50% probability) and crystal packing of complex **1b′**. Selected bond distances (Å) and angles (deg): Pd(1)−C(2) 1.986(3), Pd(1)−N(1) 2.128(2), Pd(1)−N(2) 2.0735(19), Pd(1)−I(1) 2.5671(2); C(2)−Pd(1)−N(2) 94.02(9); C(2)−Pd(1)−N(1) 172.50(9), N(2)−Pd(1)−N(1) 78.63(8), C(2)−Pd(1)−I(1) 88.66(8), N(2)−Pd(1)−I(1) 177.33(6), N(1)−Pd(1)−I(1) 98.69(6), C(1)−C(2)−Pd(1) 123.40(19), C(3)−C(2)−Pd(1) 118.16(19).

reaction of **13a** with 1 equiv of triflic acid led to the protonation of the iminoacyl nitrogen to give *trans*-[Pd{C(=NHXy)-$C_6H_4CH_2C(O)NH_2$-2}I(CNXy)$_2$]OTf (**14a**), formally containing an *N*-stabilized carbene ligand.

The reactions of the cationic complexes **2** with XyNC were attempted in order to explore the possible formation of coupling products. In the case of the NH_2 derivative **2a**, the 1:1 reaction led to the formation of a new complex that could not be conveniently characterized because of its instability, while the 1:2 reaction led to the formation of the C−N coupling product **11a** almost quantitatively. Probably, the unstable compound from the 1:1 reaction is an insertion product and the second equivalent of XyNC favors the C−N coupling by displacing one of the N atoms of the tmeda ligand, which can then act as a base. In contrast, the reactions of the NHMe and NMe_2 derivatives **2b**, **2c**, and **2b′** with 2 equiv of XyNC produced the insertion of one XyNC into the Pd−C bond and the displacement of the *O*-coordinated amide group by a second XyNC (Scheme 5) to give [Pd{C(=NXy)$C_6H_4CH_2C(O)NRR'$-2}(CNXy)(N^N)]OTf (N^N = tmeda, NRR′ = NHMe (**15b**), NMe_2 (**15c**); N^N = dbbpy, NRR′ = NHMe (**15b′**)). The use of only 1 equiv of isocyanide led to the same compounds, but half of the unreacted starting materials were recovered. The formation of organic products is probably hindered because the C−N and/or C−O coupling processes are more difficult than the C−N coupling from the primary acetamide in **2a**, and

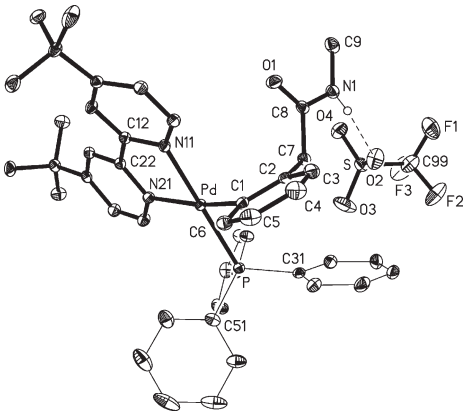


Figure 2. Thermal ellipsoid plot (50% probability) of complex **3b′**. Selected bond distances (Å) and angles (deg): Pd−C(1) 1.9906(14), Pd−N(11) 2.1070(11), Pd−N(21) 2.1749(12), Pd−P 2.2643(4), C(1)−C(2) 1.399(2), C(1)−C(6) 140.1(2); C(1)−Pd−N(11) 90.68(5), C(1)−Pd−N(21) 166.96(5), N(11)−Pd−N-(21) 77.00(4), C(1)−Pd−P 85.01(4), N(11)−Pd−P 174.92(3), N(21)−Pd−P 107.07(3), C(2)−C(1)−Pd 122.99(11), C(6)−C(1)−Pd 166.4(11).

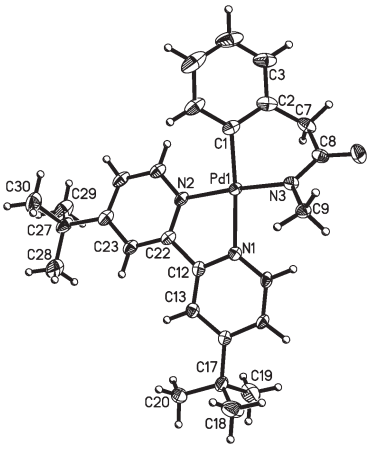
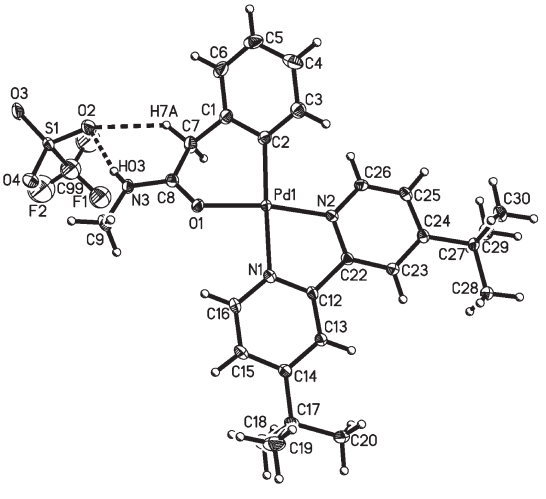


Figure 4. Thermal ellipsoid plot (50% probability) of one of the two independent molecules of the structure of complex **4b′**. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.983(4), Pd(1)−N(3) 2.012(3), Pd(1)−N(2) 2.049(3), Pd(1)−N-(1) 2.111(3), N(3)−C(8) 1.319(5), N(3)−C(9) 1.465(5), C(8)−O-(1) 1.264(5); C(1)−Pd(1)−N(3) 86.02(14), C(1)−Pd(1)−N(2) 98.02(14), N(3)−Pd(1)−N(1) 98.19(12), N(2)−Pd(1)−N(1) 77.74(12), C(8)−N(3)−C(9) 114.8(3), C(8)−N(3)−Pd(1) 123.7(3), C(9)−N(3)−Pd(1) 121.5(2), O(1)−C(8)−N(3) 124.9(4), O(1)−C(8)−C(7) 119.0(3), N(3)−C(8)−C(7) 116.1(3).



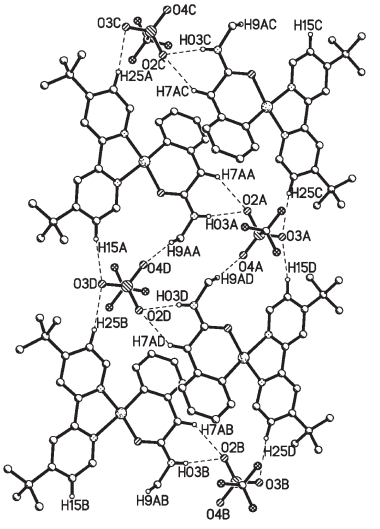


Figure 3. Thermal ellipsoid plot (50% probability) and crystal packing of complex **2b′**. Selected bond distances (Å) and angles (deg): Pd(1)−C(2) 1.991(4), Pd(1)−N(2) 2.023(3), Pd(1)−O(1) 2.031(2), Pd(1)−N(1) 2.089(3), O(1)−C(8) 1.263(4), C(8)−N(3) 1.317(4), N(3)−C(9) 1.453(4); C(2)−Pd(1)−N(2) 100.15(13), C(2)−Pd(1)−O(1) 88.74(12), N(2)−Pd(1)−N(1) 79.23(11), O(1)−Pd(1)−N(1) 91.97(10), C(8)−O(1)−Pd(1) 121.1(2), C(8)−C(7)−C(1) 110.7(3), O(1)−C(8)−N(3) 120.0(3), O(1)−C(8)−C(7) 121.7(3), N(3)−C-(8)−C(7) 118.3(3), C(8)−N(3)−C(9) 123.1(3).

thus the reaction sequence ends with the formation of the stable compound **15b**, **15b′**, or **15c**.

The amidate complexes **4a**, **4b**, and **4b′** reacted only sluggishly with XyNC. In all three cases, the main product was the C−N coupling compound **11a** or **11b**, but the reactions required heating at 60 °C in $CHCl_3$ for 16−48 h, and the organic compounds were obtained contaminated by decomposition products.

Spectroscopic Features. The methylenic protons are observed in the room-temperature ^{1}H NMR spectra of the aryl complexes **1** and **3b′** as an AB system because the aryl ligand does not lie in the coordination plane and its rotation around the Pd−C bond must be restricted. In the iminoacyl complex **10b′** such restriction is observed only at low temperatures (see Experimental Section and SI for details), while the RT spectrum shows the methylenic protons as a broad singlet. The singlet observed for the CH_2 protons in the spectra of complexes **2** and **6** must be attributed, respectively, to a fast ring flipping process that makes them equivalent and to the lower steric demand of the O atom with respect to the NXy group present in **10b′**. In the cyclic amidate complexes **4** the methylenic protons generate, at room temperature, a broad singlet (**4a**), an AB system (**4b**), or a very broad resonance (**4b′**). The latter resolves as an AB system at 233 K (see Experimental Section and SI for details). Therefore, the rate of the ring flipping process follows the order **2** > **4a** > **4b′** > **4b**. The mutual repulsion between the H6 of dbbpy or the Me group of tmeda with the R group of the amidate in complexes **4** and the absence of such repulsions in complexes **2** could account for the above-mentioned differences.

The solid-state IR spectra of the Pd complexes that contain the free acetamide group show the ν(C═O) band in the range 1636−1687 cm^{-1}, that is, at frequencies similar to or slightly higher than those corresponding to 2-(2-iodophenyl)acetamides ($C_6H_4ICH_2CONRR'$, with NRR′ = NH_2 (1659 cm^{-1}), NHMe (1641 cm^{-1}), NMe_2 (1642 cm^{-1})). The cationic cyclopalladated derivatives **2** show lower energies for this band (∼1615 cm^{-1}) because of the coordination of the amide function through the O atom, which must cause a slight decrease in the C−O bond order. The even lower energy of the ν(C═O) band found in the amidate complexes

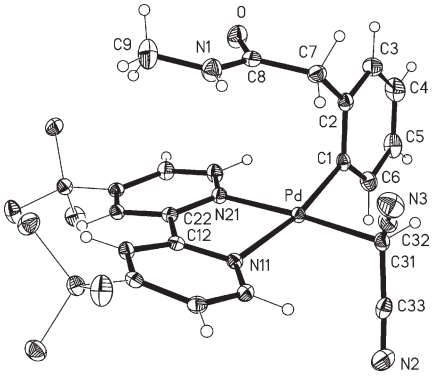


Figure 5. Thermal ellipsoid plot (50% probability) of complex **5b′**. Selected bond distances (Å) and angles (deg): Pd−C(1) 1.9925(13), Pd−N(21) 2.0793(11), Pd−C(31) 2.0903(13), Pd−N(11) 2.1402(11), O−C(8) 1.2243(17), C(8)−N(1) 1.3406(19), C(9)−N(1) 1.449(2); C(1)−Pd−N(21) 94.59(5), C(1)−Pd−C(31) 87.06(5), N(21)−Pd−C(31) 175.99(5), C(1)−Pd−N(11) 169.10(5), N(21)−Pd−N(11) 78.33(4), C(31)−Pd−N(11) 100.55(5), C(32)−C(31)−C(33) 111.95(12).

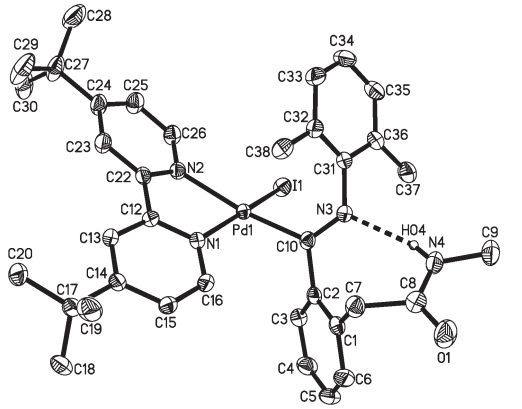
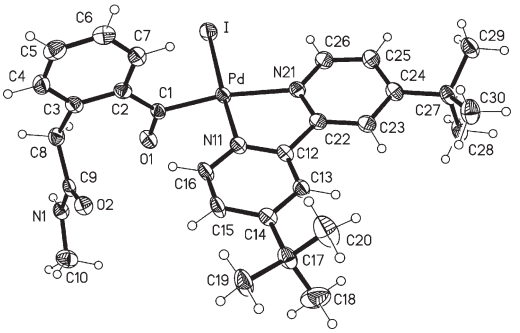


Figure 7. Thermal ellipsoid plot (50% probability) of complex **10b′**. Selected bond distances (Å) and angles (deg): Pd(1)−C(10) 1.995(2), Pd(1)−N(1) 2.0928(17), Pd(1)−N(2) 2.1557(17), Pd(1)−I(1) 2.5753(2), N(3)−C(10) 1.285(3), N(4)−C(8) 1.330(3), O(1)−C(8) 1.226(3); C(10)−Pd(1)−N(1) 97.37(7), N(1)−Pd(1)−N(2) 78.10(6), C(10)−Pd(1)−I(1) 90.25(6), N(2)−Pd(1)−I(1) 96.52(5), C(10)−N(3)−C(31) 122.77(17), C(8)−N(4)−C(9) 122.1(2), O(1)−C(8)−N(4) 123.1(2), O(1)−C(8)−C(7) 121.9(2), N(4)−C(8)−C(7) 114.9(2), N(3)−C(10)−C(2) 117.88(18), N(3)−C(10)−Pd(1) 122.49(15), C(2)−C(10)−Pd(1) 119.61(14).



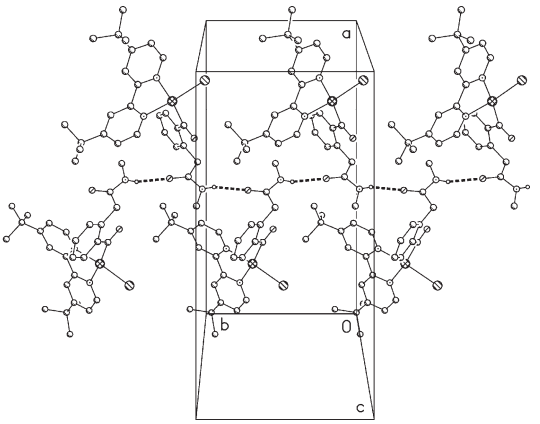


Figure 6. Thermal ellipsoid plot (50% probability) and crystal packing of complex **6b′**. Selected bond distances (Å) and angles (deg): Pd−C(1) 1.970(4), Pd−N(11) 2.085(3), Pd−N(21) 2.168(3), Pd−I 2.5820(4), O(1)−C(1) 1.211(5), C(2)−C(3) 1.431(6), C(2)−C(7) 1.396(6); C(1)−Pd−N(11) 94.52(15), C(1)−Pd−N(21) 170.39(14), N(11)−Pd−N(21) 77.57(13), C(1)−Pd−I 88.33(11), N(11)−Pd−I 174.29(9), N(21)−Pd−I 100.04(9), O(1)−C(1)−Pd 118.3(3), O(1)−C(1)−C(2) 122.6(3), C(2)−C(1)−Pd 118.8(3).

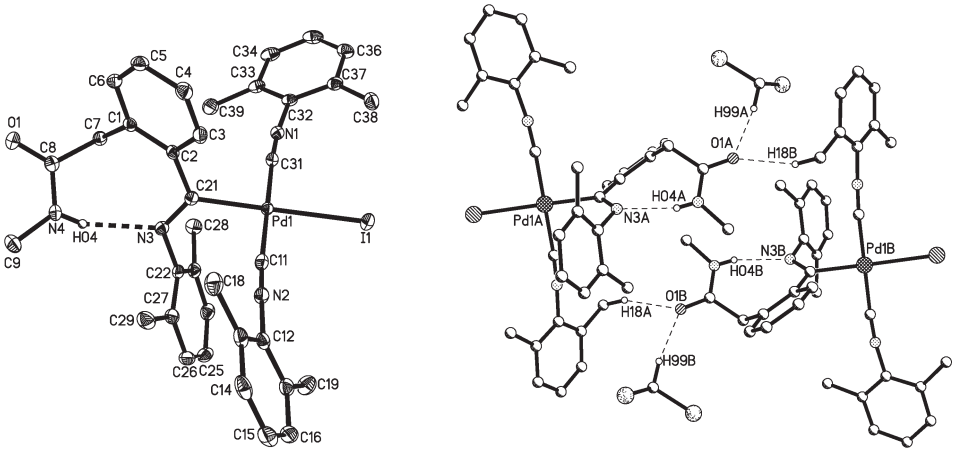


Figure 8. Thermal ellipsoid plot (50% probability) and hydrogen bonds of complex **13b**. Selected bond distances (Å) and angles (deg): Pd(1)−C(11) 1.971(2), Pd(1)−C(31) 1.978(2), Pd(1)−C(21) 2.051(2), Pd(1)−I(1) 2.7037(2), C(1)−C(2) 1.417(3), C(2)−C(3) 1.402(3), C(21)−N(3) 1.270(3), C(31)−N(1) 1.150(3), C(11)−N(2) 1.148(3), C(2)−C(21) 1.495(3); C(11)−Pd(1)−C(31) 179.05(9), C(11)−Pd(1)−C(21) 90.04(8), C(31)−Pd(1)−C(21) 89.93(8), C(11)−Pd(1)−I(1) 88.52(6), C(31)−Pd(1)−I(1) 91.55(6), C(21)−Pd(1)−I(1) 177.44(6), N(2)−C(11)−Pd(11) 175.91(19), N(3)−C(21)−Pd(1) 123.52(16), C(2)−C(21)−Pd(1) 115.62(15), N(1)−C(31)−Pd(1) 176.49(19).

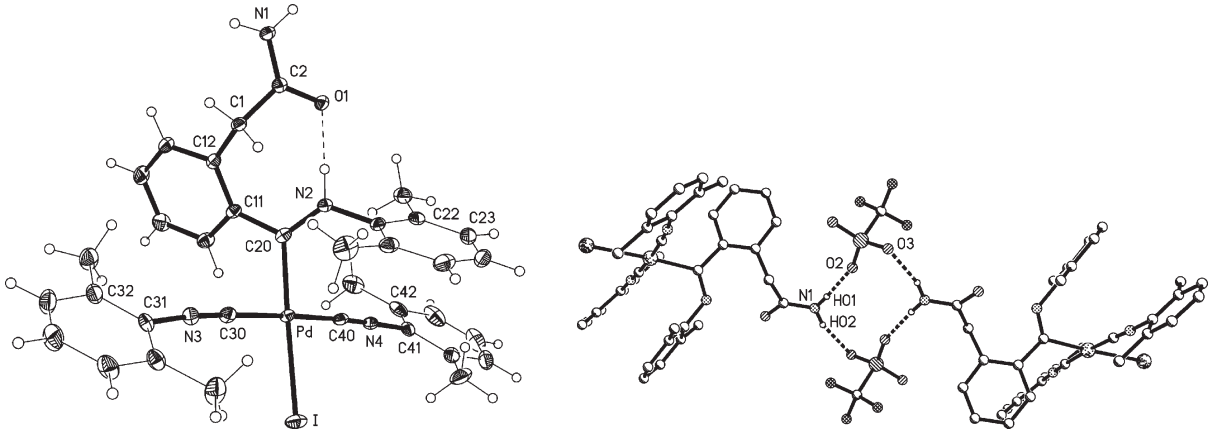


Figure 9. Thermal ellipsoid plot (50% probability) and hydrogen bonding of complex **14a**. Selected bond distances (Å) and angles (deg): Pd−C(40) 1.964(2), Pd−C(30) 1.971(2), Pd−C(20) 2.025(2), Pd−I 2.6250(2), O(1)−C(2) 1.249(3), N(1)−C(2) 1.315(3), N(2)−C(20) 1.303(3), N(2)−C(21) 1.441(3), N(3)−C(30) 1.145(3), N(3)−C(31) 1.397(3), N(4)−C(40) 1.147(3), N(4)−C(41) 1.405(3); C(40)−Pd−C(20) 91.82(8), C(30)−Pd−C(20) 89.87(9), C(40)−Pd−I 89.00(6), C(30)−Pd−I 89.48(6), C(20)−N(2)−C(21) 125.47(18), C(30)−N(3)−C(31) 174.1(2), C(40)−N(4)−C(41) 176.2(2), O(1)−C(2)−N(1) 122.4(2), O(1)−C(2)−C(1) 119.96(19), N(1)−C(2)−C(1) 117.64(19), N(2)−C(20)−C(11) 119.94(19), N(3)−C(30)−Pd 177.7(2), N(4)−C(40)−Pd 177.24(18).

4 (∼1580 cm^{-1}) is typical of metal complexes with this kind of ligand[8,39] and can be ascribed to the delocalization of the negative charge over the N−C=O group, which significantly decreases the C−O bond order.

Crystal Structures. The crystal structures of complexes **1b′** (Figure 1), **2b′**·Me_2CO (Figure 3), **3b′** (Figure 2), **4b′**·0.5CH_2Cl_2 (Figure 4), **5b′** (Figure 5), **6b′** (Figure 6), **10b′** (Figure 7), **13b**·CH_2Cl_2 (Figure 8), **14a** (Figure 9), and **15c** (Figure 10) and the organic compounds **8b**, **9**, and **11b** (see Supporting Information) were determined by means of X-ray diffraction studies. All the Pd complexes exhibit slightly distorted square-planar environments around the metal. The greatest distortions are caused by the small bite of the dbbpy ligand (angles N−Pd−N around 78°).

The aromatic ring of the aryl ligand in complexes **1b′** and **3b′** (Figures 1 and 2, respectively) is almost perpendicular to the Pd coordination mean plane, as is commonly found in ortho-substituted arylpalladium derivatives and attributed to the steric demand of the ortho substituent.[8,10,18,22,40] This is in agreement with the NMR data mentioned above. The Pd−C bond distances are normal for this type of derivative. The molecules in **1b′** are connected through three nonclassical hydrogen bonds C−H···O, giving chains along the *c* axis (Figure 1). The triflate anion in **3b′** is connected to the cation through one N−H···O hydrogen bond involving the acetamide moiety (Figure 2).

The structure of **2b′** (Figure 3) was solved as an acetone monosolvate. The acetamide group is coordinated to the Pd atom through the oxygen, forming a six-membered ring with a pseudoboat conformation. The Pd(1)−O(1) bond distance

(38) Möhrle, H.; Rohn, C. *Z. Naturforsch., B: Chem. Sci.* **2007**, *62*, 249.
(39) Yamamoto, T.; Sano, K.; Osakada, K.; Komiya, S.; Yamamoto, A.; Kushi, Y.; Tada, T. *Organometallics* **1990**, *9*, 2396.
(40) Vicente, J.; Abad, J. A.; Fernández-de-Bobadilla, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 24.

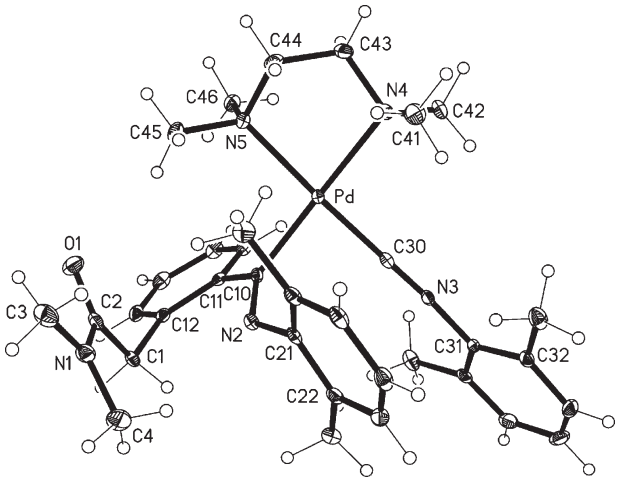


Figure 10. Thermal ellipsoid plot (50% probability) of complex **15c**. Selected bond distances (Å) and angles (deg): Pd−C(30) 1.9253(18), Pd−C(10) 2.0327(16), Pd−N(5) 2.1625(14), Pd−N(4) 2.2029(13), O(1)−C(2) 1.225(2), N(1)−C(2) 1.352(2), N(2)−C(10) 1.266(2), N(3)−C(30) 1.154(2); C(30)−Pd−C(10) 84.73(7), C(10)−Pd−N(5) 97.61(6), C(30)−Pd−N(4) 95.17(6), N(5)−Pd−N(4) 83.10(5), N(3)−C(30)−Pd 177.73(15), N(2)−C(10)−C(11) 119.42(14), C(10)−N(2)−C(21) 127.90(14).

of 2.031(2) Å is similar to that found for the ortho-palladated arylurea [Pd{κ^2*C,O*-C_6H_4NHC(O)NHTo-2}(tmeda)]OTf[15] and several *O*-coordinated amides.[41] The C(8)−O(1) bond distance of 1.263(4) Å is slightly longer than the corresponding distance in the free acetamide group of complex **1b′** (1.227(3) Å), because of the coordination to palladium through the oxygen atom. Consequently, the C(8)−N(3) bond distance of 1.317(4) Å is shorter than that found for **1b′** (1.333(4) Å). The triflate anion in **2b′** is connected to the cation through one N−H···O hydrogen bond, giving double chains parallel to the *b* axis (Figure 3).

Compound **4b′** (Figure 4) crystallized with two formula units and one CH_2Cl_2 molecule in the asymmetric unit. The amidate group is coordinated to the Pd atom through the nitrogen, forming a six-membered ring with a pseudoboat conformation. The Pd−N(3) bond distance of 2.012(3) or 2.009(3) Å is typical of palladium amidate complexes.[42] The C(8)−O(1) bond length of 1.264(5) or 1.257(5) Å is slightly longer than the corresponding distance in the free acetamide group of complex **1b′**, consistent with a significant delocalization of the negative charge over the N−C=O group.

The structure of **5b′** shows the malononitrilato ligand bonded to the Pd atom through the central carbon (Figure 5). Prior to this work, only two crystal structures of Pd complexes containing this ligand had been reported, namely, [Pd(C_6F_5)-{CH(CN)$_2$}(tmeda)][43] and [{Pd(C_6F_5)$_2$}{μ-CH(CN)$_2$}$_2$]$^{2-}$.[44]

As observed for **1b′** and **3b′**, the aromatic ring of the aryl ligand in **5b′** is practically perpendicular to the Pd coordination mean plane. The acetamide group is connected through an N−H···N hydrogen bond to one of the CN groups of a neighboring molecule, forming inversion-symmetric dimers.

The benzoyl ligand in complex **6b′** (Figure 6) is practically planar (mean deviation 0.024 Å, excluding the acetamide group), and its mean plane forms an angle of 91.8° with the mean plane of atoms Pd−I−N(11)−N(21)−C(1) (mean deviation 0.085 Å). The Pd−C bond distance is normal for this type of compound.[10,14,19] The acetamide groups of adjacent molecules are connected through N−H···O=C hydrogen bonds, thus forming infinite chains (Figure 6).

Unlike the benzoyl group in **6b′**, the iminoacyl group in **10b′** (excluding the acetamide group) is not planar (Figure 7). Thus, the mean plane of the aromatic ring (atoms C(1−6), mean deviation 0.016 Å) is rotated by 46.2° with respect to the C2−C10−N3 plane. In turn, the latter substends an angle of 72.2° to the mean Pd coordination plane (Pd−I−N(1)−N(2)−C(10), mean deviation, 0.191 Å). The particular conformation of the iminoacyl ligand appears to originate from the formation of an intramolecular hydrogen bond between the NH group and the iminoacyl N atom. The Pd(1)−C(10) bond distance of 1.995(2) Å and the arrangement of the iminoacyl ligand are similar to those found in [Pd-{C(=NXy)C_6H_4OC(O)Me-2}I(bpy)].[19]

The structure of complex **13b** (Figure 8) was solved as a CH_2Cl_2 monosolvate. The arrangement and conformation of the iminoacyl ligand are very similar to those found in **10b′**, including the intramolecular N−H···N hydrogen bond. The Pd(1)−C(21) bond distance of 2.051(2) Å is similar to that found for [Pd{C(=NXy)C_6H_4OC(O)Me-2I-(CNXy)$_2$}].[19] The molecules are connected through nonclassical hydrogen bonds C−H···O, giving dimers.

The coordination environment around the palladium atom in complex **14a** (Figure 9) is identical to that found in **13b**. The conformation and arrangement of the protonated iminoacyl ligand resemble those found for the iminoacyl ligand in **10b′** and **13b**, except that the hydrogen bond is now formed between the NH group of the protonated iminoacyl and the oxygen of the acetamide group. The two H atoms of the NH_2 group are involved in hydrogen bonds with two oxygen atoms of different triflate anions, one within the asymmetric unit and one related by inversion (Figure 9). The protonation of the iminoacyl N atom causes a slight lengthening of the C−N bond distance (1.303(3) Å) as compared to **13b** (1.270(3) Å), which reflects a decrease in the C−N bond order, while the Pd(1)−C-(20) bond distance of 2.025(2) Å is slightly shorter than that found for **13b** (2.051(2) Å). These data suggest some degree of carbene character for the Pd−C bond.

The arrangement of the iminoacyl ligand in **15c** (Figure 10) is similar to that found for **10b′** and **13b**, except that there is no intramolecular hydrogen bonding. Analogous structures have been found for [Pd{C(=NXy)C_6H_4OH-2}(CNXy)-(bpy)]OTf·Et_2O[19] and [Pd{C(=NXy)$C_6H_4NH_2$-2}(CNXy)-(bpy)]OTf.[17]

Conclusions

The present work is the first systematic study on the reactivity of ortho-palladated phenylacetamides, which includes the preparation of cyclometalated derivatives and their reactions toward CO and XyNC. We have shown that intramolecular

(41) Kiers, N. H.; Feringa, B. L.; Kooijman, H.; Spek, A. L.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1992**, 1169. Solé, D.; Vallverdú, L.; Solans, X.; Font-Bardia, M. *Chem. Commun.* **2005**, 2738. Solé, D.; Solans, X.; Font-Bardia, M. *Dalton Trans.* **2007**, 4286.

(42) Liao, C.-Y.; Chan, K.-T.; Zeng, J.-Y.; Hu, C.-H.; Tu, C.-Y.; Lee, H. M. *Organometallics* **2007**, *26*, 1692. Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154. Behrens, H.; Fröhlich, R.; Würthwein, E.-U. *Eur. J. Org. Chem.* **2005**, 3891. Haas, K.; Ehrenstorfer-Schäfers, E.-M.; Polborn, K.; Beck, W. *Eur. J. Inorg. Chem.* **1999**, 465.

(43) Ruiz, J.; Martínez, M. T.; Rodríguez, V.; López, G.; Pérez, J.; Chaloner, P.; Hitchcock, P. B. *Dalton Trans.* **2004**, 3521.

(44) Ruiz, J.; Rodríguez, V.; López, G.; Casabó, J.; Molins, E.; Miratvilles, C. *Organometallics* **1999**, *18*, 1177.

C−N and C−O reductive couplings take place under relatively mild conditions after the insertion of CO or XyNC into the Pd−C bond. Depending on the substituents on the amidic nitrogen, C−N and/or C−O couplings may occur. As far as we are aware, the palladium-mediated C−O couplings reported here are the first involving an amide function. A series of new heterocyclic compounds have been obtained, including isocoumarins, imino derivatives of isoquinoline-1,3(2*H*,4*H*)-dione, and one iminoisocoumarin.

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Supporting Information Available: Experimental procedures and spectroscopic and analytical data for **1b**, **1c**, **1b′**, **2b**, **2c**, **2b′**, **4b**, **4b′**, **6b**, **6c**, **6b′**, **13b**, **15c**, and **15b′**. Variable-temperature ^{1}H NMR spectra of **4b′** and **10b′**. X-ray structure descriptions for **8b**, **9**, and **11b**. Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and CIF files for **1b′**, **2b′**·Me_2CO, **3b′**, **4b′**·0.5CH_2Cl_2, **5b′**, **6b′**, **8b**, **9**, **10b′**, **11b**, **13b**·CH_2Cl_2, **14a**, and **15c**. This material is available free of charge via the Internet at http://pubs.acs.org.