Synthesis of Ortho-Palladated Phenol Derivatives. Study of Their Reactivity with Carbon Monoxide and Isonitriles

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The reaction of 2-ROC$_6$H$_4$I with [Pd$_2$(dba)$_3$]·dba ("Pd(dba)$_2$"; dba = dibenzylideneacetone) in the presence of the appropriate ligand results in the formation of the arylpalladium complexes *trans*-[Pd(C$_6$H$_4$OR-2)I(PPh$_3$)$_2$] (R = H (**1a**), C(O)Me (**1b**), C(O)CH=CH$_2$ (**1c**)) and [Pd(C$_6$H$_4$OR-2)I(bpy)] (bpy = 2,2′-bipyridine; R = H (**2a**), C(O)Me (**2b**)). Complexes **1b** and **1c** react with bpy in the presence of Tl(OTf) (OTf = OSO$_2$CF$_3$) to give the cationic species [Pd(C$_6$H$_4$OR-2)(bpy)(PPh$_3$)]OTf (R = C(O)Me (**3b**), C(O)CH=CH$_2$ (**3c**)). Complex **1a** reacts with carbon monoxide, yielding the insertion complex *trans*-[Pd{C(O)C$_6$H$_4$OH-2}I(PPh$_3$)$_2$] (**4a**). Complexes **2a** and **2b** can also be carbonylated to give [Pd{C(O)C$_6$H$_4$OR-2}I(bpy)] (R = H (**5a**), C(O)Me (**5b**)). Complex **4a** reacts with bpy and Tl(OTf), giving [Pd{C(O)C$_6$H$_4$OH-2}(bpy)(PPh$_3$)]OTf (**6a**). The reaction of 2-ROC$_6$H$_4$I with Pd(dba)$_2$ and isonitriles R′NC gives rise to the complexes *trans*-[Pd{C(=NR′)C$_6$H$_4$OR-2}I(CNR′)$_2$] (R = H, R′ = Xy = 2,6-dimethylphenyl) (**7a**), R′ = ^{t}Bu (**7a***); R = C(O)Me, R′ = Xy (**7b**), R′ = ^{t}Bu (**7b***)). Complexes **7a** and **7b*** can also be prepared by ligand displacement from **2a** and **2b** and XyNC and ^{t}BuNC, respectively. Complexes **2a** and **2b** react with R′NC (1:1) to give [Pd{C(=NR′)C$_6$H$_4$-OR-2}I(bpy)] (R = H, R′ = Xy (**8a**), R′ = ^{t}Bu (**8a***); R = C(O)Me, R′ = Xy (**8b**)). Complex **7a** reacts with bpy in the presence of Tl(OTf), yielding [Pd{C(=NR′)C$_6$H$_4$OH-2}(CNR′)(bpy)]-OTf (**9a**). Reaction of **5a** with R′NC gives *trans*-[Pd{C(O)C$_6$H$_4$OH-2}I(CNR′)$_2$] (R′ = Xy (**10a**), ^{t}Bu (**10a***)), which, in turn, react with further R′NC in the presence of Tl(OTf) to give [Pd-{C(O)C$_6$H$_4$OH-2}(CNR′)$_3$]OTf (R′ = Xy (**11a**), ^{t}Bu (**11a***)). Finally, the reaction of **7a** with Pd(OAc)$_2$ results in the tetrameric [Pd{κ^2(*C*,*O*)-μ_2(*O*)-C(=NXy)C$_6$H$_4$O-2}(CNXy)]$_4$ (**12**) and *trans*-[PdI$_2$(CNXy)$_2$]. Most of the reported aroyl (**4**−**6**, **10**, **11**) and iminoaroyl (**7**−**9**, **12**) derivatives are new types of palladium complexes. The crystal structures of complexes **5a**, **7a**, **7b**, **8b**, **9a**, and **12** have been determined by X-ray diffraction methods. The following scale of trans influence has been established: bpy < I < C(=NXy)C$_6$H$_4$OC(O)Me-2 ≈ C(=O)C$_6$H$_4$OH-2 < C(=NXy)C$_6$H$_4$OH-2.

Introduction

We have shown that (2-X-aryl)palladium complexes have interesting properties when X is a reactive substituent such as CHO, C(O)Me, C(O)NHR, NH$_2$, NO$_2$, CN, and CH=CH$_2$.[1−11] In this paper we report the synthesis of complexes with X = OH, OC(O)Me, and OC(O)CH=CH$_2$. These complexes seem to play an important role in some palladium-catalyzed processes,

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(1) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2000**, *19*, 752.
(2) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3067.
(3) Vicente, J.; Abad, J. A.; Rink, B.; Hernández, F.-S.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 5269.
(4) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557.
(5) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Commun.* **1997**, 959.
(6) Vicente, J.; Arcas, A.; Blasco, M. A.; Lozano, J.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 5374.
(7) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *Organometallics* **1996**, *15*, 3509.
(8) Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 1422.
(9) Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Bautista, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3093.
(10) Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G. *Organometallics* **1995**, *14*, 2677.
(11) Vicente, J.; Abad, J. A.; Jones, P. G. *Organometallics* **1992**, *11*, 3512.

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e.g., in the formation of *o*-alkynylphenols, which are intermediates in the formation of benzofurans.[12−14] Similarly, ortho-palladated O-substituted phenol derivatives may be catalytic intermediates in intramolecular cyclizations to give 4-methylcoumarin,[15,16] 1,3-benzoxazepin-2-ones,[17] or benzopyrans.[18] However, as far as we are aware, ortho-palladated phenol or phenol ester derivatives have not yet been isolated; in this work, we report on the synthesis of these types of complexes and on their reactivity with carbon monoxide and isonitriles.

The insertion of CO into the Pd−C bond, resulting in the formation of acylpalladium derivatives, constitutes a key step in the palladium-catalyzed carbonylation of organic substrates in laboratory synthesis and also in industrial processes.[19−24] These CO insertions are also relevant in the palladium-catalyzed copolymerization of CO and unsaturated organic substrates.[25−39] This is the reason for the extensive study of insertion reactions.[21,40−44] However, most studies of insertion reactions of CO into Pd−C bonds have been devoted to alkyl, mainly methyl, derivatives.[24,40,43−50] Only mononuclear phenyl- or alkyl-substituted phenyl[46,51−56] and dinuclear 1,4-phenylene and 4,4′-biphenyl[57] palladium complexes have been carbonylated. The rates of reaction of a variety of *trans*-[Pd(Ar)X(PPh_3)$_2$] (Ar = C_6H_4R-4, R = H, NO_2, Me, CN, CF_3, OMe; X = Cl, Br, I) complexes with CO have been studied, but the resulting complexes have not been isolated.[58] We have isolated the first carbonylation products of functionalized arylpalladium(II) complexes, [Pd($C_6H_4NH_2$-2)I(bpy)] and [Pd(C_6H_4-NH_2-2)I(PR_3)] (R = Ph, C_6H_4Me-4).[2,5] Norbornene,[59,60] norbornadiene,[61] allenes,[62] or internal alkynes[63] react with *o*-iodophenol in the presence of carbon monoxide and a palladium catalyst to afford coumaranone, chromone, or coumarin derivatives. In this paper, we report the carbonylation reactions of some ortho-palladated complexes of phenol and some of its derivatives that could be intermediates in some of these catalytic systems.

Insertion reactions of isonitriles into Pd−C bonds also constitute a subject of great interest,[4,44,45,57,64−69] since they can lead to new types of organopalladium[4,44,45,57,64−79]

(12) Botta, M.; Summa, V.; Corelli, F.; Dipietro, G.; Lombardi, P. *Tetrahedron: Asymmetry* **1996**, *7*, 1263.
(13) Arcadi, A.; Cacchi, S.; Delrosario, M.; Fabrizi, G.; Marinelli, F. *J. Org. Chem.* **1996**, *61*, 9280.
(14) Lütjens, H.; Scammells, P. J. *Tetrahedron Lett.* **1998**, *39*, 6581.
(15) Catellani, M.; Chiusoli, G. P.; Fagnola, M. C.; Solari, G. *Tetrahedron Lett.* **1994**, *35*, 5919.
(16) Catellani, M.; Chiusoli, G. P.; Marzolini, G.; Rossi, E. *J. Organomet. Chem.* **1996**, *525*, 65.
(17) Bocelli, G.; Catellani, M.; Chiusoli, G. P.; Cugini, F.; Lasagni, B.; Mari, M. N. *Inorg. Chim. Acta* **1998**, *270*, 123.
(18) Söderberg, B. J.; Rector, S. R.; O'Neil, S. *Tetrahedron Lett.* **1999**, *40*, 3657.
(19) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.
(20) Tsuji, J. *Palladium Reagents and Catalysts*, Wiley: Chichester, U.K., 1995.
(21) Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433.
(22) Negishi, E.; Coperet, C.; Ma, S. M.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5904.
(23) Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1027.
(24) Lin, Y. S.; Yamamoto, A. *Organometallics* **1998**, *17*, 3466.
(25) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303.
(26) van Asselt, R.; Gielens, E.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977.
(27) 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.
(28) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.
(29) Abu-Surrah, A.; Rieger, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2475.
(30) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213.
(31) Nozaki, K.; Naomasa, S.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779.
(32) Safir, A. L.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 643.
(33) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 0.
(34) Kacker, S.; Kim, J. S.; Sen, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 7, 1251.
(35) Carfagna, C.; Formica, M.; Gatti, G.; Musco, A.; Pierleoni, A. *Chem. Commun.* **1998**, 1113.
(36) Aeby, A.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1999**, 655.
(37) Brinkmann, P. H. P.; Luinstra, G. A. *J. Organomet. Chem.* **1999**, *572*, 193.
(38) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Travaglia, M.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M. *Organometallics* **1999**, *18*, 3061.
(39) Parlevliet, F. J.; Zuideveld, M. A.; Kiener, C.; Kooijman, H.; Spek, A. L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1999**, *18*, 3394.
(40) Yamamoto, A. *J. Organomet. Chem.* **1995**, *500*, 337.
(41) Cavell, K. J. *Coord. Chem. Rev.* **1996**, *155*, 209.
(42) Groen, J. H.; de Jong, B. J.; Ernsting, J. M.; van Leeuwen, P. W. N. M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1999**, *573*, 3 and references therein.
(43) Gutierrez, E.; Nicasio, M. C.; Paneque, M.; Ruiz, C.; Salazar, V. *J. Organomet. Chem.* **1997**, *549*, 167.
(44) Campora, J.; Graiff, C.; Palma, P.; Carmona, E.; Tiripicchio, A. *Inorg. Chim. Acta* **1998**, *269*, 191.
(45) Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917.
(46) Delis, J. G. P.; Rep, M.; Rülke, R. E.; van Leeuwen, P.; Vrieze, K.; Fraanje, J.; Goubitz, K. *Inorg. Chim. Acta* **1996**, *250*, 87.
(47) Ankersmit, H. A.; Loken, B. H.; Kooijman, H.; Spek, A. L.; Vrieze, K.; van Koten, G. *Inorg. Chim. Acta* **1996**, *252*, 141.
(48) Ankersmit, H. A.; Veldman, N.; Spek, A. L.; Eriksen, K.; Goubitz, K.; Vrieze, K.; van Koten, G. *Inorg. Chim. Acta* **1996**, *252*, 203.
(49) 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.
(50) Toth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388.
(51) Monteil, F.; Kalck, P. *J. Organomet. Chem.* **1994**, *482*, 45.
(52) Moser, W. R.; Wang, A. W.; Kjeldahl, N. K. *J. Am. Chem. Soc.* **1988**, *110*, 2816.
(53) Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1987**, *6*, 1640.
(54) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683.
(55) Anderson, G. K. *Organometallics* **1983**, *2*, 665.
(56) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890.
(57) Kim, Y. J.; Song, S. W.; Lee, S. C.; Lee, S. W.; Osakada, K.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **1998**, 1775.
(58) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.
(59) Grigg, R.; Khalil, H.; Levett, P.; Virica, J.; Sridharan, V. *Tetrahedron Lett.* **1994**, *35*, 3197.
(60) Moinet, C.; Fiaud, J. C. *Synlett* **1997**, 97.
(61) An, Z. W.; Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1989**, *371*, C51.
(62) Okuro, K.; Alper, H. *J. Org. Chem.* **1997**, *62*, 1566.
(63) Kadnikov, D. V.; Larock, R. C. *Org. Lett.* **2000**, *2*, 3643.
(64) Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; Vanleeuwen, P.; Veldman, N.; Spek, A. L.; Vanneer, F. J. R. *Organometallics* **1997**, *16*, 2948.
(65) Alias, F. M.; Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1997**, *16*, 301.
(66) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1554.
(67) Onitsuka, K.; Segawa, M.; Takahashi, S. *Organometallics* **1998**, *17*, 4335.
(68) Alias, F. M.; Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1998**, *17*, 5620.
(69) Ito, Y.; Miyake, T.; Hatano, S.; Shima, R.; Ohara, T.; Suginome, M. *J. Am. Chem. Soc.* **1998**, *120*, 11880.
(70) Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15.
(71) Onitsuka, K.; Joh, T.; Takahashi, S. *J. Organomet. Chem.* **1994**, *464*, 247.
(72) Otsuka, S.; Ataka, K. *J. Chem. Soc., Dalton Trans.* **1976**, 327.
(73) Crociani, B.; Sala, M.; Polo, A.; Bombieri, G. *Organometallics* **1986**, *5*, 1369.
(74) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531.

complexes and because they may be important for organic synthesis.[4,69,79−85]

Experimental Section

Reactions were carried out without precautions to exclude atmospheric moisture, unless otherwise stated. The IR and C, H, and N analyses and melting point determinations were carried out as described elsewhere.[10] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ in a Varian Unity 300 or a Bruker Unity 200. Chemical shifts were referenced to TMS (^1H and $^{13}C\{^1H\}$) and PO_4H_3 (^{31}P). Chromatographic separations were carried out by TLC on silica gel (70−230 mesh).

Synthesis of 2-Iodophenol Esters.[86] **$C_6H_4OC(O)CH{=}CH_2$-I-2.** A suspension of 2-iodophenol (500 mg, 2.23 mmol), acryloyl chloride (205 mg, 2.23 mmol), and K_2CO_3 (1 g, 7,24 mmol) in acetone (10 mL) was refluxed for 3 h. After addition of water (20 mL) and extraction with Et_2O (3 × 5 mL), the organic phase was dried with anhydrous $MgSO_4$ and the solvents evaporated. The resulting crude ester was chromatographed through silica gel with 1.5:1 *n*-hexane/Et_2O. Evaporation of the eluents gave the ester as a colorless clear oil. Yield: 550 mg, 90%. IR (cm^{-1}): ν(CO) 1745. ^1H NMR (200 MHz, $CDCl_3$; ppm): 7.85 (d, C_6H_4, 1 H, $^3J_{HH}$ = 9.6 Hz), 7.37 (dd, C_6H_4, 1H, $^3J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 7.3 Hz), 7.12 (d, C_6H_4, 1H, $^3J_{HH}$ = 9.6 Hz), 7.00 (dd, C_6H_4, 1H, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 9.3 Hz), 6.80 (dd, vinyl H (trans), 1H, $^3J_{HH}$ = 18.0 Hz, $^2J_{HH}$ = 1.3 Hz), 6.36 (dd, vinyl H, 1H, $^3J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 12.0 Hz), 6.05 (dd, vinyl H (cis), 1H, $^3J_{HH}$ = 12.0 Hz, $^2J_{HH}$ = 1.3 Hz).

$C_6H_4\{OC(O)Me\}$-I-2. A suspension of 2-iodophenol (240 mg, 1.09 mmol), acetic anhydride (112 mg, 1.09 mmol), and K_2CO_3 (3 g, 21,72 mmol) in acetone (10 mL) was stirred for 30 min. The solution was filtered through anhydrous $MgSO_4$, and the solvent was evaporated. The resulting crude ester was chromatographed through silica gel with 1.5:1 *n*-hexane/Et_2O. Evaporation of the eluents gave the ester as a colorless clear oil. Yield: 214 mg, 75%. IR (cm^{-1}): ν(CO) 1785. ^1H NMR (200 MHz, $CDCl_3$; ppm): 7.82 (d, C_6H_4, 1H, $^3J_{HH}$ = 7.8 Hz), 7.37 (dd, C_6H_4, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.8 Hz), 7.09 (d, C_6H_4, 1H, $^3J_{HH}$ = 10.0 Hz), 7.00 (dd, C_6H_4, 1H, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 7.8 Hz), 2.36 (s, 3H, Me).

Synthesis of Complexes. *trans*-$[Pd(C_6H_4OH\text{-}2)I(PPh_3)_2]$ (1a). "Pd(dba)$_2$" (400 mg, 0.7 mmol), PPh_3 (367 mg, 0.14 mmol), and 2-iodophenol (175 mg, 0.8 mmol) were mixed in dry degassed toluene (10 mL) and stirred for 4 h. After evaporation of the solvent and extraction of the residue with CH_2Cl_2 (10 + 2 × 3 mL), the combined organic extracts were filtered over anhydrous $MgSO_4$. The resulting solution was concentrated (2 mL), and a mixture of the complex and dba was precipitated with *n*-hexane. Purification by chromatography through silica gel with 1:1.5 Et_2O/*n*-hexane gave a solid, which was recrystallized from CH_2Cl_2/*n*-hexane to give **1a** as a yellow powder. Yield: 120 mg, 21%. Mp: 161 °C. ^1H NMR (300 MHz, $CDCl_3$; ppm): 7.78−7.48 (m, PPh_3, 12H), 7.39−7.22 (m, PPh_3, 18H), 6.57 (d, C_6H_4, 1H, $^3J_{HH}$ = 7.8 Hz), 6.38 (dd, C_6H_4, 1H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.8 Hz), 6.03 (dd, C_6H_4, 1H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.2 Hz), 5.78 (d, C_6H_4, 1H, $^3J_{HH}$ = 7.2 Hz), 4.99 (s, OH, 1H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 155.05 (t, COH, $^3J_{CP}$ = 3.0 Hz), 144.03 (t, Pd−C, $^2J_{CP}$ = 4.4 Hz), 134.71 (t, *o*-C of PPh_3, $^2J_{CP}$ = 6.2 Hz), 131.60 (t, P−C, $^1J_{PC}$ = 23.6 Hz), 129.93 (s, *p*-C of PPh_3), 127.65 (t, *m*-C of PPh_3, $^3J_{CP}$ = 5.2 Hz), 124.52, 120.03 (2 C), 114.31 (s, C_6H_4 CH). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; ppm): 22.84. Anal. Calcd for $C_{42}H_{35}IOP_2Pd$: C, 59.28; H, 4.15. Found: C, 58.92; H, 3.98.

***trans*-$[Pd\{C_6H_4[OC(O)Me]\text{-}2\}I(PPh_3)_2]$ (1b).** "Pd(dba)$_2$" (240 mg, 0.42 mmol), PPh_3 (230 mg, 0.88 mmol), and the corresponding 2-iodophenyl ester (131 mg, 0.5 mmol) were mixed in dry degassed toluene (10 mL) and stirred for 4 h. After evaporation of the solvent and extraction of the residue with CH_2Cl_2 (10 + 2 × 3 mL), the combined organic extracts were filtered over anhydrous $MgSO_4$. The resulting solution was evaporated to approximate 2 mL. Purification by chromatography through silica gel with 1:1.5 Et_2O/*n*-hexane gave a solid, which was recrystallized from CH_2Cl_2/*n*-hexane to give **1b** as a white powder. Yield: 138 mg, 42%. Mp: 308 °C dec. IR (cm^{-1}): ν(CO) 1760. ^1H NMR (200 MHz, $CDCl_3$; ppm): 7.62−7.51 (m, PPh_3, 12H), 7.34−7.19 (m, PPh_3, 18H), 6.48 (d, C_6H_4, 1H, $^3J_{HH}$ = 8.0 Hz), 6.39 (dd, C_6H_4, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.6 Hz), 6.23 (d, C_6H_4, 1H, $^3J_{HH}$ = 7.6 Hz), 6.01 (dd, C_6H_4, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.6 Hz), 2.22 (s, Me, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 168.70 (s, C=O), 151.22, 150.24 (s, C−O and C−Pd), 137.70 (d, *p*-C of PPh_3, $^4J_{CP}$ = 4.4 Hz), 134.88 (t, *o*-C of PPh_3, $^3J_{CP}$ = 6.5 Hz), 132.13 (t, C−P, $^1J_{CP}$ = 23.5 Hz), 129.80 (s, CH C_6H_4), 127.65 (t, *m*-C of PPh_3, $^2J_{CP}$ = 5.0 Hz), 125.15, 122.87, 121.15 (s, CH C_6H_4), 21.84 (s, Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; ppm): 22.59. Anal. Calcd for $C_{44}H_{37}IO_2P_2Pd$: C, 59.18; H, 4.16. Found: C, 59.19; H, 4.15.

***trans*-$[Pd\{C_6H_4[OC(O)CH{=}CH_2]\text{-}2\}I(PPh_3)_2]$ (1c).** The same procedure as for **1b** was used, starting from "Pd(dba)$_2$" (229 mg, 0.40 mmol), PPh_3 (210 mg, 0.80 mmol), and the corresponding 2-iodophenyl ester (140 mg, 0.49 mmol) to prepare **1c** as a yellow powder. Yield: 192 mg, 53%. Mp: 156 °C dec. IR (cm^{-1}): ν(CO) 1726. ^1H NMR (300 MHz, $CDCl_3$; ppm): 8.22−8.03 (m, PPh_3, 12H), 7.86−7.69 (m, PPh_3, 18H), 7.09 (d, vinyl H, 1H, $^3J_{HH}$ = 15.5 Hz), 7.10 (d, C_6H_4, 1H, $^3J_{HH}$ = 9 Hz), 7.00−6.77 (m, C_6H_4 and vinyl H, 3H), 6.53−6.48 (m, C_6H_4 and vinyl H, 2H), $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 164.32 (s, C=O), 151.23, 150.49 (C−O and C−Pd), 137.92 (s, C_6H_4, CH), 134.90 (t, *o*-C of PPh_3, $^2J_{CP}$ = 6.4 Hz), 132.11 (t, *i*-C PPh_3, $^1J_{CP}$ = 23.6 Hz), 131.51 (=CH_2), 129.75 (s, *p*-C of PPh_3), 128.91 (CH=), 127.62 (t, *m*-C of PPh_3, $^3J_{CP}$ = 5.2 Hz), 125.13, 122.93, and 121.04 (s, C_6H_4, CH). Anal. Calcd for $C_{45}H_{34}IO_2P_2Pd$: C, 59.78; H, 3.92. Found: C, 59.92; H, 3.80.

$[Pd(C_6H_4OH\text{-}2)I(bpy)]$ (2a). "Pd(dba)$_2$" (121 mg, 0.21 mmol), bpy (66 mg, 0.42 mmol), and *o*-iodophenol (110 mg, 0.5 mmol) were added to dry degassed toluene (7 mL). After 2.5 h at 0 °C, the solvent was evaporated and the residue was extracted with CH_2Cl_2 (10 + 2 × 3 mL). The combined extracts were filtered over anhydrous $MgSO_4$ and the resulting solution concentrated (2 mL). Addition of Et_2O precipitated a solid, which was recrystallized from CH_2Cl_2/Et_2O and dried in a desiccator in vacuo over P_2O_5 to give **2a** as an orange solid. Yield: 54 mg, 54% (crude); 35 mg, 35% (recrystallized). Mp: 185 °C. IR (cm^{-1}): ν(OH) 3422. ^1H NMR (200 MHz, $CDCl_3$; ppm): 9.61 (d, bpy, 1H, $^3J_{HH}$ = 5.1 Hz), 8.12−8.00 (m, bpy, 3H), 7.52−7.42 (m, bpy and C_6H_4, 2H), 7.41−7.27 (m, bpy and C_6H_4, 1H), 7.01−6.96 (m, bpy and C_6H_4, 1H), 7.66−7.21 (m, bpy and C_6H_4, 1H), 6.97−6.93 (m, C_6H_4, 1H), 6.80−6.71 (m, C_6H_4, 2H), 5.82 (s, OH, 1H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 156.81, 153.94, 152.86 (quaternary C), 150.48, 151.35, 138.87, 138.84 (bpy CH), 135.86, 126.99, 126.75, 125.35, 122.00, 121.61, 120.63, 113.86 (bpy CH and C_6H_4 CH). Anal.

(75) Delis, J. G. P.; Aubel, P. G.; Vanleeuwen, P.; Vrieze, K.; Veldman, N.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1995**, 2233.
(76) Dupont, J.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3193.
(77) Wouters, J. M. A.; Klein, R. A.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Organometallics* **1993**, *12*, 3864.
(78) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 438.
(79) Campora, J.; Gutierrez, E.; Monge, A.; Palma, P.; Poveda, M. L.; Ruiz, C.; Carmona, E. *Organometallics* **1994**, *13*, 1728.
(80) Tanase, T.; Fukushima, T.; Nomura, T.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1994**, *33*, 32.
(81) Yamamoto, Y.; Yamazaki, H. *Synthesis* **1976**, 750.
(82) O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1165.
(83) Gehrig, K.; Klaus, A. J.; Rys, P. *Helv. Chim. Acta* **1983**, *66*, 2603.
(84) Veya, P.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.
(85) Albinati, A.; Pregosin, P. S.; Rüedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046.
(86) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans.* **1975**, 795.

Calcd for $C_{16}H_{13}IN_2OPd$: C, 39.84; H, 2.72; N, 5.81. Found: C, 39.89; H, 2.59; N, 5.88.

[Pd{C_6H_4[OC(O)Me]-2}I(bpy)] (2b). The same procedure as for **1b** was used, starting from "$Pd(dba)_2$" (257 mg, 0.45 mmol), bpy (70 mg, 0.45 mmol), and the corresponding 2-iodophenyl ester (130 mg, 0.5 mmol) in toluene (7 mL) to prepare **2b** as a bright yellow powder. Yield: 148 mg, 63%. Mp: 120 °C dec. IR (cm^{-1}): ν(CO) 1757. ^1H NMR (200 MHz, $CDCl_3$; ppm): 9.64 (d, bpy, 1H, $^3J_{HH}$ = 6.0 Hz), 8.10−7.97 (m, bpy, 4H), 7.76 (d, bpy, 1H, $^3J_{HH}$ = 4.0 Hz), 7.52−7.42 (m, bpy and C_6H_4, 2H), 7.41−7.27 (m, bpy and C_6H_4, 1H), 7.01−6.96 (m, bpy and C_6H_4, 2H), 6.85−6.81 (m, C_6H_4, 1H), 2.21 (s, Me, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 170.83 (s, C═O), 155.50, 154.09, 153.93 (quaternary C), 153.18, 151.35 (bpy C−H), 138.69, 137.64 (bpy C−H), 135.30 (quaternary C), 126.76, 126.38, 125.06, 124.50, 121.62, 121.57, 121.44 (C_6H_4 C−H and bpy C−H), 22.03 (Me). Anal. Calcd for $C_{18}H_{15}IN_2O_2Pd$: C, 41.21; H, 2.88; N, 5.34. Found: C, 41.18; H, 3.28; N, 5.10.

[Pd{C_6H_4[OC(O)Me-2]}(bpy)PPh_3)]OTf (3b). To a suspension of Tl(OTf) (OTf = OSO_2CF_3; 23.0 mg, 0.065 mmol) in CH_2Cl_2 (7 mL) were added complex **1b** (55 mg, 0.061 mmol) and, 2−3 min later, bpy (9.53 mg, 0.061 mmol), and the mixture was stirred for 14 h. The resulting suspension was filtered over Celite, and the filtrate was concentrated to dryness to give a bright yellow solid, which was finally recrystallized from CH_2Cl_2/Et_2O to give **3b**. Yield: 38 mg, 77%. Mp: 161 °C. IR (cm^{-1}): ν(CO) 1746, $\nu(SO_3)$ 1268, 1152. ^1H NMR (200 MHz, $CDCl_3$; ppm): 8.78−8.70 (m, aromatic H of bpy, 2H), 8.22−8.14 (m, aromatic H of bpy, 2H), 7.63−7.27 (m, aromatic H of PPh_3, bpy, 20H), 7.20−6.3 (m, aromatic H of bpy and/or C_6H_4, 5H), 2.16 (s, Me, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 169.39 (C═O), 155.71, 155.40, 151.70 (quaternary C), 150.82, 150.38 (aromatic CH), 145.22 (d, Pd−C, $^2J_{PC}$ = 12 Hz), 141.44, 141.33, 135.41, 135.34 (aromatic CH), 134.42 (d, *o*-C of PPh_3, $^2J_{PC}$ = 11.9 Hz), 131.88 (d, *p*-C of PPh_3, $^4J_{PC}$ = 2.6 Hz), 129.18, 129.29 (d, *m*-C of PPh_3, $^3J_{PC}$ = 11.1 Hz), 126.73, 126.48, 126.20, 125.78, 124.79, 124.13, 122.84 (aromatic CH). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; ppm): 33.11. Anal. Calcd for $C_{37}H_{30}F_3N_2O_5PPdS$: C, 54.93; H, 3.74; N, 3.46; S, 3.96. Found: C, 54.68; H, 3.50; N, 3.24; S, 3.69.

[Pd(C_6H_4{OC(O)C_2H_3-2})(bpy)PPh_3]OTf (3c). The same procedure as for **3b** was used, starting from Tl(OTf) (27.5 mg, 0.080 mmol) in CH_2Cl_2 (7 mL) and **1c** (70 mg, 0.078 mmol), to prepare yellow **3c**, except that concentrating the filtrate to dryness led to a yellow foam, which was stirred with Et_2O for 1 h to remove some PPh_3; Et_2O was decanted, and the solid was dried in vacuo. Yield: 57 mg, 91.3%. Mp: 158 °C. IR (cm^{-1}): ν(CO) 1734, $\nu(SO_3)$ 1276, $\nu(SO_3)$ 1152. ^1H NMR (300 MHz, $CDCl_3$; ppm): 9.79−9.73 (m, aromatic H of bpy, 2H), 8.22−8.16 (m, aromatic H of bpy, 2H), 7.75−7.21 (m, aromatic H of PPh_3, bpy and C_6H_4, 21H), 7.05−6.95 (m, aromatic H of bpy and/or C_6H_4, 2H), 6.78 (dd, C_6H_4, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.0 Hz), 6.94 (d, phenyl CH, 1H, $^3J_{HH}$ = 8.5 Hz), 6.30 (d, terminal vinyl H (trans), $^3J_{HH}$ = 16.0 Hz, 1H), 6.40 (dd, vinyl H, 1H, $^3J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 10.0 Hz), 6.31 (d, vinyl H (cis), 1H, $^3J_{HH}$ = 12.0 Hz), 6.05 (d, terminal vinyl H (cis), 1H, $^3J_{HH}$ = 12.0 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 164.59 (C═O), 155.71, 155.38, 151.68 (quaternary C), 150.90, 150.34 (CH, bpy), 145.40 (d, Pd−C, $^2J_{PC}$ = 11.9 Hz), 143.29, 141.46, 141.32, 135.45, 135.38 (CH, bpy), 134.45 (d, *o*-C of PPh_3, $^2J_{PC}$ = 12 Hz), 132.60 (═CH_2), 132.15 (CH), 132.00 (═CH), 131.87 (d, *p*-C of PPh_3, $^4J_{PC}$ = 3 Hz), 129.17 (P−C; one part of the doublet, the other part might be below the next PPh_3 *m*-C signal), 129.80 (d, *m*-C of PPh_3, $^3J_{PC}$ = 11.0 Hz), 128.61, 128.37, 128.11, 126.71, 126.43, 126.23, 125.89, 124.78, 124.06, 122.80 (aromatic CH). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; ppm): 33.82. Anal. Calcd for $C_{38}H_{30}F_3N_2O_5PPdS$: C, 55.59; H, 3.68; N, 3.41; S, 3.91. Found: C, 55.18; H, 3.70 N, 3.73; S, 4.20.

***trans*-[Pd{C(O)C_6H_4OH-2}I{PPh_3)$_2$] (4a).** CO was bubbled through a solution of **1a** (80 mg, 0.09 mmol) CH_2Cl_2 (10 mL) for 45 min. The solution was stirred for a further 1 h under an atmosphere of CO and concentrated (2 mL), and addition of *n*-hexane precipitated a solid, which was filtered and washed with *n*-hexane (10 mL) to give **4a** as a yellow solid. Yield: 69 mg, 84%. Mp: 194 °C dec. IR (cm^{-1}): ν(CO) 1570. ^1H NMR (200 MHz, $CDCl_3$; ppm): 9.72 (s, OH, 1H), 8.64 (d, C_6H_4 H ortho to C═O, $^3J_{HH}$ = 7.2 Hz, 1H), 7.61−7.58 (m, PPh_3, 12H), 7.29−7.20 (m, PPh_3, 18H), 6.97 (dd, C_6H_4, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.2 Hz), 6.01 (dd, C_6H_4, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.0 Hz), 6.94 (d, C_6H_4, 1H, $^3J_{HH}$ = 8.5 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 245.57 (s, CO), 156.75 (s, COH), 135.19 (t, C_6H_4 CH), $^4J_{CP}$ = 2.4 Hz), 134.88 (t, *o*-C of PPh_3, $^2J_{CP}$ = 6.2 Hz), 133.55 (s, C_6H_4 CH), 131.09 (t, C−P, $^1J_{CP}$ = 22.9 Hz), 130.30 (s, *p*-C of PPh_3), 128.00 (t, *m*-C of PPh_3, $^3J_{CP}$ = 2.1 Hz), 125.27 (t, C(O)−C_{arom}, $^3J_{PC}$ = 12 Hz), 118.39, 116.29 (s, C_6H_4 CH). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; ppm): 18.88. Anal. Calcd for $C_{43}H_{35}IO_2P_2Pd$: C, 58.76; H, 4.01. Found: C, 58.09; H, 4.00.

[Pd{C(O)C_6H_4OH-2}I(bpy)] (5a). CO was bubbled through a solution of **2a** (80 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) for 30 min. The solution was stirred for a further 1 h under an atmosphere of CO and concentrated (2 mL), and addition of Et_2O precipitated a solid, which was filtered and washed with Et_2O (10 mL) to give **5a** as a red-orange solid. Yield: 78 mg, 92%. Mp: 268 °C dec. IR (cm^{-1}): ν(CO) 1596. ^1H NMR (200 MHz, DMSO-d_6; ppm): 10.25 (s, OH, 1H), 8.64−8.58 (m, bpy and C_6H_4, 3H), 8.30−8.25 (m, bpy and C_6H_4, 3H), 7.80−7.61 (m, bpy and C_6H_4, 3H), 7.30−7.27 (m, C_6H_4 or bpy H, 1H), 6.81−6.73 (m, C_6H_4 or bpy H, 2H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): not sufficiently soluble. Anal. Calcd for $C_{17}H_{13}IN_2O_2Pd$: C, 39.99; H, 2.57; N 5.49. Found: C, 39.86; H, 2.42; N, 5.49.

[Pd{C(O)C_6H_4OH-2}(bpy)PPh_3)]OTf (6a). To a suspension of Tl(OTf) (25.3 mg, 0.072 mmol) in CH_2Cl_2 (7 mL) was added complex **4a** (63 mg, 0.072 mmol). After 5 min, bpy (11.2 mg, 0.072 mmol) was added and the resulting mixture stirred for 6 h. The suspension was filtered over Celite to give a yellow solution, which was concentrated (2 mL). Addition of *n*-hexane gave a solid, which was recrystallized from CH_2Cl_2/*n*-hexane to give **6a** as a bright yellow powder. Yield: 49 mg, 86%. Mp: 121 °C dec. IR (cm^{-1}): ν(CO) 1600, $\nu(SO_3)$ 1266, 1148. ^1H NMR (300 MHz, $CDCl_3$; ppm): 10.08 (s, OH, 1H), 8.81 (d, bpy H, 2H, $^3J_{HH}$ = 8.4 Hz), 8.61 (d, C_6H_4 ortho to C═O, 1H, $^3J_{HH}$ = 8.1 Hz), 8.22 (dd, bpy H, 2H, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 8.1 Hz), 7.68−7.62 (m, aromatic H, 7H), 7.57−7.49 (m, aromatic H, 3H), 7.46−7.37 (m, aromatic H, 7H), 7.32−7.26 (m, aromatic H, 3H), 6.87 (dd, C_6H_4, 1H, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 6.3 Hz), 6.35 (d, C_6H_4, 1H, $^3J_{HH}$ = 8.4 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 235.98 (CO), 157.54 (quaternary C, COH), 155.01 (quaternary C), 150.17, 141.69 (CH, bpy), 135.59, 135.36 (CH, bpy), 134.25 (d, *o*-C of PPh_3, $^2J_{PC}$ = 12.5 Hz), 132.01 (d, *p*-C of PPh_3, $^4J_{PC}$ = 2.2 Hz), 129.29(d, *m*-C of PPh_3, $^3J_{PC}$ = 11.1 Hz), 128.61, 128.37, 126.88, 125.05 (aromatic CH), 122.05 (quaternary C), 119.81, 117.14 (C_6H_4 CH). The signal of P−C is probably obscured by the signals of *m*-C of PPh_3. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; ppm): 29.44. Anal. Calcd for $C_{36}H_{28}F_3N_2O_5PPdS$: C, 54.39; H, 3.55; N, 3.52; S, 4.03. Found: C, 54.78; H, 3.48; N, 3.24; S, 4.25.

***trans*-[Pd{C(═NXy)C_6H_4OH-2}I(CNXy)$_2$] (7a). Method A.** "$Pd(dba)_2$" (240 mg, 0.42 mmol) and XyNC (115 mg, 0.85 mmol) were added to dry degassed toluene (10 mL) at 0 °C and stirred under N_2. After 5 min, C_6H_4OH-I-2 (300 mg, 1.36 mmol) was added and the reaction mixture stirred for a further 4 h and for 20 h more at room temperature. The resulting suspension was evaporated to dryness, the residue was extracted with CH_2Cl_2, and the extract was filtered over anhydrous $MgSO_4$. The orange filtrate was concentrated to 2−3 mL, and Et_2O was added. After a few minutes of stirring complex **7a** precipitated as a pale yellow solid. Diffraction-quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **7a**. Yield: 130 mg, 64% (calculated assuming eqs 1−3; see below).

Method B. To a solution of **2a** (60 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added XyNC (44 mg, 0.37 mmol), and the mixture was stirred for 3 h. The solution was concentrated (2−3 mL), and *n*-hexane was added to give a suspension. The solid was filtered off and washed with *n*-hexane (10 mL) to give **7a** as a pale yellow powder. Yield: 50 mg, 56%. Mp: 195 °C dec. IR (cm^{-1}): ν(C≡N) 2176, ν(C=N) 1556. ^1H NMR (200 MHz, $CDCl_3$; ppm): 13.66 (s, OH, 1H), 8.61 (d, H of C_6H_4 ortho to C=N, 1H, $^3J_{HH}$ = 7.0 Hz), 7.38−7.19 (m, aromatic H of C_6H_4 and isonitrile, 3H), 7.08−6.96 (m, aromatic H of C_6H_4 and isonitrile, 9H), 2.20 (s, Me, 12H), 2.16 (s, Me, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; ppm): 188.19 (C=N), 158.10 (COH), 147.79 (quaternary C, −NC), 136.70 (CH), 136.04 (quaternary C, C−Me), 131.75 (CH), 130.20 (CH), 128.25 (CH), 128.08 (CH), 124.60 (CH), 118.38 (CH), 116.21 (aromatic CH), 18.85, 18.57 (Me). Anal. Calcd for $C_{33}H_{32}IN_3OPd$: C, 55.05; H, 4.48; N, 5.84. Found: C, 55.20; H, 4.42; N, 5.78.

trans*-[Pd{C(=N^{t}Bu)C$_6$H$_4$OH-2}I(CN^{t}Bu)$_2$] (7a*).** Method A for **7a** was used, starting from "$Pd(dba)_2$" (240 mg, 0.42 mmol), ^{t}BuNC (70 mg, 0.84 mmol), and C_6H_4(OH)-I-2 (111 mg, 0.504 mmol). Reaction time: 1 h at 0 °C and 2 h at room temperature. The CH_2Cl_2 solution was concentrated, and a large excess of *n*-hexane was added. The solvent was decanted and the solid dried in vacuo to give **7a as a bright yellow solid. Yield: 130 mg, 81% (calculated assuming eqs 1−3; see below). Mp: 141 °C dec. IR (cm^{-1}): ν(C≡N) 2198, ν(C=N) 1572. ^1H NMR (300 MHz, $CDCl_3$; ppm): 15.89 (vb s, OH, 1H), 8.46 (d, H of C_6H_4 ortho to C=N, 1H, $^3J_{HH}$ = 9.0 Hz), 7.20 (dd, C_6H_4, 1H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 9.0 Hz), 6.83 (m, C_6H_4, 1H), 6.79 (d, H of C_6H_4 ortho to OH, 1H, $^3J_{HH}$ = 7.5 Hz), 1.63 (s, ^{t}Bu, 9H), 1.37 (s, 2x^{t}Bu, 18H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 182.03 (C=N), 159.56 (COH), 136.57 (CH, C_6H_4), 130.56 (CH, C_6H_4), 128.99, 127.53 (quaternary C and terminal ^{t}BuNC), 117.01 (CH, C_6H_4), 116.13 (CH, C_6H_4), 65.80, 57.02 (quaternary C of ^{t}Bu), 31.06, 29.65 (Me). Anal. Calcd for $C_{21}H_{32}IN_3OPd$: C, 43.80; H, 5.60; N, 7.30. Found: C, 43.76; H, 5.60 N, 7.35.

***trans*-[Pd{C(=NXy)C$_6$H$_4$OC(O)Me-2}I(CNXy)$_2$] (7b).** Method A for **7a** was used, starting from "$Pd(dba)_2$" (240 mg, 0.42 mmol), XyNC (165 mg, 1.26 mmol), and 2-$MeCO_2C_6H_4I$ (132 mg, 0.50 mmol). Reaction time: 4 h at 0 °C and 3 days at room temperature. The CH_2Cl_2 solution was concentrated and *n*-hexane added, causing the precipitation of a green powder. A concentrated CH_2Cl_2 solution was subjected to preparative thin-layer chromatography using 1:1 Et_2O/*n*-hexane through silica gel. The pink fraction was collected and extracted with CH_2Cl_2. This solution was concentrated (2 mL), *n*-hexane was added very slowly to form two layers, and the flask was stored at −15 °C. Over 3 days, complex **7b** precipitated as a yellow solid that did not need further purification. Diffraction-quality crystals were grown by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **7b**. Yield: 182 mg, 57%. Mp: 213 °C. IR (cm^{-1}): ν(C≡N) 2182, ν(CO) 1766, ν(C=N) 1586. ^1H NMR (300 MHz, $CDCl_3$; ppm): 8.61 (d, H of C_6H_4 ortho to C=N, 1H, $^3J_{HH}$ = 7.5 Hz), 7.42−6.94 (m, aromatic H of C_6H_4 and isonitrile, 9H), 7.08−6.96 (m, aromatic H of C_6H_4 and isonitrile, 3H), 2.33 (s, Me, 3H), 2.19 (s, Me, 12H), 2.13 (s, Me, 6H).$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; ppm): 172.30 (C=N), 169.71 (C=O), 150.16, 147.42, 134.04, 137.20 (quaternary C), 135.80 (CH), 132.15, 131.95 (quaternary C), 130.61 (CH), 130.15 (quaternary C), 129.69, 129.18, 128.67, 127.10, 126.19 (CH), 125.34 (quaternary C), 124.18, 122.79, 122.44 (CH), 22.00 (MeC(O)), 18.78, 18,55, 18,43 (Me). Anal. Calcd for $C_{35}H_{34}IN_3O_2Pd$: C, 55.17; H, 4.50; N, 5.51. Found: C, 55.40; H, 4.38; N, 5.99.

trans*-[Pd{C(=N^{t}Bu)C$_6$H$_4$OC(O)Me-2}I(CN^{t}Bu)$_2$] (7b*).** To a solution of **2b** (50 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added ^{t}BuNC (24 mg, 0.30 mmol) (the initially yellow solution immediately became pale yellow), and the mixture was stirred for a further 3 h. After 3 h the clear reaction mixture was evaporated to approximately 2−3 mL; addition of *n*-hexane precipitated a solid, which was filtered off, washed with a further 10 mL of *n*-hexane, and air-dried to give **7b as a pale yellow powder. Yield: 37 mg, 60%. Mp: 144 °C dec. IR (cm^{-1}): ν(C≡N) 2190, ν(CO) 1758, ν(C=N) 1636. ^1H NMR (300 MHz, $CDCl_3$; ppm): 7.59−7.56 (m, H of C_6H_4 ortho to C=N, 1H), 7.27−7.22 (m, C_6H_4, 2H), 6.98 (m, H of C_6H_4 ortho to OH, 1H), 2.25 (s, Me, 3H), 1.55 (s, ^{t}Bu, 9H), 1.47 (s, 2 × ^{t}Bu, 18H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 173.17 (C=N), 168.97 (C=O), 144.48 (COH), 136.01 (quaternary C), 131.45, 128.18, 125.54, 123.51 (CH), 57.97, 56.60 (quaternary C of ^{t}Bu), 30.00, 29.78 (^{t}Bu), 21.34 (Me). Anal. Calcd for $C_{23}H_{34}IN_3O_2Pd$: C, 44.71; H, 5.55; N, 6.80. Found: C, 44.54; H, 5.49; N, 6.77.

[Pd{C(=NXy)C$_6$H$_4$OH-2}I(bpy)] (8a). XyNC (25 mg, 0.19 mmol) was added to a solution of **2a** (100 mg, 0.21 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 8 h, the resulting suspension filtered, and the solid washed with a mixture of CH_2Cl_2 (10 mL) and Et_2O (5 mL) to give **8a** as a yellow solid. Yield: 70 mg, 54%. Mp: 248 °C dec. IR (cm^{-1}): ν(C=N) 1536. NMR: not sufficiently soluble. Anal. Calcd for $C_{25}H_{22}IN_3OPd$: C, 48.92; H, 3.61; N 6.85. Found: C, 47.21; H, 3.74; N, 6.87. The insolubility of **8a** prevented recrystallization.

[Pd{C(=N^{t}Bu)C$_6$H$_4$OH-2}I(bpy)] (8a*). ^{t}BuNC (9 mg, 0.11 mmol) was added to a solution of **2a** (63 mg, 0.11 mmol) in CH_2Cl_2 (10 mL) at 0 °C and the mixture stirred for 3 h. The solvent was evaporated, the residue dissolved in CH_2Cl_2 (2 mL), and this solution chromatographed through silica gel with 1.5:1 CH_2Cl_2/Et_2O as eluant. The yellow band was collected and extracted with acetone. Evaporation of the solvent and recrystallization of the residue from CH_2Cl_2/Et_2O gave **8a*** as a yellow-orange powder. Yield: 41 mg, 66%. Mp: 256 °C dec. IR (cm^{-1}): ν(C=N) 1598. ^1H NMR (200 MHz, acetone-d_6; ppm): 13.90 (s, OH, 1 H), 9.50 (d, bpy, 1H, $^3J_{HH}$ = 5.3 Hz), 9.06 (dd, bpy, 1H, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 8.0 Hz), 8.61−8.09 (m, bpy, 5H), 7.83−7.66 (m, bpy, 2H), 7.22−7.00 (m, bpy and C_6H_4, 2H), 6.66−6.58 (m, C_6H_4, 2H), 1.68 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: not sufficiently soluble. Anal. Calcd for $C_{21}H_{22}IN_3OPd$: C, 44.59; H, 3.92; N 7.43. Found: C, 45.21; H, 4.01; N, 7.62.

[Pd{C(=NXy)C$_6$H$_4$[OC(O)Me]-2}I(bpy)] (8b). XyNC (22 mg, 0.17 mmol) was added to a solution of **2b** (87 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The resulting solution was slowly warmed to room temperature and stirred for a further 14 h. The solution was concentrated (2 mL), and addition of *n*-hexane caused the precipitation of a yellow-orange powder, which was purified by chromatography through silica gel using 1.5:1 CH_2Cl_2/Et_2O. Diffraction-quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **8b**. Yield: 77 mg, 69%. Mp: 215 °C dec. IR (cm^{-1}): ν(CO) 1768, ν(C=N) 1614. ^1H NMR (300 MHz, $CDCl_3$; ppm): 9.42 (d, bpy, $^3J_{HH}$ = 7.0 Hz, 1H), 9.27 (dd, bpy, 1H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 8.1 Hz), 8.55 (d, aromatic H, $^3J_{HH}$ = 5.7 Hz, 1H), 8.01−7.90 (m, aromatic H, 4H), 7.45−6.62 (m, aromatic H, 8H), 2.14 (b s, Me, 6H), 2.10 (s, Me, 3H). $^{13}C\{^1H\}$ NMR: not sufficiently soluble. Anal. Calcd for $C_{27}H_{24}IN_3O_2Pd$: C, 49.45; H, 3.69; N 6.41. Found: C, 49.96; H, 3.55; N, 6.33.

[Pd{C(=NXy)C$_6$H$_4$OH-2}(CNXy)(bpy)]OTf (9a). Complex **7a** (46 mg, 0.064 mmol) was added to a suspension of Tl(OTf) (25 mg, 0.071 mmol) in CH_2Cl_2 (7 mL). After 5 min, bpy (11 mg, 0.011 mmol) was added and the mixture stirred for a further 14 h. The resulting suspension was filtered, the filtrate was concentrated (1 mL), and an excess of Et_2O was added to precipitate the pale yellow, flocculent complex **9a**. Yield: 43 mg, 74%. Mp: 185 °C dec. IR (cm^{-1}): ν(C≡N) 2158, ν(C=N) 1564, ν(SO_3) 1268, 1090. ^1H NMR (200 MHz, $CDCl_3$; ppm): 13.36 (s, OH, 1H), 8.83−8.80 (m, aromatic H, 2H), 8.63 (dd, aromatic H, 1H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz), 8.36−8.26 (m, aromatic H, 3H), 8.09 (d, aromatic H, 1H, $^3J_{HH}$ = 4.8 Hz), 7.70 (dd, aromatic H, 1H, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 6.1 Hz), 7.50−6.91 (m, aromatic H, 10H), 2.19 (s, Me, 6H), 1.99 (s, Me, 3H), 1.85 (s, Me, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; ppm): 188.75 (C=N), 159.35, 156.60, 153.32 (quaternary C), 150.65 (CH),

150.11, 147.67 (quaternary C), 142.51, 142.22 (CH), 135.72 (quaternary C), 135.39, 133.09, 131.15, 128.56, 128.27, 128.24, 127.32, 125.19 (CH), 125.14, 122.74 (quaternary C), 119.21, 117.00 (CH), 18.56 (Me), 15.23 (Me). Anal. Calcd for $C_{35}H_{31}F_3N_4O_4SPd$: C, 54.80; H, 4.07; N, 7.30; S, 4.18. Found: C, 55.03; H, 4.32; N, 7.35; S, 3.68.

***trans*-[Pd{C(O)C$_6$H$_4$OH-2}I(CNXy)$_2$] (10a).** CO was bubbled through a solution of **2a** (60 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) for 40 min. The resulting deep orange solution was stirred for a further 30 min under an atmosphere of CO. The flask was then cooled in an ice bath, and XyNC (33 mg, 0.25 mmol) was added, causing a change of color of the reaction mixture from orange to yellow. After 3 h of further stirring at 0 °C, the solution was concentrated (2 mL) and Et_2O was added. The resulting suspension was filtered and the solid washed with Et_2O (10 mL) to give **10a** as a red-orange powder. Yield: 62 mg, 84%. Mp: 129 °C dec. IR (cm^{-1}): ν(C≡N) 2182, ν(CO) 1626. ^{1}H NMR (200 MHz, $CDCl_3$; ppm): 10.79 (s, OH, 1H), 8.75 (d, H of C_6H_4 ortho to C═O, $^3J_{HH}$ = 7.1 Hz, 1H), 7.44 (dd, aromatic H of C_6H_4 or isonitrile, 1H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.2 Hz), 7.26−7.04 (m, C_6H_4 and isonitrile H, 7H), 6.91 (d, C_6H_4, 1H, $^3J_{HH}$ = 8.2 Hz), 2.29 (s, Me, 12H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$; ppm): 230.03 (C═O), 156.25 (COH), 137.78, 136.20, 135.00, 130.28 (CH), 128.43 (quaternary C), 119.80, 116.67 (CH C_6H_4), 18.51 (Me). Anal. Calcd for $C_{25}H_{24}IN_2OPd$: C, 48.65; H, 3.76; N 4.54. Found: C, 48.10; H, 3.63; N, 4.62.

trans*-[Pd{C(O)C$_6$H$_4$OH-2}I(CN^{t}Bu)$_2$] (10a*).** Complex **10a was similarly prepared from **2a** (70 mg, 0.15 mmol) and ^{t}BuNC (36 mg, 0.44 mmol). Orange-brown **10a*** was precipitated with *n*-hexane. Yield: 59 mg, 78%. Mp: 128 °C dec. IR (cm^{-1}): ν(C≡N) 2206, ν(CO) 1618. ^{1}H NMR (200 MHz, $CDCl_3$; ppm): 10.78 (s, OH, 1H), 8.54 (d, H of C_6H_4 ortho to C═O, $^3J_{HH}$ = 8.0 Hz, 1H), 7.43 (dd, C_6H_4, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.1 Hz), 7.23−7.03 (m, C_6H_4, 1H), 6.89 (d, C_6H_4, 1H, $^3J_{HH}$ = 8.2 Hz), 1.40 (s, ^{t}Bu, 18H). ^{13}C (^{1}H) NMR (50 MHz, $CDCl_3$; ppm): 230.93 (C═O), 156.20 (COH), 137.61 (CH C_6H_4), 135.13 (quaternary C), 134.58 (CH C_6H_4), 127.80, 125.85, 123.92 (quaternary C), 119.44, 116.49 (CH C_6H_4), 58.36 (quaternary C of ^{t}Bu), 29.72 (^{t}Bu). Anal. Calcd for $C_{17}H_{23}INO_2Pd$: C, 40.46; H, 4.59; N 5.55. Found: C, 40.27; H, 4.07; N, 5.33.

[Pd{C(O)C$_6$H$_4$OH-2}(CNXy)$_3$]OTf (11a). CO was bubbled through a solution of **2a** (64 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) for 30 min, and the resulting deep orange solution was stirred for a further $^1/_2$ h under an atmosphere of CO. The flask was cooled to 0 °C, XyNC (139 mg, 1.06 mmol) was added (causing decolorization), and the mixture was stirred for 15 min. Tl(OTf) (50 mg, 0.14 mmol) was added, and the resulting suspension stirred for 4 h more at 0 °C and filtered over Celite. The filtrate was concentrated (2 mL), and addition of Et_2O precipitated a solid, which was filtered and washed with Et_2O (10 mL) to give **11a** as a white powder. Yield: 58 mg, 57%. Mp: 97 °C dec. IR (cm^{-1}): ν(C≡N) 2186, ν(CO) 1622. ^{1}H NMR (200 MHz, $CDCl_3$; ppm): 10.31 (s, OH, 1H), 8.37 (d, H of C_6H_4 ortho to C═O, $^3J_{HH}$ = 6.6 Hz, 1H), 7.43 (dd, aromatic H of C_6H_4 or isonitrile, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.6 Hz), 7.26−6.96 (m, C_6H_4 and isonitrile H, 11H), 2.25 (b s, Me, 18H). ^{13}C (^{1}H) NMR (50 MHz, $CDCl_3$; ppm): **11a** decomposed in $CDCl_3$ solution after 1 h. Anal. Calcd for $C_{35}H_{32}F_3N_3O_5PdS$: C, 54.59; H, 4.19; N, 5.46; S, 4.16. Found: C, 54.26; H, 4.26; N, 5.68; S, 4.01.

[Pd{C(O)C$_6$H$_4$OH-2}(CN^{t}Bu)$_3$]OTf (11a*). Complex **11a*** was similarly prepared from **2a** (64 mg, 0.13 mmol), ^{t}BuNC (90 mg, 1.06 mmol), and Tl(OTf) (50 mg, 0.14 mmol). White **11a*** was precipitated by addition of *n*-hexane. Yield: 62 mg, 71%. Mp: 88 °C dec. IR (cm^{-1}): ν(C≡N) 2224, ν(CO) 1586. ^{1}H NMR (200 MHz, $CDCl_3$; ppm): 10.42 (s, OH, 1H), 8.24 (d, H of C_6H_4 ortho to C═O, $^3J_{HH}$ = 7.5 Hz, 1H), 7.43 (dd, C_6H_4, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.6 Hz), 7.20 (dd, C_6H_4, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.6 Hz), 6.93 (d, C_6H_4, $^3J_{HH}$ = 8.2 Hz, 1H), 1.61 (s, ^{t}Bu, 9H), 1.43 (s, ^{t}Bu, 18H). ^{13}C (^{1}H) NMR (50 MHz, $CDCl_3$; ppm): **11a*** decomposed in $CDCl_3$ solution after 1 h. Anal. Calcd for $C_{23}H_{32}F_3N_3O_5PdS$: C, 44.13; H, 5.15; N, 6.71; S,5.12. Found: C, 43.96; H, 5.31; N, 6.93; S, 5.29.

[Pd{κ^2(*C*,*O*)-μ_2(*O*)-C(═NXy)C$_6$H$_4$O-2}(CNXy)]$_4$ (12). To a yellow suspension of **7a** (25 mg, 0.035 mmol) in acetone (10 mL) was added $Pd(OAc)_2$ (4 mg, 0.017 mmol) at room temperature. After 2.5 h, the mixture was evaporated to dryness, the residue was dissolved in CH_2Cl_2 (2 mL), and Et_2O was added to precipitate a solid that was filtered, washed with *n*-hexane (5 mL), and finally air-dried to give **12** as a yellow solid. Diffraction-quality crystals were grown by slow diffusion of *n*-hexane into a very dilute solution of **12** in CH_2Cl_2. Yield: 13 mg, 81%. Mp: 154 °C dec. IR (cm^{-1}): ν(C≡N) 2184, ν(C═N) 1642. ^{1}H NMR (300 MHz, $CDCl_3$; ppm): 7.83 (d, H of C_6H_4 ortho to C═N, 4H, $^3J_{HH}$ = 7.8 Hz), 7.29−7.13 (m, aromatic H of isonitrile, 12 H), 6.80−6.71 (m, aromatic H, 12 H), 6.47 (dd, C_6H_4, 4H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.2 Hz), 6.32 (d, C_6H_4 1-H, 4H, $^3J_{HH}$ = 8.4 Hz), 6.22 (dd, C_6H_4, 4H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.5 Hz), 2.22 (s, Me, 24H), 2.20 (s, Me, 24H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$; ppm): 169.75 (C═N), 151.87 (COH), 134.46 (CH), 132.38 (PdCNR′), 132.05 (CH), 129.05 (CH), 128.19 (quaternary C, Pd−*C*(═NXy)C$_6$H$_4$−), 127.61, 127.42 (CH), 126.89 (quaternary C, C−Me), 126.76, 123.12, 116.90, 115.36 (CH), 19.30, 18.52 (Me). Anal. Calcd for $C_{96}H_{88}N_8O_4Pd_4$: C, 62.55; H, 4.81; N, 6.08. Found: C, 63.23; H, 4.86; N, 5.76.

The complex $[PdI_2(CNXy)_2]$ is obtained on workup of the mother liquors from **12**. Yield: 9 mg, 83%. Mp: 129 °C dec. IR (cm^{-1}): ν(C≡N) 2194. ^{1}H NMR (300 MHz, $CDCl_3$; ppm): 7.16 (m, H ortho to CMe, 4 H), 7.13 (m, H meta to CMe, 2 H), 2.57 (s, Me, 12H). Anal. Calcd for $C_{18}H_{18}I_2N_2Pd$: C, 34.73; H, 2.91; N, 4.50. Found: C, 35.15; H, 2.86; N, 4.66.

X-ray Structure Determinations. A summary of X-ray data is presented in Table 1.

Data Collection. Data were recorded at low temperature using Mo Kα radiation. Appropriate absorption corrections (multiscan for area detector data, ψ-scan for others) were applied.

Structure Refinement. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Göttingen, Germany). Hydrogen atoms were refined as follows: OH, restrained in **7a**, rigid group in **5a**, **12**; methyls, riding in solvent of **9a**, otherwise rigid; all others riding.

Special Features. The isonitrile C31−C38 in compound **7b** is disordered over two sites with occupation factors 0.64/0.36. Compound **9a** crystallizes with one ether molecule, which is well-ordered. The structure of **12** contained badly resolved residual electron density disordered about the 4-fold axis. This was arbitrarily refined as two carbon sites. Quoted values for *M* and related parameters of **12** do not include solvent.

Results and Discussion

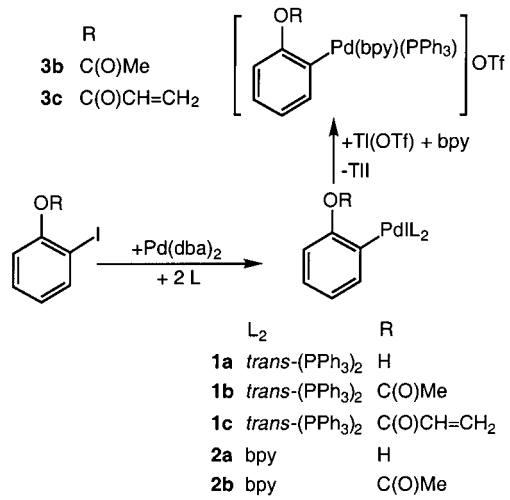
Synthesis of Complexes 1−3. 2-Iodophenol and its derivatives 2-ROC$_6$H$_4$I, where R = C(O)Me, C(O)-CH═CH$_2$, react with $[Pd_2(dba)_3]$·dba ("Pd(dba)$_2$") in the presence of neutral ligands to give the products of the oxidative addition reactions. Thus, the reaction in the presence of 2 equiv of PPh_3 results in the formation of *trans*-[Pd(C$_6$H$_4$OR-2)I(PPh$_3$)$_2$] (R = H (**1a**), C(O)Me (**1b**), C(O)CH═CH$_2$ (**1c**)) (Scheme 1). Similarly, the use of 2,2′-bipyridine (bpy) led to complexes [Pd(C$_6$H$_4$OR-2)I-(bpy)] (R = H (**2a**), C(O)Me (**2b**)), although the reaction of C$_6$H$_4$[OC(O)CH═CH$_2$]-I-2 with "Pd(dba)$_2$" in the presence of bpy failed to give the corresponding complex. Such a procedure has been shown to be useful for the synthesis of organopalladium complexes containing

Table 1. Details of Data Collection and Structure Refinement for the Complexes 5a, 7a, 7b, 8b, 9a, and 12

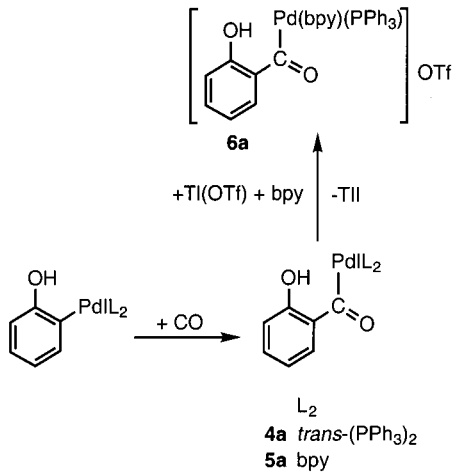
	5a	7a	7	8b	9a·$C_4H_{10}O$	12
chem formula	$C_{17}H_{13}IN_2O_2Pd$	$C_{33}H_{32}IN_3OPd$	$C_{35}H_{34}IN_3O_2Pd$	$C_{27}H_{24}IN_3O_2Pd$	$C_{39}H_{41}F_3N4O_5PdS$	$C_{96}H_{88}N_8O_4Pd_4$
cryst habit	yellow column	colorless column	pale yellow lath	orange prism	colorless tablet	yellow block
cryst size/mm	0.25 × 0.05 × 0.04	0.7 × 0.2 × 0.15	0.7 × 0.2 × 0.06	0.26 × 0.09 × 0.07	0.45 × 0.4 × 0.12	0.15 × 0.10 × 0.10
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	triclinic	orthorhombic	monoclinic	triclinic	tetragonal
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2_1/n$	$P\bar{1}$	$P4/n$
a/Å	8.8284(3)	9.0188(14)	14.8140(18)	10.0568(8)	8.5339(3)	19.5269(14)
b/Å	9.2319(4)	16.689(2)	20.550(2)	13.3006(12)	14.9785(4)	19.5269(14)
c/Å	10.7891(3)	21.851(3)	21.620(3)	18.6197(16)	17.2207(4)	12.2839(12)
α/deg	74.104(3)	112.344(8)	90	90	112.118(3)	90
β/deg	89.026(3)	90.559(10)	90	103.876(3)	95.685(3)	90
γ/deg	76.708(4)	98.875(10)	90	90	101.822(3)	90
V/Å^3	822.04	2997.1	6581.4	2417.9	1957.95	4683.8
Z	2	4	8	4	2	2
D_c/g cm^{-3}	2.063	1.595	1.538	1.802	1.427	1.307
M_r	510.59	719.92	761.95	655.79	841.22	1843.34
F(000)	488	1432	3040	1288	864	1872
diffractometer	Siemens SMART	Siemens P4	Siemens P4	Bruker SMART	Siemens SMART	Bruker SMART
T/°C	−100	−100	−100	−130	−100	−130
$2\theta_{max}$/deg	52	50	50	60	56.6	52.7
μ(Mo Kα)/mm^{-1}	3.0	1.68	1.54	2.07	0.59	0.81
transmissn	0.45−0.99	0.79−0.93	0.68−0.89	0.81−0.96	0.89−0.99	0.77−0.98
no. of rflns measd	4775	13 576	5815	19 897	13 301	29 815
no. of unique rflns	3181	10 263	5783	7041	9338	4796
R_{int}	0.043	0.016	0.17	0.041	0.017	0.101
$R(F > 4\sigma(F))^a$	0.058	0.025	0.039	0.038	0.034	0.038
$R_w(F^2$, all rflns)^b	0.139	0.053	0.068	0.084	0.084	0.111
no. of params	209	723	421	310	483	261
no. of restraints	49	171	586	69	3	233
S^c	1.00	0.95	0.79	0.98	1.05	0.91
max Δρ/e Å^{-3}	0.92	0.41	0.39	1.3	0.60	1.54

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program. ^{c} $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

Scheme 1



Scheme 2



nitrogen[87,88] or phosphorus[89] donor ligands, and we have recently applied it to the synthesis of ortho-palladated anilines.[2,5] The trans geometry of **1a**−**c** was confirmed by the appearance of one singlet in their ^{31}P NMR spectra. Complexes **1b**,**c** react with bpy in the presence of Tl(OTf) (OTf = OSO_2CF_3) to give the cationic species [Pd(C_6H_4OR-2)(bpy)(PPh_3)]OTf (R = C(O)Me (**3b**), C(O)-CH=CH_2 (**3c**)) (Scheme 1). As far as we are aware, these are the first ortho-palladated complexes of phenol and its derivatives.

CO Insertions. We have tested the reactions of complexes **1** and **2** with carbon monoxide, observing that the ortho-palladated phenol derivatives **1a** and **2a** insert CO to give the aroylpalladium complexes *trans*-[Pd{C(O)C_6H_4OH-2}I(PPh_3)$_2$] (**4a**) and [Pd{C(O)C_6H_4OH-2}I(bpy)] (**5a**) (Scheme 2). With the palladated acetic acid esters **1b** and **2b** a partial carbonylation takes place; in the case of **1b** the isolated solid is unreacted **1a** with a very small amount of another compound

(87) Vanasselt, R.; Vrieze, K.; Elsevier, C. J. *J. Organomet. Chem.* **1994**, *480*, 27.
(88) Markies, B. A.; Canty, A. J.; Degraaf, W.; Boersma, J.; Janssen, M. D.; Hogerheide, M. P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1994**, *482*, 191.
(89) Wallow, T. I.; Goodson, F. E.; Novak, B. M. *Organometallics* **1996**, *15*, 3708.

(detected by ^{1}H NMR) that could be the expected CO-inserted species. **2b** is partially carbonylated to give a 40:60 mixture of **2b** and a compound which is probably the compound [Pd{C(O)C$_6$H$_4$O[C(O)Me]-2}I(bpy)]. An increase in either the reaction time or the temperature did not change the 40:60 ratio of the mixture. The palladated acrylic acid ester does not react at all with CO under our conditions. We conclude that the reactivity of our compounds toward CO insertion is dependent mainly on the nature of the ortho OR group, the reactivity order being OH ≫ OC(O)Me > OC(O)CH=CH$_2$. Complex **4a** reacts with bpy and Tl(OTf) to give the cationic aroyl complex [Pd{C(O)C$_6$H$_4$OH-2}(bpy)(PPh$_3$)]-OTf (**6a**). These carbonylated compounds are characterized by the presence in their ^{1}H NMR spectra of a signal at ca. 8.6 ppm, corresponding to the aryl proton ortho to the carbonyl group (see Experimental Section).

The only previously isolated aroylpalladium complexes derived from carbonylation of arylpalladium derivatives are of two kinds: *trans*-[Pd{C(O)C$_6$H$_4$R-4}-XL$_2$] (R = C$_6$H$_4$PdI(PEt$_3$)$_2$, PdI(PEt$_3$)$_2$, X = I, L = PEt$_3$;[57] R = H, X = Br, L = PPh$_3$,[51,52] X = I, L = PCy$_3$, PMe$_2$-Ph[53] PMePh$_2$[54]) and [Pd{C(O)C$_6$H$_4$R-4}(μ-X)L]$_2$ (R = H, Me, L = PPh$_3$, X = I;[56] R = H, L = PBu$_3$, X = Cl[55]). We have recently reported the complexes [Pd{C(O)C$_6$H$_4$R-2}IL$_2$] (R = NH$_2$, N=CHPh, L$_2$ = 2 PR$_3$, bpy) and some of their derivatives [Pd{C(O)C$_6$H$_4$NH$_2$-2}L$_2$]OTf.[2] Therefore, these complexes and those reported here are the products of the first carbonylation reactions of functionalized aryl palladium complexes and also the first not containing phosphines as ligands.

Reactions with Isonitriles. The addition of 2-ROC$_6$H$_4$I (R = H, C(O)Me) to a mixture of "Pd(dba)$_2$" and the isonitrile R′NC (R′ = C$_6$H$_3$Me$_2$-2,6 (Xy), ^{t}Bu) in toluene yields the isonitrile-inserted complexes *trans*-[Pd{C(=NR′)C$_6$H$_4$OR-2}I(CNR′)$_2$] (R = H, R′ = Xy (**7a**), ^{t}Bu (**7a***); R = C(O)Me, R′ = Xy (**7b**), ^{t}Bu (**7b***)) (Scheme 3). Complex **7b*** was obtained impurified by dba but was prepared using a different method (see below). Instead of the required 3:1:1 molar ratio of reagents R′NC:2-ROC$_6$H$_4$I:Pd, an excess of the arene and, in the case of **7a** and **7a***, substoichiometric amounts of the isonitrile were used (3.2:1:2 (**7a**), 1.2:1:2 (**7a***), 1.2:1:3 (**7b**)). When these reactions were carried out with the stoichiometric ratio R′NC:Pd, it was not possible to isolate complexes **7a** and **7a***. The homologous complex using ^{t}BuNC and 2-CH$_2$=CHC(O)OC$_6$H$_4$I seems to be in the mixture obtained in the corresponding reaction, as indicated by the NMR spectra, but it could not be isolated as an analytically pure compound, nor could the analogous complex with XyNC be obtained.

The reaction between isonitriles and Pd(0) complexes have been shown to give "Pd(CN^{t}Bu)$_2$" (eq 1).[90]

$$\text{"Pd(dba)}_2\text{"} + 2\text{R′NC} \rightarrow \text{"Pd(CNR′)}_2\text{"} \qquad (1)$$

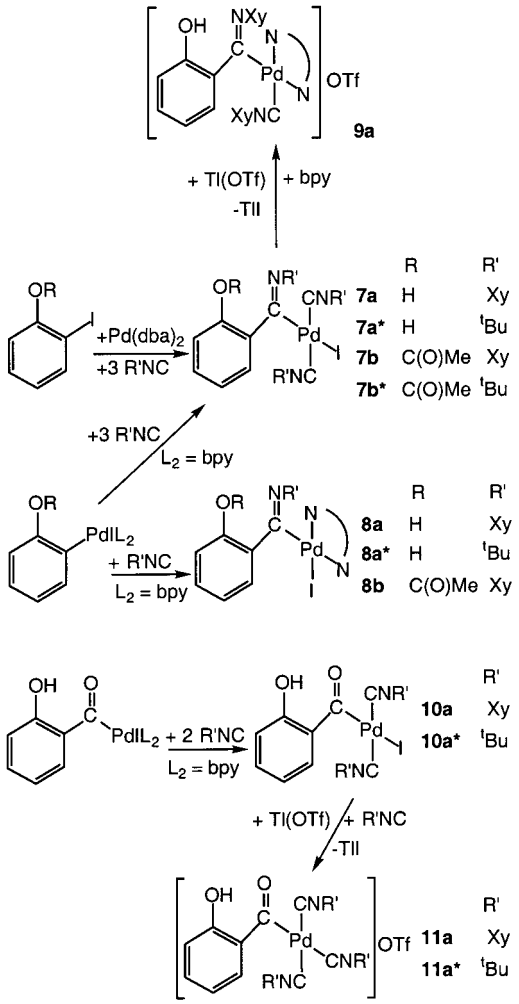
$$\text{"Pd(CNR′)}_2\text{"} + \text{RX} \rightarrow [\text{Pd(R)X(CNR′)}_2] \qquad (2)$$

$$[\text{Pd(R)X(CNR′)}_2] \rightarrow {}^2/_3[\text{Pd}\{\text{C}(=\text{NR′})\text{R}\}\text{X(CNR′)}_2] + {}^1/_3\text{"Pd(R)X"} \qquad (3)$$

Reactions between acyl, aroyl, and alkyl chlorides and "Pd(CN^{t}Bu)$_2$" give the complexes [Pd(R)X(CN^{t}Bu)$_2$] (eq 2; R = MeC(O), PhC(O), (CH$_2$)$_2$CO$_2$Et, CH(Ph)CO$_2$Et, CH$_2$CO$_2$Me, X = Cl) but not insertion products.[91] Otsuka showed that similar complexes with R = CH$_2$Ph, X = Br, I could be isolated by reacting "Pd(CN^{t}Bu)$_2$" with XR but with X = Cl the complex [Pd{C(=N^{t}Bu)CH$_2$Ph}-Cl(CN^{t}Bu)]$_2$ was obtained.[72] Similarly, the reaction of "Pd(CN^{t}Bu)$_2$" with *trans*-BrCH=CHCO$_2$Me gave [Pd-{C(=N^{t}Bu)CH=CHCO$_2$Me}Br(CN^{t}Bu)]$_2$. In our case, such dimeric complexes were not obtained. We assume that the resulting [Pd(R)I(CNR′)$_2$] (or the corresponding dimeric complex) quickly decomposes to give **7a** or **7a*** and some polymeric complex (eq 3) that could be responsible of the formation of the mixture observed when using the 3:1 stoichiometric amount of the isonitrile. When R = C(O)Me, X = I, and R′ = Xy, the intermediate [Pd(R)I(CNR′)$_2$] would be stable and could react with more isonitrile to give **7b**.

Insertion reactions of isonitriles with organopalladium complexes have been widely studied, but the above-mentioned work of Otsuka[72] is the only precedent of the method we describe here. However, as already mentioned, the results are different, and the complexes involved are alkyl instead of aryl palladium complexes. Iminoacyl and -aroyl palladium complexes have been obtained (i) by reacting isonitriles with

Scheme 3



(90) Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994.
(91) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180.

alkyl,[45,64,67,70,72,78,83,84,92−94] aryl,[4,45,57,76,78,85,93,95−97] alkynyl,[67,71,74,98] or other organopalladium complexes[68,72,73,99] (ii) via a transmetalation reaction involving an organosodium[68] or organomercury compound[100] and a palladium isonitrile complex, or (iii) by thermal rearrangement of an organo(isonitrile)palladium complex.[101−103]

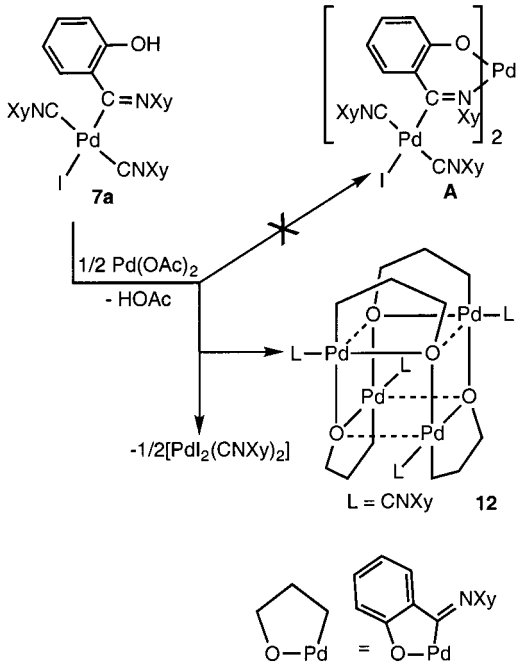
Complex **7a** or **7b*** can also be prepared by ligand displacement from **2a** or **2b** and XyNC or ^{t}BuNC, respectively, in an 1:3 molar ratio. The bpy ligand is substituted by two isonitriles, and a third isonitrile inserts into the Pd−C bond (Scheme 3). This method complements the previous one, since complex **7b*** can now be obtained as a pure compound. However, when **2b** is reacted with XyNC in a 1:3 molar ratio, the isonitrile inserts into the C−Pd bond but does not replace bpy, giving complex **8b** (see below).

Most of the many reported iminoaroyl palladium complexes obtained by insertion of an isonitrile into a C−Pd bond have some additional phosphorus, nitrogen, oxygen, or sulfur donor ligand(s). The only exceptions are the complexes $[Pd\{\mu\text{-}C(=NR')R\}X]_2$ (R = C_6F_5, R′ = Me, *p*-tolyl, X = halide),[104] $[Pd\{\mu\text{-}C(=NR')R\}XL]$ (R = C_6F_5, R′ = Me, X = Cl, L = MeNC;[101] R = R′ = Ph, *p*-$MeOC_6H_4$, X = Cl, L = RNC),[100] and $[Pd\{C(=NR')R\}Cl(CNR'')]$ (R = 2-$C_6H_4CH_2NMe_2$, R′ = *p*-MeC_6H_4, R″ = ^{t}Bu)[96] and the doubly inserted complex $[Pd\{\{C(=NR')\}_2R\}Cl(CNR')_2]$ (R = 2-$C_6H_4N_2Ph$, R′ = C_6H_{11}).[97] The complexes **7** thus represent a new type of iminoaroyl palladium complex.

When complexes **2a**,**b** react with R′NC in a 1:1 ratio, the bpy ligand is not displaced by the isonitrile, which inserts into the corresponding aryl−palladium bond to give the iminoaroyl palladium derivatives $[Pd\{C(=NR')C_6H_4OR\text{-}2\}I(bpy)]$ (R = H, R′ = Xy (**8a**), ^{t}Bu (**8a***); R = C(O)Me, R′ = Xy (**8b**)). As mentioned above, complex **8b** is obtained even if an excess of the isonitrile is used. The only known complexes related to **8** are $[Pd\{C(=NR')R\}X(L_2)]$, where R = Me, R′ = Xy, ^{t}Bu, CH_2-tosyl, X = Cl, and L_2 = bpy, phen;[64] they thus represent a new type of iminoaroyl palladium complexes.

In an attempt to prepare the doubly inserted complex $[Pd\{\{C(=NXy)\}_2C_6H_4OH\text{-}2\}(CNXy)(bpy)]^+$, we reacted **7a** with bpy in the presence of Tl(OTf), which however led instead to the substitution of one isonitrile and the iodide by bpy to form the cationic complex $[Pd\{C(=NXy)C_6H_4OH\text{-}2\}(CNXy)(bpy)]OTf$ (**9**). It is noteworthy that bpy replaces XyNC, whereas this ligand replaces bpy in complex **2a** to give **7a**. We are not aware of the existence of any complex related to **9**.

Scheme 4



We have attempted the coinsertion of CO and R′NC, and thus, we have (i) reacted the CO-inserted complex **5a** with R′NC in a 1:2 ratio, whereupon only displacement of the bpy ligand occurs, giving *trans*-$[Pd\{C(O)C_6H_4OH\text{-}2\}I(CNR')_2]$ (R′ = Xy (**10a**), ^{t}Bu (**10a***)), and (ii) reacted these complexes with further R′NC in the presence of Tl(OTf), whereby only the cationic complexes $[Pd\{C(O)C_6H_4OH\text{-}2\}(CNR')_3]OTf$ (R′ = Xy (**11a**), ^{t}Bu (**11a***)) were obtained (Scheme 3).

In an attempt to prepare a trinuclear complex such as **A** (Scheme 4) by reaction of **7a** with $Pd(OAc)_2$ in a 2:1 molar ratio, exploiting the acidity of the phenolic proton, we obtained instead an easily separable mixture of $[PdI_2(CNXy)_2]$ and the tetrameric $[Pd\{\kappa^2(C,O)\text{-}\mu_2(O)\text{-}C(=NXy)C_6H_4O\text{-}2\}(CNXy)]_4$ (**12**). Therefore, although the expected acid−base reaction took place, the resulting "naked" Pd(II) removed the iodo and one isonitrile ligand from each molecule of **7a**, giving $[PdI_2(CNXy)_2]$. The structure of **12** has been confirmed by X-ray diffraction, as shown below.

Spectroscopic Properties. The ^{1}H NMR signal corresponding to the OH group in complex **1a** or **2a** appears as a singlet at 4.99 or 5.82 ppm, respectively. This signal is shifted to much higher frequency in the CO-inserted complexes (**4a**, 9.72 ppm; **6a**, 10.08 ppm; **5a**, 10.25 ppm) or still higher in the isonitrile-inserted complexes (**7a**, 13.66 ppm; **7a***, 15.89 ppm; **8a***, 13.90 ppm; **9a**, 13.36 ppm). These changes may be associated with to the deshielding caused by an intramolecular hydrogen bond between the OH group and the carbonyl oxygen or the imine nitrogen, which would result in the formation of a six-membered ring (Chart 1). This has been confirmed by X-ray diffraction studies carried out for **5a**, **7a**, and **9a** (see below). Complexes **10a**, **10a***,

(92) Campora, J.; Hudson, S. A.; Massiot, P.; Maya, C. M.; Palma, P.; Carmona, E.; Martinez Cruz, L. A.; Vegas, A. *Organometallics* **1999**, *18*, 5225.
(93) Yamamoto, Y.; Tanase, T.; Yanai, T.; Asano, T.; Kobayashi, K. *J. Organomet. Chem.* **1993**, *456*, 287.
(94) Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196.
(95) Zografidis, A.; Polborn, K.; Beck, W.; Markies, B. A.; van Koten, G. *Z. Naturforsch., B* **1994**, *49*, 1494.
(96) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1980**, *41*, 229.
(97) van Baar, J. F.; Klerks, J. M.; Overbosch, P.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1976**, *112*, 95.
(98) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem. Eur. J.* **2000**, *6*, 983.
(99) Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683.
(100) Crociani, B.; Nicolini, M.; Richards, R. L. *J. Organomet. Chem.* **1976**, *104*, 259.
(101) Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1982**, 2389.
(102) Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E. *J. Organomet. Chem.* **1983**, *254*, 371.
(103) Usón, R.; Forniés, J.; Espinet, P.; Pueyo, L.; Lalinde, E. *J. Organomet. Chem.* **1986**, *299*, 251.
(104) Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E.; García, A.; Jones, P. G.; Meyer-Bäse, K.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 259.

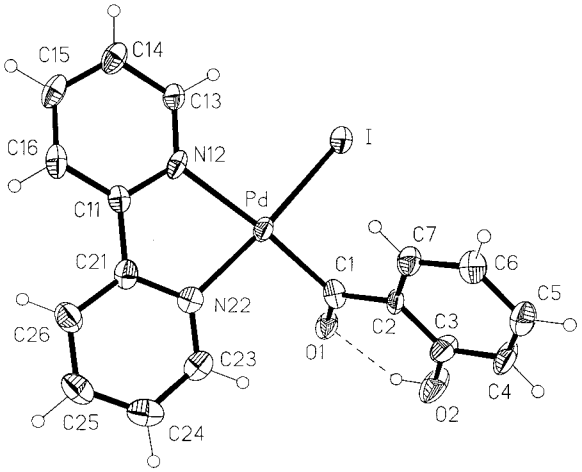
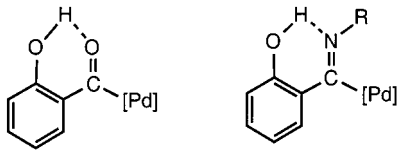


Figure 1. Thermal ellipsoid plot of complex **5a** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(1), 1.998(10); Pd−N(22), 2.102(8); Pd−N(12), 2.159(7); Pd−I, 2.5883(9); C(1)−O(1), 1.202(11); C(1)−Pd−N(22), 95.4(3); N(22)−Pd−N(12), 78.4(3); C(1)−Pd−I, 87.7(3); N(12)−Pd−I, 98.4(2).

Chart 1



11a, and **11a*** show a singlet at 10.79, 10.78, 10.31, and 10.42 ppm, respectively, shifts very similar to those of **4a**, **6a**, and **5a**. In consequence, we propose a hydrogen bond between the OH and the carbonyl oxygen in these complexes. In *o*-hydroxyacetophenone the OH proton resonance appears at 12.25 ppm. We have reported similar intramolecular hydrogen bonding in *trans*-[Pd{C(O)$C_6H_4NH_2$-2}I(PMe_3)$_2$] between the aroyl oxygen and one of the ortho NH_2 protons.[2]

The band assignable to ν(OH) in complexes with R = H is clearly observed only in the case of **2a**. In all other cases it is weak and broad and has not been assigned. Those complexes with R = C(O)Me show one band from ν(CO) in the narrow range 1768−1746 cm^{-1}, 17−39 cm^{-1} lower than in C_6H_4{OC(O)Me}-I-2 (1785 cm^{-1}). This is probably because of the lower electron-withdrawing effect on the aryl ligand of the ortho groups in the complexes ("$PdIL_2$" in **1b**, **2b**, **3b**; "{C(=NR′)}$PdIL_2$" in **7b**, **7b***, **8b**) compared to that of the iodine substituent in the starting compound. Similarly, complexes **1c** and **3c** show ν(CO) bands at lower frequencies (1726 and 1734 cm^{-1}, respectively) than the corresponding one in the iodoarene C_6H_4OC(O)CH=CH_2−I-2 (1745 cm^{-1}). The band corresponding to ν(C≡N) appears in the region 2224−2190 or 2192−2158 cm^{-1} for complexes containing ^{t}BuNC or XyNC, respectively. The band corresponding to ν(C=N) appears in a wide range (1642−1536 cm^{-1}). The factor with the greatest effect on the frequency of this band is the nature of the group R, because, other groups being equal, $\nu(C{=}N)_{C(O)Me} - \nu(C{=}N)_H$ = 30−78 cm^{-1}. Certainly, the intramolecular O−H···N hydrogen bonding must be responsible for this effect ($\nu(C{=}N)_{C(O)Me}$ = 1636−1586 cm^{-1}; $\nu(C{=}N)_H$ = 1572−1536 cm^{-1}). As expected,[64] $\nu(C{=}N)_{^tBu} > \nu(C{=}N)_{Xy}$ for the same R but the difference is lower than that ascribable to R (16−62 cm^{-1}), giving the following order of ν(C=N): **7b*** > **7b** > **7a*** > **7a**; **8b** > **8a*** > **8a**.

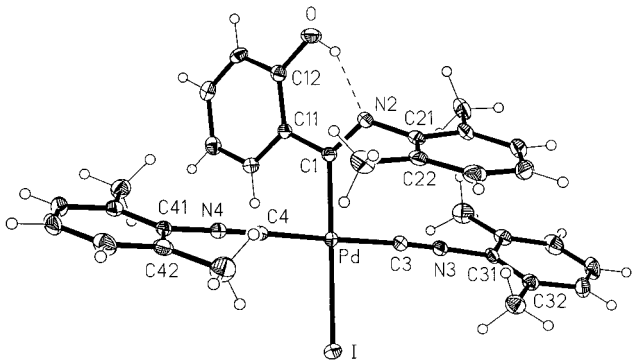


Figure 2. Thermal ellipsoid plot of one of the two independent molecules of the complex **7a** (30% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(3), 1.979(3); Pd−C(4), 1.982(3); Pd−C(1), 2.044(3); Pd−I, 2.7009(5); O−C(12), 1.350(4); N(2)−C(1), 1.282(4); N(3)−C(3), 1.147(4); N(4)−C(4), 1.146-(4); C(3)−Pd−C(1), 91.32(11); C(4)−Pd−C(1), 87.61(11); C(3)−Pd−I, 91.22(8); C(4)−Pd−I, 89.74(8); C(1)−N(2)−C(21), 123.8(2); C(3)−N(3)−C(31), 169.5(3); C(4)−N(4)−C(41), 179.0(3); N(3)−C(3)−Pd, 174.6(3); N(4)−C(4)−Pd, 177.5(3).

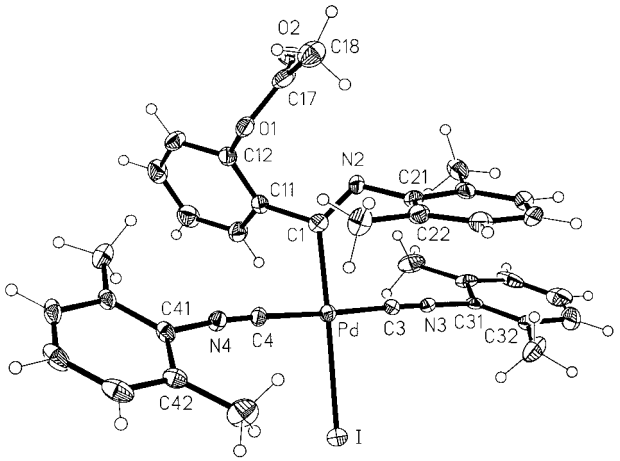


Figure 3. Thermal ellipsoid plot of the complex **7b** (30% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(3), 1.954(5); Pd−C(4), 1.977(5); Pd−C(1), 2.058(5); Pd−I, 2.7121(6); O(1)−C(17), 1.365(7); O(1)−C(12), 1.407(6); O(2)−C(17), 1.193(6); N(2)−C(1), 1.259(6); N(3)−C(3), 1.157(5); N(4)−C(4), 1.139-(5); C(3)−Pd−C(1), 90.0(2); C(4)−Pd−C(1), 87.7(2); C(3)−Pd−I, 91.60(15); C(4)−Pd−I, 90.62(15); C(17)−O(1)−C(12), 115.4(4); C(1)−N(2)−C(21), 124.0(5); C(3)−N(3)−C(31), 172.8(6); C(4)−N(4)−C(41), 174.7(5); N(3)−C(3)−Pd, 178.0(5); N(4)−C(4)−Pd, 177.7(5).

X-ray Crystal Structures of Complexes 5a, 7a, 7b, 8b, 9a, and 12. The structures of these complexes show the usual square-planar arrangement about the palladium atom (**5a** (Figure 1), **7a** (Figure 2), **7b** (Figure 3), **8b** (Figure 4), **9a** (Figure 5) and **12** (Figure 6)). The crystal structure of **7a** involves two independent but essentially similar molecules (rms deviation of all non-H atoms 0.11 Å). In those complexes with bpy, the geometry is distorted because of the small bite angle of this ligand. The different Pd−I and Pd−N bond distances can be used to order the trans influence of some ligands. Thus, the Pd−I bond distances (in Å) are

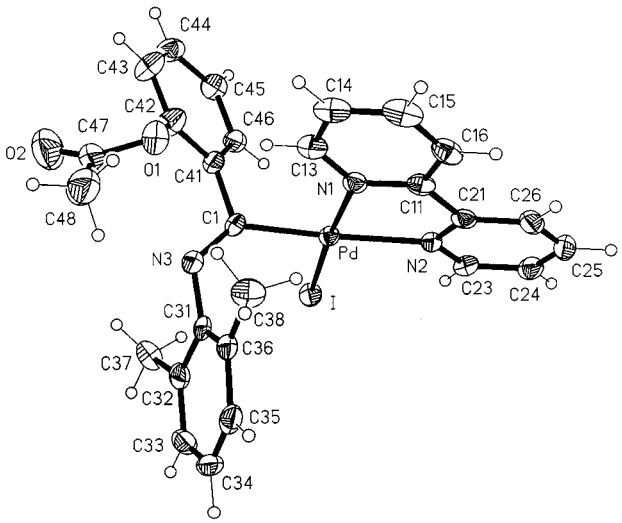


Figure 4. Thermal ellipsoid plot of the complex **8b** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(1), 1.994(4); Pd−N(1), 2.114(3); Pd−N(2), 2.153(3); Pd−I, 2.5904(4); N(3)−C(1), 1.267(5); C(42)−O(1), 1.424(5); C(47)−O(2), 1.190(6); C(47)−O(1), 1.326(6); C(1)−Pd−N(1), 95.85(14); C(1)−Pd−N(2), 173.12(14); N(1)−Pd−N(2), 77.28(12); C(1)−Pd−I, 88.89(10); N(1)−Pd−I, 175.07(9); N(2)−Pd−I, 97.98(9); C(1)−N(3)−C(31), 126.6(3).

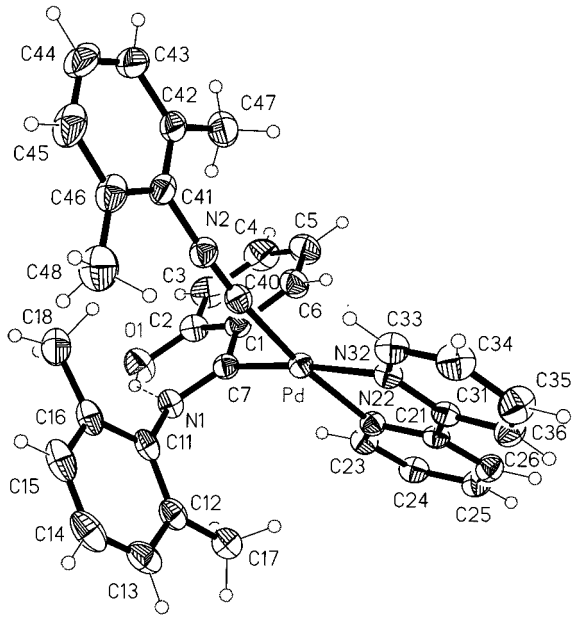


Figure 5. Thermal ellipsoid plot of the cation of complex **9a** (30% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(40), 1.926(2); Pd−C(7), 2.017(2); Pd−N(22), 2.0739(18); Pd−N(32), 2.1173(19); O(1)−C(2), 1.348(3); N(1)−C(7), 1.283(3); C(40)−Pd−C(7), 85.68(9); C(7)−Pd−N(22), 96.27(8); C(40)−Pd−N(32), 99.40(9); N(22)−Pd−N(32), 78.98(7); C(7)−N(1)−C(11), 124.1(2); C(40)−N(2)−C(41), 172.6(2); N(2)−C(40)−Pd, 173.8(2).

2.5883(9) (**5a**), 2.7009(5) (**7a**), 2.7121(6) (**7b**), and 2.5904(4) (**8b**). Therefore, the order of trans influence is bpy ≪ C(=NXy)C_6H_4OC(O)Me-2 < C(=NXy)C_6H_4OH-2. The Pd−N bond distances (in Å) in bpy complexes are as follows: trans to I, 2.102(8) (**5a**) and 2.114(5) (**8b**); trans to C(=O)C_6H_4OH-2, 2.159(7) (**5a**); trans to C(=NXy)-

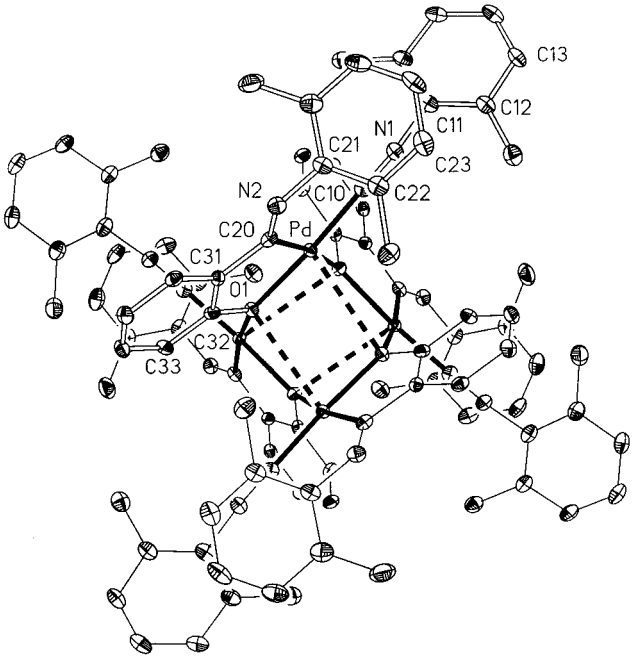


Figure 6. Thermal ellipsoid plot of complex **12** (30% probability levels) with the labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(10), 1.926(5); Pd−C(20), 2.004(4); Pd−O(1), 2.052(3); Pd−O(1)#1, 2.195(3); O(1)−Pd#2, 2.195(3); C(10)−N(1), 1.155(6); C(10)−Pd−C(20), 96.0(2); C(20)−Pd−O(1), 84.99(16); C(10)−Pd−O(1)#1, 93.68(16); O(1)−Pd−O(1)#1, 85.09(13); C(32)−O(1)−Pd, 111.1(3); C(32)−O(1)−Pd#2, 123.1(3); Pd−O(1)−Pd#2, 122.50(14); N(1)−C(10)−Pd, 170.8(4); C(10)−N(1)−C(11), 173.3(5); C(20)−N(2), 1.265(6).

C_6H_4OC(O)Me-2, 2.153(3) (**8b**). If the values for the neutral complexes are compared, the order of trans influence is I < C(=NXy)C_6H_4OC(O)Me-2 ≈ C(=O)C_6H_4-OH-2. In the cationic complex **9b**, the order of trans influence is XyNC < C(=NXy)C_6H_4OH-2. When the Pd−C(=NXy)C_6H_4OC(O)Me-2 bond distances in **7b** (2.058(5) Å) and in **8b** (1.994(4) Å) are compared, the order of trans influence is bpy < I. Therefore, from the above series we propose the following scale of trans influence: bpy < I < C(=NXy)C_6H_4OC(O)Me-2 ≈ C(=O)C_6H_4OH-2 < C(=NXy)C_6H_4OH-2. The aroyl and iminoaroyl C−Pd bond distances only depend on the nature of the trans ligand because the related pairs of complexes **5a** (1.998(10) Å)/**8b** (1.994(4) Å), with bpy trans, and **7a** (2.044(3) Å)/**7b** (2.058(5) Å), with iodo trans, have similar C−Pd bond distances.

An intramolecular hydrogen bond is established between the OH group at O(2) and the carbonyl oxygen O(1) in **5a** (O−H, 0.84 Å; OH···O, 1.83 Å; O···O, 2.559(9) Å; O−H···O, 144.2(4)°), from the OH group to the imine N(2) nitrogen in both molecules of **7a** (O−H, 0.76(3) Å; H···N, 1.90(3) Å; 1.89(3) Å; O···N, 2.584(3), 2.579(3) Å; O−H···N, 151(3), 150(4)°) and from O(1)−H to N(1) in **9a** (O−H, 0.84 Å; H···N, 1.83 Å; O···N, 2.571(3) Å; O−H···N, 144.2(4)°) giving a six-membered ring (Chart 1). This type of interaction may reasonably be postulated as the cause of the high frequency of the ^{1}H NMR resonance observed for the OH proton and the low frequency of the ν(C=N) band in these and related complexes (see above). The following additional nonclassical hydrogen bonds are observed: **5a**,

C(23)−H(23)···O(2) with H···O = 2.46 Å and C H···O = 139°; **9a**, seven H bonds to triflate and ether oxygens, of which the shortest is C(34)−H(34)···O(2) with H···O = 2.45 Å, C−H···O = 167°.

The X-ray diffraction study of **12** (Figure 6) reveals a tetrameric structure with crystallographic 4-fold symmetry, consisting of a highly distorted cubic array of alternating palladium and oxygen atoms; the nonbonded axial Pd···O contacts along the open sides of the cube are typically long at 3.097(3) Å. A schematic representation of the structure is shown in Scheme 4. Each palladium atom displays a distorted-square-planar geometry formed with a chelating C,O iminoacylphenolato ligand, XyNC, and the oxygen atom of an adjacent fragment. The oxygen atoms are unsymmetrically bonded to two palladium atoms (Pd−O(1), 2.052(3) Å; Pd−O(1)#, 2.195(3) Å). The shorter bond distances correspond to those in the chelating ligand. A search of the Cambridge Crystallographic Database revealed only two precedents for this type of structure in palladium complexes, [Pd{κ^3(*C*,*N*,*O*)-μ_2(*O*)-C_6H_4(CHMeN=CHC_6H_4O-2)-2}]$_4$[105] (**B**) and [Pd{κ^2(*P*,*O*)-μ(*O*)-$Ph_2P(C_6H_3$(OH)-3-O-6}Br]$_4$[106] (**C**). These complexes, obtained by routes completely different from that of **12**, have in common with it the presence of a chelating $(E-X-Y-O)^{n-}$ ligand (**12**, E = C, *n* = 2; **B**, E = N, *n* = 1; **C**, E = P, *n* = 1). Complex **B** has been found to catalyze the allylic oxidation of cyclohexene.[105]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **5a**, **7a**, **7b**, **8b**, **9a**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(105) Yang, H.; Khan, M. A.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 210.
(106) Sembiring, S. B.; Colbran, S. B.; Craig, D. C.; Scudder, M. L. *J. Chem. Soc., Dalton Trans.* **1995**, 3731.