

New Palladacycles Containing Terdentate $[C,N,O]^n$ ($n = 0, 1, 2$) or Tetridentate $[N,C,O,N']^n$ ($n = 1, 2$) Ligands. The First 1,2-Dihydroquinazoline-4-yl Complexes

José Vicente, María Teresa Chicote,* and Antonio Jesús Martínez-Martínez

Grupo de Química Organometálica, Departamento de Química Inorgánica, Universidad de Murcia, Apartado 4021, 30071 Murcia, Spain

Peter G. Jones[‡]

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 23329, 38023, Braunschweig, Germany

Delia Bautista[§]

SAI, Universidad de Murcia, Apartado 4021, 30071 Murcia, Spain

Received March 5, 2008

The reaction of $IC_6H_4[NHC(Me)CHC(O)Me]-2$ (IAr) with $[Pd_2(dba)_3] \cdot dba$ ("Pd(dba)₂", dba = dibenzylideneacetone) gives, in the presence of bidentate ligands N[^]N (1:1:1), *cis*-[PdI(Ar)(N[^]N)] (N[^]N = 4,4'-*tert*-butyl-2,2'-bipyridine = 'Bubpy (**1**), *N,N,N',N'*-tetramethylethylenediamine = tmeda (**2**)). These complexes react with PPh₃ (1:2) to give *trans*-[PdI(Ar)(PPh₃)₂] (**3**) or with TfO (TfO = CF₃SO₃) to give [Pd{C,C-C₆H₄{NH=C(Me)CHC(O)Me}-2}(N[^]N)]TfO (N[^]N = 'Bubpy (**4**), tmeda (**5**)), which, in turn, react with neutral monodentate ligands (L, 1:1) to give complexes [Pd(Ar)(N[^]N)(L)] (N[^]N = 'Bubpy, L = PPh₃ (**6**), N[^]N = tmeda, L = PPh₃ (**7**), 'BuNC (**8**)). The reaction of IAr with "Pd(dba)₂" and RNC (R = Xy, 'Bu) in 1:1:2 molar ratio produces a mixture containing [Pd₂I₂(CNXy)₄] (**9**, Xy = C₆H₃Me₂-2,6) or *trans*-[PdI₂{C(=NH'Bu)Ar}(CN'Bu)] (**10**), respectively, but using an excess of RNC (1:1:5 molar ratio), complexes *trans*-[PdI{C(=NR)Ar}(CNR)₂] (R = 'Bu (**11**), Xy (**12**)) are obtained instead. Complex **5** reacts with XyNC (1:1) to give the dimeric complex [Pd{μ-N,C,N',O-N(Xy){=CC₆H₄{NC(Me)CHC(Me)O}-2}}]₂ (**13**), which reacts with excess HTfO to give [Pd{μ-N,C,N',O-N(Xy){=CC₆H₄{N=C(Me)CH₂C(O)Me}-2}}]₂(TfO)₂ (**14a**) or with neutral monodentate ligands (L) to give neutral mononuclear pincer complexes [Pd{C,N,O-C(=NXy)C₆H₄{NC(Me)CHC(Me)O}-2}(L)] (L = PPh₃ (**15**), 'BuNC (**16a**), XyNC (**17**)), which react with excess of HTfO to give the corresponding dicationic [Pd{C,N,O-C(=NHXy)C₆H₄{N=C(Me)CH₂C(O)Me}-2}(PPh₃)](TfO)₂ (**18**) or monocationic pincer derivatives [Pd{C,N,O-C(=NHXy)C₆H₄{NC(Me)CHC(Me)O}-2}(CNR)]TfO (R = 'Bu (**19**), Xy (**20**)), respectively. The reaction of complex **11** or **12** with AgClO₄ (1:1) or that of **14a** with PPh₃ (1:2) affords [Pd{C,N,O-C(=NHR)C₆H₄{NC(Me)CHC(Me)O}-2}L]X (X/R/L = ClO₄/^tBu/^tBuNC (**21**), ClO₄/Xy/XyNC (**22**), TfO/Xy/PPh₃ (**23**)), analogues of **19** or **20**, respectively. The reaction of **21** with Na₂CO₃ (2:1) allowed the synthesis of [Pd{C,N,O-C(=N'Bu)C₆H₄{NC(Me)CHC(Me)O}-2}(CN'Bu)] (**16b**). The reaction of **1** or **3** with HI and XyNC in 1:1:2 or 1:1:1 molar ratio, respectively, produces the first 1,2-dihydroquinazoline-4-yl complexes *trans*-[PdI₂{C(=NXy)C(Me){CH₂C(O)Me}NHC₆H₄-2}(L)] (L = XyNC (**24**), PPh₃ (**25**)). The crystal structures of complexes **1**, **3**, **5**, **7**, **10**, **13**, **14a**, **17**, **21**, **22**, and **24** have been determined. Single crystals of complex [Pd{μ-O,N,C,N'-OC(Me)CHC(Me)NC₆H₄C=NXY}{μ-N,C,N',O-N(Xy){=CC₆H₄{NC(Me)CH₂C(Me)O}-2}}]TfO (**14b**) were obtained alongside those of **14a**, and the corresponding crystal structure was also solved.

Introduction

In the chemistry of palladium, the search for multidentate ligands has been increasing during the past few years mainly with the purpose of preparing tailor-made organometallic

complexes that could display interesting activity in areas such as organic synthesis, catalysis, or materials science.^{1a–d} In addition to classical palladacycles with monoanionic bidentate ligands, interest is growing in cyclometalated palladium compounds containing terdentate ligands that impose severe restrictions on the coordination sphere of the metal, thus modifying its reactivity.^{1e–g}

One of our research interests is the synthesis of *ortho*-functionalized arylpalladium complexes and the study of their reactivity toward unsaturated molecules such as CO, isocyanides, alkenes, alkynes, or carbodiimides. The ability of the Pd–C bond to insert unsaturated molecules is thought to be one of

* To whom correspondence should be addressed. E-mail: mch@um.es. WWW: <http://www.um.es/gqo/>.

[‡] To whom correspondence regarding the X-ray diffraction studies of complexes **1**, **5**, **7**, **10**, **14a**, **14b**, **21**, **22**, and **24**, should be addressed. E-mail: p.jones@tu-bs.de.

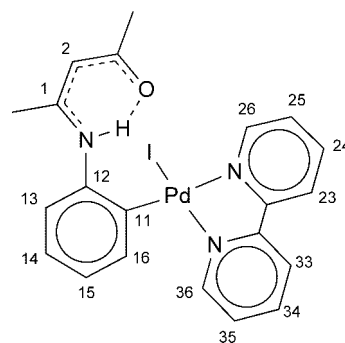
[§] To whom correspondence regarding the X-ray diffraction study of complexes **3**, **13**, and **17** should be addressed. E-mail: dbc@um.es.

the key steps in many palladium-catalyzed reactions. We believe that synthesizing and studying such species could open the way to the discovery of new reactivity patterns. Our studies in this field over the past few years have given us the opportunity to prepare novel types of organometallic complexes as well as various organic products.^{1h-k} In particular, we described recently a Pd-C,N,C-pincer complex that is an efficient precatalyst in Heck and Suzuki cross-coupling processes.² In addition, the present study involves formation of *ortho*-substituted aryl complexes that must be intermediates in a reported palladium-catalyzed synthesis of 2,3-disubstituted indoles.^{3a}

Quite a few palladium complexes with terdentate C,N,O-ligands have been reported.^{1a,3b-1,4-9} In most cases they have been prepared by treating an appropriate hydrazone, semicarbazone, imine, quinoline, or diarylazo derivative with [Pd(OAc)₂] or with Li₂[PdCl₄], sometimes in the presence of a base. The carbon atom bonded to Pd is generally sp² hybridized and, in most cases, belongs to an aryl ligand. In a few examples, it belongs to thiophene,⁴ pyrrole,⁵ or ferrocenyl^{7a,7b,8,9} fragments, and only one Pd-C(sp³)NO pincer complex has been reported.⁶ In the majority of such complexes both the Pd-O-N and Pd-C-N cycles are five-membered, although a few examples are known for Pd-O-N in which there are six-membered rings.⁷ Two complexes have also been reported with Pd-O-N and Pd-C-N in six- and seven-membered rings, respectively, the latter resulting from the insertion of RC≡CR (R = Ph,⁸ CO₂Me)⁹ into a Pd-C_{ferrocenyl} bond.

In this paper we report the reactivity of a functionalized aryl ligand (see Chart 1), selected in view of the nature and

Chart 1



disposition of its potential donor atoms, which, after the insertion of unsaturated molecules into the Pd-C_{aryl} bond, could lead to novel types of pincer complexes. In fact, 10 new ligands are present in the complexes here described, including aryl, iminoacyl, mono- and dianionic C,N,O-pincer, and 1,2-dihydroquinazolin-4-yl ligands, some of which are connected through a rich acid/base chemistry.

Experimental Section

When not otherwise stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Molar conductivities were measured on a ca. 5×10^{-4} mol·L⁻¹ acetone solution with a Crison Micro CM2200 conductimeter. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded in Varian 200, 300, or 400 NMR spectrometers. Chemical shifts are referred to TMS (¹H, ¹³C) or H₃PO₄ (³¹P). The NMR assignments follow the atom-numbering scheme depicted in Chart 1 and, in some cases, were performed with the help of APT, HMQC, and HMBC experiments. [Pd₂(dba)₃]·dba [Pd(dba)₂, dba = dibenzylideneacetone] was prepared as reported in the literature,¹⁰ TiTfO was obtained from HTfO (TfO = CF₃SO₃) and Ti₂CO₃ (Fluka), tmeda, XyNC, ^tBuNC, and PPh₃ were purchased from Fluka, ^tBubpy and AgClO₄·H₂O were purchased from Aldrich, and HI (57%) was purchased from Riedel de Haën. The solvents were distilled before use.

Synthesis of IC₆H₄NHC(Me)CHC(O)Me-2 (IAR; 4-(2-iodophenylamino)pent-3-en-2-one). In order to avoid the use of benzene, we have slightly modified the procedure reported by Sakamoto.³ To a solution of 2-iodoaniline (10.64 g, 48.6 mmol) in a mixture of CHCl₃ and EtOH (70/20, v/v) were added freshly distilled acetylacetone (5 mL, 48.6 mmol), *p*-toluenesulfonic acid monohydrate (1 g, 5.26 mmol), and anhydrous MgSO₄ (10 g). The reaction mixture was refluxed for 6 h and filtered. The yellow solution was concentrated to dryness. The oily residue was dissolved in CHCl₃ (30 mL) and washed with H₂O (3 × 20 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated to give an oily material. Upon the addition of Et₂O (1 mL) and *n*-hexane (10 mL) and cooling the solution at -30 °C overnight, colorless crystals of IAR formed, which were filtered off and suction dried. Yield: 7.6 g, 52%. Mp: 56 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.85 (s, 3 H, MeCN), 2.13 (s, 3 H, C(O)Me), 5.25 (s, 1 H, CH), 6.92 (td, 1 H, H15, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 7.16 (dd, 1 H, H16, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 7.33 (td, 1 H, H14, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 7.87 (dd, 1 H, H13, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 12.29 (s, 1 H, NH). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 19.6 (MeCN), 29.2, (C(O)Me), 97.5 (C11), 97.7 (C2), 127.0 (C15), 127.7

(10) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, U. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

- (1) (a) Solé, D.; Díaz, S.; Soláns, X.; Font-Bardía, M. *Organometallics* **2006**, 25, 1995. (b) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, 105, 2527. (c) Bedford, R. B. *Chem. Commun.* **2003**, 1787. (d) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (e) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **2001**, 40, 3750. (f) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, 103, 1759. (g) Singleton, J. T. *Tetrahedron* **2003**, 59, 1837. (h) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2006**, 25, 1851. (i) Vicente, J.; Abad, J. A.; López-Nicolás, R. M. *Tetrahedron Lett.* **2005**, 46, 5839. (j) Vicente, J.; Abad, J. A.; Foertsch, W.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2004**, 23, 4414. (k) Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G. *Organometallics* **2004**, 23, 4711.
- (2) Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G.; Nájera, C.; Botella-Segura, L. *Organometallics* **2005**, 24, 5044.
- (3) (a) Sakamoto, T.; Nagano, T.; Kondo, Y.; Yamanaka, H. *Synthesis* **1990**, 215. (b) Nonoyama, M.; Sugimoto, M. *Inorg. Chim. Acta* **1979**, 35, 131. (c) Tollari, S.; Palmisano, G.; Demartin, F.; Grassi, M.; Magnaghi, S.; Cenini, S. J. *J. Organomet. Chem.* **1995**, 488, 79. (d) Vila, J. M.; Pereira, T.; Ortigueira, J. M.; Torres, M. L.; Castiñeiras, A.; Lata, D.; Fernández, J. J.; Fernández, A. *J. Organomet. Chem.* **1998**, 556, 21. (e) Fernández, A.; López-Torres, M.; Suárez, A.; Ortigueira, J. M.; Pereira, T.; Fernández, J. J.; Vila, J. M.; Adams, H. J. *J. Organomet. Chem.* **2000**, 598, 1. (f) Das, S.; Pal, S. J. *J. Organomet. Chem.* **2004**, 689, 352. (g) Albert, J.; González, A.; Granell, J.; Moragas, R.; Puerta, C.; Valera, P. *Organometallics* **1997**, 16, 3775. (h) Albert, J.; González, A.; Granell, J.; Moragas, R.; Solans, X.; Font Bardia, M. *J. Chem. Soc. Dalton Trans.* **1998**, 1781. (i) Cativiela, C.; Falvello, L. R.; Gines, J. C.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **2001**, 25, 344. (j) Fernández, A.; Pereira, E.; Fernández, J. J.; López-Torres, M.; Suárez, A.; Mosteiro, R.; Vila, J. M. *Polyhedron* **2002**, 21, 39. (k) Fernández, A.; Vázquez-García, D.; Fernández, J. J.; López-Torres, M.; Suárez, A.; Castro-Juiz, S.; Vila, J. M. *New J. Chem.* **2002**, 26, 398. (l) Steiner, E.; L'Epplattienier, F. A. *Helv. Chim. Acta* **1978**, 61, 2264.
- (4) Nonoyama, M. *J. Inorg. Nucl. Chem.* **1980**, 42, 297.
- (5) Nonoyama, M. *Inorg. Chim. Acta* **1988**, 145, 53.
- (6) Yoneda, A.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Organometallics* **1994**, 13, 4912.
- (7) (a) Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 3785. (b) Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *Organometallics* **1998**, 17, 3437. (c) Yang, H.; Khan, M. A.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 210.
- (8) Zhao, G.; Wang, Q. G.; Mak, T. C. W. *J. Organomet. Chem.* **574**, 311–317 1999, 574, 311.
- (9) Perez, S.; Lopez, C.; Caubet, A.; Solans, X.; Font-Bardía, M.; Roig, A.; Molins, E. *Organometallics* **2006**, 25, 596.

(C16), 128.7 (C14), 139.4 (C13), 140.9 (C12), 159.6 (C1), 196.5 (CO). IR (cm⁻¹): $\nu_{\text{C=O}}$ 1610.

Synthesis of [PdI(Ar)(N[^]N)] [N[^]N = 'Bubpy (1), tmeda (2)]. To a suspension of Pd(dba)₂ (mg/mmol for 1: 183.6/0.32, for 2: 225.0/0.39) in toluene (20 mL), under a nitrogen atmosphere, were added the appropriate bidentate ligand (N[^]N/mg/mmol for 1: 'Bubpy = 4,4'-*tert*-butyl-2,2'-bipyridine/85.7/0.32, for 2: tmeda = *N,N,N',N'*-tetramethylethylenediamine/45.5/0.39) and IAr (mg/mmol for 1: 96.1/0.32, for 2: 117.8/0.39) with an interval of 10 min. The reaction mixture was stirred (1: 2.5 h; 2: 2 h) and concentrated under vacuum to dryness, and the solid residue was stirred with CH₂Cl₂ (20 mL). The resulting suspension was filtered through a short pad of Celite to remove some metallic palladium, and the orange (1) or yellow (2) filtrate was concentrated to ca. 2 mL. Upon the addition of Et₂O (5 mL) and *n*-hexane (20 mL), 1 precipitated along with some dba. The crude product was refluxed in *n*-hexane (30 mL) for 15 min, and the suspension was filtered while hot. The yellow solid collected was recrystallized from CH₂Cl₂/Et₂O and air-dried to give pure 1. In the case of 2, Et₂O (30 mL) was added, and the resulting suspension was stirred in a water/ice bath for 30 min to convert the initially oily material into a yellow solid that was filtered off, recrystallized from CH₂Cl₂/Et₂O, and suction dried.

1. Yield: 140 mg, 67%. Mp: 182 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.38 (s, 9 H, 'Bu), 1.41 (s, 9 H, 'Bu), 1.90 (s, 3 H, MeCN), 1.99 (s, 3 H, C(O)Me), 5.08 (s, 1 H, CH), 6.87–6.91 (m, 1 H, H14), 6.94–6.99 (m, 2 H, H13 + H15), 7.31 (dd, 1 H, H 25, ³J_{HH} = 6 Hz, ⁴J_{HH} = 1.8 Hz), 7.45–7.50 (m, 3 H, H16 + H26 + H35), 7.93 (d, 1 H, H33, ⁴J_{HH} = 1.8 Hz), 7.95 (d, 1 H, H23, ⁴J_{HH} = 1.8 Hz), 9.45 (d, 1 H, H36, ³J_{HH} = 6 Hz), 12.40 (br, 1 H, NH). ¹³C{¹H} NMR (100.81 MHz, CDCl₃): δ 21.2 (MeCN), 29.3 (C(O)Me), 30.7 (Me, 'Bu), 30.8 (Me, 'Bu), 35.8 (CMe₃), 35.9 (CMe₃), 96.9 (C2), 118.5 (C33) 119.2 (C23), 123.9 (C13 or C15), 124.1 (C25), 124.2 (C35), 125.4 (C13 or C15), 124.4 (C14), 138.3 (C16), 142.8 (C11 or C12), 143.1 (C11 or C12), 149.7 (C26), 153.0 (C36), 154.4 (C22 or C32), 156.6 (C22 or C32), 162.0 (C1), 163.4 (C24 or C34), 163.6 (C24 or C34), 194.7 (CO). IR (cm⁻¹): $\nu_{\text{C=O}}$ 1600. Anal. Calcd for C₂₉H₃₆IN₃OPd: C, 51.53; H, 5.37; N, 6.22. Found: C, 51.40; H, 5.42; N, 6.09. Crystals of 1·0.5Et₂O suitable for an X-ray diffraction study were obtained by the liquid diffusion method using Et₂O and *n*-hexane.

2. Yield: 136 mg, 67%. Mp: 182 °C, dec. ¹H NMR (200 MHz, CDCl₃): δ 2.00 (s, 3 H, MeCN), 2.10 (s, 3 H, C(O)Me), 2.45 (s, 3 H, Me, tmeda), 2.50–3.50 (various m, 4 H, CH₂, tmeda), 2.57 (s, 3 H, Me, tmeda), 2.67 (s, 6 H, Me, tmeda), 5.21 (s, 1 H, CH), 6.77–6.90 (m, 3 H, Ar), 7.16–7.24 (m, 1 H, Ar), 13.07 (br, 1 H, NH). ¹³C{¹H} NMR (100.81 MHz, CDCl₃): δ 20.4 (MeCN), 29.1 (C(O)Me), 48.5 (Me, tmeda), 48.6 (Me, tmeda), 50.5 (Me, tmeda), 50.6 (Me, tmeda), 58.6 (CH₂, tmeda), 62.0 (CH₂, tmeda), 96.7 (C2), 123.0 (CH, Ar), 124.1 (CH, Ar), 124.4 (CH, Ar), 136.8 (CH, Ar), 140.2 (C11 or C12, Ar), 142.3 (C11 or C12, Ar), 162.1 (C1), 194.2 (CO). IR (cm⁻¹): $\nu_{\text{C=O}}$ 1600. Anal. Calcd for C₁₇H₂₈IN₃OPd: C, 38.99; H, 5.39; N, 8.02. Found: C, 38.90; H, 5.24; N, 8.05.

Synthesis of trans-[PdI(Ar)(PPh₃)₂] (3). To a suspension of 1 (200.0 mg, 0.296 mmol) in Et₂O (20 mL) was added PPh₃ (170.8 mg, 0.65 mmol), and the reaction mixture was stirred at room temperature for 30 min. The resulting suspension was filtered, and the solid was washed with Et₂O (5 mL), recrystallized from CH₂Cl₂/Et₂O, and air-dried to give 3 as a pale yellow solid. Yield: 232 mg, 84%. Mp: 188 °C (dec). ¹H NMR (300 MHz, CDCl₃): δ 1.03 (s, 3 H, MeCN), 2.21 (s, 3 H, C(O)Me), 4.83 (s, 1 H, CH), 6.05 (d, 1 H, Ar, ³J_{HH} = 8 Hz), 6.38 (t, 1 H, Ar, ³J_{HH} = 8 Hz), 6.52 (t, 1 H, Ar, ³J_{HH} = 8 Hz), 7.16–7.32 (m, 19 H, PPh₃ + Ar), 7.54–7.59 (m, 12 H, PPh₃), 12.67 (1 H, NH). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 20.4 (MeCN), 29.4 (C(O)Me), 96.9 (C2), 121.9 (CH, Ar), 122.9 (CH, Ar), 123.2 (CH, Ar), 127.6 (vt, *meta*-C, PPh₃, *N* = 10.6 Hz), 129.6 (*para*-C, PPh₃), 131.9 (vt, *ipso*-C, PPh₃, *N* = 47 Hz), 135.1 (vt, *ortho*-C, PPh₃, *N* = 12 Hz), 135.7 (vt, CH, Ar,

N = 9 Hz), 142.4 (vt, C, Ar, *N* = 6 Hz), 151.8 (vt, C, Ar, *N* = 7 Hz), 157.3 (C1), 193.5 (CO). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 21.3. IR (cm⁻¹): $\nu_{\text{C=O}}$ 1600. Anal. Calcd for C₄₇H₄₂INOP₂Pd: C, 60.56; H, 4.54; N, 1.50. Found: C, 60.68; H, 4.86; N, 1.62. Crystals of 3·0.89CH₂Cl₂·0.55Et₂O suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH₂Cl₂ and Et₂O.

Synthesis of [Pd{C,C-C₆H₄[NH=C(Me)CHC(O)Me]-2}(N[^]N)]-TfO [N[^]N = 'Bubpy (4), tmeda (5)]. To a solution of 1 or 2 (mg/mmol for 4: 300/0.44, for 5: 99/0.19, respectively) in acetone (20 mL) was added TfO (mg/mmol: 156.9/0.44 mmol, 67.2/0.19, respectively). A suspension immediately formed that was stirred for 2 (4) or 1 (5) h and filtered through a short pad of Celite. The solution was concentrated under vacuum to ca. 1 mL, and Et₂O (20 mL) was added to precipitate an oily material, which was converted into a pale yellow powder by stirring the suspension in an ice/water bath for 15 min. The suspension was filtered and the yellow solid was recrystallized from CH₂Cl₂/Et₂O (4) or acetone/Et₂O (5) and suction dried.

4. Yield: 113 mg, 77%. Mp: 176 °C (dec). ¹H NMR (400 MHz, acetone-*d*₆, -60 °C): δ 1.38 (s, 9 H, 'Bu), 1.42 (s, 9 H, 'Bu), 2.14 (s, 3 H, C(O)Me), 2.65 (s, 3 H, MeCN), 4.46 (s, 1 H, CH), 7.10–7.20 (m, 4 H, Ar), 7.85 (d, 1 H, H25 or H35, ³J_{HH} = 6 Hz), 7.91 (d, 1 H, H25 or H35, ³J_{HH} = 6 Hz), 8.52 (d, 1 H, H26 or H36, ³J_{HH} = 6 Hz), 8.83 (s, 1 H, H23 or H33), 8.88 (s, 1 H, H23 or H33), 9.25 (d, 1 H, H26 or H36, ³J_{HH} = 6 Hz), 12.98 (s, 1 H, NH). ¹³C{¹H} NMR (150 MHz, acetone-*d*₆, -60 °C): δ 23.7 (MeCN), 29.4 (Me, 'Bu), 29.4 (Me, 'Bu), 31.5 (C(O)Me), 35.8 (CMe₃), 35.9 (CMe₃), 51.3 (C2), 116.9 (CH), 121.1 (q, TfO, ¹J_{CF} = 315 Hz), 121.1 (C23 or C33), 121.2 (C23 or C33), 124.2 (C25 or C35), 124.2 (C25 or C35), 125.4 (CH), 129.1 (CH), 137.8 (CH), 143.0 (C11 or C12), 148.9 (C26 or C36), 148.9 (C11 or C12), 150.3 (C26 or C36), 155.0 (C22 or C32), 155.4 (C22 or C32), 164.6 (C24 or C34), 164.7 (C24 or C34), 185.6 (C1), 195.4 (CO). IR (cm⁻¹): 1682, 1614. Λ_{M} (Ω⁻¹ cm² mol⁻¹): 157. Anal. Calcd for C₃₀H₃₆F₃N₃O₄PdS: C, 51.62; H, 5.20; N, 6.02; S, 4.59. Found: C, 51.45; H, 5.38; N, 6.08; S, 4.42.

5. Yield: 70.1 mg, 68%. Mp: 168 °C. ¹H NMR (300 MHz, acetone-*d*₆): δ 2.15 (s, 3 H, C(O)Me), 2.42 (s, 3 H, Me, tmeda), 2.50–3.23 (various m, 4 H, CH₂, tmeda), 2.58 (s, 3 H, MeCN), 2.86 (s, 3 H, Me, tmeda), 2.87 (s, 3 H, Me, tmeda), 2.89 (s, 3 H, Me, tmeda), 3.71 (s, 1 H, CH), 6.96–7.16 (m, 4 H, Ar), 12.32 (br, 1 H, NH). ¹³C{¹H} NMR (75 MHz, acetone-*d*₆): δ 24.4 (MeCN), 31.9 (C(O)Me), 47.4 (Me, tmeda), 48.3 (Me, tmeda), 49.7 (Me, tmeda), 50.3 (Me, tmeda), 52.1 (C2), 60.5 (CH₂, tmeda), 62.4 (CH₂, tmeda), 117.7 (CH), 125.7 (CH), 129.3 (CH), 135.9 (CH), 144.1 (C), 144.7 (C), 184.7 (C1), 196.2 (CO). IR (cm⁻¹): $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$ 1674, 1622. Λ_{M} (Ω⁻¹ cm² mol⁻¹): 145. Anal. Calcd for C₁₈H₂₈F₃N₃O₄PdS: C, 39.60; H, 5.17; N, 7.70; S, 5.87. Found: C, 39.60; H, 5.27; N, 7.93; S, 5.63. Crystals of 5 suitable for an X-ray diffraction study were obtained from acetone-*d*₆ and Et₂O by the liquid diffusion method.

Synthesis of [Pd(Ar)(N[^]N)(L)] [N[^]N = 'Bubpy, L = PPh₃ (6), N[^]N = tmeda, L = PPh₃ (7), 'BuNC (8)]. To a solution of 4 (mg/mmol for 6: 75/0.11) or 5 (mg/mmol for 7: 155/0.28, for 8: 200/0.37) in acetone (20 mL) was added the appropriate ligand (L/mg/mmol for 6: PPh₃/31/0.12, for 7: PPh₃/82/0.32, for 8: (L/μL/mmol): 'BuNC/41.4/0.37). After 1 (6, 7) or 2.5 (8) h of stirring, the reaction mixture was filtered through a short pad of Celite, the solution was concentrated under vacuum to ca. 1 mL, and Et₂O (20 mL) was added. An oily material formed that was converted into a solid upon stirring for 30 min with Et₂O (6: 30 mL in an ice/water bath, 7: 30 mL at room temperature, 8: 5 × 5 mL in an ice/water bath). The suspension was filtered, and the solid was washed with Et₂O (3 × 3 mL) and suction dried (8 was additionally dried in an oven at 80 °C for 4 h) to give the desired compound as a very pale yellow (6, 7) or yellow (8·1.5H₂O) solid.

6. Yield: 101 mg, 98%. Mp: 157 °C. ^1H NMR (300 MHz, CDCl_3): δ 1.34 (s, 3 H, *MeCN*), 1.38 (s, 9 H, ^tBu), 1.41 (s, 9 H, ^tBu), 2.04 (s, 3 H, *C(O)Me*), 4.99 (s, 1 H, CH), 6.70 (m, 1 H, Ar), 6.84 (m, 1 H, Ar), 6.95–7.02 (m, 2 H, Ar), 7.15 (m, 1 H, Ar), 7.23 (m, 1 H, Ar), 7.30–7.36 (m, 7 H, Ar), 7.43–7.56 (m, 10 H, Ar), 8.27 (m, 2 H, Ar), 13.08 (br, 1 H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 20.1 (Me), 29.2 (Me), 30.1 (Me, ^tBu), 30.2 (Me, ^tBu), 35.7 (*CMe*₃), 35.8 (*CMe*₃), 98.1 (C2), 120.3 (CH, Ar), 120.5 (CH, Ar), 123.4 (CH, Ar), 124.0 (CH, Ar), 124.3 (CH, Ar), 124.5 (CH, Ar), 125.4 (CH, Ar), 128.7 (d, *ipso*-C, PPh_3 , $J_{\text{CP}} = 53$ Hz), 129.0 (d, *meta*-C, PPh_3 , $J_{\text{CP}} = 11$ Hz), 131.8 (d, *para*-C, PPh_3 , $J_{\text{CP}} = 2$ Hz), 134.7 (d, *ortho*-C, PPh_3 , $J_{\text{CP}} = 12$ Hz), 135.3 (d, C16, $J_{\text{CP}} = 3$ Hz), 140.8 (d, C12, $J_{\text{CP}} = 2$ Hz), 148.0 (d, C11, $J_{\text{CP}} = 13$ Hz), 149.3 (C26), 159.3 (C36), 155.5 (C22 or C32), 155.6 (C22 or C32), 159.0 (C1), 165.4 (C24 or C34), 165.6 (C24 or C34), 195.4 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): δ 33.0. IR (cm^{-1}): $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$, $\nu_{\text{C=N}}$, 1614, 1556. Λ_{M} ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 152. Anal. Calcd for $\text{C}_{48}\text{H}_{51}\text{F}_3\text{N}_3\text{O}_4\text{PPdS}$: C, 60.03; H, 5.35; N, 4.37; S, 3.34. Found: C, 59.99; H, 5.68; N, 4.04; S, 3.17.

7. Yield: 211 mg, 92%. Mp: 182 °C (dec). ^1H NMR (300 MHz, CDCl_3): δ 1.35 (s, 3 H, *MeCN*), 1.90 (s, 3 H, Me, *tmeda*), 2.18 (s, 3 H, Me, *tmeda*), 2.24 (s, 3 H, *C(O)Me*), 2.29 (m, 1 H, CH_2 , *tmeda*), 2.32 (d, 3 H, Me, *tmeda*, $J_{\text{HP}} = 2$ Hz), 2.56–2.61 (m, 1 H, CH_2 , *tmeda*), 2.77 (d, 3 H, Me, *tmeda*, $J_{\text{HP}} = 2$ Hz), 3.28 (m, 1 H, CH_2 , *tmeda*), 3.73 (m, 1 H, CH_2 , *tmeda*), 5.20 (s, 1 H, CH), 6.51 (m, 1 H, Ar), 6.84 (m, 2 H, Ar), 7.30–7.47 (m, 16 H, PPh_3 + Ar), 7.57 (m, 1 H, Ar), 13.69 (br, 1 H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 19.8 (*MeCN*), 29.4 (*C(O)Me*), 47.6 (Me, *tmeda*), 50.6 (Me, *tmeda*), 51.7 (Me, *tmeda*), 61.1 (CH_2 , *tmeda*), 61.9 (CH_2 , *tmeda*), 97.8 (C2), 122.0 (C13 or C15), 121.0 (q, TFO, $J_{\text{CF}} = 320$ Hz), 123.7 (C13 or C15), 125.1 (C14), 128.4 (d, *ipso*-C, PPh_3 , $J_{\text{CP}} = 51$ Hz), 128.8 (d, *meta*-CH, PPh_3 , $J_{\text{CP}} = 11$ Hz), 131.2 (d, *para*-CH, PPh_3 , $J_{\text{CP}} = 3$ Hz), 134.6 (d, *ortho*-CH, PPh_3 , $J_{\text{CP}} = 11$ Hz), 136.2 (d, C16, $J_{\text{CP}} = 3$ Hz), 141.4 (d, C12, $J_{\text{CP}} = 3$ Hz), 145.4 (d, C11, $J_{\text{CP}} = 13$ Hz), 159.1 (C1), 195.2 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ 26.8. IR (cm^{-1}): $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$ 1602, 1556. Λ_{M} ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 153. Anal. Calcd for $\text{C}_{36}\text{H}_{43}\text{F}_3\text{N}_3\text{O}_4\text{PPdS}$: C, 53.50; H, 3.36; N, 5.20; S, 3.97. Found: C, 53.57; H, 5.72; N, 5.05; S, 3.76. Crystals of **7**·2 CH_2Cl_2 were obtained from CH_2Cl_2 and Et_2O by the liquid diffusion method.

8·1.5 H_2O . Yield: 168 mg, 70%. Mp: 55 °C. ^1H NMR (400 MHz, CDCl_3): δ 1.36 (s, 9 H, ^tBu), 1.56 (br, 3 H, H_2O), 2.05 (s, 3 H, Me), 2.11 (s, 3 H, Me), 2.39 (s, 3 H, Me, *tmeda*), 2.63 (s, 3 H, Me, *tmeda*), 2.79 (s, 3 H, Me, *tmeda*), 2.86 (s, 3 H, Me, *tmeda*), 2.58–3.10 (various m, 4 H, CH_2 , *tmeda*), 5.21 (s, 1 H, CH), 6.92–7.01 (m, 2 H, Ar), 7.05–7.10 (m, 1 H, Ar), 7.40 (dd, 1 H, Ar, $J_{\text{HH}} = 7$ Hz, $J_{\text{HH}} = 2$ Hz), 13.27 (br, 1 H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 20.0 (Me), 29.3 (Me), 29.8 (Me, ^tBu), 48.7 (Me, *tmeda*), 49.6 (Me, *tmeda*), 50.1 (Me, *tmeda*), 51.0 (Me, *tmeda*), 59.0 (CH_2 , *tmeda*), 59.3 (*CMe*₃), 62.6 (CH_2 , *tmeda*), 97.5 (C2), 120.7 (q, TFO, $J_{\text{CF}} = 320$ Hz), 123.0 (CH, Ar), 125.1 (CH, Ar), 125.2 (CH, Ar), 135.8 (CH, Ar), 140.1 (C), 141.5 (C), 159.2 (C1), 195.6 (CO). IR (cm^{-1}): ν_{NH} , 3508, $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$ 1601, 1567, 1557. Λ_{M} ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 156. Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{F}_3\text{N}_4\text{O}_{5.5}\text{PdS}$: C, 42.11; H, 6.15; N, 8.54; S, 4.89. Found: C, 41.94; H, 6.03; N, 8.34; S, 5.07.

Synthesis of $[\text{PdI}_2(\text{CNXy})_4]$ (9**).** A suspension of $\text{Pd}(\text{dba})_2$ (250 mg, 0.43 mmol), XyNC (114.1 mg, 0.87 mmol), and *I*Ar (130.9 mg, 0.43 mmol) in toluene was stirred under a nitrogen atmosphere for 4.5 h. The solvent was removed under vacuum, the residue was stirred with CH_2Cl_2 (10 mL), and the suspension was filtered. The solution was concentrated to dryness, and the residue was stirred with Et_2O (5 mL) in an ice/water bath. The orange solid was filtered, washed with Et_2O (3 $\times$ 3 mL), and suction dried. Yield: 16%. Mp: 217 °C. ^1H NMR (300 MHz, CDCl_3): δ 2.53 (s, 6 H, Me, *Xy*), 7.10, 7.22 (AB₂ system, 3 H, CH, *Xy*, $J_{\text{AB}} = 9$ Hz). IR (cm^{-1}):

$\nu_{\text{C=N}}$ 2152. Anal. Calcd for $\text{C}_{36}\text{H}_{36}\text{I}_2\text{N}_4\text{Pd}_2$: C, 43.62; H, 3.64; N, 5.68. Found: C, 43.64; H, 3.53; N, 5.92.

Synthesis of $\text{trans-}[\text{PdI}_2\{\text{C}(\text{=NH}^t\text{Bu})\text{Ar}\}(\text{CN}^t\text{Bu})]$ (10**).** To a suspension of $\text{Pd}(\text{dba})_2$ (250 mg, 0.43 mmol) in toluene (10 mL) were successively added $^t\text{BuNC}$ (98 μL , 0.87 mmol) and *I*Ar (130.9 mg, 0.43 mmol) under nitrogen with a 10 min interval. After 2.5 h of stirring, the resulting suspension was filtered, and the brown solid was washed with toluene (3 $\times$ 3 mL) and stirred with CH_2Cl_2 (10 mL). The suspension was filtered through a short pad of Celite, the solution was concentrated to ca. 1 mL, and Et_2O (15 mL) was added to precipitate a yellow solid that was recrystallized from CH_2Cl_2 and Et_2O and suction dried. Yield: 84.7 mg, 28%. Mp: 184 °C (dec). ^1H NMR (300 MHz, CDCl_3): δ 1.49 (s, 9 H, ^tBu), 1.62 (s, 3 H, Me), 1.81 (s, 9 H, ^tBu), 1.95 (s, 3 H, Me), 4.99 (s, 1 H, CH), 6.89 (d, 1 H, Ar, $J_{\text{HH}} = 7$ Hz), 7.29–7.37 (m, 2 H, Ar), 8.83 (dd, 1 H, Ar, $J_{\text{HH}} = 8$ Hz, $J_{\text{HH}} = 2$ Hz), 11.04 (br, 1 H, NH^tBu), 11.94 (br, 1 H, NHAr). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 22.0 (*MeCN*), 28.1 (*C(O)Me*), 30.0 (Me, ^tBu), 30.1 (Me, ^tBu), 61.0 (*CMe*₃), 98.5 (C2), 126.9 (CH, Ar), 128.6 (CH, Ar), 130.0 (CH, Ar), 131.5 (C), 137.2 (CH, Ar), 139.2 (C), 163.4 (C1), 196.1 (CO). IR (cm^{-1}): $\nu_{\text{C=N}}$ 2202, $\nu_{\text{C=O}}$, $\nu_{\text{C=N}}$ 1600, 1590. Anal. Calcd for $\text{C}_{21}\text{H}_{31}\text{I}_2\text{N}_3\text{OPd}$: C, 35.94; H, 4.45; N, 5.99. Found: C, 36.06; H, 4.33; N, 5.97. Crystals of **10** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH_2Cl_2 and Et_2O .

Synthesis of $\text{trans-}[\text{PdI}\{\text{C}(\text{=NR})\text{Ar}\}(\text{CNR})_2]$ [R** = ^tBu (**11**), **Xy** (**12**)].** To a solution of **1** (mg/mmol for **11**: 220/0.32, for **12**: 132/0.19) in CH_2Cl_2 (20 mL) was added the appropriate RNC (R/ mL/mmol for **11**: ^tBu /0.18/1.59, R/mg/mmol for **12**: *Xy*/128.1/0.98). After 1 h of stirring, the solution was concentrated under vacuum (1 mL). Upon addition of *n*-pentane (**11**, 20 mL) or Et_2O (**12**, 20 mL), a yellow suspension formed. In the case of **11**, the suspension was stirred in an ice/water bath for 10 min and filtered. The yellow solid was washed with Et_2O (2 $\times$ 1 mL), recrystallized from CH_2Cl_2 /*n*-pentane, and suction dried. For **12** the suspension was filtered and the solid recrystallized from CH_2Cl_2 / Et_2O and suction dried to give **12** as a yellow solid.

11. Yield: 180 mg, 86%. Mp: 135 °C. ^1H NMR (300 MHz, CDCl_3): δ 1.48 (s, 18 H, ^tBu), 1.56 (s, 9 H, ^tBu), 1.93 (s, 3 H, *MeCN*), 2.04 (s, 3 H, *C(O)Me*), 5.14 (s, 1H, CH), 7.02–7.04 (m, 1 H, Ar), 7.18–7.25 (m, 2 H, Ar), 7.46–7.51 (m, 1 H, Ar), 11.96 (br, 1 H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3): δ 20.6 (*CNMe*), 29.2 (*MeC(O)*), 29.6 (Me, ^tBu), 30.7 (Me, ^tBu), 57.9 (*CMe*₃), 58.1 (*CMe*₃), 97.8 (C2), 125.3 (CH, Ar), 127.1 (CH, Ar), 127.2 (CH, Ar), 130.3 (CH, Ar), 132.8 (C), 139.2 (C), 159.6 (C1), 166.6 (*C=N* ^tBu), 194.6 (CO). IR (cm^{-1}): $\nu_{\text{C=N}}$ 2192, $\nu_{\text{C=O}}$, $\nu_{\text{C=N}}$ 1640–1574 br. Anal. Calcd for $\text{C}_{26}\text{H}_{39}\text{IN}_4\text{OPd}$: C, 47.54; H, 5.98; N, 8.53. Found: C, 47.51; H, 5.99; N, 8.69.

12. Yield: 138 mg, 91%. Mp: 162 °C (dec). ^1H NMR (400 MHz, CDCl_3): δ 1.93 (s, 3 H, *MeCN*), 1.95 (s, 3 H, *C(O)Me*), 2.16 (s, 6 H, Me, *Xy*), 2.23 (s, 12 H, Me, *Xy*), 5.19 (s, 1H, CH), 6.80–6.85 (m, 3 H), 6.99–7.07 (m, 4 H), 7.12–7.14 (m, 1 H), 7.18–7.24 (m, 2 H), 7.29–7.35 (m, 2 H), 8.11 (dd, 1 H, $J_{\text{HH}} = 8$ Hz, $J_{\text{HH}} = 2$ Hz), 12.64 (br, 1 H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 18.8 (Me, *Xy*), 19.0 (Me, *Xy*), 20.1 (*MeCN*), 29.1 (*C(O)Me*), 98.7 (C2), 123.3 (CH, Ar), 125.6 (CH, Ar), 126.9 (C), 127.1 (CH, Ar), 127.8 (CH, Ar), 127.9 (CH, Ar), 128.8 (CH, Ar), 129.9 (CH, Ar), 131.2 (CH, Ar), 135.1 (C), 135.7 (C), 135.8 (C), 141.1 (C), 150.0 (C), 155.2 (C), 159.1 (C1), 174.2 (*C=N* ^tBu), 195.6 (CO). IR (cm^{-1}): $\nu_{\text{C=N}}$ 2181 s, $\nu_{\text{C=O}}$, $\nu_{\text{C=N}}$ 1620–1556 br. Anal. Calcd for $\text{C}_{38}\text{H}_{39}\text{IN}_4\text{OPd}$: C, 56.98; H, 4.91; N, 6.99. Found: C, 57.01; H, 5.16; N, 7.08.

Synthesis of $[\text{Pd}\{\mu\text{-}N, \text{C}, N', O\text{-}N(\text{Xy})\}(\text{=CC}_6\text{H}_4\{\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{O}\}\text{-}2)]_2$ (13**).** To a solution of **5** (200 mg, 0.37 mmol) in acetone (20 mL) was added XyNC (48 mg, 0.37 mmol). After 2.5 h of stirring, the solution was filtered, and the solvent removed under vacuum to dryness. The residue was stirred with MeOH (20 mL)

at 0 °C for 15 min, the suspension was filtered, and the solid was suction dried and then in an oven at 80 °C for 4 h to give **13** as an orange solid. Yield: 98 mg, 63%. Mp: 242 °C (dec). ¹H NMR (300 MHz, CDCl₃): δ 1.70 (s, 3 H, C(O)Me), 1.97 (s, 3 H, Me, Xy), 2.12 (s, 3 H, MeCN), 2.69 (s, 3 H, Me, Xy), 4.92 (s, 1 H, CH), 5.96 (dd, 1 H, Ar, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 6.26 (t, 1 H, Ar, ³J_{HH} = 8 Hz), 6.74–7.07 (various m, 5 H, Ar). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 18.7 (Me, Xy), 19.0 (Me, Xy), 22.4 (MeCN), 26.1 (C(O)Me), 104.7 (C2), 120.1 (CH, Ar), 121.6 (CH, Ar), 123.6 (CH, Ar), 125.2 (CH, Ar), 127.8 (CH, Ar), 128.0 (CH, Ar), 129.4 (CH, Ar), 130.1 (C), 131.0 (C), 140.0 (C), 147.8 (C), 155.8 (C), 161.8 (C1), 183.4 (C=NXY), 207.8 (CO). IR (cm⁻¹): ν_{C=O}, ν_{C=N} 1565, 1563, 1550. Anal. Calcd for C₄₀H₄₀N₄O₂Pd₂: C, 58.48; H, 4.91; N, 6.82. Found: C, 58.76; H, 5.14; N, 6.69. (FAB⁺): (m/z, %) 820 (M⁺, 100) 410 (M⁺/2, 93). Crystals of **13** suitable for an X-ray diffraction study were obtained from CH₂Cl₂/MeOH by the liquid diffusion method.

Synthesis of [Pd{μ-N,C,N',O-N(Xy)}{=CC₆H₄[N=C(Me)-CH₂C(O)Me]-2}]₂(TfO)₂ (14a**).** To a solution of **13** (150 mg, 0.17 mmol) in CH₂Cl₂ (7 mL) was added an excess of HTfO (0.1 mL, 1.13 mmol). After 1.5 h of stirring, the solution was concentrated under vacuum to dryness. The residue was stirred with Et₂O (5 mL), and the suspension was filtered. The solid was washed with Et₂O (3 × 3 mL), suction dried, and heated in an oven at 80 °C for 4 h to give **14a**·2H₂O as a pale yellow solid. Yield: 192.5 mg, 99%. Mp: 181 °C (dec). ¹H NMR (300 MHz, acetone-*d*₆): δ 1.81 (s, 3 H, Me, Xy), 2.36 (s, 3 H, C(O)Me), 2.65 (s, 3 H, MeCN), 2.74 (s, 3 H, Me, Xy), 3.35 (br, 4 H, H₂O), 4.79, 5.11 (AB system, 2 H, CH₂, J_{AB} = 20 Hz), 6.43 (d, 1 H, Ar, ³J_{HH} = 8 Hz), 6.95–7.00 (m, 2 H, Ar), 7.13–7.26 (m, 2 H, Ar), 7.42 (t, 1 H, Ar, ³J_{HH} = 8 Hz), 7.55 (m, 1 H, Ar). ¹³C{¹H} NMR (75 MHz, acetone-*d*₆): δ 18.4 (Me, Xy), 19.0 (Me, Xy), 24.8 (MeCN), 31.5 (C(O)Me), 56.7 (CH₂), 123.4 (CH, Ar), 124.6 (CH, Ar), 128.1 (CH, Ar), 129.1 (CH, Ar), 129.5 (CH, Ar), 129.8 (CH, Ar), 130.3 (C), 131.9 (C), 132.4 (CH, Ar), 141.7 (C), 146.5 (C), 151.8 (C), 178.3 (C1) 200.5 (C=NXY), 209.9 (CO). IR (cm⁻¹): ν_{C=O}, ν_{C=N} 1672, 1592, 1578, 1557. Λ_M (Ω⁻¹ cm² mol⁻¹): 264.9. Anal. Calcd for C₄₂H₄₆F₆N₄O₁₀Pd₂S₂: C, 43.57; H, 4.00; N, 4.84; S, 5.54. Found: C, 43.69; H, 3.86; N, 4.98; S, 5.11. Crystals of **14a**·Et₂O·Me₂CO and **14b** suitable for X-ray diffraction studies were obtained from acetone and Et₂O by the liquid diffusion method.

Synthesis of [Pd{C,N,O-C(=NXY)C₆H₄[NC(Me)CHC(Me)O]-2}(L)] [L = PPh₃ (15**), 'BuNC (**16a**)].** To a solution of **13** (mg/mmol for **15**: 90/0.10, for **16a**: 200/0.23) in degassed CHCl₃ (20 mL) was added the appropriate ligand (L/mg/mmol for **15**: PPh₃/55/0.21; L/μL/mmol for **16a**: 'BuNC/65/0.58). The resulting solution was refluxed under nitrogen atmosphere (**15**, 10.5 h) or heated in a Carius tube (**16a**, at 65 °C, 9 h), and then the solvent was removed under vacuum. For **15**, the oily residue was stirred with *n*-pentane (3 × 2 mL) at 0 °C until a solid formed that was filtered off, suction dried, and then heated in an oven at 80 °C for 4 h to give **15**. In the case of **16a** the residue was dissolved in Et₂O (20 mL), the solution was filtered through a short pad of Celite, the filtrate was concentrated under vacuum to dryness, and the residue was stirred with *n*-pentane (2 mL) at 0 °C for 15 min. The suspension was filtered and the yellow solid collected and washed with *n*-pentane (2 × 2 mL) and suction dried to give **16a**·H₂O, which could not be dehydrated even after heating in an oven at 80 °C for 4 h.

15. Yield: 82 mg, 58%. Mp: 199 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.46 (s, 6 H, Me, Xy), 1.76 (s, 3 H, C(O)Me), 2.27 (s, 3 H, MeCN), 5.01 (s, 1 H, CH), 6.41 (d, 2 H, ³J_{HH} = 4 Hz), 6.61 (m, 1 H), 6.71 (s, 1 H), 6.72 (s, 1 H), 6.98 (m, 2 H), 7.28–7.38 (m, 9 H), 7.71 (m, 6 H). ¹³C{¹H} (75 MHz, CDCl₃): δ 18.1 (Me, Xy), 23.3 (d, MeCN, ⁴J_{CP} = 5 Hz), 26.9 (C(O)Me), 103.3 (C2), 120.7 (d, CH, Ar, ⁴J_{CP} = 3 Hz), 120.8 (CH, Ar), 122.0 (CH, Ar), 124.6 (CH, Ar), 124.7 (CMe, Xy), 127.3 (*meta*-CH, Xy), 127.8 (d, *meta*-CH, PPh₃, ³J_{CP} = 10 Hz), 128.6 (CH, Ar), 129.9 (d, *para*-

CH, PPh₃, ⁴J_{CP} = 2 Hz), 131.8 (d, *ipso*-C, PPh₃, ¹J_{CP} = 46 Hz), 134.9 (d, *ortho*-CH, PPh₃, ²J_{CP} = 12 Hz), 140.2 (C), 150.5 (d, C, J_{CP} = 8 Hz), 153.8 (C), 162.8 (C1), 179.0 (d, C = NXY, ²J_{CP} = 5 Hz), 182.3 (CO). ³¹P{¹H} (121 MHz, CDCl₃): δ 31.15. IR (cm⁻¹): ν_{C=O}, ν_{C=N}, ν_{C=C} 1611, 1589, 1557, 1415. Anal. Calcd for C₃₈H₃₅N₂O₂OPd: C, 67.81; H, 5.24; N, 4.16. Found: C, 67.41; H, 5.63; N, 4.03.

16a·H₂O. Yield: 136.8 mg, 60%. Mp: 197 °C (dec). ¹H NMR (200 MHz, CDCl₃): δ 1.22 (s, 9 H, 'Bu), 1.57 (br, 2 H, H₂O), 1.95 (s, 3 H, C(O)Me), 2.17 (s, 6 H, Me, Xy), 2.33 (s, 3 H, MeCN), 5.01 (s, 1 H, CH), 6.85–6.99 (m, 4 H, Ar), 7.09–7.21 (m, 2 H, Ar), 7.98 (dd, 1 H, Ar, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 19.4 (Me, Xy), 24.3 (MeCN), 27.4 (C(O)Me), 29.9 (CMe₃), 56.6 (CMe₃), 102.8 (C2), 120.4 (CH, Ar), 122.3 (CH, Ar), 123.0 (CH, Ar), 125.2 (CH, Ar), 126.9 (*ortho*-C, Xy), 127.6 (*meta*-CH, Xy), 129.8 (CH, Ar), 142.3 (C), 152.9 (*ipso*-C, Xy), 154.8 (C), 163.2 (C1), 178.4 (C=NXY), 182.8 (CO). IR (cm⁻¹): ν_{C=N} 2199, ν_{C=O}, ν_{C=N}, ν_{C=C} 1628, 1583, 1562. Anal. Calcd for C₂₅H₃₁N₃O₃Pd: C, 58.65; H, 6.10; N, 8.21. Found: C, 58.82; H, 6.25; N, 8.17.

Synthesis of [Pd{C,N,O-C(=N^tBu)C₆H₄[NC(Me)CHC(Me)O]-2}(CN^tBu)] (16b**).** To a solution of **21** (60 mg, 0.11 mmol) in acetone (20 mL) was added Na₂CO₃ (7 mg, 0.07 mmol). The resulting suspension was stirred at room temperature for 5 h and then concentrated to dryness under vacuum. The residue was stirred with Et₂O (2 × 10 mL), and the suspension was filtered. The solution was concentrated under vacuum to dryness to give **16b** as a yellow solid. Yield: 49 mg, 100%. Mp: 206 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.47 (s, 9 H, 'Bu), 1.53 (s, 9 H, 'Bu), 1.98 (s, 3 H, C(O)Me), 2.18 (s, 3 H, MeCN), 4.96 (s, 1 H, CH), 6.73 (t, 1 H, ³J_{HH} = 7 Hz), 6.86 (d, 2 H, ³J_{HH} = 8 Hz), 7.02 (t, 1 H, ³J_{HH} = 7 Hz), 7.49 (d, 1 H, ³J_{HH} = 8 Hz). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 22.8 (MeCN), 27.3 (C(O)Me), 30.0 (Me, 'Bu), 31.1 (Me, 'Bu), 54.9 (CMe₃), 102.8 (C2), 119.2 (CH, Ar), 122.9 (CH, Ar), 124.9 (CH, Ar), 128.6 (CH, Ar), 146.3 (C), 152.4 (C), 162.9 (C1), 167.7 (C=N^tBu), 182.1 (CO). IR (cm⁻¹): ν_{C=N} 2186, ν_{C=O}, ν_{C=N}, ν_{C=C} 1615, 1579–1541 (br). Anal. Calcd for C₂₁H₂₉N₃OPd: C, 56.57; H, 6.56; N, 9.42. Found: C, 56.20; H, 6.80; N, 9.39.

Synthesis of [Pd{C,N,O-C(=NXY)C₆H₄[NC(Me)CHC(Me)O]-2}(CNXY)] (17**).** To a solution of **2** (120 mg, 0.22 mmol) in CH₂Cl₂ (20 mL) was added XyNC (57.1 mg, 0.44 mmol). After 15 h of stirring, the solution was concentrated under vacuum to dryness. The residue was stirred with *n*-hexane (20 mL), and the white suspension was filtered to remove (H₂tmeda)I₂. The filtrate was concentrated under vacuum to dryness, and the residue was stirred with *n*-hexane (2 × 1.5 mL) at –30 °C. The suspension was filtered, and the solid was suction dried to give **17** as an orange solid. Yield: 104.2 mg, 84%. Mp: 190 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 1.95 (s, 3 H, C(O)Me), 2.21 (s, 6 H, Me, Xy), 2.22 (s, 6 H, Me, Xy), 2.35 (s, 3 H, MeCN), 5.04 (s, 1 H, CH), 6.26 (t, 1 H, ³J_{HH} = 8 Hz), 6.72 (d, 2 H, ³J_{HH} = 8 Hz), 6.92 (t, 1 H, ³J_{HH} = 7 Hz), 6.98 (d, 2 H, ³J_{HH} = 8 Hz), 7.13 (m, 2 H), 7.20 (td, 1 H, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz), 8.02 (dd, 1 H, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1.5 Hz). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 18.5 (Me, Xy), 19.4 (Me, Xy), 24.2 (MeCN), 27.3 (C(O)Me), 103.0 (C2), 120.5 (CH, Ar), 122.8 (CH, Ar), 123.2 (CH, Ar), 125.3 (CH, Ar), 126.7 (*ipso*-C, Xy), 127.3 (*meta*-CH, Xy), 127.3 (*meta*-CH, Xy), 128.7 (CH, Ar), 129.9 (CH, Ar), 134.4 (*ipso*-C, Xy), 141.9 (C), 153.0 (C), 154.8 (C), 163.3 (C1), 178.2 (C=NXY), 182.9 (CO). IR (cm⁻¹): ν_{C=N} 2170, ν_{C=O}, ν_{C=N}, ν_{C=C} 1633, 1556, 1520. Anal. Calcd for C₂₉H₂₉N₃OPd: C, 64.27; H, 5.39; N, 7.75. Found: C, 63.92; H, 5.47; N, 7.67. Crystals of **17** suitable for an X-ray diffraction study grew upon cooling a solution of the crude product in a mixture of Et₂O/*n*-hexane (1:1) at 4 °C.

Synthesis of [Pd{C,N,O-C(=NHXY)C₆H₄[N=C(Me)CH₂C(O)Me]-2}(PPh₃)](TfO)₂ (18**).** To a solution of **15** (60 mg, 0.09 mmol) in CH₂Cl₂ (5 mL) was added HTfO (0.1 mL, 1.13 mmol). After 3 h

of stirring, the solution was concentrated under vacuum to dryness. The residue was washed with Et₂O (3 × 5 mL, at 0 °C), recrystallized with CH₂Cl₂ and *n*-pentane at 0 °C, filtered under nitrogen, and dried by suction for 4 h to give **18**·2H₂O. Yield: 59.1 mg, 65%. Mp: 101 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.73 (s, 6 H, Me, Xy), 2.24 (s, 3 H, C(O)Me), 2.71 (s, 3 H, MeCN), 4.33 (br, 4 H, H₂O), 4.88 (br, 2 H, CH₂), 6.43 (d, 1 H, Ar, ³J_{HH} = 7 Hz), 6.94–6.98 (m, 3 H, Ar), 7.18 (t, 1 H, ³J_{HH} = 7 Hz), 7.56–7.85 (m, 17 H, Ar), 8.98 (br, 1 H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 17.9 (Me, Xy), 24.6 (MeCN), 30.9 (C(O)Me), 56.3 (CH₂), 120.42 (q, TFO, ¹J_{CF} = 317 Hz), 124.6 (CH, Ar), 129.6 (CH, Ar), 129.7 (CH, Ar), 130.0 (d, *meta*-CH, PPh₃, ³J_{CP} = 11 Hz), 130.5 (CH, Ar), 132.7 (CH, Ar), 133.4 (*para*-CH, PPh₃), 134.9 (d, *ortho*-CH, PPh₃, ²J_{CP} = 12 Hz), 136.5 (CH, Ar), 148.3 (C), 153.1 (C), 180.2 (C1), 191.5 (C=NXY), 216.8 (CO). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 33.9. IR (cm⁻¹): ν_{C=O}, ν_{C=N}, ν_{C=C} 1660–1515 br. Λ_M (Ω⁻¹ cm² mol⁻¹): 241.5. Anal. Calcd for C₄₀H₄₁F₆N₂O₉PPdS₂: C, 47.60; H, 4.09; N, 2.78; S, 6.35. Found: C, 47.24; H, 3.99; N, 2.70; S, 6.47.

Synthesis of [Pd{C,N,O-C(=NHXY)C₆H₄{NC(Me)CHC(O)Me}-2}(L)]TfO [BuNC (19), XyNC (20)]. To a solution of **16a** (for **19**: 100 mg, 0.20 mmol) or **17** (for **20**: 85 mg, 0.16 mmol) in CH₂Cl₂ (5 mL) was added HTfO (0.1 mL, 1.13 mmol). After 1 (**19**) or 3 h (**20**) of stirring, the solution was concentrated under vacuum to dryness. The residue was stirred with Et₂O (2 mL) at 0 °C for 15 min, and the resulting suspension was filtered. The solid collected was washed with Et₂O (3 × 3 mL) and suction dried to give an orange solid. Additionally, **19** was heated in an oven at 80 °C for 4 h.

19. Yield: 90.8 mg, 73%. Mp: 192 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 1.27 (s, 9 H, 'Bu), 1.98 (s, 3 H, C(O)Me), 2.35 (s, 3 H, MeCN), 2.45 (s, 6 H, Me, Xy), 5.13 (s, 1 H, CH), 6.99–7.17 (m, 4 H, Ar), 7.26–7.32 (m, 1 H, Ar), 7.42 (t, 1H, ³J_{HH} = 8 Hz), 8.22 (d, 1 H, ³J_{HH} = 8 Hz), 12.23 (s, 1 H, NH). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 18.9 (Me, Xy), 24.0 (MeCN), 26.3 (C(O)Me), 29.8 (Me, 'Bu), 58.5 (CMe₃), 105.0 (C2), 120.3 (q, TFO, ¹J_{CF} = 319 Hz), 121.1 (CH), 124.9 (CH), 125.7 (CH), 128.5 (*meta*-CH, Xy), 129.4 (CH), 134.7 (C), 135.8 (CH), 136.7 (C), 141.1 (C), 158.0 (C), 163.5 (C1), 183.3 (C=NXY), 216.4 (CO). IR (cm⁻¹): ν_{C=N} 2212, ν_{C=O}, ν_{C=N}, ν_{C=C} 1569, 1544, 1524. Λ_M (Ω⁻¹ cm² mol⁻¹): 165.3. Anal. Calcd for C₂₆H₃₀F₃N₃O₄PdS: C, 48.49; H, 4.70; N, 6.52; S, 4.98. Found: C, 48.94; H, 4.85; N, 6.61; S, 5.10.

20. Yield: 86.5 mg, 80%. Mp: 186 °C (dec). ¹H NMR (300 MHz, CDCl₃): δ 1.98 (s, 3 H, C(O)Me), 2.21 (s, 6 H, Me, Xy), 2.39 (s, 3 H, MeCN), 2.50 (s, 6 H, Me, Xy), 5.18 (s, 1H, CH), 6.63 (t, 1 H, ³J_{HH} = 8 Hz), 6.88 (d, 2 H, ³J_{HH} = 7 Hz), 7.06–7.11 (m, 4 H), 7.22–7.27 (m, 1 H), 7.46 (m, 1 H), 8.27 (d, 1 H, ³J_{HH} = 7 Hz), 12.4 (br, 1 H, NH). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 18.4 (Me, Xy), 19.0 (Me, Xy), 24.0 (MeCN), 26.1 (C(O)Me), 105.3 (C2), 120.3 (q, TFO, ¹J_{CF} = 319 Hz), 121.3 (CH), 125.2 (CH), 126.0 (CH), 128.0 (*meta*-CH, Xy), 128.3 (*meta*-CH, Xy), 129.7 (CH), 130.2 (CH), 134.6 (*ortho*-C, Xy), 134.7 (*ortho*-C, Xy), 136.1 (CH), 136.5 (C), 140.9 (C), 158.2 (C), 163.7 (C1), 183.3 (C=NXY), 216.6 (CO). IR (cm⁻¹): ν_{C=N} 2207, ν_{C=O}, ν_{C=N}, ν_{C=C} 1589, 1563, 1545, 1520. Λ_M (Ω⁻¹ cm² mol⁻¹): 142.7. Anal. Calcd for C₃₀H₃₀F₃N₃O₄PdS: C, 52.07; H, 4.37; N, 6.07; S, 4.63. Found: C, 51.63; H, 4.64; N, 5.98; S, 4.72.

Synthesis of [Pd{C,N,O-C(=NHR)C₆H₄{NC(Me)CHC(Me)O}-2}(CNR)]ClO₄ [R = 'Bu (21), Xy (22)]. To a solution of **11** (for **21**: 60 mg, 0.07 mmol) or **12** (for **22**: 60 mg, 0.08 mmol) in acetone (5 mL) was added 1 equiv of AgClO₄·H₂O. The resulting suspension was stirred for 30 min, and the solvent was removed under vacuum to dryness. The residue was stirred with CH₂Cl₂ (10 mL) for 10 min, and the suspension was filtered through a short pad of Celite. The red filtrate was concentrated to ca. 1 mL, and Et₂O (20 mL) was added to precipitate an orange-red solid, which was recrystallized from CH₂Cl₂/Et₂O (three times for **21**, twice for

22) and suction dried to give **21**·H₂O or **22**·H₂O. After heating in an oven at 80 °C for 6 h, **21** decomposed and **22** did not dehydrate.

21·H₂O. Yield: 29.6 mg, 74%. Mp: 137 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 1.61 (s, 9 H, 'Bu), 1.64 (s, 3 H, H₂O), 1.81 (s, 9 H, 'Bu), 2.04 (s, 3 H, C(O)Me), 2.27 (s, 3 H, MeCN), 5.15 (s, 1 H, CH), 6.91 (d, 1 H, ³J_{HH} = 8 Hz), 7.04 (td, 1 H, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 7.33 (td, 1 H, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 7.88 (d, 1 H, ³J_{HH} = 8 Hz), 9.73 (br, 1 H, NH). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 23.0 (MeCN), 25.8 (C(O)Me), 29.7 (Me, 'Bu), 30.3 (Me, 'Bu), 59.7 (CMe₃), 60.1 (CMe₃), 105.4 (C2), 120.1 (CH, Ar), 124.2 (CH, Ar), 125.1 (CH, Ar), 134.7 (CH, Ar), 140.7 (C), 154.2 (C), 162.9 (C1), 181.8 (C=N'Bu), 215.6 (CO). IR (cm⁻¹): ν_{C=N} 2204. Λ_M (Ω⁻¹ cm² mol⁻¹): 163.3. Anal. Calcd for C₂₁H₃₂ClN₃O₆Pd: C, 44.69; H, 5.72; N, 7.45. Found: C, 44.99; H, 5.85; N, 7.65. Crystals of **21** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH₂Cl₂ and Et₂O.

22·H₂O. Yield: 33 mg, 68%. Mp: 280 °C (dec). ¹H NMR (300 MHz, CDCl₃): δ 1.63 (br, 2 H, H₂O), 1.98 (s, 3 H, C(O)Me), 2.20 (s, 6 H, Me, Xy), 2.38 (s, 3 H, MeCN), 2.50 (s, 6 H, Me, Xy), 5.19 (s, 1 H, CH), 6.63 (t, 1 H, ³J_{HH} = 8 Hz), 6.89 (d, 2 H, ³J_{HH} = 8 Hz), 7.05–7.30 (m, 5 H), 7.48 (td, 1 H, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz), 8.23 (d, 1 H, ³J_{HH} = 8 Hz), 11.78 (br, 1 H, NH). ¹³C{¹H} NMR (300 MHz, CDCl₃): δ 18.4 (Me, Xy), 19.1 (Me, Xy), 24.1 (MeCN), 26.1 (C(O)Me), 105.3 (C2), 121.4 (CH, Ar), 125.5 (CH, Ar), 125.6 (CH, Ar), 127.9 (CH, Ar), 128.3 (CH, Ar), 129.9 (CH, Ar), 130.3 (CH, Ar), 134.6 (*ortho*-C, Xy), 134.7 (*ortho*-C, Xy), 136.4 (CH, Ar), 140.7 (C), 163.7 (C1), 183.3 (C=NXY), 217.1 (CO). IR (cm⁻¹): ν_{C=N} 2204 s. Λ_M (Ω⁻¹ cm² mol⁻¹): 170.5. Anal. Calcd for C₂₉H₃₂ClN₃O₆Pd: C, 52.74; H, 4.89; N, 6.36. Found: C, 52.79; H, 4.78; N, 6.45. Crystals of **22**·CHCl₃ suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CHCl₃ and Et₂O.

Synthesis of [Pd{C,N,O-C(=NHXY)C₆H₄{NC(Me)CHC(Me)O}-2}PPh₃]TfO (23). To a solution of **14a** (150 mg, 0.13 mmol) in degassed CHCl₃ (20 mL) was added PPh₃ (81.6 mg, 0.31 mmol), and the solution was stirred in a Carius tube at 65 °C for 10 h. The solution was concentrated under vacuum to ca. 1 mL, and Et₂O (20 mL) was added. The collected solid was recrystallized from CH₂Cl₂ and Et₂O and dried in an oven at 80 °C for 24 h. Yield: 124 mg, 58%. Mp: 114 (dec) °C. ¹H NMR (300 MHz, CDCl₃): δ 1.66 (s, 3 H, C(O)Me), 1.79 (s, 6 H, Me, Xy), 2.34 (s, 3H, MeCN), 5.18 (s, 1 H, CH), 6.17 (d, 1 H, ³J_{HH} = 8 Hz), 6.51 (t, 1 H, ³J_{HH} = 8 Hz), 6.98 (d, 2 H, ³J_{HH} = 8 Hz), 7.07 (d, 1 H, ³J_{HH} = 8 Hz), 7.16 (t, 1 H, ³J_{HH} = 8 Hz), 7.33 (t, 1 H, ³J_{HH} = 8 Hz), 7.53–7.71 (m, 15 H, PPh₃), 9.08 (br, 1 H, NH). ¹³C{¹H} (50 MHz, CDCl₃): δ 18.1 (Me, Xy), 23.4 (d, MeCN, ⁴J_{CP} = 6 Hz), 25.8 (C(O)Me), 106.1 (C2), 121.9 (d, CH, Ar, ⁴J_{CP} = 3 Hz), 123.4 (CH, Ar), 125.2 (CH, Ar), 126.3 (d, *ipso*-C, PPh₃, ¹J_{CP} = 50 Hz), 129.4 (CH, Ar), 129.5 (d, *meta*-CH, PPh₃, ³J_{CP} = 11 Hz), 129.9 (CH, Ar), 132.2 (CMe, Xy), 132.6 (d, *para*-CH, PPh₃, ⁴J_{CP} = 3 Hz), 134.8 (d, *ortho*-CH, PPh₃, ²J_{CP} = 12 Hz), 136.1 (CH, Ar), 136.7 (C), 137.5 (d, C, ¹J_{CP} = 1 Hz), 158.4 (C), 164.1 (C1), 182.9 (C=NXY), 223.0 (d, CO, ³J_{CP} = 8 Hz). ³¹P{¹H} (121 MHz, CDCl₃): δ 35.1. IR (cm⁻¹): ν_{C=O}, ν_{C=N}, ν_{C=C} 1584, 1548, 1516. Λ_M (Ω⁻¹ cm² mol⁻¹): 163.5. Anal. Calcd for C₃₉H₃₆F₃N₂O₄PPdS: C, 56.90; H, 4.41; N, 3.40; S, 3.90. Found: C, 56.90; H, 4.74; N, 3.44; S, 3.84.

Synthesis of trans-[PdI₂{C(=NXY)C(Me){CH₂C(O)Me}NH-C₆H₄-2}(CNXY)] (24). To a solution of **1** (140 mg, 0.21 mmol) and CH₂Cl₂ (15 mL) were successively added HI (28 μL, 0.21 mmol) and XyNC (54.3 mg, 0.42 mmol). After being stirred for 3.5 h the solution was concentrated under vacuum to dryness. The residue was stirred with Et₂O (2 mL), and the suspension was filtered. The solid collected was suction dried to give **24** as a yellow solid. Yield: 144.1 mg, 87%. Mp: 195 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 1.50 (s, 3 H, MeCN), 2.06 (s, 3 H, C(O)Me), 2.45 (s, 6 H, Me, Xy), 2.48 (s, 3 H, Me, Xy), 2.75 (s, 3 H, Me, Xy), 2.86, 3.84 (AB, 2 H, CH₂, J_{AB} = 18 Hz), 5.70 (s, 1 H, NH),

Table 1. Crystal Data and Structure Refinement of Complexes 1·0.5Et₂O, 3·0.89CH₂Cl₂·0.55Et₂O, 5, 10, and 13

	1·1/2Et ₂ O	3·0.89CH ₂ Cl ₂ ·0.55Et ₂ O	5	7·2CH ₂ Cl ₂	10	13
formula	C ₃₁ H ₄₁ IN ₃ O _{1.5} Pd	C _{50.12} H _{49.34} Cl _{1.77} INO _{1.55} P ₂ Pd	C ₁₈ H ₂₈ F ₃ N ₃ O ₄ PdS	C ₃₈ H ₄₇ Cl ₄ F ₃ N ₃ O ₄ PPdS	C ₂₁ H ₃₁ I ₂ N ₃ OPd	C ₄₀ H ₄₀ N ₄ O ₂ Pd ₂
fw	712.97	1048.67	545.89	978.02	701.69	821.56
temperature (K)	133(2)	100(2)	133(2)	133(2)	153(2)	298(2)
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic	triclinic	orthorhombic
space group	C2/c	P $\bar{1}$	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P $\bar{1}$	Pbca
a (Å)	28.5877(18)	12.1163(5)	12.8466(11)	17.7886(18)	10.0442(8)	19.0732(12)
b (Å)	10.1558(6)	13.7556(6)	12.9925(11)	13.7537(13)	10.8695(9)	15.3618(11)
c (Å)	21.7712(14)	15.5580(7)	13.6154(11)	35.728(4)	13.2366(11)	24.6074(16)
α (deg)	90	87.638(2)	90	90	111.027(2)	90
β (deg)	91.275(4)	80.440(2)	90	98.698(4)	92.493(2)	90
γ (deg)	90	64.323(2)	90	90	106.846(2)	90
volume (Å ³)	6319.3(7)	2303.11(17)	2272.5(3)	8640.7(15)	1273.28(18)	7209.9(8)
Z	8	2	4	8	2	8
ρ _{calcd} (Mg m ⁻³)	1.499	1.512	1.596	1.504	1.830	1.514
μ(Mo Kα) (mm ⁻¹)	1.593	1.284	0.961	0.817	3.169	1.037
F(000)	2872	1057	1112	4000	676	3328
cryst size (mm)	0.14 × 0.07 × 0.07	0.15 × 0.07 × 0.05	0.18 × 0.10 × 0.10	0.4 × 0.4 × 0.12	0.14 × 0.12 × 0.03	0.24 × 0.13 × 0.08
θ range (deg)	1.87 to 28.70	1.64 to 28.23	2.17 to 30.51	1.15 to 25.03	1.67 to 28.70	1.66 to 26.37
no. of rflns coll	60 040	26 727	45 144	102 372	14 479	75 487
no. of indep rflns/R _{int}	8157/0.046	10 315/0.037	6937/0.072	15 260/0.127	6424/0.062	7371/0.052
transmissn	0.897–0.760	0.939–0.831	no abs corr	0.908–0.439	0.896–0.594	0.922–0.789
no. of restraints/params	60/328	0/549	0/281	819/995	1/269	0/441
goodness-of-fit on F ²	1.02	1.05	0.98	1.21	0.98	1.38
R ₁ (I > 2σ(I))	0.0298	0.0424	0.0313	0.114	0.0434	0.0519
wR ₂ (all rflns)	0.0706	0.0887	0.0662	0.253	0.0721	0.104
largest diff peak/hole (e Å ⁻³)	0.81/−0.35	1.10/−0.60	0.72/−0.43	2.16/−3.63	0.96/−0.95	0.69/−0.64

6.65 (d, 1 H, Ar, ³J_{HH} = 8 Hz), 6.98–7.08 (m, 3 H, Ar), 7.13–7.20 (m, 3 H, Ar), 7.25–7.29 (m, 1 H, Ar), 7.36 (m, 1 H, Ar), 8.85 (d, 1 H, Ar, ³J_{HH} = 8 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 19.1 (Me), 23.3 (Me), 23.4 (Me), 23.6 (Me), 31.7 (Me), 47.1 (CH₂), 74.1 (C1), 114.8 (CH), 119.6 (CH, Ar), 127.8 (*meta*-CH, Xy), 128.5 (C), 129.0 (CH, Ar), 129.5 (CH, Ar), 129.6 (CH, Ar), 130.0 (CH, Ar), 134.9 (C), 136.4 (CH, Ar), 136.5 (C), 137.6 (C), 139.5 (C), 142.2 (CH, Ar), 142.4 (C), 206.5 (CO), 219.2 (CPd). IR (cm⁻¹): ν_{NH} 3348, 3286; ν_{C=O}, ν_{C=C} 1614.2, 1570.9, 1562.3, 1518.0. Anal. Calcd for C₂₉H₃₁I₂N₃OPd: C, 43.66; H, 3.92; N, 5.27. Found: C, 43.42; H, 4.10; N, 5.20. Crystals of **24** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH₂Cl₂ and Et₂O.

Synthesis of *trans*-[PdI₂{C(=NXy)C(Me){CH₂C(O)Me}NH-C₆H₄-2](PPh₃)] (25). To a solution of **3** (250 mg, 0.27 mmol) in CH₂Cl₂ (20 mL) were successively added HI (57%, 36 μL, 0.27 mmol) and XyNC (35 mg, 0.27 mmol). After 6 h of stirring the solution was concentrated under vacuum to ca. 1 mL and Et₂O (20 mL) was added. The suspension was stirred at 0 °C for 15 min and filtered. The orange solid was collected, washed with Et₂O (3 × 3 mL), and dried by suction and then in an oven at 80 °C for 4 h to give **25**·H₂O. Yield: 135.4 mg, 53%. Mp: 212 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 1.50 (s, 3 H, *Me*CN), 1.56 (s, 2 H, H₂O), 2.02 (s, 3 H, C(O)*Me*), 2.51 (s, 3 H, Me, Xy), 2.75 (s, 3 H, Me, Xy), 2.85, 3.91 (AB, 2 H, CH₂, J_{AB} = 18 Hz), 5.64 (s, 1 H, NH), 6.62 (d, 1 H, ³J_{HH} = 8 Hz), 6.97 (d, 1 H, ³J_{HH} = 8 Hz), 7.29–7.45 (m, 19 H), 8.62 (d, 1 H, ³J_{HH} = 7 Hz). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 23.3 (*Me*CN), 23.8 (Me, Xy), 23.9 (Me, Xy), 31.7 (C(O)*Me*), 47.1 (CH₂), 74.2 (d, C1, ²J_{CP} = 6 Hz), 114.7 (CH, Ar), 119.7 (CH, Ar), 127.5 (d, *meta*-CH, PPh₃, ³J_{CP} = 10 Hz), 128.4 (d, C, ³J_{CP} = 4 Hz), 128.9 (CH, Ar), 129.6 (CH, Ar), 129.7 (d, *para*-C, PPh₃, ⁴J_{CP} = 2 Hz), 130.1 (CH, Ar), 133.2 (d, *ipso*-C, PPh₃, ¹J_{CP} = 43 Hz), 135.0 (d, *ortho*-CH, ²J_{CP} = 11 Hz), 135.3 (C), 136.1 (CH, Ar), 138.4 (C, Ar), 139.3 (d, C, J_{CP} = 5 Hz), 141.7 (d, C, J_{CP} = 3 Hz), 142.8 (CH, Ar), 206.7 (CO), 221.4 (d, CPd, ²J_{CP} = 174 Hz). ³¹P{¹H} (121 MHz, CDCl₃): δ 14.5. IR (cm⁻¹): ν_{NH} 3385; ν_{C=O}, ν_{C=C} 1614, 1568, 1514. Anal. Calcd for C₃₈H₃₉I₂N₂O₂PPd: C, 48.20; H, 4.15; N, 2.96. Found: C, 48.13; H, 3.85; N, 2.99.

X-ray Structure Determinations of Complexes 1, 3, 5, 7, 10, 13, 14a, 14b, 17, 21, 22, and 24. For clarity, solvent contents are

omitted here, but are defined in Tables 1 and 2. Figures 1–12 show the ellipsoid representations.

Complexes **3**, **13**, and **17** were measured on a Bruker Smart APEX diffractometer. Data were collected using monochromated Mo Kα radiation in ω scan mode. Other structures were measured on a Bruker Smart 1000 diffractometer in ω and φ scan modes. Absorption corrections were applied on the basis of multiscans (program SADABS). All structures were refined anisotropically on F². The NH hydrogens were refined freely, the ordered methyl groups were refined using rigid groups (AFIX 137), and the other hydrogens were refined using a riding model. *Special features and exceptions:* Complex **1**: A substantial region of electron density, presumably disordered solvent, could not be assigned satisfactorily. The effects of this solvent were therefore removed mathematically using the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands). A notional amount of 4 diethyl ether per cell (half per asymmetric unit) was added to the formula; molar mass and other derived parameters were adjusted accordingly. Complex **3**: The solvent sites were refined as superpositions of dichloromethane and Et₂O. Complex **5**: The Flack parameter refined to −0.03(2); the compound crystallizes by chance in a chiral space group. No absorption correction was applied. Complex **7**: The crystal quality was poor (the asymmetric unit contains four dichloromethane molecules and diffraction is accordingly weak). Nonetheless, the structure could be unambiguously established despite the poor R values. Methyl hydrogens (except those at C10 and C11) were included using a riding model assuming perfect staggering (AFIX 33). NH hydrogens were included using a riding model assuming planarity at nitrogen (AFIX 43). Complex **10**: The absorption correction was numerical, based on face-indexing. Complex **14a**: The acetone molecule is well resolved, but the ether only moderately resolved; its methyl H's were included using AFIX 33. Complex **14b**: H atoms at C5 and C10 were refined freely. There is no evidence for disorder involving mutually alternative sites for these groups. The methyl hydrogens at C37 are poorly resolved, and the group may be rotationally disordered. The triflate is disordered over two sites with occupation 55:45. The acetone is disordered over a 2-fold axis; its H atoms were not included in the refinement. Complex **21**: Both perchlorates are disordered over two sites (ca. 7:3 and 1:1, respectively), each by rotation about one Cl–O bond. The butyl group at C18' is disordered over two sites (ca. 3:1).

Table 2. Crystal Data and Structure Refinement of Complexes 14a, 14b, 17, 21, 22, and 24

	14a • Et ₂ O • Me ₂ CO	14b • 1/2 Me ₂ CO	17	21	22 • CHCl ₃	24
formula	C ₄₉ H ₅₈ F ₆ N ₄ O ₁₀ Pd ₂ S ₂	C _{42.5} H ₄₄ F ₃ N ₄ O _{5.5} Pd ₂ S	C ₂₉ H ₂₉ N ₃ OPd	C ₂₁ H ₃₀ ClN ₃ O ₃ Pd	C ₃₀ H ₃₁ Cl ₄ N ₃ O ₃ Pd	C ₂₉ H ₃₁ I ₂ N ₃ OPd
fw	1253.91	1000.68	541.95	546.33	761.78	797.77
temperature (K)	133(2)	133(2)	100(2)	133(2)	133(2)	133(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	15.7388(11)	30.039(3)	11.0431(5)	13.9120(11)	7.5612(3)	9.8875(2)
<i>b</i> (Å)	20.4783(12)	13.873(2)	15.1683(6)	23.1974(16)	15.6521(6)	19.6683(4)
<i>c</i> (Å)	16.6344(11)	24.189(3)	22.8535(9)	16.0669(11)	15.8294(6)	16.0188(3)
α (deg)	90	90	85.293(2)	90	113.260(3)	90
β (deg)	93.788(4)	124.729(4)	78.629(2)	113.257(3)	97.223(3)	102.8630(10)
γ (deg)	90	90	89.107(2)	90	103.022(3)	90
volume (Å ³)	5349.6(6)	8284.4(18)	3740.3(3)	4763.8(6)	1627.90(11)	3037.01(10)
<i>Z</i>	4	8	6	8	2	4
ρ_{calcd} (Mg m ⁻³)	1.557	1.605	1.444	1.523	1.554	1.745
μ (Mo K α) (mm ⁻¹)	0.830	0.983	0.770	0.927	0.941	2.669
<i>F</i> (000)	2552	4048	1668	2240	772	1544
cryst size (mm)	0.30 × 0.25 × 0.12	0.15 × 0.11 × 0.06	0.27 × 0.19 × 0.08	0.4 × 0.4 × 0.2	0.4 × 0.2 × 0.08	0.37 × 0.25 × 0.18
θ range (deg)	1.58 to 30.51	1.65 to 26.37	1.56 to 28.16	1.59 to 30.51	1.44 to 30.51	1.67 to 30.51
no. of rflns coll	126 390	54 513	42 981	102 353	39 421	64 652
no. of indep rflns/ <i>R</i> _{int}	16 337/0.058	8470/0.097	16 639/0.028	14 529/0.027	9890/0.029	9238/0.024
transmissn	0.907–0.751	0.943–0.836	0.941–0.819	0.836–0.745	0.929–0.791	0.645–0.519
no. of restraints/params	55/668	615/579	48/938	135/650	18/425	0/335
goodness-of-fit on <i>F</i> ²	1.06	1.07	1.06	1.06	1.05	1.05
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0380	0.050	0.0363	0.0246	0.0313	0.0216
<i>wR</i> ₂ (all rflns)	0.0907	0.134	0.0821	0.0637	0.0763	0.0542
largest diff peak/hole (e Å ⁻³)	1.05/–0.66	1.64/–0.90	0.73/–0.40	0.71/–0.76	0.68/–0.57	1.38/–0.93

Complex **22**: The chloroform is disordered over two sites (ca. 65:35). Complex **24**: The methyl hydrogens at C27 are poorly resolved.

Results and Discussion

Synthesis. The oxidative addition of IC₆H₄{NHC(Me)-CHC(O)Me}-2 (IAr) to Pd(dba)₂ was studied in the presence of various ligands, the nature of which proved to be decisive in the reaction course. Thus, with bidentate N^N ligands (1:1:1, at room temperature, in toluene under nitrogen atmosphere) the reaction gave complexes [PdI(Ar)(N^N)] (N^N = 4,4'-*tert*-butyl-2,2'-bipyridine = 'Bubpy' (**1**), *N,N,N',N'*-tetramethylethylenediamine = tmeda (**2**)) in good yield (Scheme 1). Some metallic palladium formed, which was removed by filtration through a short pad of Celite. Complex **1** is partly soluble in Et₂O and precipitated along with some dibenzylideneacetone

upon the addition of a Et₂O/*n*-hexane mixture. To remove dba, the crude product was refluxed in *n*-hexane and the resulting suspension filtered while hot. The reaction of **1** with PPh₃ (1:2) in Et₂O gave *trans*-[PdI(Ar)(PPh₃)₂] (**3**), which precipitated from the reaction mixture. When the reaction was carried out using a 1:1 molar ratio of the reagents, **3** was also obtained, and the unreacted half of the starting complex **1** was recovered from the mother liquor. Complex **3** results by replacement of the chelating N^N ligand by PPh₃ and an isomerization process that

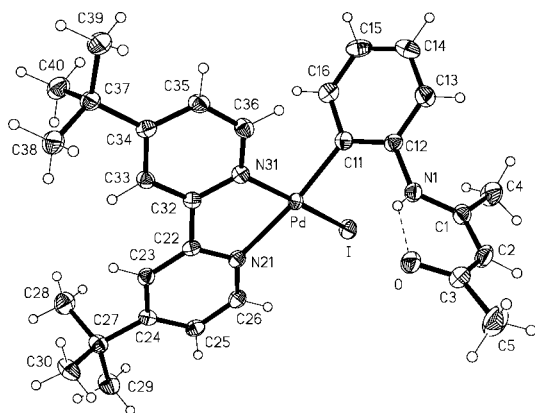


Figure 1. Thermal ellipsoid representation plot (50% probability) of complex **1** • 0.5Et₂O. Selected bond lengths (Å) and angles (deg): Pd–N(31) = 2.0741(19), Pd–N(21) = 2.1281(19), Pd–I = 2.5700(3), Pd–C(11) = 1.993(2), C(11)–C(12) = 1.395(3), N(1)–C(12) = 1.427(3), N(1)–C(1) = 1.346(3), C(1)–C(2) = 1.376(4), C(2)–C(3) = 1.413(4), O–C(3) = 1.256(3), C(11)–Pd–N(31) = 94.87(8), N(31)–Pd–N(21) = 78.47(7), C(11)–Pd–I = 88.11(7), N(21)–Pd–I = 98.09(5), C(1)–N(1)–C(12) = 126.6(2), N(1)–C(1)–C(2) = 121.2(2), C(1)–C(2)–C(3) = 123.8(2), O–C(3)–C(2) = 123.7(2).

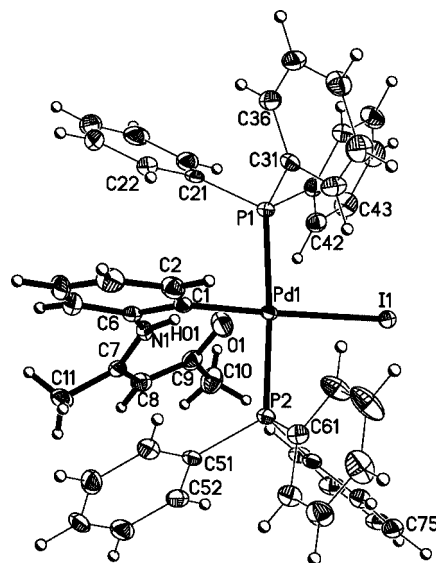


Figure 2. Thermal ellipsoid representation plot (50% probability) of complex **3**. Selected bond lengths (Å) and angles (deg): Pd(1)–P(2) = 2.3250(9), Pd(1)–P(1) = 2.3349(9), Pd(1)–I(1) = 2.6901(3), Pd(1)–C(1) = 2.020(3), C(1)–C(6) = 1.395(5), C(6)–N(1) = 1.419(5), N(1)–C(7) = 1.339(4), C(7)–C(8) = 1.390(5), C(8)–C(9) = 1.412(5), C(9)–O(1) = 1.255(4), C(1)–Pd(1)–P(2) = 87.81(9), C(1)–Pd(1)–P(1) = 87.46(9), P(2)–Pd(1)–I(1) = 91.77(2), P(1)–Pd(1)–I(1) = 92.60(2), C(7)–N(1)–C(6) = 129.9(3), N(1)–C(7)–C(8) = 120.2(3), C(7)–C(8)–C(9) = 124.2(3), O(1)–C(9)–C(8) = 123.9(3).

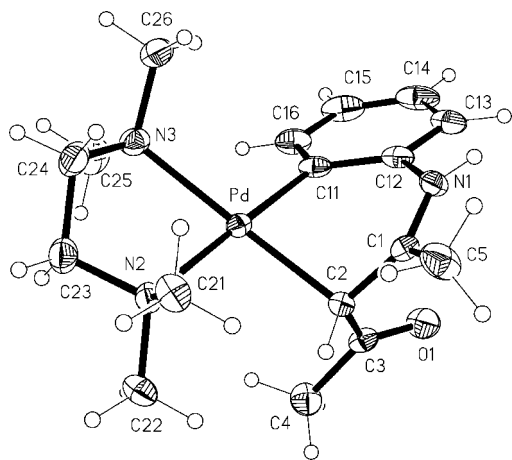


Figure 3. Thermal ellipsoid representation plot (50% probability) of the cation of complex **5**. Selected bond lengths (Å) and angles (deg): Pd–C(2) = 2.089(2), Pd–N(3) = 2.166(2), Pd–N(2) = 2.197(2), Pd–C(11) = 2.009(3), C(12)–N(1) = 1.420(4), C(1)–N(1) = 1.306(3), C(1)–C(2) = 1.451(4), C(2)–C(3) = 1.494(4), O(1)–C(3) = 1.213(3), C(11)–Pd–C(2) = 84.87(10), C(11)–Pd–N(3) = 97.39(9), C(2)–Pd–N(2) = 94.20(9), N(3)–Pd–N(2) = 83.59(8), C(1)–N(1)–C(12) = 124.2(2), N(1)–C(1)–C(2) = 121.3(2), C(1)–C(2)–C(3) = 117.3(2), O(1)–C(3)–C(2) = 123.3(3).

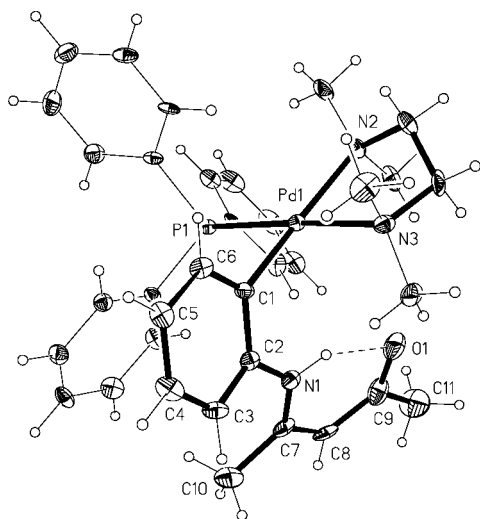


Figure 4. Thermal ellipsoid representation plot (30% probability) of one of the two independent cations of complex **7**. See Supporting Information for bond lengths and angles.

is probably promoted by the great transphobia^{11–14} of the Ph₃P/Ar ligand pair.¹⁵ These results contrast with those obtained by reacting equimolecular amounts of IC₆H₄N(R)(CH₂)_nC(O)R' (R = benzyl, R' = Me, *n* = 3; R = Me, R' = NMe₂, CO₂Me, *n* = 2), Pd(dba)₂, and PPh₃, affording four-membered C,N palladacyclic complexes.^{1a,16}

The reactions of **1** or **2** with TlTfO (TfO = CF₃SO₃, 1:1 in acetone) precipitated TlI immediately, and the 4-pallada-3,4-

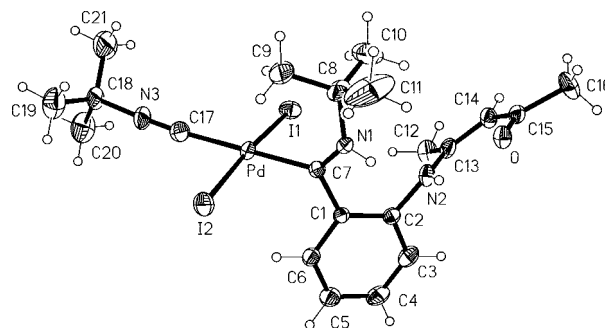


Figure 5. Thermal ellipsoid representation plot (50% probability) of complex **10**. Selected bond lengths (Å) and angles (deg): Pd–C(17) = 2.014(5), Pd–I(1) = 2.6076(5), Pd–I(2) = 2.6164(5), Pd–C(7) = 1.991(4), N(1)–C(7) = 1.293(5), N(1)–C(8) = 1.502(5), C(1)–C(7) = 1.497(5), N(2)–C(2) = 1.440(5), N(2)–C(13) = 1.323(6), C(13)–C(14) = 1.375(6), C(14)–C(15) = 1.409(6), C(15)–O = 1.258(5), N(3)–C(17) = 1.141(5), C(7)–Pd–I(1) = 89.46(11), C(17)–Pd–I(1) = 91.29(14), C(7)–Pd–I(2) = 88.71(11), C(17)–Pd–I(2) = 90.62(14), N(1)–C(7)–Pd = 127.1(3), C(7)–N(1)–C(8) = 131.5(4), N(1)–C(7)–C(1) = 115.8(3), C(13)–N(2)–C(2) = 126.7(4), N(2)–C(13)–C(14) = 121.1(4), O–C(15)–C(14) = 122.2(4), N(3)–C(17)–Pd = 175.2(4), C(17)–N(3)–C(18) = 176.7(5).

dihydroquinolinium complexes [Pd{C,C-C₆H₄{NH=C(Me)CHC(O)Me}-2}(N^N)]TfO (N^N = 'Bubpy' (**4**), tmeda (**5**)) were isolated in moderate yields (Scheme 1). The coordination to Pd of the methine carbon, after removal of the iodo ligand, can be attributed to the electronic delocalization over the N–C–C–O skeleton (see below), which confers negative charge on the methine C atom (and also the O atom, with a positive charge at N), to the more carbophilic than oxophilic character of Pd, as expected for a soft cation, and to the six-membered nature of the chelate ring. The Pd–C(sp³) bond in these complexes is easily cleaved upon the addition of NaI or neutral ligands L (1:1) to give the starting complexes (**1** or **2**) or cationic derivatives [Pd(Ar)(N^N)(L)] (N^N = 'Bubpy', L = PPh₃ (**6**), N^N = tmeda, L = PPh₃ (**7**), 'BuNC (**8**)), respectively, in good yields. Complex **8** was obtained along with a small amount of the complex resulting from the insertion of 'BuNC into the Pd–C_{aryl} bond (**16b**, see below), which was isolated from the mother liquor.

(11) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D.; Jones, P. G. *Organometallics* **2005**, *24*, 2516.

(12) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557.

(13) Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587. Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454. Vicente, J.; Arcas, A.; Gálvez-López, M. D.; Jones, P. G. *Organometallics* **2006**, *25*, 4247.

(14) Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fischer, A. K. *Organometallics* **2001**, *20*, 2704.

(15) Albert, J.; Bosque, R.; Cadena, J. M.; Granell, J. R.; Muller, G.; Ordinas, J. I. *Tetrahedron: Asymmetry* **2000**, *11*, 3335. Albert, J.; Cadena, J. M.; Delgado, S.; Granell, J. J. *Organomet. Chem.* **2000**, *603*, 235. Albert, J.; Cadena, J. M.; Granell, J. R.; Solans, X.; Font Bardia, M. *Tetrahedron: Asymmetry* **2000**, *11*, 1943. Larraz, C.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **2000**, *24*, 623. Lohner, P.; Pfeffer, M.; Fischer, J. J. *Organomet. Chem.* **2000**, *607*, 12. Fernandez, S.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **2000**, *602*, 151. Albert, J.; Bosque, R.; Cadena, J. M.; Delgado, S.; Granell, J. J. *Organomet. Chem.* **2001**, *634*, 83. Amatore, C.; Bahsoun, A. A.; Jutand, A.; Meyer, G.; Ntepe, A. N.; Ricard, L. *J. Am. Chem. Soc.* **2003**, *125*, 4212. Carbayo, A.; Cuevas, J. Y.; Garcia Herbosa, G.; Garcia Granda, S.; Miguel, D. *Eur. J. Inorg. Chem.* **2001**, 2361. Carbayo, A.; Cuevas, J. V.; Garcia Herbosa, G. *J. Organomet. Chem.* **2002**, *658*, 15. Crespo, M.; Granell, J.; Solans, X.; Fontbardia, M. *J. Organomet. Chem.* **2003**, *681*, 143. Fernandez, A.; Vazquez Garcia, D.; Fernandez, J. J.; López Torres, M.; Suarez, A.; Castro Juiz, S.; Vila, J. M. *Eur. J. Inorg. Chem.* **2002**, 2389. Fernandez-Rivas, C.; Cardenas, D. J.; Martin-Matute, B.; Monge, A.; Gutierrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998. Jalil, M. A.; Fujinami, S.; Nishikawa, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1091. López, C.; Caubet, A.; Pérez, S.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **2003**, *681*, 82. Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 555. Ng, J. K. P.; Chen, S.; Li, Y.; Tan, G. K.; Koh, L. L.; Leung, P. H. *Inorg. Chem.* **2007**, *46*, 5100. Casas, J. M.; Fornies, J.; Fuertes, S.; Martin, A.; Sicilia, V. *Organometallics* **2007**, *26*, 1674.

(16) Solé, D.; Vallverdú, L.; Soláns, X.; Font-Bardia, M.; Bonjoch, J. *J. Am. Chem. Soc.* **2003**, *125*, 1587. Solé, D.; Serrano, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 7270.

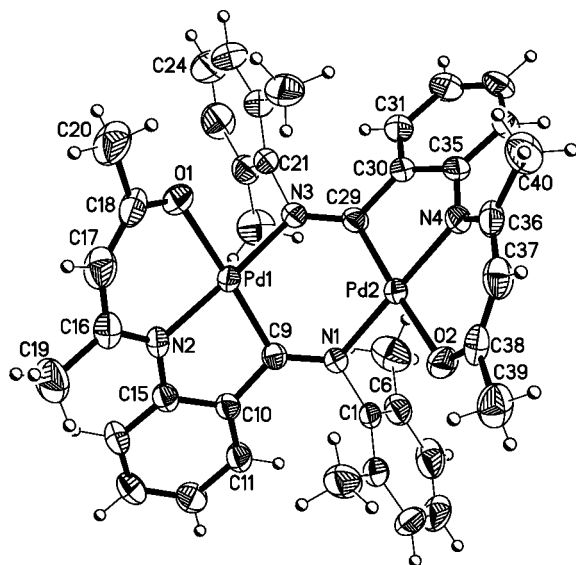


Figure 6. Thermal ellipsoid representation plot (50% probability) of complex **13**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(9) = 1.954(4), Pd(1)–N(2) = 2.002(3), Pd(1)–O(1) = 2.067(3), Pd(1)–N(3) = 2.068(3), Pd(2)–C(29) = 1.931(4), Pd(2)–N(4) = 2.013(3), Pd(2)–N(1) = 2.067(3), Pd(2)–O(2) = 2.072(3), N(1)–C(9) = 1.290(5), N(1)–C(1) = 1.448(5), N(3)–C(29) = 1.294(5), N(3)–C(21) = 1.447(5), N(2)–C(16) = 1.329(5), N(4)–C(36) = 1.326(6), C(16)–C(17) = 1.401(7), C(36)–C(37) = 1.395(7), C(17)–C(18) = 1.386(8), C(37)–C(38) = 1.391(7), O(1)–C(18) = 1.257(6), O(2)–C(38) = 1.270(5), C(9)–Pd(1)–N(2) = 82.82(15), N(2)–Pd(1)–O(1) = 93.20(14), C(9)–Pd(1)–N(3) = 96.99(15), O(1)–Pd(1)–N(3) = 87.85(13), C(29)–Pd(2)–N(4) = 81.44(15), C(29)–Pd(2)–N(1) = 96.36(14), N(4)–Pd(2)–O(2) = 92.58(13), N(1)–Pd(2)–O(2) = 89.99(12), C(15)–N(2)–Pd(1) = 110.1(2), C(35)–N(4)–Pd(2) = 110.6(3), C(10)–C(9)–Pd(1) = 109.8(3), C(30)–C(29)–Pd(2) = 111.1(3), C(18)–O(1)–Pd(1) = 119.2(3), C(38)–O(2)–Pd(2) = 119.0(3), O(1)–C(18)–C(17) = 126.7(4), O(2)–C(38)–C(37) = 127.3(4), N(2)–C(16)–C(17) = 122.3(4), N(4)–C(36)–C(37) = 122.4(4), C(16)–N(2)–Pd(1) = 123.1(3), C(36)–N(4)–Pd(2) = 122.3(3).

When the oxidative addition of IAr to Pd(dba)₂ was carried out in the presence of RNC ligands (R = C₆H₃Me₂-2,6 (Xy), ^tBu, 1:1:2, at room temperature, in toluene under nitrogen atmosphere) complex mixtures (by NMR) formed, from which only low yields of [Pd₂I₂(CNXy)₄]¹⁷ (**9**, 16%) or *trans*-[PdI₂{C(=NH^tBu)Ar}(CN^tBu)] (**10**, 28%) (Scheme 1), respectively, could be isolated, while the expected [PdI(Ar)(CNR)₂] compounds, analogous to **3**, were not detected. Complex **9** has been prepared recently¹⁷ from [Pd₂(μ-I)₂(P^tBu₃)₂] and XyNC; it was identified only by its elemental analyses and IR spectrum, but no NMR data were reported. Previous syntheses of this type of complexes involved comproportionation reactions of Pd(0) and Pd(II) isocyanide derivatives.¹⁸ We have postulated the formation of **9** in the decomposition of *trans*-[Pd{C(O)C₆H₄NHC(O)NHTo-2}I(CNXY)₂]² and have isolated other members of the family [Pd₂X₂(CNR)₄] (X/R = Cl/^tBu,¹¹ Xy;¹² Br/^tBu,¹⁹ Xy²⁰) by reacting aryl or alkyl palladium complexes with isocyanides.

(17) Durà-Vilà, V.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2000**, 600, 198.

(18) Otsuka, S.; Tatsuno, Y.; Ataka, K. *J. Am. Chem. Soc.* **1971**, 93, 6705. Rettig, M. F.; Kirk, E. A.; Maitlis, P. M. *J. Organomet. Chem. Chem.* **1976**, 111, 113. (c) Boehm, J. R.; Balch, A. L. *Inorg. Chem.* **1977**, 16, 778.

(19) Vicente, J.; Saura-Llamas, I.; Gruenwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, 21, 3587.

(20) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2003**, 22, 1967.

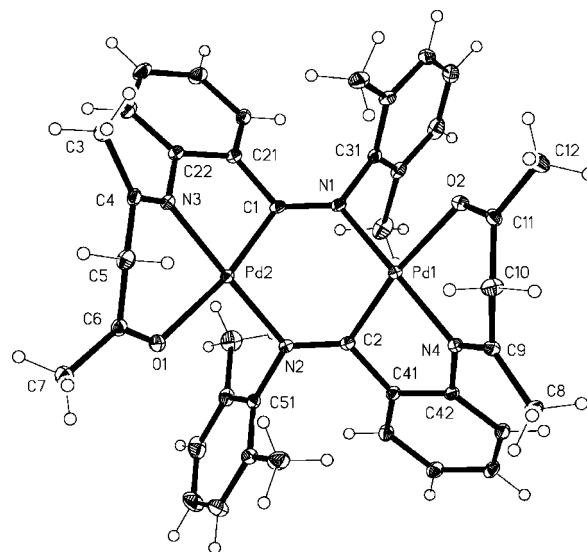


Figure 7. Thermal ellipsoid representation plot (30% probability) of the cation of complex **14a**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(2) = 1.937(2), Pd(1)–N(4) = 2.008(2), Pd(1)–N(1) = 2.040(2), Pd(1)–O(2) = 2.1263(18), Pd(2)–C(1) = 1.943(3), Pd(2)–N(3) = 2.008(2), Pd(2)–N(2) = 2.050(2), Pd(2)–O(1) = 2.1298(19), C(1)–N(1) = 1.283(3), C(2)–N(2) = 1.291(3), C(11)–O(2) = 1.233(3), C(10)–C(11) = 1.499(4), C(9)–C(10) = 1.506(4), C(9)–N(4) = 1.283(3), C(42)–N(4) = 1.433(3), C(2)–C(41) = 1.491(3), C(6)–O(1) = 1.231(3), C(5)–C(6) = 1.510(4), C(4)–C(5) = 1.511(4), C(4)–N(3) = 1.285(3), C(22)–N(3) = 1.437(3), C(1)–C(21) = 1.494(3), C(31)–N(1) = 1.450(3), C(51)–N(2) = 1.451(3), C(2)–Pd(1)–N(4) = 81.72(9), C(2)–Pd(1)–N(1) = 94.93(9), N(4)–Pd(1)–O(2) = 88.85(8), N(1)–Pd(1)–O(2) = 94.57(8), C(1)–Pd(2)–N(3) = 81.59(10), C(1)–Pd(2)–N(2) = 95.26(9), N(3)–Pd(2)–O(1) = 88.60(8), N(2)–Pd(2)–O(1) = 94.48(8), N(1)–C(1)–Pd(2) = 124.60(18), N(2)–C(2)–Pd(1) = 123.96(18), C(1)–N(1)–Pd(1) = 121.69(17), C(2)–N(2)–Pd(2) = 122.12(17), N(3)–C(4)–C(5) = 119.3(2), N(4)–C(9)–C(10) = 119.1(2), C(6)–C(5)–C(4) = 118.1(2), C(11)–C(10)–C(9) = 118.4(2), O(1)–C(6)–C(5) = 122.8(2), O(2)–C(11)–C(10) = 124.3(2), C(4)–N(3)–Pd(2) = 123.70(18), C(9)–N(4)–Pd(1) = 125.48(18), C(6)–O(1)–Pd(2) = 120.37(18), C(11)–O(2)–Pd(1) = 119.95(17).

We have studied the reactions of complexes **1** and **2** with RNC (R = Xy, ^tBu) and found that the results depend on (1) the molar ratio of the reagents, (2) the R substituent in the isocyanide, and (3) the N^{Ar} ligand present in the starting palladium complex. Thus, when **1** or **2** is treated with five or more equivalents of isocyanide, complex *trans*-[PdI{C(=NR)Ar}(CNR)₂] (R = ^tBu (**11**), Xy (**12**); Scheme 1) forms in almost quantitative yield. The process involves insertion of one RNC into the Pd–Ar bond, the replacement of N^{Ar} by two RNC ligands, and a *cis* to *trans* isomerization process probably driven by the different transphobia^{11–14} between ligands. Similar results have been previously found in the reactions of various [PdX(Ar)(N^{Ar})] complexes with isocyanide,^{2,14,19,21,22} although, in some cases, polyinsertion processes have also been observed.²¹

The reaction of **5** with XyNC (1:1 molar ratio) also involved the insertion of the isocyanide into the Pd–Ar bond, but,

(21) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, 21, 4454. Van Baar, J. F.; Klerkz, J. M.; Overbosch, P.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1976**, 112, 95.

(22) Uson, R.; Fornies, J.; Espinet, P.; Lalinde, E.; Jones, P. G.; Sheldrick, G. M. *J. Organomet. Chem.* **1983**, 253, C47. Uson, R.; Fornies, J.; Espinet, P.; García, A.; Tomás, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, 282, C35.

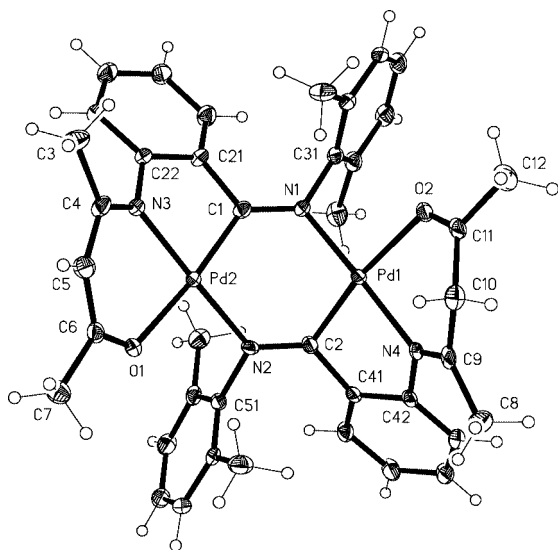


Figure 8. Thermal ellipsoid representation plot (30% probability) of complex **14b**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(2) = 1.932(6), Pd(1)–N(4) = 2.026(5), Pd(1)–N(1) = 2.043(5), Pd(1)–O(2) = 2.131(4), Pd(2)–C(1) = 1.949(6), Pd(2)–N(3) = 1.989(5), Pd(2)–N(2) = 2.048(5), Pd(2)–O(1) = 2.078(4), C(1)–N(1) = 1.286(7), C(2)–N(2) = 1.282(7), C(11)–O(2) = 1.219(8), C(10)–C(11) = 1.498(9), C(9)–C(10) = 1.500(9), C(9)–N(4) = 1.284(8), C(42)–N(4) = 1.441(8), C(2)–C(41) = 1.503(8), C(6)–O(1) = 1.266(7), C(5)–C(6) = 1.394(9), C(4)–C(5) = 1.412(9), C(4)–N(3) = 1.318(8), C(22)–N(3) = 1.412(7), C(1)–C(21) = 1.487(8), C(31)–N(1) = 1.470(7), C(51)–N(2) = 1.456(7), C(2)–Pd(1)–N(4) = 81.3(2), C(2)–Pd(1)–N(1) = 95.1(2), N(4)–Pd(1)–O(2) = 88.30(18), N(1)–Pd(1)–O(2) = 95.45(17), C(1)–Pd(2)–N(3) = 81.8(2), C(1)–Pd(2)–N(2) = 95.4(2), N(3)–Pd(2)–O(1) = 90.78(18), N(2)–Pd(2)–O(1) = 92.14(17), N(1)–C(1)–Pd(2) = 124.3(4), N(2)–C(2)–Pd(1) = 124.0(4), C(1)–N(1)–Pd(1) = 122.0(4), C(2)–N(2)–Pd(2) = 122.7(4), N(3)–C(4)–C(5) = 121.3(6), N(4)–C(9)–C(10) = 119.1(6), C(6)–C(5)–C(4) = 128.3(6), C(11)–C(10)–C(9) = 120.5(6), O(1)–C(6)–C(5) = 126.2(6), O(2)–C(11)–C(10) = 124.4(6), C(4)–N(3)–Pd(2) = 123.3(4), C(9)–N(4)–Pd(1) = 125.0(4), C(6)–O(1)–Pd(2) = 120.4(4), C(11)–O(2)–Pd(1) = 120.8(4).

additionally, deprotonation of the iminic nitrogen by the tmeda ligand takes place, resulting in a *C,N,O*-pincer fragment that, in the absence of an additional ligand, dimerizes upon the coordination of the pendant iminoacyl nitrogen atom to give the β -ketiminato complex $[\text{Pd}\{\mu\text{-}N,C,N',O\text{-}N(\text{Xy})\}=\text{CC}_6\text{H}_4\{\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{O}\}\text{-}2\}]_2$ (**13**) (Scheme 2). The byproducts, $1/2$ (H_2tmeda)(TfO) $_2$ + $1/2$ tmeda, were removed by washing the crude reaction mixture with cold MeOH. The insertion of the isocyanide is probably responsible for the change of coordination of the *ortho* substituent, because otherwise the resulting *C,C*-palladacycle would be a seven-membered ring. Instead, deprotonation of the iminium proton by the replaced tmeda ligand allows formation of a five-membered *C,N*-palladacycle, which, together with the six-membered chelate ring resulting from the *O*-enolato coordination, leads to a pincer complex. The reaction of **13** with an excess of HTfO produced protonation of both methine groups in the *ortho* substituent, resulting in the formation of the dicationic complex $[\text{Pd}\{\mu\text{-}O,N,C,N'\text{-}OC(\text{Me})\text{CH}_2\text{C}(\text{Me})\text{NC}_6\text{H}_4\text{C}=\text{NXY}\}]_2(\text{TfO})_2$ (**14a**; Scheme 2). When formation of single crystals of **14a** was attempted, single crystals of the monoprotonated complex $[\text{Pd}\{\mu\text{-}O,N,C,N'\text{-}OC(\text{Me})\text{CHC}(\text{Me})\text{NC}_6\text{H}_4\text{C}=\text{NXY}\}\{\mu\text{-}N,C,N',O\text{-}N(\text{Xy})\}=\text{CC}_6\text{H}_4\{\text{NC}(\text{Me})\text{CH}_2\text{C}(\text{Me})\text{O}\}\text{-}2\}]\text{TfO}$ (**14b**) were also isolated, which allowed the study of both complexes by

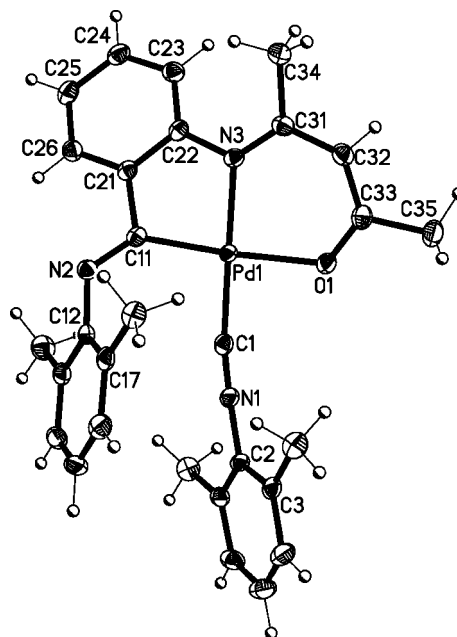


Figure 9. Thermal ellipsoid representation plot (50% probability) of complex **17**. Selected bond lengths (Å) and angles (deg) for one of the independent molecules: Pd(1)–C(1) = 1.958(2), Pd(1)–C(11) = 1.988(2), Pd(1)–N(3) = 2.031(2), Pd(1)–O(1) = 2.0928(17), N(1)–C(1) = 1.150(3), N(2)–C(11) = 1.269(3), N(2)–C(12) = 1.408(3), C(11)–C(21) = 1.497(3), C(21)–C(22) = 1.397(3), N(3)–C(22) = 1.419(3), N(3)–C(31) = 1.332(3), C(31)–C(32) = 1.409(4), C(32)–C(33) = 1.390(4), O(1)–C(33) = 1.277(3), C(1)–Pd(1)–C(11) = 97.11(10), C(11)–Pd(1)–N(3) = 83.14(9), C(1)–Pd(1)–O(1) = 87.50(9), N(1)–C(1)–Pd(1) = 170.6(2), N(2)–C(11)–Pd(1) = 133.73(19), C(11)–N(2)–C(12) = 125.5(2), C(21)–C(11)–Pd(1) = 108.89(16), C(22)–C(21)–C(11) = 117.1(2), C(21)–C(22)–N(3) = 114.4(2), C(22)–N(3)–Pd(1) = 111.59(15), C(31)–N(3)–Pd(1) = 122.92(17), N(3)–C(31)–C(32) = 123.1(2), C(33)–C(32)–C(31) = 128.9(2), O(1)–C(33)–C(32) = 127.2(2), C(33)–O(1)–Pd(1) = 121.00(16).

X-ray diffraction. The 1:1 reaction between **13** and HTfO produced a solid, for which the ^1H NMR spectrum showed broad resonances at room temperature. At low temperature (-40°C), signals corresponding to **13** and a different complex containing four Me resonances, probably **14b** (1:2 molar ratio), were observed. Recrystallization of the isolated mixture led to an increase in the proportion of **13**. This suggests that **14b** is in an equilibrium displaced to the formation **13**. Reactions of **14a** with half an equivalent of Na_2CO_3 or with 1 equiv of **13** gave respectively either a complex mixture or the starting materials.

Dinuclear complexes with bridging iminoacyl ligands were known previously, and the crystal structures of seven of them have been reported.^{22,23} However, apart from the iminoacyl ligands, these complexes bear from two to four additional ligands in order to attain the tetracoordination of the Pd atoms, whereas **13**, **14a**, and **14b** contain only iminoacyl ligands.

Complex **13** is robust, and its iminoacyl bridges do not split unless it is refluxed in CHCl_3 with phosphine or isocyanide ligands for at least 9 h, giving mononuclear neutral *C,N,O*-pincer

(23) Uson, R.; Fornies, J.; Espinet, P.; Lalinde, E.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1982**, 2389. Uson, R.; Fornies, J.; Espinet, P.; Lalinde, E.; García, A.; Jones, P. G.; Meyer-Base, K.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 259. Dupont, J.; Pfeffer, M.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, 6, 899. Zografidis, A.; Polborn, K.; Beck, W.; Markies, B. A.; van Koten, G. Z. *Naturforsch., B: Chem. Sci.* **1994**, 49, 1494. Canovese, L.; Visentin, F.; Santo, C.; Levi, C.; Dolmella, A. *Organometallics* **2007**, 26, 5590.

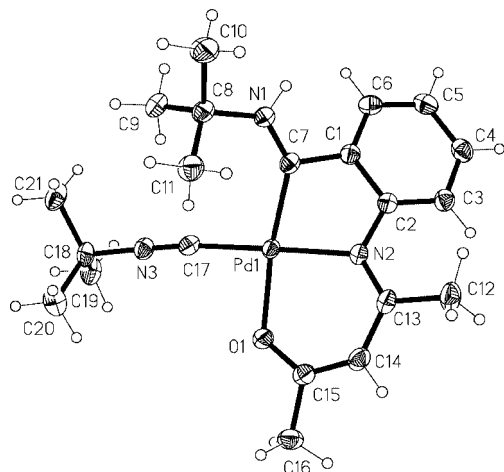


Figure 10. Thermal ellipsoid representation plot (50% probability) of the cation of complex **21**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(17) = 1.9831(17), Pd(1)–C(7) = 1.9883(16), Pd(1)–N(2) = 2.0045(14), Pd(1)–O(1) = 2.0506(12), O(1)–C(15) = 1.282(2), C(14)–C(15) = 1.393(3), C(13)–C(14) = 1.400(2), N(2)–C(13) = 1.332(2), N(2)–C(2) = 1.414(2), C(1)–C(2) = 1.409(2), N(1)–C(7) = 1.301(2), N(1)–C(8) = 1.500(2), N(3)–C(17) = 1.148(2), C(17)–Pd(1)–C(7) = 101.53(7), C(7)–Pd(1)–N(2) = 80.09(6), C(17)–Pd(1)–O(1) = 87.13(6), N(2)–Pd(1)–O(1) = 91.71(5), C(15)–O(1)–Pd(1) = 122.06(11), O(1)–C(15)–C(14) = 126.65(16), C(15)–C(14)–C(13) = 127.81(16), N(2)–C(13)–C(14) = 122.10(15), C(2)–N(2)–Pd(1) = 111.07(10), C(1)–C(2)–N(2) = 113.90(14), C(2)–C(1)–C(7) = 113.21(14), N(1)–C(7)–C(1) = 116.43(15), N(1)–C(7)–Pd(1) = 134.46(13), C(7)–N(1)–C(8) = 130.10(15), N(3)–C(17)–Pd(1) = 173.29(15).

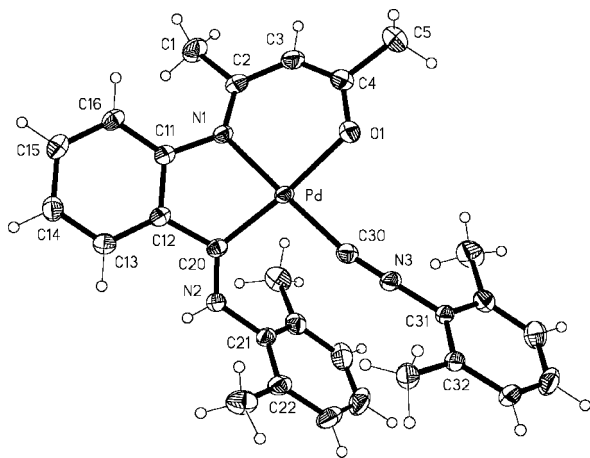


Figure 11. Thermal ellipsoid representation plot (50% probability) of the cation of complex **22**. Selected bond lengths (Å) and angles (deg): Pd–C(20) = 1.9659(18), Pd–C(30) = 1.9677(18), Pd–N(1) = 2.0110(14), Pd–O(1) = 2.0441(13), O(1)–C(4) = 1.283(2), C(3)–C(4) = 1.387(3), C(2)–C(3) = 1.408(3), N(1)–C(2) = 1.330(2), N(1)–C(11) = 1.414(2), C(11)–C(12) = 1.409(2), C(12)–C(20) = 1.475(2), N(2)–C(20) = 1.301(2), N(2)–C(21) = 1.443(2), N(3)–C(30) = 1.151(2), N(3)–C(31) = 1.404(2), C(20)–Pd–C(30) = 99.66(7), C(20)–Pd–N(1) = 81.76(6), C(30)–Pd–O(1) = 85.73(6), N(1)–Pd–O(1) = 92.86(6), C(4)–O(1)–Pd = 121.29(13), O(1)–C(4)–C(3) = 126.80(18), C(4)–C(3)–C(2) = 128.30(17), N(1)–C(2)–C(3) = 122.56(17), C(2)–N(1)–Pd = 122.26(12), C(11)–N(1)–Pd = 112.12(10), C(12)–C(11)–N(1) = 114.38(15), C(12)–C(20)–Pd = 110.90(12), C(20)–N(2)–C(21) = 125.79(16), N(3)–C(30)–Pd = 169.51(16), C(30)–N(3)–C(31) = 174.99(19).

complexes [Pd{C,N,O-C(=NXY)C₆H₄{NC(Me)CHC(Me)O}-2}(L)] (L = PPh₃ (**15**), 'BuNC (**16a**), XyNC (**17**)) (Scheme 2).

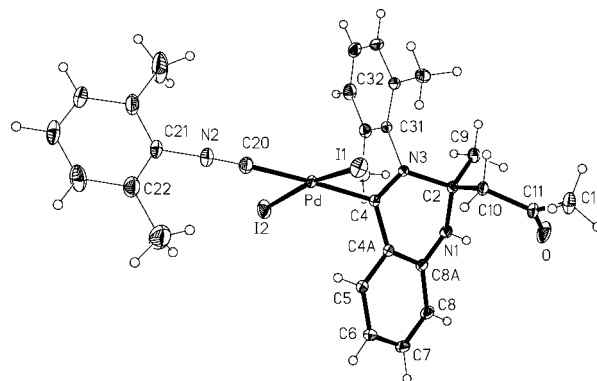


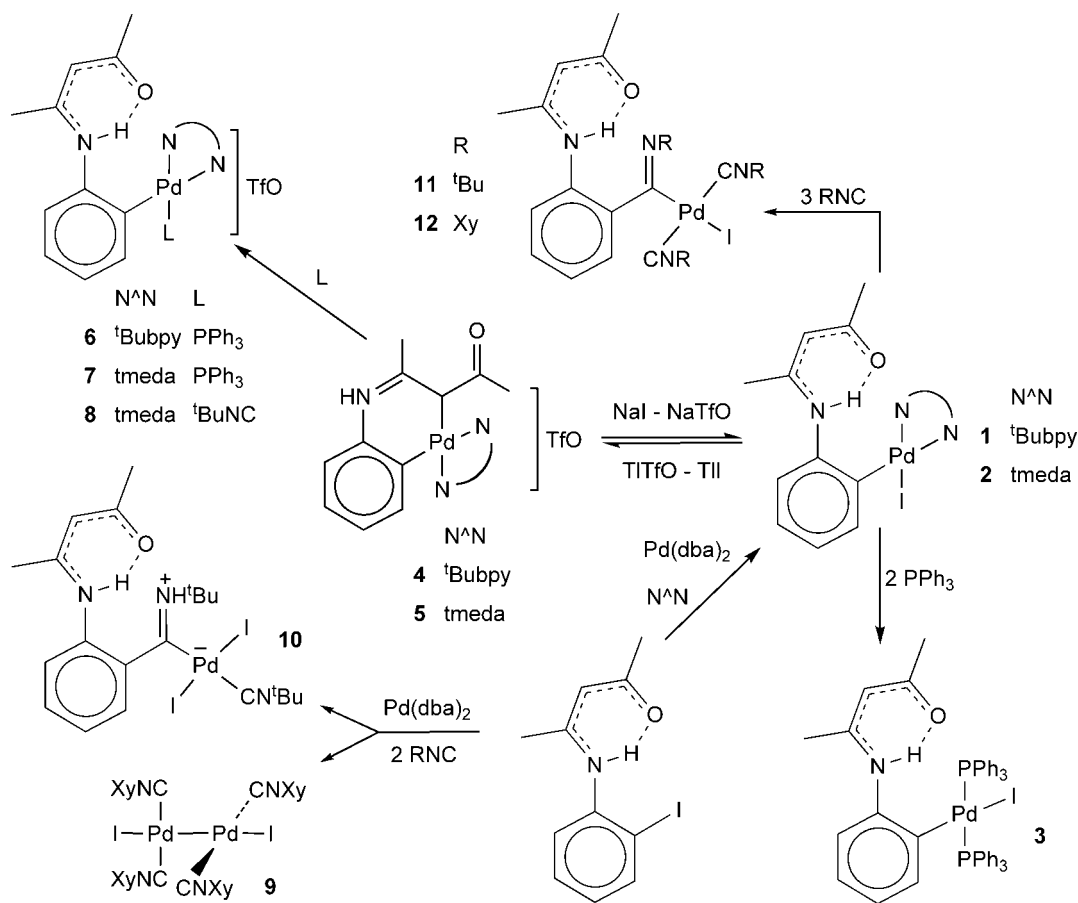
Figure 12. Thermal ellipsoid representation plot (30% probability) of complex **24**. Selected bond lengths (Å) and angles (deg): Pd–C(20) = 2.0056(19), Pd–C(4) = 2.0130(16), Pd–I(2) = 2.60390(19), Pd–I(1) = 2.61461(18), N(3)–C(4) = 1.330(2), C(2)–N(3) = 1.526(2), N(1)–C(2) = 1.443(2), N(1)–C(8A) = 1.359(2), C(4A)–C(8A) = 1.417(2), C(4)–C(4A) = 1.451(2), N(2)–C(20) = 1.141(2), C(20)–Pd–C(4) = 176.49(7), C(20)–Pd–I(2) = 86.73(6), C(4)–Pd–I(2) = 94.51(5), C(20)–Pd–I(1) = 90.70(6), C(4)–Pd–I(1) = 87.47(5), I(2)–Pd–I(1) = 168.930(70), N(3)–C(4)–C(4A) = 117.01(14), C(4)–N(3)–C(2) = 119.10(13), N(1)–C(2)–N(3) = 105.11(13), C(8A)–N(1)–C(2) = 117.72(15), N(1)–C(8A)–C(4A) = 118.07(16), C(8A)–C(4A)–C(4) = 118.24(16), N(2)–C(20)–Pd = 177.1(2), C(20)–N(2)–C(21) = 177.3(2).

These complexes are soluble even in *n*-pentane, which accounts for the moderate isolated yields (58–62%). Complex **13** does not react with PPNCl (PPN = PPh₃=N=PPh₃) after 10 h refluxing in CHCl₃.

Compound **15** was protonated by excess HTfO at both the methine carbon and the imine nitrogen to give [Pd{C,N,O-C(=NHXY)C₆H₄{N=C(Me)CH₂C(O)Me}-2}(PPh₃)](TfO)₂ (**18**), containing a neutral C,N,O-pincer ligand. However, under the same reaction conditions, protonation of **16a** or **17** occurs only at the imine nitrogen, giving complexes [Pd{C,N,O-C(=NHXY)C₆H₄{NC(Me)CHC(Me)O}-2}(L)]TfO (L = 'BuNC (**19**), XyNC (**20**)), containing a monoanionic C,N,O-pincer ligand (Scheme 2). The greater nucleophilic character of the CH carbon in **15** compared to that in the homologous **17** suggests that the XYNC ligand is more electron-withdrawing than PPh₃. Complexes [Pd{C,N,O-C(=NHR)C₆H₄{NC(Me)CHC(Me)O}-2}(CNR)]ClO₄ (R = 'Bu (**21**), Xy (**22**)), homologues of **19** and **20**, were obtained by reacting **11** or **12**, respectively, with AgClO₄ (1:1, in acetone, Scheme 2). In these reactions, the coordination vacancy at the Pd center promotes a rare isocyanide replacement by an O donor ligand; the NH deprotonation by the imine N, required for the formation of the monoanionic C,N,O-pincer ligand, shows again, as in the synthesis of **19** and **20**, the greater nucleophilic character of the imine N than the methine carbon.

Complexes **21** and **22** were isolated together with a small amount of replaced isocyanide, and their purification required repeated recrystallization from CH₂Cl₂ and Et₂O, thus lowering the yield somewhat. Both complexes crystallized as hydrates (with 1.5 or 1 molecule of water, respectively, from ¹H NMR data and elemental analyses). After being heated at 80 °C for 6 h, **21** decomposed and **22** did not dehydrate. The treatment of these complexes with M₂CO₃ (M = Na, Tl, 1:0.5, Scheme 2) affords complexes **16b** and **17**. Complex [Pd{C,N,O-C(=NHXY)C₆H₄{NC(Me)CHC(Me)O}-2}PPh₃]TfO (**23**), the PPh₃ homologue of **19**–**22**, forms in the reaction of **15** with the equimolar amount of HTfO, but is better obtained by reacting **14a** with PPh₃ (1:2, 65 °C, 10 h). In this reaction, the dimer is

Scheme 1



split and one proton migrates from the methylene to the imine N atom (Scheme 2). As far as we are aware, complexes **13–23**, along with one cobalt²⁴ and two other palladium complexes^{2,25} bearing *C,C,O*-, *C,N,N*-, and *C,N,C*-pincer ligands, respectively, are the only pincer complexes of any transition metal in which at least one metalated carbon atom belongs to an iminoacyl fragment.²⁶

We have mentioned above that reaction of **1** or **2** with excess *XyNC* gives **12**. However, reactions of **1–3** with *XyNC* in a 1:2 (**1**, **2**) or 1:1.5 (**3**) Pd:*XyNC* molar ratio afford different products depending on the nature of the neutral ligands present in the starting complex. Thus, the reaction of the *tmeda* complex **2** with *XyNC* (1:2) produced half an equivalent each of (H₂*tmeda*)I₂ and free *tmeda*, as in the synthesis of **13**, along with the neutral pincer complex **17** (Scheme 2). However, when **1** or **3** was reacted with *XyNC* in 1:2 or 1:1.5 molar ratio, respectively, a mixture was obtained of half an equivalent each of **17** and the 1-*H*-2-methyl-2-aceton-yl-3-*xylyl*-1,2-dihydroquinazolin-4-yl derivative *trans*-[Pd₂{C(=N*Xy*)C(Me){CH₂C(O)Me}-NHC₆H₄-2}L] (L = *XyNC* (**24**), PPh₃ (**25**)) (Scheme 3), which can easily be separated because **17** is soluble in Et₂O.

Scheme 4 shows a reasonable reaction pathway to explain these results. Reaction of complexes **1–3** with 1 equiv of *XyNC* should afford complex **A** after the insertion of the isocyanide into the Pd–C bond. This intermediate reacts with another equivalent of *XyNC* to afford **17**, L₂ (*t*Bubpy, *tmeda*, or 2 PPh₃),

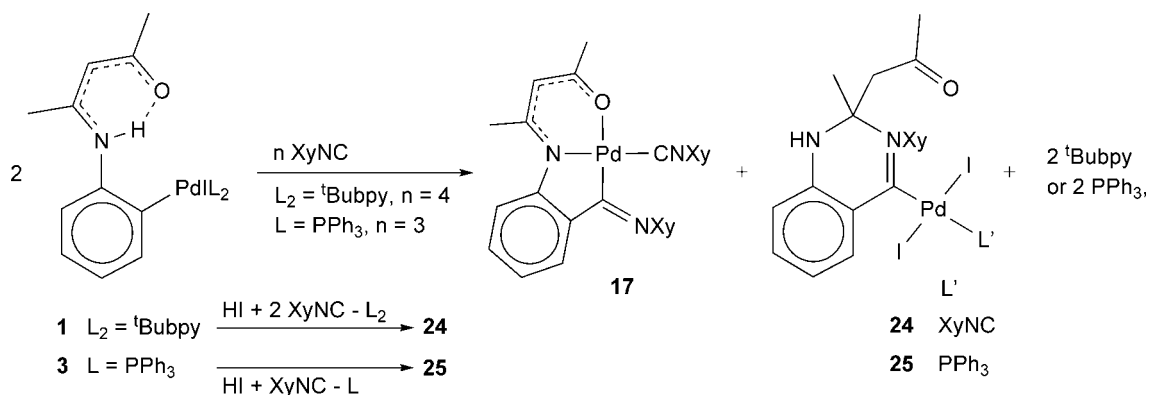
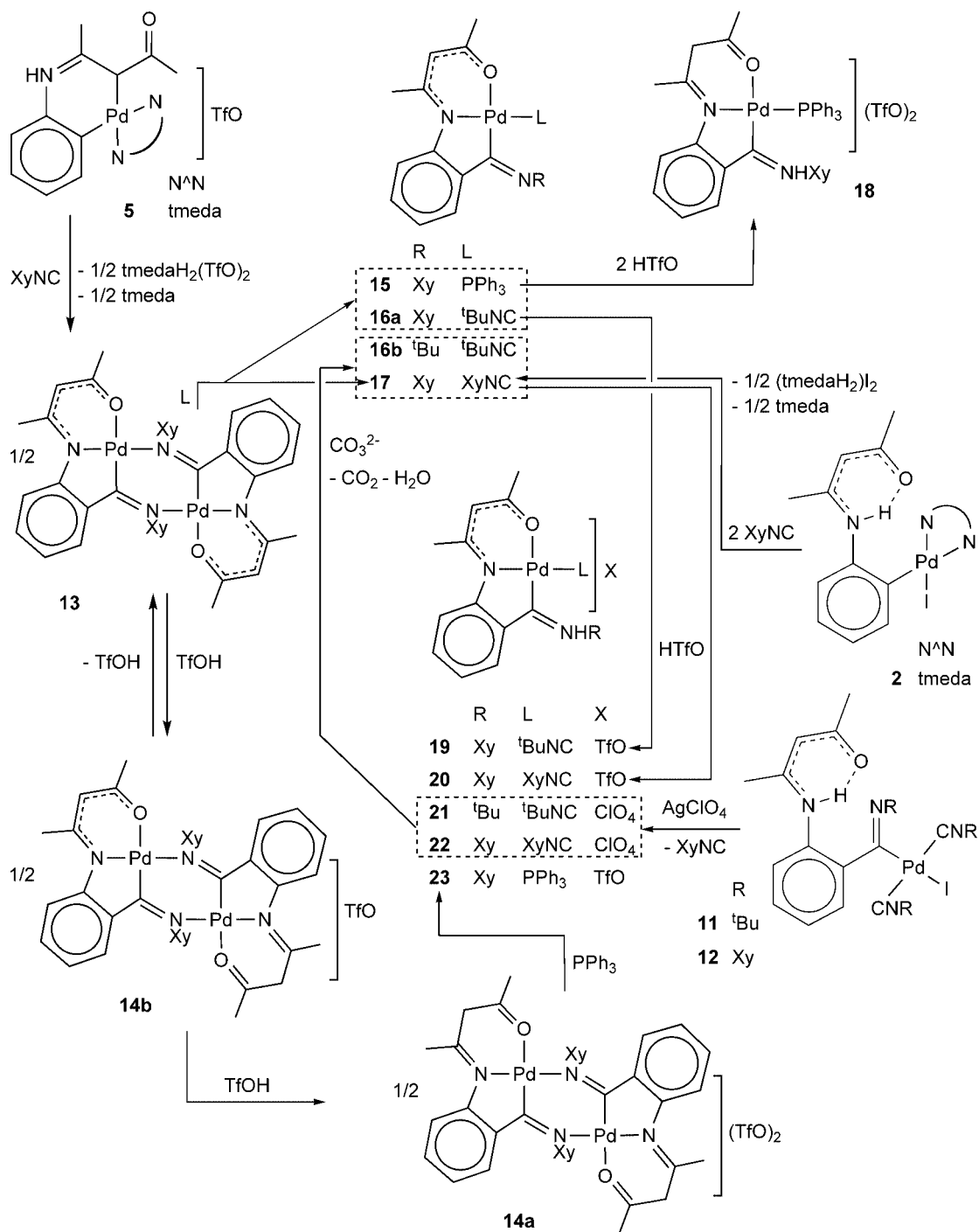
and HI. When L₂ = *tmeda*, this base neutralizes all HI formed, giving 0.5 equiv of the salt (H₂*tmeda*)I₂ and leaving an unreacted 0.5 equiv of *tmeda*. However, when L₂ = *t*Bubpy, the imine nitrogen of the still unreacted complex **A** is more nucleophilic than free L₂, and the HI formed, together with the still unreacted *XyNC*, affords **B** (L' = *XyNC*), which is an analogue of **10**. However, the NH addition to the C(Me)–CH bond required in **B** to give **24** does not occur in **10** because of the less acidic character of the *t*BuNH group. When L = PPh₃, the reaction is similar, but only 1 equiv of L is replaced (L' = PPh₃). This proposal is supported by the synthesis of pure **24** in 87% yield from **1**, HI, and *XyNC* in 1:1:2 molar ratio. Similarly, **25** was obtained from the reaction of **3** with HI and *XyNC* (1:1:1). The source of **24** is not **17** because it does not react with HI. As far as we are aware, **24** and **25** are the first 1,2-dihydroquinazolin-4-yl complexes of any metal. Complexes **24** and **25**, like **10**, adopt a *trans* geometry, in spite of the strong C/C and C/P transphobia,^{11–14} because this is the most common structure for a diiodo complex.

The pincer ligands in complexes **20** and **22** or in **17** can be viewed as resulting from the quinazolinyl ligand present in **24**, after cleavage of the N–C bond formed in its synthesis, mono- or dideprotonation, respectively (Scheme 5), and removal of the two iodo ligands. In fact, we have succeeded in preparing **22** or **17** in almost quantitative yield by reacting **24** with 2 equiv of AgClO₄ (room temperature, acetone, 30 min) or 1 equiv of Ti₂CO₃ (refluxing in acetone, 30 min), respectively. We assume that the cleavage of the C–N bond of the quinazolinyl ligand and the deprotonation of the methylene group affording **22** occur through complex **C** (Scheme 5), whose dicationic nature confers it a markedly acid character. Therefore, **22** is formed, like its

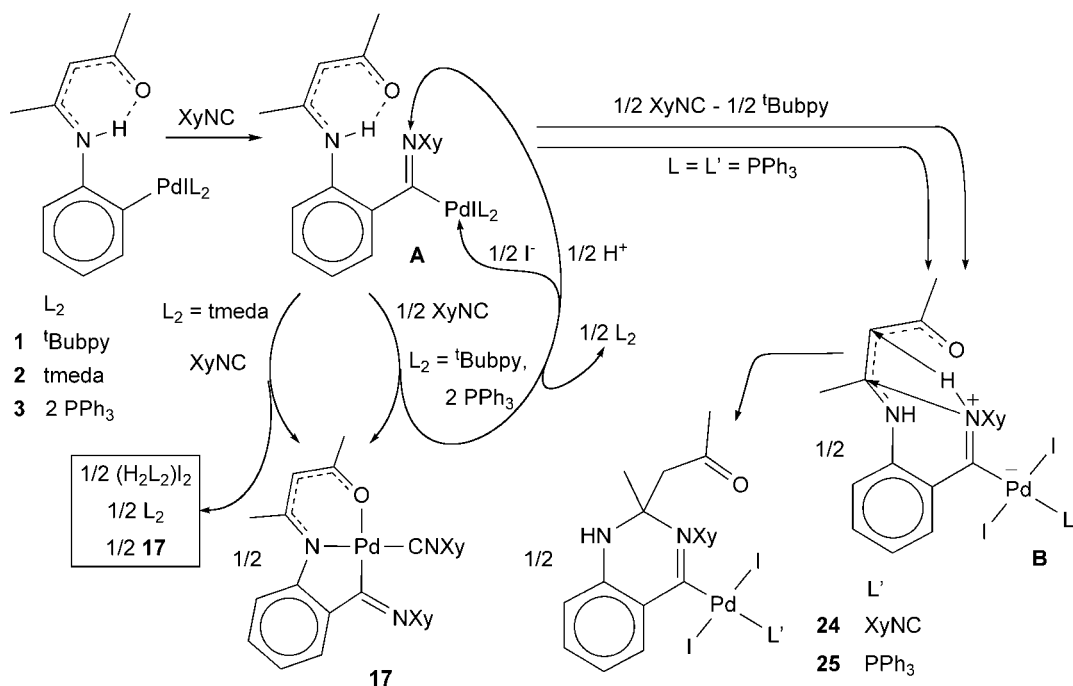
(24) Yamamoto, Y.; Tanase, T.; Sugano, K. *J. Organomet. Chem.* **1995**, 486, 21.

(25) Kim, Y. J.; Chang, X. H.; Han, J. T.; Lim, M. S.; Lee, S. W. *Dalton Trans.* **2004**, 3699.

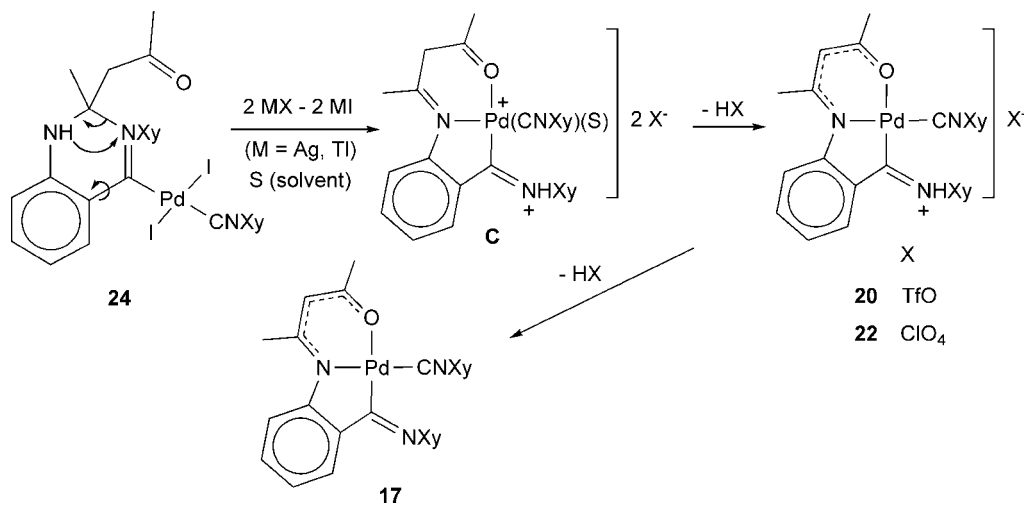
(26) CCDC CSD version 5.28 (November 2006, updated May 2, 2007), 2006.



Scheme 4



Scheme 5



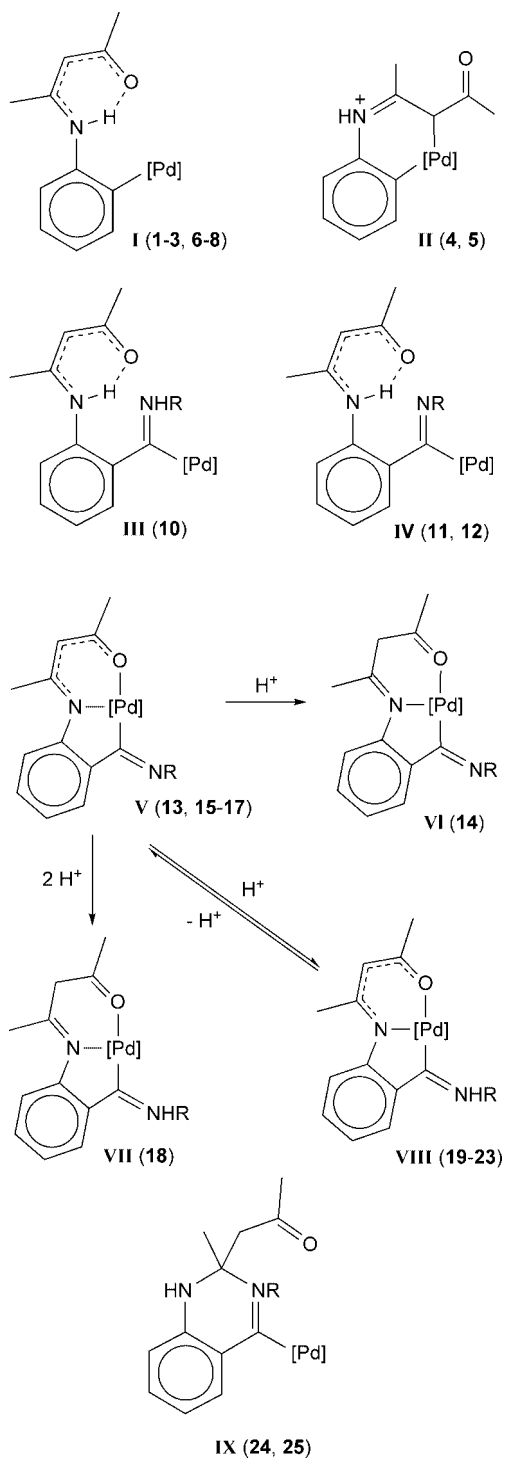
homologue **20**, in the presence of a strong acid (HClO₄ or TfOH, respectively). The reaction of **24** with Tl₂CO₃ causes the deprotonation of the intermediate **20**, giving **17**.

It is noteworthy that, apart from the ability of the aryl ligand Ar to act as monocoordinate (**I**, Chart 2) or *C,C*-chelating (**II**), the insertion of RNC into the Pd–C_{aryl} bond gives rise to seven different ligands, some of them mutually related through acid/base reactions. These include monocoordinate neutral (**III**) and monoanionic (**IV**) iminoacyl ligands; terdentate dianionic (**V**), monoanionic (**VI**, **VII**), or neutral (**VIII**) *C,N,O*-pincer ligands, and the 1,2-dihydroquinazolin-4-yl ligand (**IX**). Additionally, in complexes **13** and **14** the *C,N,O*-pincer ligands use their pendant iminoacyl nitrogen atoms to coordinate a second metal center, thus acting as dianionic or monoanionic tetradentate *N,C,N,O*-bridging pincer ligands.

X-ray Crystal Structures. The crystal structures of complexes **1**, **3**, **5**, **7**, **10**, **13**, **14a**, **14b**, **17**, **21**, **22**, and **24** have been determined, although that of **7** is of poor quality (see above). The two independent cations of **7** are closely similar, as are those of **21** and three independent molecules of **17**.

All the structures display some common features. Thus, in all cases, the Pd atom is in a distorted square-planar environment; the mean deviations from planarity for the Pd atom and its four immediate neighbors is ≤ 0.05 Å except for **24** (0.10 Å, associated with the nonlinearity of the I–Pd–I moiety, angle 168.93(1)°). When *N,N* chelating ligands are present, the N–Pd–N angles are less than 90° (**1**, 'Bubpy, 78.47(7)°; **5**, **7**, tmeda, 83.59(8)°, 83.4(4)°, respectively). In the pincer complexes **13**, **14a**, **14b**, **21**, and **22** the C–Pd–N angles in the five-membered ring are narrower (82.82(15)° and 81.44(15)°, 81.72(9)°, 81.8(2)°, 80.096(6)°, 81.16(6)°, respectively) than the N–Pd–O angle in the more flexible six-membered ring (93.20(14)° and 92.58(13)°, 88.85(9)° and 88.60°, 88.30(18)° and 90.78(18)°, 91.71(5)°, 92.86(6)°, respectively). The Pd–C_{Ar} bond distances in complexes **1**, **3**, **5**, and **7** (1.993–2.009 Å) or the Pd–C_{imine} in complexes **10**, **13**, **14a**, **14b**, **17**, **21**, **22**, and **24** (1.931(4)–2.0130(16) Å) are in the ranges found in aryl or iminoacyl complexes of Pd previously reported (Pd–C_{aryl}, 1.96–2.06 Å; Pd–C_(=N), 1.95–2.07 Å).²⁶

Chart 2



Most bond distances at the *ortho* substituent of the aryl ligand in complexes **1**, **3**, **7**, and **10** or pincer complexes **13**, **14b**, **17**, **21**, and **22** (N–C(Me): 1.318(8)–1.346(3) Å, C(Me)–CH: 1.375(6)–1.412(9) Å, CH–C(O)Me: 1.386(8)–1.499(4) Å, C–O: 1.233(3)–1.283(2) Å) are intermediate between those reported for single and double bonds ($C_{sp^2}-N_{sp^3}$: 1.416 Å, $C_{sp^2}=N_{sp^3}$: 1.316 Å; $C_{sp^2}-C_{sp^2}$: 1.455 Å, $C_{sp^2}=C_{sp^2}$: 1.326 Å; $C_{sp^2}-C_{sp^2}(C=O)$: 1.464 Å, $C_{sp^2}=C_{sp^2}(C=O)$: 1.340 Å; $C_{sp^2}-O$: 1.333 Å, $C_{sp^2}=O$: 1.210 Å).²⁷ In the schemes we have represented this situation by showing an electronic delocalization over the N–C–C–O group.

(27) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Table 3. Classical Hydrogen Bonds (Å, deg)

complex	D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
1	N(1)–H(1)...O	0.80(3)	1.99(3)	2.665(3)	141(3)
3	N(1)–H(1)...O(1)	0.79(4)	2.00(4)	2.664(4)	142(3)
5	N(1)–H(1)...O(2)	0.81(3)	2.05(3)	2.841(3)	166(3)
7	N(1)–H(1)...O(1)	0.88	1.93	2.662(14)	139.0
	N(1')–H(1')...O(1')	0.88	1.91	2.649(13)	141.0
10	N(1)–H(1)...O#1	0.81(3)	2.07(3)	2.863(4)	168(4)
	N(2)–H(2)...O	0.81(3)	2.10(4)	2.647(4)	125(4)
	N(2)–H(2)...O#1	0.81(3)	2.35(3)	3.072(5)	149(4)
	#1: 1-x, 1-y, -z				
21	N(1)–H(1)...O(2)	0.83(2)	2.27(2)	3.092(2)	169(2)
	N(1')–H(1')...O(2')	0.80(2)	2.46(2)	3.220(2)	160(2)
22	N(2)–H(2)...O(2)	0.76(2)	2.18(3)	2.924(2)	168(2)
24	N(1)–H(1)...O#1	0.81(3)	2.16(3)	2.957(2)	169(2)
	#1: 2-x, 1-y, 2-z				

In complexes **5**, **14a**, and **14b**, the coordination or protonation of the methine group interrupts the electronic delocalization over the N–C–C–O group, making the N–C(Me) (1.306(3)–1.283(3) Å) and C–O (1.213(3)–1.233(3) Å) distances shorter and the MeC(N)–C (1.451(4)–1.511(4) Å) and C–C(O)Me (1.494(4)–1.510(4) Å) lengths longer than those in their precursors, approaching N=C and C=O double bonds or C–C single bonds, respectively. The $C_{sp^2}-C_{sp^3}-C_{sp^2}$ angles are rather wide (117.3(2)°, 118.1(2)°, 118.4(2)°) for an sp^3 carbon.

Pd–O distances are shorter in the anionic pincer ligand (2.0441(13)–2.0922(18) Å) than that in the cationic ligand (2.1263(18)–2.131(4) Å), as expected for the stronger enolato O–Pd than carbonyl O–Pd bond.

The C=NXY bond distances in **17** (1.269(3), 1.274(3), 1.271(3) Å) are similar to those found in other iminoacyl palladium complexes and shorter than the C=NHR lengths in its cationic homologues (R = ^tBu (**21**), Xy (**22**), 1.301(2) Å) or in **10** (N(1)–C(7) = 1.293(5) Å), which, in turn, are similar to that found in the only similar structurally characterized palladium complex, namely, [Pd{C(Me)=NHXY}Cl(dppe)]BF₄ (1.291(6) Å).²⁸

In the dinuclear complexes, the central N(1)–C(9)–N(3)–C(29) (**13**) or C(1)–N(1)–C(2)–N(2) (**14a,b**) fragment is planar (mean deviation, 0.04, 0.03, 0.02 Å, respectively), and this plane subtends the Pd–C–N plane angles of 35.6°, 37.1° (**13**), 37.3°, 34.4° (**14a**), and 37.1°, 33.9° (**14b**), leading to a boat conformation.

The *trans* influence sequence $C_{aryl} > C_{sp^3} > PPh_3 > I$ is responsible for the slightly different Pd–N bond distances in complexes containing N^N chelating ligands **1** (2.1281(19) vs 2.0741(19) Å), **5** (2.197(2) vs 2.166(2) Å), and **7** (2.207(10) vs 2.190(9) Å). All other structural parameters are unremarkable.

Intramolecular classical hydrogen bonds of the form N–H...O are observed in complexes **1**, **3**, **7**, and **10**. Intermolecular or cation/anion N–H...O hydrogen bonds between the NH group of the *ortho* substituent with the oxygen of the carbonyl group (**10**, **24**) or a triflate anion (**5**) or between the iminoacyl NH and one oxygen of the ClO₄[−] anion (**21**, **22**; in **21** the ordered perchlorate oxygen is involved, the other three are disordered about the local 3-fold axis) or the carbonyl oxygen (**10**; dimer formation, Figure 16) are also observed (Table 3).

“Weak” hydrogen bonds of the form C–H...O, C–H...F, or C–H...I and in some cases C–H...Pd (H...I and H...Pd distances of about 3.0–3.3 Å indicate the borderline nature of the contacts) are present in several of the complexes; for reasons of space, these are not included in Table 3 (see

(28) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4511.

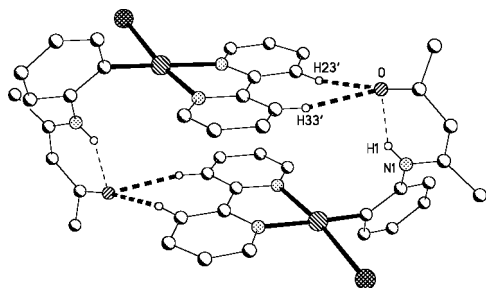


Figure 13. Dimer formation via bifurcated $(\text{C-H})_2 \cdots \text{O}$ interactions in complex **1**. The distance between the stacked ring centroids is 3.7 Å. The symmetry operator is $1/2-x, 1/2-y, 1-z$.

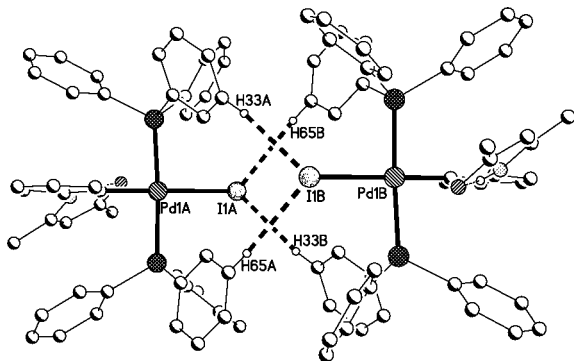


Figure 14. Dimer formation via bifurcated $(\text{C-H})_2 \cdots \text{I}$ interactions in complex **3**. The symmetry operator is $1-x, -y, -z$.

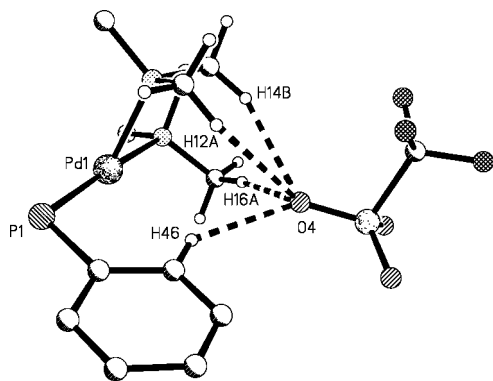


Figure 15. "Tetrafurcate" hydrogen bond system $(\text{C-H})_4 \cdots \text{O}$ in complex **7**. The $\text{H} \cdots \text{O}$ distances lie in the range 2.41–2.65 Å.

Supporting Information). The effects of the more important weak interactions (a subjective assessment!) may be summarized as follows. Compound **1**: Molecules are arranged in pairs across inversion centers by bifurcated $(\text{C-H})_2 \cdots \text{O}$ interactions from the bipy ligands (Figure 13). **3**: Molecules are arranged in pairs by bifurcated $(\text{C-H})_2 \cdots \text{F}$ interactions from the triphenylphosphine ligands (Figure 14). Compound **5**: Two $\text{C-H} \cdots \text{O}$ interactions to the carbonyl oxygen and three $\text{C-H} \cdots \text{O}$ and two $\text{C-H} \cdots \text{F}$ to the triflate result in a complex three-dimensional packing (not shown). Compound **7**: Twelve $\text{C-H} \cdots \text{O}$ and three $\text{C-H} \cdots \text{F}$ interactions to the triflate result in thick layers of residues parallel to the xy plane at $z \approx 1/4, 3/4$ (not shown); one interesting feature is a $(\text{C-H})_4 \cdots \text{O}$ system (Figure 15). Compound **10**: The intramolecular contact $\text{H9A} \cdots \text{Pd}$ is very short at 2.53 Å. Compound **14a**: Seven $\text{C-H} \cdots \text{O}$ interactions to the triflate and one to the acetone lead to a complex three-dimensional packing (not shown). Compound **14b**: The triflate disorder makes a discussion of limited value. It is surprising that only

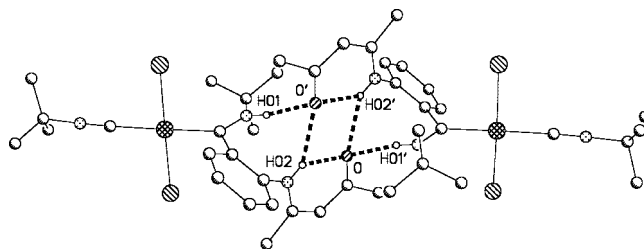


Figure 16. Dimer formation in complex **10** via classical hydrogen bonds (including a three-center interaction).

one of the three presumably activated hydrogens at C5 and C10 makes a short contact to a triflate. Compound **21**: The disordered perchlorates preclude a meaningful discussion of $\text{H} \cdots \text{O}$ interactions. There is an intramolecular $\text{Pd1} \cdots \text{H11A}$ contact of 2.69 Å; in the second cation it is 2.84 Å. The two independent molecules are arranged such that O1' of the second molecule makes an axial contact of 3.23 Å to Pd1. Compound **22**: The perchlorate oxygens are acceptors in one classical and four $\text{C-H} \cdots \text{O}$ interactions, forming layers parallel to $(01\bar{1})$ (Figure 17). Compound **24**: The structural role of "borderline" $\text{H} \cdots \text{Pd}$ and $\text{H} \cdots \text{I}$ contacts is well illustrated here. The hydrogens H33 and H34 are involved in a bifurcated contact to Pd (3.39, 2.96 Å) over an inversion center, and H34 is additionally close to the neighboring I atom (3.33 Å). Combined with the classical hydrogen bond, the overall effect is to form ribbons of molecules parallel to $[101]$ (Figure 18). There is also an intramolecular contact $\text{Pd} \cdots \text{H5}$ of 2.76 Å.

NMR Spectroscopy. The replacement of iodine in IAr by a $[\text{Pd}]$ or C(=NR)[Pd] moiety (complexes **1–3**, **6–8**, or **10–12**, respectively) produces changes in the shielding of a few nuclei of the *ortho* substituent of Ar. Thus, most *MeCN*, *C(O)Me*, CH, and NH resonances appear in the ranges 2.00–1.62, 2.24–1.95, 5.21–4.99, and 12.67–11.94 ppm, respectively, which compare well with those of IAr at 1.85, 2.13, 5.25, and 12.29 ppm. However, *MeCN* protons in **3** (1.03 ppm), **6** (1.34 ppm), and **7** (1.35) and CH proton in **3** (4.83 ppm) appear outside the above ranges, probably because of their shielding by one of the aryl rings of PPh_3 (see Figures 2 and 4). In contrast, the NH protons in complexes **6–8** (13.08–13.69 ppm) are significantly deshielded with respect to ArI, because they are cationic, although the NH proton in the neutral complex **2** (13.07 ppm) is also deshielded. Similarly, carbon *MeCN* (22.0–19.8 ppm), *C(O)Me* (31.5–28.1 ppm), C2 (98.7–97.7 ppm), C1 (163.4–157.3 ppm), and CO (196.1–193.5) nuclei resonate near the corresponding values in ArI at 19.6, 29.2, 97.7, 159.6, and 196.5 ppm, respectively, although it is noticeable that in all complexes *MeCN* and CO resonances are deshielded (by 0.2–2.4 ppm) and shielded (by 0.4–3 ppm), respectively, with respect to ArI.

C1 coordination of the Ar ligand in **4** and **5** causes, with respect to their precursors (Scheme 1), deshielding of *MeCN* protons (by 0.75 and 0.58 ppm, respectively), probably because of their cationic nature, and shielding of the CH proton (by 0.62 and 1.50 ppm, respectively), because of metal coordination. It is surprising that the NH proton in **4** is deshielded by 0.58 ppm with respect to that in **1** but shielded by 0.75 ppm in **5** with respect to **2**.

Pincer complexes **13**, **15–17**, and **19–22** show resonances corresponding to the proton at 2.38–2.12 (*MeCN*), 2.04–1.70 (*C(O)Me*), and 5.19–4.92 (CH) ppm and to carbon at 24.3–22.4 (*MeCN*), 27.4–25.8 (*C(O)Me*), 105.4–102.8 (C2), and 163.7–161.8 (C1) ppm regardless of the nuclearity or the charge of the

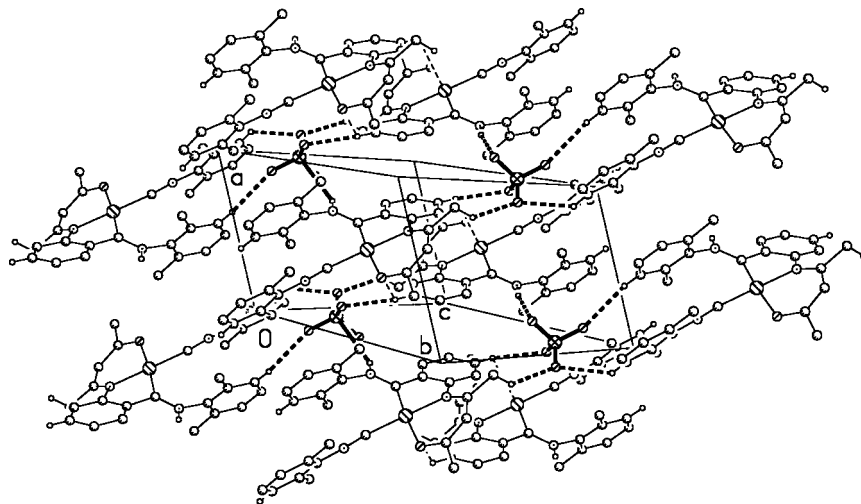


Figure 17. Packing diagram of complex **22**. Perchlorates are drawn with thick bonds; H...O interactions are indicated by thick dashed bonds. One layer parallel to (011) is shown.

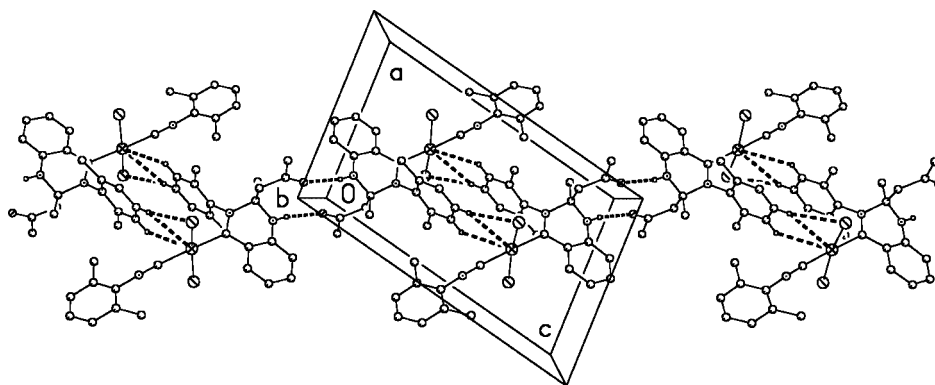


Figure 18. Packing diagram of complex **24**. H...O, H...Pd, and H...I interactions are indicated by thick dashed bonds. The net effect is to form a ribbon of molecules parallel to [101].

complex. However, the resonance for the CO carbon nucleus is deshielded for cationic complexes **19–22** (215.6–217.1 ppm) and the neutral dinuclear complex **13** (207.8 ppm) with respect to neutral **15–17** complexes (182.9–182.1 ppm).

The mono- or diprotonation of the pincer ligands in **13** or **15** deshields mainly the *Me*CN and C(O)*Me* protons and the C1 carbon nuclei (by 0.53 or 0.44, by 0.66 or 0.48, and by 16.5 or 17.4 ppm, respectively) in complex **14a** or **18**, respectively, and the CO carbon nucleus in **18** (by 34.5 ppm).

The resonance from the iminoacyl carbon bonded to Pd appears for the non-pincer complexes **11** and **12** at 166.5 and 174.2, respectively, for the neutral (**15–18**) or cationic (**19–22**) pincer derivatives in the ranges 178.2–179.0 and 181.8–183.3 ppm, respectively, or for the dicationic complexes **14a** and **18** at 200.5 and 191.5 ppm, respectively, which is probably related to the positive charge supported by the palladium atom in each case.

In complexes **24** and **25** we assigned the resonance of the quinazolyl carbon bonded to palladium on the basis of a recent paper²⁹ reporting a Pd complex bearing a C–C(=NEt₂)CH=CHPh ligand *trans* to PPh₃, in which the C

atom bonded to Pd was shown in the ¹³C{¹H} NMR spectrum to appear at 228 ppm with a ²*J*_{CP} coupling constant of 147 Hz.

Conclusions

The study of the reactivity of the functionalized iodoarene IAr toward Pd(dba)₂ in the presence of various N donor ligands, and the insertion reaction of isocyanides into the Pd–C_{aryl} bond present in the resulting *ortho*-palladated derivatives, has allowed us to prepare a wide variety of complexes containing novel aryl, iminoacyl, or *C,N,O*-pincer ligands as well as some 1,2-dihydroquinazolin-4-ylpalladium complexes, which, as far as we are aware, are the first such derivatives of any metal. The complexes described are connected through a rich acid/base chemistry.

Acknowledgment. Dedicated to Profs. Juan Forniés, M. Pilar García, José Gimeno, and Miguel Yus on the occasion of their 60th birthday (1947 was an excellent vintage!). We thank Ministerio de Ciencia y Tecnología and FEDER for financial support (CTQ2004–05396) and for a grant to A.J.M.M.

Supporting Information Available: CIF files for complexes **1**, **3**, **5**, **7**, **10**, **13**, **14a**, **14b**, **17**, **21**, **22**, and **24**. Nonclassical hydrogen bond parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM800205G

(29) Albéniz, A. C.; Espinet, P.; Pérez-Mateo, A.; Nova, A.; Ujaque, G. *Organometallics* **2006**, 1293.