ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 5693–5707 5693
DOI: 10.1021/om1005403

Reactivity of *ortho*-*β*-Enaminone-phenyl Palladium Complexes. Insertion of CO into the Pd−C Bond to Give the First Acyl C,N,O-Pincer Complexes. Sequential Insertion of Dimethylacetylenedicarboxylate into the Enaminone C−H Bond and of Isocyanide into the Pd−C Bond. A New Photooxigenation/Cyclization Process†

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

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

Delia Bautista

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

Received May 31, 2010

Insertion of CO into the Pd−C_{aryl} bond of complexes [PdI{C_6H_4{NHC(Me)CHC(O)Me}-2}(N^N)] afforded the benzoyl derivatives [PdI{C(O)C_6H_4{NHC(Me)CHC(O)Me}-2}(N^N)] [N^N = 4,4′-di-*tert*-butyl-2,2′-dipyridyl (^{t}Bubpy) (**1a**), *N,N,N′,N′*-tetramethylethylenediamine (tmeda) (**1b**)]. The reactions of [Pd{*C,C*-C_6H_4{NH=C(Me)CHC(O)Me}-2}(tmeda)]OTf (OTf = CF_3SO_3) with excess CO and tmeda (2:1) or HOTf (1:1) produced the dinuclear benzoyl complex [{Pd{*C,N,O*-{C(O)C_6H_4{NC(Me)CHC(O)Me}-2}$_2$(μ-tmeda)] (**2**) or [Pd_2{μ-*O,C,N,O′*-{O=CC_6H_4{NC(Me)-CHC(O)Me}-2}$_2$}] (**3**), respectively. The latter reacted with anionic or neutral ligands to give complexes Bu_4N[{Pd{*C,N,O*-{C(O)C_6H_4{NC(Me)CHC(O)Me}-2}$_2$(μ-OH)] (**4**), Q[Pd{*C,N,O*-{C-(O)C_6H_4{NC(Me)CHC(O)Me}-2}}Cl] [Q = PPN (**5a**), NMe_4 (**5b**)], or [{Pd{*C,N,O*-{C(O)C_6H_4-{NC(Me)CHC(O)Me}-2}L] (L = CN^tBu (**6a**), CNXy (**6b**), PPh_3 (**6c**), NH_3 (**6d**), NH_2Me (**6e**), MeCN (**6f**), dmso (**6g**)), respectively. The reaction of dimethylacetylenedicarboxylate (DMAD) with [PdI-{C_6H_4{NHC(Me)CHC(O)Me}-2}(tmeda)] (1:1) afforded [PdI{C_6H_4{NHC(Me)C{*Z*-C(CO_2Me)=CH(CO_2Me)}C(O)Me}}-2}(tmeda)] (**7*Z***), resulting from the insertion of the alkyne into the C-(sp^2)−H bond of the enaminone substituent. **7*Z*** isomerized into the *E* analogue (**7*E***) when heated in toluene at 95 °C and reacted in two steps with $AgClO_4$ and XyNC (1:1:2) to give the C,N,O-pincer derivative Pd{*C,N,*O-{C(=NXy)C_6H_4{NC(Me)C{C(CO_2Me)=CHCO_2Me)}C(O)Me}-2}(CNXy)] (**8**) as a mixture of the *Z* and *E* isomers. The latter complex converted, after a photochemical oxygenation, into the palladacycle [Pd{*C,N,O*-{C(=NXy)C_6H_4{N(dmoc)}-2](CNXy)]·2$CHCl_3$ (**9**), where the imino substituent dmoc is the cycle 1,2-di(methoxycarbonyl)-3-oxocyclopent-1-ene-4-yl. Compound **8** or **9** reacted with triflic or picric acid to give the species Pd{*C,N,*O-{C(=NHXy)C_6H_4-{NC(Me)C{C(CO_2Me)=CHCO_2Me)}C(O)Me}-2}(CNXy)]OTf (**10**) or [Pd{*C,N,O*-{C(=NXy)C_6-H_4{N(dmoc)}-2](CNXy)]·Hpic (**11**; Hpic = picric acid), respectively. The crystal structures of complexes **2**, **3**, **5a**, **6b**, **6c**, **6e**, **7*Z***, **7*E***, and **10** have been determined.

Introduction

We are studying the synthesis of ortho-functionalized aryl metal complexes and their reactivity toward unsaturated molecules (isocyanides,[1−11] CO,[1,3,5,9,11−16] alkynes,[3−6,11,12,17−19] alkenes,[3,20] allenes,[19,20] carbodiimides,[21,22] isothiocyanates,[9,22] nitriles,[22,23] cyanamides[22]). These reactions are of interest because they are involved in many stoichiometric and catalytic palladium-mediated organic transformations.[3,5,6,9,10,12−14,17,24]

† Part of the Dietmar Seyferth Festschrift. Dedicated to Prof. Dietmar Seyferth, on occasion of his retirement as Editor-in-Chief of Organometallics, for his outstanding contribution to organometallic chemistry.

*To whom correspondence should be addressed. E-mail: jvs1@um.es (J.V.), mch@um.es (M.T.C.), dbc@um.es (D.B.). WWW: http://www.um.es/gqo/.

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

(2) Vicente, J.; Abad, J. A.; Frankland, A. D.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272. Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Rink, B.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **2004**, *23*, 1292. Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G. *Organometallics* **2004**, *23*, 4711. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D.; Jones, P. G. *Organometallics* **2005**, *24*, 2516. Vicente, J.; Chicote, M. T.; Vicente-Hernández, I.; Bautista, D. *Inorg. Chem.* **2007**, *46*, 8939.

Published on Web 08/04/2010

Recently, we have described some aryl palladium complexes ortho-functionalized with a β-enaminone substituent and their reactivity toward isocyanides. The functionalized aryl ligand was designed with the hope that novel types of pincer complexes would result upon the insertion of unsaturated molecules into the $Pd-C_{aryl}$ bond and that novel reactivity patterns could be found caused by the severe restrictions imposed on the coordination sphere of the metal by the tridentate ligand. Our expectations were more than fulfilled since, by reacting these aryl complexes with isocyanides under different reaction conditions, not only C,N,O-pincer but also bridging iminoacyl derivatives, related to each other through acid/base processes, were obtained.[8] These findings prompted us to study the reactivity of the same starting materials toward CO and alkynes.

Carbonylation reactions incorporate carbon monoxide, the currently most important C_1 building block, into different organic substrates. These reactions, usually carried out in the presence of a nucleophile and catalyzed by palladium complexes, are assumed to take place through acylpalladium intermediates. Their outstanding significance is mainly based on the fact that they have given access, both at laboratory and industrial levels, to valuable products such as alcohols, aldehydes, carboxylic acids, anhydrides, acid fluorides, esters, or amides and to a variety of heterocycles including lactones, lactams, oxazoles, thiazoles, and imidazoles, as compiled in some recent reviews.[25] Although most carbonylation reactions have been carried out with alkyl derivatives, a few carbonylation products of arylpalladium(II) complexes have been reported.[1,3,5,8,9,12,13,15,16,26]

On the other hand, although the reactions of alkynes with metal complexes have led to an enormous amount and variety of complexes resulting from the coordination of the alkyne in various manners or its insertion into different M−X (X = H, C, S, P, etc.) bonds, only a few examples are known in which the alkyne reacts with the ligands present in the complex. In particular, only three complexes have been characterized by X-ray crystallography, in which DMAD inserts into the C−H or S−H bond of chelating diphosphanylmethanide,[27] σ-ferrocenyl,[28] or bridging hydrosulfide[29] ligands, respectively, none of them containing palladium.

(3) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Förtsch, W.; Jones, P. G. *Organometallics* **2004**, *23*, 4414.
(4) Vicente, J.; Abad, J. A.; López-Serrano, J.; Clemente, R.; Ramírez de Arellano, M. C.; Jones, P. G.; Bautista, D. *Organometallics* **2003**, *22*, 4248.
(5) Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G.; Nájera, C.; Botella-Segura, L. *Organometallics* **2005**, *24*, 5044.
(6) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557.
(7) Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Bautista, D. *Organometallics* **2009**, *28*, 5915.
(8) Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Jones, P. G.; Bautista, D. *Organometallics* **2008**, *27*, 3254.
(9) Vicente, J.; Saura-Llamas, I.; García-López, J. A.; Bautista, D. *Organometallics* **2009**, *28*, 448.
(10) Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587.
(11) Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683.
(12) Vicente, J.; Saura-Llamas, I.; Turpín, J.; Bautista, D.; Ramírez de Arellano, C.; Jones, P. G. *Organometallics* **2009**, *28*, 4175.
(13) Vicente, J.; Saura-Llamas, I.; García-López, J. A.; Calmuschi-Cula, B.; Bautista, D. *Organometallics* **2007**, *26*, 2768.
(14) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2003**, *22*, 1967.
(15) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem.—Eur. J.* **1999**, *5*, 3066.
(16) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Commun.* **1997**, 959.
(17) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *J. Organomet. Chem.* **1992**, *436*, C9. Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G. *Inorg. Chim. Acta* **1994**, *222*, 1. Vicente, J.; Abad, J. A.; Fernández-de-Bobadilla, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 24. Vicente, J.; Abad, J. A.; Gil-Rubio, J. *Organometallics* **1996**, *15*, 3509. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2000**, *19*, 752. Vicente, J.; Abad, J. A.; López-Pelaez, B.; Martínez-Viviente, E. *Organometallics* **2002**, *21*, 58.
(18) Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G. *Organometallics* **1995**, *14*, 2677. Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2535. Vicente, J.; Saura-Llamas, I.; Ramírez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529. Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 1422. Vicente, J.; Martínez-Viviente, E.; Fernandez-Rodriguez, M.-J.; Jones, P. G. *Organometallics* **2009**, *28*, 5845.
(19) Vicente, J.; Abad, J. A.; Bergs, R.; Ramírez de Arellano, M. C.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2000**, *19*, 5597. Vicente, J.; Abad, J. A.; Lopez-Saez, M.-J.; Jones, P. G. *Organometallics* **2010**, *29*, 409.
(20) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2008**, *27*, 3978.
(21) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2006**, *25*, 1851.
(22) Vicente, J.; Abad, J. A.; Lopez-Saez, M.-J.; Jones, P. G. *Chem.—Eur. J.* **2010**, *16*, 661.
(23) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 6001.
(24) (a) Holton, R. A. *Tetrahedron Lett.* **1977**, *18*, 355. (b) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1980**, *41*, 229. (c) Barr, N.; Dyke, S. F.; Quessy, S. N. *J. Organomet. Chem.* **1983**, *253*, 391. (d) O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1165. (e) Ryabov, A. D. *Synthesis* **1985**, 233. (f) Ryabov, A. D.; Sakodinskaya, I. K.; Dvoryantsev, S. N.; Eliseev, A. V.; Yatsimirsky, A. K.; Kuz'mina, L. G.; Struchkov, Y. T. *Tetrahedron Lett.* **1986**, *27*, 2169. (g) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (h) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 2386. (i) Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116. (j) Beydoun, N.; Pfeffer, M. *Synthesis* **1990**, 729. (k) Maassarani, F.; Pfeffer, M.; Borgne, G. L. *Organometallics* **1990**, *9*, 3003. (l) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. (m) Beydoun, N.; Pfeffer, M.; Decian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3693. (n) Dupont, J.; Pfeffer, M.; Theurel, L.; Rotteveel, M. A.; Decian, A.; Fischer, J. *New J. Chem.* **1991**, *15*, 551. (o) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Organomet. Chem.* **1991**, *406*, 309. (p) Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335. (q) Pfeffer, M.; Sutter, J. P.; Rotteveel, M. A.; Decian, A.; Fischer, J. *Tetrahedron* **1992**, *48*, 2427. (r) Pfeffer, M.; Sutter, J. P.; Decian, A.; Fischer, J. *Organometallics* **1993**, *12*, 1167. (s) Wensbo, D.; Eriksson, A.; Jeschke, T.; Annby, U.; Gronowitz, S.; Cohen, L. A. *Tetrahedron Lett.* **1993**, *34*, 2823. (t) Larock, R. C.; Doty, M. J.; Cacchi, S. J. *J. Org. Chem.* **1995**, *60*, 3270. (u) Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214. (v) Negishi, E.; Coperet, C.; Ma, S. M.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5904. (w) Fagnola, M. C.; Candiani, I.; Visentin, G.; Cabri, W.; Zarini, F.; Mongelli, N.; Bedeschi, A. *Tetrahedron Lett.* **1997**, *38*, 2307. (x) Dyker, G.; Markwitz, H. *Synthesis* **1998**, 1750. (y) Park, S. S.; Choi, J. K.; Yum, E. K.; Ha, D. C. *Tetrahedron Lett.* **1998**, *39*, 627. (z) Ma, C. R.; Liu, X. X.; Yu, S.; Zhao, S.; Cook, J. M. *Tetrahedron Lett.* **1999**, *40*, 657. (aa) Catellani, M.; Motti, E.; Ghelli, S. *Chem. Commun.* **2000**, 2003. (bb) Kadnikov, D. V.; Larock, R. C. *Org. Lett.* **2000**, *2*, 3643. (cc) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2001**, *20*, 2767. (dd) Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2001**, *66*, 412. (ee) Zhang, H. M.; Larock, R. C. *Org. Lett.* **2001**, *3*, 3083. (ff) Zhang, H. F.; Hussain, I.; Brust, M.; Cooper, A. I. *Chem. Commun.* **2006**, 2539.
(25) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114. Veige, A. S. *Polyhedron* **2008**, 27. Trzeciak, A. M.; Ziołkowski, J. J. *Coord. Chem. Rev.* **2005**, *249*, 2308. Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402.
(26) Dupont, J.; Pfeffer, M.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 899. Cinellu, M. A.; Gladiali, S.; Minghetti, G. *J. Organomet. Chem.* **1989**, *363*, 401. Negishi, E.; Zhang, Y.; Shimoyama, I.; Wu, G. *J. Am. Chem. Soc.* **1989**, *111*, 8018. Dupont, J.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3193. Suzaki, Y.; Osakada, K. *Organometallics* **2003**, *22*, 2193. Lindsell, W. E.; Palmer, D. D.; Preston, P. N.; Rosair, G. M.; Jones, R. V. H.; Whitton, A. J. *Organometallics* **2005**, *24*, 1119. Komine, N.; Tsutsuminai, S.; Hirano, M.; Komiya, S. *J. Organomet. Chem.* **2007**, *692*, 4486. Sergeev, A. G.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2008**, *130*, 15549.
(27) Ruiz, J.; Quesada, R.; Riera, V.; Castellano, E.; Piro, O. *Organometallics* **2004**, *23*, 175.

Herein we report a family of palladium complexes bearing monocoordinate or C,N,O-pincer benzoyl ligands, which result from the insertion of CO into the Pd−C_{aryl} bond of some β-enaminone-substituted aryl complexes under different reaction conditions. Complexes with a monocoordinate benzoyl ligand spontaneously lose CO at room temperature: slowly in the solid state and faster in solution. The current interest in acyl complexes resides in the fact that some of them behave as CO-releasing molecules (CORMs), which are relevant in view of the versatile properties of CO and its recently recognized participation in important biological processes causing antioxidative, vasodilator, anti-inflammatory, antiapoptotic, and antiproliferative effects.[30,31] Additionally, decarbonylation of acyl complexes by thermal or photochemical means has been reported to afford aryl or perfluoroalkyl complexes not accessible through more conventional ways.[32] As far as we are aware, the complexes described here are the first acyl C,N,O-pincer derivatives of any metal.[33,34] The crystal structures we describe include the first palladium example of a very small family of complexes bearing a bridging acyl ligand[35−39] and a dipalladium complex with a bridging *N,N′*-tmeda ligand, of which only a few precedents are known,[40] including one of palladium.[41]

We also report that dimethylacetylenedicarboxylate (DMAD) inserts into the C−H bond of the β-enaminone substituent instead of into the C−Pd bond. The attack of DMAD on various β-enaminones has been reported recently.[42,43] In addition, we have found that the resulting complex inserts an isocyanide into the Pd−C bond, which, in turn, undergoes a photooxygenation process giving rise to an unprecedented palladium pincer derivative and acetic acid.

Experimental Section

General Procedures. When not stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. The molar conductivities were measured with a CRISON micro CM 2200 conductimeter on ca. 5×10^{-4} M solutions in acetone. 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. The NMR assignments were performed, in some cases, with the help of APT, HMQC, and HMBC experiments. Schemes 1, 2 and 5 show the atom numbering used in the NMR assignments. CO (Air Products), HOTf, PPh_3, XyNC, ^{t}BuNC, tmeda, bpy, ^{t}Bubpy (Fluka), NH_2Me, $AgClO_4$ (Sigma-Aldrich), DMAD (Alfa Aesar), Hpic (Probus), NH_3 (Carburos Metálicos), MeCN, and dmso (SDS) were obtained from commercial sources. $[Pd_2(dba)_3]\cdot$dba ("$Pd(dba)_2$"),[44] [PdI{C_6H_4-{NHC(Me)CHC(O)Me}-2}(N^N)] (N^N = tbbpy, tmeda), and [Pd{*C,C*-C_6H_4{NH=C(Me)CHC(O)Me}-2}(tmeda)]OTf[8] were prepared as reported in the literature. The solvents were distilled before use.

Synthesis of [PdI{C(O)C_6H_4{NHC(Me)CHC(O)Me}-2}(N^N)] [N^N = ^{t}Bubpy (1a), tmeda (1b)]. CO was bubbled for 5 min through a solution of [PdI{C_6H_4{NHC(Me)CHC(O)Me}-2}-(N^N)] (for **1a**, N^N = 4,4′-di-*tert*-butyl-2,2′-dipyridyl = ^{t}Bubpy, 300 mg, 0.44 mmol; for **1b**, N^N = *N,N,N′,N′*-tetramethylethylenediamine = tmeda, 600 mg, 1.15 mmol) in CH_2Cl_2 (3 mL), and the solution was stirred under a CO atmosphere for 16 (**1a**) or 18 (**1b**) h. Upon the addition of cold Et_2O (25 mL, 0 °C; for **2b** under a CO atmosphere) a suspension formed, which was stirred in a water/ice bath (0 °C) for 5 (**1a**) or 15 (**1b**) min and filtered. The solid collected was washed with Et_2O (3 × 3 mL) and dried by suction to give **1a** or **1b** as a yellow solid. **1b** was stored at 4 °C under CO atmosphere.

1a. Yield: 260 mg, 83%. Mp: 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.420 (s, 9 H, ^{t}Bu), 1.423 (s, 9 H, ^{t}Bu), 1.92 (s, 3 H, Me[8]), 2.00 (s, 3 H, Me[11]), 4.93 (s, 1 H, H[9]), 7.03 (d, 1 H, Ar, $^3J_{HH}$ = 7 Hz), 7.26 (m, 1 H, Ar), 7.39 ("t", 1 H, Ar, $^3J_{HH}$ = 7 Hz), 7.43 (d, 1 H, ^{t}Bubpy, $^3J_{HH}$ = 6 Hz), 7.46 (d, 1 H, ^{t}Bubpy, $^3J_{HH}$ = 6 Hz), 7.93 (s, 1 H, ^{t}Bubpy), 7.97 (s, 1 H, tbbpy), 8.00 (d, 1 H, Ar, $^3J_{HH}$ = 7 Hz), 8.32 (d, 1 H, ^{t}Bubpy, $^3J_{HH}$ = 6 Hz), 9.25 (d, 1 H, ^{t}Bubpy, $^3J_{HH}$ = 6 Hz), 12.81 (br, 1 H, NH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.2 (Me[8]), 28.6 (Me[11]), 30.3 (Me, ^{t}Bu), 30.4 (Me, ^{t}Bu), 35.3 (*C*Me_3), 35.4 (*C*Me_3), 96.5 (C[9]), 117.6 (CH, tbbpy) 118.4 (CH), 123.1 (CH), 123.8 (CH), 126.0 (CH), 127.7 (CH), 130.0 (CH), 131.2 (CH), 136.5 (C), 138.8 (C), 150.1 (CH), 151.9 (CH), 153.4 (C), 154.8 (C), 160.6 (C[7]), 162.9 (C), 163.1 (C), 194.7 (C[10]), 224.1 (C[12]). IR (cm^{-1}): ν(C=O) 1652. Anal. Calcd for $C_{30}H_{36}N_3O_2IPd$: C, 51.19; H, 5.15; N, 5.97. Found: C, 50.90; H, 5.45; N, 6.11.

1b. Yield: 530 mg, 84%. Mp: 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.03 (s, 3 H, C[8]), 2.10 (s, 3 H, Me[11]), 2.45−2.96 (various m, 4 H, CH_2, tmeda), 2.53 (br s, 6 H, Me, tmeda), 2.59 (br s, 6 H, Me, tmeda), 5.31 (s, 1 H, H[9]), 6.98 (d, 1 H, Ar, $^3J_{HH}$ = 8 Hz), 7.29 (t, 1 H, Ar, $^3J_{HH}$ = 7 Hz), 7.36 (td, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.43 (d, 1 H, Ar, $^3J_{HH}$ = 7 Hz), 12.70 (s, 1 H, NH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.0 (Me[8]), 29.4 (Me[11]), 48.9 (Me, tmeda), 50.0 (Me, tmeda), 57.7 (CH_2, tmeda), 61.5 (CH_2, tmeda), 99.7 (C[9]), 125.0 (CH, Ar), 126.4 (CH, Ar), 131.1 (CH, Ar), 134.1 (C, Ar), 135.0 (CH, Ar), 135.2 (C, Ar), 160.0 (C[7]), 195.7 (C[10]), 222.3 (C[12]). IR (cm^{-1}): ν(C=O) 1628. Anal. Calcd for $C_{18}H_{28}N_3O_2IPd$: C, 39.18; H, 5.11; N, 7.62. Found: C, 38.55; H, 4.99; N, 7.49.

Synthesis of [{Pd{*C,N,O*-{C(O)C_6H_4{NC(Me)CHC(O)Me}-2}$_2$(μ-tmeda)] (2). To a suspension of [Pd{*C,C*-C_6H_4{NH=C(Me)CHC(O)Me}-2}(tmeda)]OTf[8] (530 mg, 0.97 mmol) in acetone (5 mL) was added tmeda (0.15 mL, 1.0 mmol), and after 5 min of stirring, CO was bubbled through the reaction

(28) Onitsuka, K.; Yoshida, T.; Adachi, T.; Yoshida, T.; Sonogashira, K. *Chem. Lett*. **1995**, 233.
(29) Kaneko, Y.; Suzuki, T.; Isobe, K. *Organometallics* **1998**, *17*, 996.
(30) Alberto, R.; Motterlini, R. *Dalton Trans*. **2007**, 1651.
(31) Hartinger, C. G.; Dyson, P. J. *Chem. Soc. Rev*. **2009**, *38*, 391.
(32) King, R. G.; Bisnette, M. B. *J. Organomet. Chem*. **1964**, *2*, 1651.
(33) https://scifinder.cas.org/
(34) *Cambridge Structural Database*, version 5.30; Cambridge Crystallographic Data Centre: Cambridge, U.K., November 2008, Updated September 2009; www.ccdc.cam.ac.uk.
(35) Acha, F.; Ciganda, R.; Garralda, M. A.; Hernandez, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Dalton Trans*. **2008**, 4602. Acha, F.; Garralda, M. A.; Hernandez, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R.; Zarandona, M. *Eur. J. Inorg. Chem*. **2006**, 3893.
(36) Mason, M. R.; Song, B.; Han, Y.; Hu, X. *Inorg. Chim. Acta* **2008**, *361*, 3332.
(37) Schweiger, M. J.; Nagel, U.; Beck, W. *J. Organomet. Chem*. **1988**, *355*, 289.
(38) Funaioli, T.; Cavazza, C.; Marchetti, F.; Fachinetti, G. *Inorg. Chem*. **1999**, *38*, 3361.
(39) Mason, M. R.; Song, B.; Kirschbaum, K. *J. Am. Chem. Soc*. **2004**, *126*, 11812.
(40) Kheradmandan, S.; Fox, T.; Schmalle, H. W.; Venkatesan, K.; Berke, H. *Eur. J. Inorg. Chem*. **2004**, *2004*, 3544. Lee, H. K.; Lam, T. S.; Lam, C. K.; Li, H. W.; Fung, S., M. *New J. Chem*. **2003**, *27*, 1310.
(41) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun*. **2007**, *28*, 2033.
(42) Moradi, S.; Rajabi Mehr, F.; Baharvand, A.; Rostami, C. *Iranian J. Chem. Chem. Eng*. **2008**, *27*, 17.
(43) Simunek, P.; Pesková, M.; Bertolasi, V.; Lycka, A.; Machácek, C. *Eur. J. Org. Chem*. **2004**, *2004*, 5055. Ali, A. A.; Winzerberg, K. N. *Aust. J. Chem*. **2005**, *58*, 870.
(44) Takahashi, Y.; Ito, S.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun*. **1970**, 1065.

mixture for 10 min. An orange solution initially formed, which converted into a suspension within a few minutes. The suspension was further stirred under a CO atmosphere for 6 h and concentrated under vacuum (1 mL), and H_2O (25 mL) was added. The suspension was filtered, and the solid collected was washed with Et_2O (3 × 5 mL) and dried by suction to give **2** as an orange solid. Yield: 268.8 mg, 76%. Mp: 170 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.91 (s, 3 H, Me^{11}), 2.25 (s, 3 H, Me^8), 2.69 (s, 6 H, Me, tmeda), 3.39 (s, 2 H, CH_2), 4.97 (s, 1 H, H^9), 6.78 (t, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz), 7.10 (d, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz), 7.22 (td, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz), 7.36 (dd, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 24.3 (Me^8), 27.9 (Me^{11}), 51.2 (Me, tmeda), 60.2 (CH_2), 103.2 (C^9), 120.6 (CH, Ar), 122.7 (CH, Ar), 122.9 (CH, Ar), 132.1 (CH, Ar), 139.8 (C), 157.1 (C), 164.2 (C^7), 185.6 (C^{10}), 216.3 (C^{12}). IR (cm^{-1}): ν(C═O), 1653. Anal. Calcd for $C_{30}H_{38}N_4O_4Pd_2$: C, 49.29; H, 5.24; N, 7.66. Found: C, 48.85; H, 5.13; N, 7.93. FAB$^+$ MS: (*m*/*z*, %) 732.0 [M$^+$, 8], 423.0 [{Pd{*C,N,O*-{C(O)C$_6$H$_4$}{NC(Me)CHC(O)Me}-2}{tmeda} − 1 H}$^+$, 84]. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a CH_2Cl_2 solution of **2**.

Synthesis of [Pd$_2${μ-*O,C,N,O*′-{O═CC$_6$H$_4${NC(Me)CHC(O)Me}-2}$_2$}] (3). CO was bubbled through a suspension of [Pd{*C,C*-C$_6$H$_4${NH═C(Me)CHC(O)Me}-2}(tmeda)]OTf[8] (800 mg, 1.47 mmol) in acetone (10 mL) for 15 min. HOTf (130 μL, 1.49 mmol) was added, and the stirring was continued for 1 h while the reaction mixture was kept under a CO atmosphere. Acetone (50 mL) was added to the resulting suspension, and the mixture was filtered through a short pad of Celite. The solution was concentrated under vacuum to dryness, the residue was stirred with acetone (5 mL), and the suspension was filtered. The solid collected was washed with acetone (3 × 5 mL) and dried by suction to give a brown-red solid containing **3** with traces of colloidal palladium, which were removed by treating the crude product with MeCN (70 mg, 1.7 mmol) in acetone (15 mL), filtering the resulting solution through a short pad of Celite, concentrating under vacuum to dryness, stirring the residue with acetone, filtering the suspension, washing the solid with Et_2O, and drying the solid by suction. Yield: 407 mg, 90%. Mp: 177 °C (dec). ^{1}H and ^{13}C NMR spectra could only be measured in dmso-d_6 solution and coincide with those of **6g** in the same solvent. IR (cm^{-1}): ν(C═O), ν(C═C), 1604, 1567, 1549, 1519. Anal. Calcd for $C_{24}H_{22}N_2O_4Pd_2$: C, 46.85; H, 3.60; N, 4.55. Found: C, 46.31; H, 3.48; N, 4.42. Crystals of **3** suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a $CHCl_3$ solution of complex **6f**.

Synthesis of Bu$_4$N[{Pd{*C,N,O*-{C(O)C$_6$H$_4${NC(Me)CHC(O)Me}-2}$_2$(μ-OH)}] (4). To a suspension of **3** (33 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was added (Bu$_4$N)OH (0.05 mL, 1 M solution in MeOH). After 30 min of stirring the resulting solution was concentrated under vacuum to 1 mL, Et_2O (20 mL) was added, and the resulting suspension was filtered. The brown solid collected was dissolved in CH_2Cl_2 (1 mL) and filtered though a short pad of anhydrous $MgSO_4$, and the solution was dropped into stirred *n*-hexane (20 mL). The suspension was filtered and the solid was dried by suction to give **4** as a yellow powder. Yield: 30 mg, 69%. Mp: 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.87 (t, 6 H, CH_3, NBu_4, $^3J_{HH}$ = 7.2 Hz), 1.37 (m, 4 H, CH_2, NBu_4), 1.53 (m, 4 H, CH_2, NBu_4), 1.80 (s, 3 H, C^{11}), 2.18 (s, 3 H, Me^8), 3.45 (m, 4 H, CH_2, NBu_4), 4.79 (s, 1 H, H^9), 6.67 (t, 1 H, Ar, $^3J_{HH}$ = 7.0 Hz), 7.07−7.14 (m, 2 H, Ar), 7.35 (d, 1 H, Ar, $^3J_{HH}$ = 6.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 13.8 (Me, NBu_4), 19.8 (CH_2, NBu_4), 24.2 (CH_2, NBu_4), 24.7 (Me^8), 28.1 (Me^{11}), 58.7 (CH_2, NBu_4), 102.4 (C^9), 120.0 (CH, Ar), 121.5 (CH, Ar), 122.2 (CH, Ar), 131.4 (CH, Ar), 140.0 (C), 158.2 (C), 162.2 (C^7), 185.6 (C^{10}), 217.4 (C^{12}). Λ_M = 140 Ω^{-1} cm^2 mol^{-1} (6.13 × 10^{-4} mol L^{-1}). IR (cm^{-1}): ν(C═O), 1666. Anal. Calcd for $C_{40}H_{59}N_3O_5Pd_2$: C, 54.92; H, 6.80; N, 4.80. Found: C, 54.66; H, 7.20; N, 4.87.

Synthesis of PPN[Pd{*C,N,O*-{C(O)C$_6$H$_4${NC(Me)CHC(O)Me}-2}}Cl] (5a). To a suspension of **3** (100 mg, 0.16 mmol) in $CHCl_3$ (10 mL) was added (PPN)Cl (186.6 mg, 0.33 mmol). The reaction mixture was stirred for 5 h and filtered through a short pad of Celite. The solution was concentrated under vacuum (1 mL), and cold Et_2O (0 °C, 20 mL) was added. After 15 min of stirring in an ice/water bath the suspension was filtered and the solid collected was washed with Et_2O (3 × 5 mL), recrystallized from CH_2Cl_2/Et_2O, and dried first by suction and then in an oven at 70 °C for 8 h to give **5a** as a yellow solid. Yield: 253 mg, 88%. Mp: 184 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.90 (s, 3 H, Me^{11}), 2.19 (s, 3 H, Me^8), 4.85 (s, 1 H, H^9), 6.59 (m, 1 H, Ar), 7.13 (d, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz), 7.06 (m, 1 H, Ar), 7.30 (d, 1 H, Ar, $^3J_{HH}$ = 7 Hz), 7.41−7.51 (various m, 24 H, ortho- + meta-PPN), 7.67 (m, 6 H, para-PPN). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 24.2 (Me^8), 28.1 (Me^{11}), 102.2 (C^9), 119.7 (CH, Ar), 121.1 (CH, Ar), 122.6 (CH, Ar), 126.7 (dd, ipso-C, PPN, $^1J_{CP}$ = 108 Hz, $^3J_{CP}$ = 2 Hz), 129.4 (m, ortho-PPN), 130.6 (CH, Ar), 131.8 (m, meta-PPN), 133.8 (para-PPN), 140.4 (C), 157.0 (C), 162.3 (C^7), 185.5 (Me^{10}), 212.4 (Me^{12}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 21.2. Λ_M = 135 Ω^{-1} cm^2 mol^{-1} (5.49 × 10^{-4} mol L^{-1}). IR (cm^{-1}): ν(C═O), 1661. Anal. Calcd for $C_{48}H_{41}ClN_2O_2P_2Pd$: C, 65.39; H, 4.69; N, 3.18. Found: C, 65.26; H, 4.92; N, 3.23. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion on *n*-pentane into a solution of **5a** in CH_2Cl_2.

Synthesis of Me$_4$N[Pd{*C,N,O*-{C(O)C$_6$H$_4${NC(Me)CHC(O)Me}-2}}Cl] (5b). To a suspension of **3** (55.5 mg, 0.09 mmol) in acetone (20 mL) was added anhydrous (Me_4N)Cl (35.5 mg, 0.32 mmol). The reaction mixture was stirred for 1.5 h and filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), and cold Et_2O (0 °C, 20 mL) was added. The suspension was filtered, and the solid collected was recrystallized from CH_2Cl_2 and Et_2O and dried first by suction and then in an oven at 70 °C under vacuum for 10 h to give **5b** as a yellow solid. Yield: 53.2 mg, 71%. Mp: 192 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.87 (s, 3 H, Me^{11}), 2.25 (s, 3 H, Me^8), 3.49 (s, 12 H, NMe_4), 4.89 (s, 1 H, H^9), 6.71 (t, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz), 7.13 (d, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz), 7.18 (t, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz), 7.25 (d, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 24.5 (Me^8), 28.3 (Me^{11}), 56 (NMe_4), 102.8 (C^9), 120.3 (CH, Ar), 122.3 (CH, Ar), 122.5 (CH, Ar), 131.9 (CH, Ar), 139.6 (C), 157.3 (C), 163.4 (C^7), 185.5 (C^{10}), 214.4 (C^{12}). Λ_M = 118 Ω^{-1} cm^2 mol^{-1} (9.40 × 10^{-4} mol L^{-1}). IR (cm^{-1}): ν(C═O), 1654. Anal. Calcd for $C_{16}H_{23}ClN_2O_2Pd$: C, 46.06; H, 5.56; N, 6.71. Found: C, 45.82; H, 5.84; N, 6.68.

Synthesis of [{Pd{*C,N,O*-{C(O)C$_6$H$_4${NC(Me)CHC(O)Me}-2}L] [L = ^{t}BuNC (6a), XyNC (6b), PPh$_3$ (6c), MeNH$_2$ (6d), NH$_3$ (6e), MeCN (6f), dmso (6g)]. To a suspension of **3** (for **6a**, **6b**, 80 mg, 0.13 mmol; for **6c**, 150 mg, 0.24 mmol; for **6d**, 160 mg, 0.26 mmol; for **6e**, 90 mg, 0.15 mmol; for **6f**, 77 mg, 0.13 mmol; for **6g** 34 mg, 0.06 mmol) in acetone (**6a**−**c**, 15 mL) or CH_2Cl_2 (for **6d**, 5; for **6e**, 10; for **6f**, 0.5; for **6g**, 2 mL) was added the appropriate L ligand (for **6a**, ^{t}BuNC, 24.9 μL, 0.26 mmol; for **6b**, XyNC, 34.1 mg, 0.26 mmol; for **6c**, PPh_3, 127.7 mg, 0.49 mmol; for **6d**, $MeNH_2$ 8 M in abs. EtOH, 77.8 μL, 0.62 mmol; for **6e**, NH_3 was bubbled for 10 min; for **6f**, MeCN, 15 mg, 0.37 mmol; for **6g**, dmso, 36 mg, 0.46 mmol). The reaction mixture was stirred for 3 h (**6a**, **b**), 5 h (**6c**), 2 h (**6d**, **6e** under NH_3 atmosphere), or 10 min (**6f**, **6g**). In the cases of **6b** and **6c** a suspension formed, which was concentrated under vacuum (2 mL). For **6b**, the suspension was filtered, and the solid collected was washed with acetone (1 mL) and Et_2O (5 mL) and dried by suction, while for **6c**, Et_2O (20 mL) was added, the suspension was filtered, and the solid collected was recrystallized form CH_2Cl_2/Et_2O and dried in an oven at 65 °C for 10 h. For **6f** *n*-hexane (20 mL) was added, the resulting suspension was stirred in an ice−water bath for 15 min, allowed to stand at −20 °C overnight, and filtered, and the solid was collected and dried under nitrogen. For **6g** the

reaction mixture was concentrated to dryness, the oily residue was stirred with *n*-pentane at 0 °C for 15 min, the resulting suspension was filtered, and the solid collected was washed with *n*-pentane (2 mL) and dried with a nitrogen stream and then in an oven under vacuum at 70 °C for 10 h. In all other cases, the reaction mixture was filtered through a short pad of Celite and the solution was concentrated under vacuum to dryness (**6a**, **6d**) or to 2 mL (**6e**). The oily residue was stirred with *n*-pentane (**6a**, 5; **6d**, 20 mL) in an ice−water bath for 15 min, the suspension was filtered, and the solid collected was washed with cold *n*-pentane (**6a**, 2 × 1; **6d**, 3 × 3 mL) and dried by suction. For **6e**, the resulting suspension was stirred at 0 °C for 15 min and filtered, and the solid washed with Et_2O (5 mL) and dried by suction.

6a: yellow powder. Yield: 78 mg, 76%. Mp: 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.59 (s, 9 H, ^{t}Bu), 2.0 (s, 3 H, Me^{11}), 2.30 (s, 3 H, Me^8), 5.01 (s, 1 H, H^9), 6.82 (td, 1 H, Ar, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.15 (d, 1 H, Ar, $^3J_{HH}$ = 8 Hz), 7.24 (ddd, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.38 (dd, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 24.7 (Me^8), 27.8 (Me^{11}), 30.0 (C*Me*$_3$), 57.6 (*C*Me$_3$), 103.1 (C^9), 120.8 (CH, Ar), 123.0 (CH, Ar), 123.7 (CH, Ar), 132.5 (CH, Ar), 139.0 (C), 157.1 (C), 164.2 (C^7), 185.3 (C^{10}), 212.5 (C^{12}). IR (cm^{-1}): ν(C≡N), 2198; ν(C=O), 1660. Anal. Calcd for $C_{17}H_{20}N_2O_2Pd$: C, 52.25; H, 5.16; N, 7.17. Found: C, 52.20; H, 5.38; N, 7.13.

6b: yellow powder. Yield: 79.4 mg, 70%. Mp: 184 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.02 (s, 3 H, Me^{11}), 2.33 (s, 3 H, Me^8), 2.52 (s, 6 H, Me, Xy), 5.06 (s, 1 H, H^9), 6.80 (td, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.11 (d, 2 H, meta-Xy, $^3J_{HH}$ = 7 Hz), 7.16−7.30 (various m, 3 H, Ar + ortho-Xy), 7.40 (dd, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.7 (Me, Xy), 24.7 (Me^8), 27.8 (Me^{11}), 103.2 (C^9), 120.8 (CH, Ar), 123.0 (CH, Ar), 123.9 (CH, Ar), 126.2 (ipso-C, Xy), 127.9 (meta-Xy), 129.5 (para-Xy), 132.7 (CH, Ar), 135.9 (C, ortho-Xy), 138.9 (Pd−*C*NXy), 148.0 (C), 157.2 (C), 164.1 (C^7), 185.6 (C^{10}), 212.5 (C^{12}). IR (cm^{-1}): ν(C≡N), 2181; ν(C=O), 1666. Anal. Calcd for $C_{21}H_{20}N_2O_2Pd$: C, 57.48; H, 4.59; N, 6.38. Found: C, 57.31; H, 4.68; N, 6.44. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion on *n*-pentane into a solution of **6b** in $CHCl_3$.

6c·H$_2$O: yellow powder. Yield: 242 mg, 86%. Mp: 213 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.53 (s, 2 H, H_2O), 1,74 (s, 3 H, Me^{11}), 2.32 (s, 3 H, Me^8), 4.98 (s, 1 H, H^9), 6.76 (td, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.15 (d, 1 H, Ar, $^3J_{HH}$ = 8 Hz), 7.21−7.26 (various m, 2 H, Ar), 7.33−7.44 (various m, 9 H, PPh_3), 7.60−7.65 (various m, 6 H, PPh_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 24.4 (d, Me^8, $^4J_{CP}$ = 4 Hz), 27.4 (Me^{11}), 103.0 (C^9), 120.8 (d, CH, Ar, $^4J_{CP}$ = 4 Hz), 122.6 (CH, Ar), 123.9 (CH, Ar), 128.0 (d, meta-CH, PPh_3, $^3J_{CP}$ = 11 Hz), 130.1 (d, para-CH, PPh_3, $^4J_{CP}$ = 2 Hz), 131.0 (d, ipso-C. PPh_3, $^1J_{CP}$ = 46 Hz), 132.3 (CH, Ar), 134.8 (d, ortho-CH, PPh_3, $^2J_{CP}$ = 12 Hz), 140.1 (d, C, J_{CP} = 3 Hz), 156.6 (C), 163.9 (C^7), 185.2 (C^{10}), 216.8 (C^{12}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 35.6. IR (cm^{-1}): ν(C=O), 1659. Anal. Calcd for $C_{30}H_{28}NO_3PPd$: C, 61.29; H, 4.80; N, 2.38. Found: C, 61.37; H, 4.64; N, 2.53. Crystals of **6c** suitable for an X-ray diffraction study were obtained by slow diffusion on *n*-pentane into a solution of **6c** in Et_2O.

6d: yellow powder. Yield: 155 mg, 88%. Mp: 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.96 (s, 3 H, Me^{11}), 2.33 (s, 3 H, Me^8), 2.71 (t, 3 H, NH_2*Me*, $^3J_{HH}$ = 7 Hz), 2.83 (s br, 2 H, NH_2), 4.97 (s, 1 H, H^9), 6.83 (m, 1 H, Ar), 7.22−7.27 (m, 2 H, Ar), 7.42−7.44 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 25.2 (Me^8), 28.0 (Me^{11}), 31.3 (NH_2*Me*), 103.3 (C^9), 120.6 (CH, Ar), 122.8 (CH, Ar), 123.0 (CH, Ar), 132.6 (CH, Ar), 139.3 (C), 158.0 (C), 163.9 (C^7), 185.3 (C^{10}), 219.2 (C^{12}). IR (cm^{-1}): ν(NH) 3308, 3257 ; ν(C=O), 1654. Anal. Calcd for $C_{13}H_{16}N_2O_2Pd$: C, 46.10; H, 4.76; N, 8.27. Found: C, 46.37; H, 4.94; N, 8.29.

6e: yellow powder. Yield: 65 mg, 69%. Mp: 188 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.90 (s, 3 H, Me^{11}), 2.32 (s, 3 H, Me^8), 2.46 (s br, 3 H, NH_3), 4.97 (s, 1 H, H^9), 6.82 (m, 1 H, Ar), 7.23−7.29 (m, 2 H, Ar), 7.35−7.37 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25 °C): δ 25.5 (Me^8), 28.0 (C(O)*Me*), 103.3 (CH), 121.0 (CH, Ar), 123.0 (CH, Ar), 123.2 (CH, Ar), 133.0 (CH, Ar), the quaternary carbons are not observed because of the scarce solubility of **6e**. IR (cm^{-1}): ν(NH) 3357, 3306, 3145; ν(C=O), 1650. Anal. Calcd for $C_{12}H_{14}N_2O_2Pd$: C, 44.40; H, 4.35; N, 8.63. Found: C, 44.43; H, 4.32; N, 8.56. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a solution of the complex in CH_2Cl_2.

6f: yellow powder. Yield: 83 mg, 92%. Mp: 114 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.00 (s, 3 H, Me^{11}), 2.33 (s, 6 H, Me^8 + *Me*C≡N), 5.00 (s, 1 H, H^9), 6.81 (t, 1 H, Ar, $^3J_{HH}$ = 8 Hz), 7.19−7.27 (various m, 2 H, Ar), 7.42 (d, 1 H, Ar, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 1.87 (*Me*C≡N), 25.0 (Me^8), 28.0 (Me^{11}), 103.3 (C^9), 116.4 (Me*C*≡N), 120.5 (CH, Ar), 123.0 (CH, Ar), 123.4 (CH, Ar), 132.6 (CH, Ar), 138.4 (C), 157.9 (C), 164.2 (C^7), 185.9 (C^{10}), 211.5 (C^{12}). IR (cm^{-1}): ν(C=O), 1659; ν(CC) + ν(CN) + ν(CO), 1585, 1547, 1519. Anal. Calcd for $C_{14}H_{14}N_2O_2Pd$: C, 48.23; H, 4.05; N, 8.03. Found: C, 47.95; H, 4.25; N, 8.03.

6g·0.5H$_2$O: deep yellow powder. Yield: 37 mg, 85%. Mp: 103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.66 (s, 1 H, H_2O), 2.02 (s, 3 H, C^{11}), 2.36 (s, 3 H, Me^8), 3.21 (s, 6 H, dmso), 5.07 (s, 1 H, H^9), 6.85 (t, 1 H, Ar, $^3J_{HH}$ = 7.6 Hz), 7.20 (d, 1 H, Ar, $^3J_{HH}$ = 7.6 Hz), 7.27 (td, 1 H, Ar, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 7.43 (d, 1 H, Ar, $^3J_{HH}$ = 7.5 Hz); (400 MHz, dmso-d_6, 25 °C) δ 1.92 (s, 3 H, Me^{11}), 2.31 (s, 3 H, Me^8), 5.11 (s, 1 H, H^9), 6.88 (t, 1 H, Ar, $^3J_{HH}$ = 6.5 Hz), 7.29 (d, 1 H, Ar, $^3J_{HH}$ = 6.5 Hz), 7.34−7.38 (m, 2 H, Ar). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ 24.8 (Me^8), 28.1 (Me^{11}), 42.5 (Me, dmso), 103.9 (C^9), 120.8 (CH, Ar), 123.3 (CH, Ar), 124.2 (CH, Ar), 133.3 (CH, Ar), 138.4 (C), 157.1 (C), 164.2 (C^7), 186.7 (C^{10}), the (*C*(O)Pd) resonance (C^{12}) is not observed; (100 MHz, dmso-d_6, 25 °C) δ 24.4 (Me^8), 27.7 (Me^{11}), 103.5 (C^9), 121.1 (2 CH, Ar), 123.3 (CH, Ar), 133.6 (CH, Ar), 137.9 (C), 156.5 (C), 164.5 (C), 185.4 (C^{10}), 213.3 (C^{12}). IR (cm^{-1}): ν(C=O), 1658, ν(S=O), 1101.[45] Anal. Calcd for $C_{14}H_{18}NO_{3.5}PdS$: C, 42.60; H, 4.60; N, 3.55; S, 8.12. Found: C, 42.88; H, 4.35; N, 3.60; S, 7.98.

Synthesis of (*Z*)-[PdI{C$_6$H$_4$}{NHC(Me)C{C(CO$_2$Me)=CH-(CO$_2$Me)}{C(O)Me}}-2}(tmeda)] (7*Z*). To a solution of [PdI-{C$_6$H$_4$}{NHC(Me)CHC(O)Me}-2}(tmeda)] (553 mg, 1.06 mmol) in $CHCl_3$ (10 mL) was added dimethylacetylenedicarboxylate (DMAD, 130 μL, 1.06 mmol). The reaction mixture was stirred at room temperature for 10 h and concentrated under vacuum to dryness. The residue was dissolved in CH_2Cl_2 (1 mL), Et_2O (20 mL) was added, and the suspension was stirred at 0 °C for 20 min and then filtered. The solid collected upon filtration was washed with Et_2O (4 × 1.5 mL) and dried by suction to give **7*Z*** as a pale orange solid contaminated with a small amount of the *E* isomer (molar ratio 20:1), which could not be removed after repeated recrystallizations or by chromatography. Yield: 591 mg, 86%. Mp: 153−154 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.05 (s, 3 H, Me^8), 2.24 (s, 3 H, Me^{11}), 2.37 (s, 3 H, Me, tmeda), 2.57 (s, 3 H, Me, tmeda), 2.62 (s, 3 H, Me, tmeda), 2.68 (s, 3 H, Me, tmeda), 2.40−3.30 (several m, 4 H, CH_2, tmeda), 3.78 (s, 3 H, Me$^{14\text{ or }17}$), 3.84 (s, 3 H, Me$^{14\text{ or }17}$), 6.15 (s, 1 H, H^{15}), 6.80 (dd, 1 H, H^6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 6.88 (td, 1 H, H$^{4\text{ or }5}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 6.91 (td, 1 H, H$^{4\text{ or }5}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.25 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 14.13 (s, 1 H, NH). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ 18.8 (Me^8), 28.5 (Me^{11}), 48.3 (Me, tmeda), 48.4 (Me, tmeda), 50.6 (Me, tmeda), 50.9 (Me, tmeda), 51.9 (Me$^{14\text{ or }17}$), 52.4 (Me$^{14\text{ or }17}$), 58.6 (CH_2, tmeda), 62.0 (CH_2, tmeda), 104.4 (C^9), 123.1 (CH, Ar), 125.0 (CH, Ar), 125.1 (CH, Ar), 127.3 (C^{15}), 136.8 (CH, Ar), 141.1 (C$^{1\text{ or }2}$), 142.0 (C$^{1\text{ or }2}$), 147.4 (C^{12}), 163.3 (C^7), 165.6 (C$^{13\text{ or }16}$), 169.1 (C$^{13\text{ or }16}$), 192.5 (C^{10}). IR (cm^{-1}):

(45) Vicente, J.; Arcas, A.; Borrachero, M. V.; Molíns, E. M., C. *J. Organomet. Chem.* **1989**, *359*, 127.

$\nu_{asym}(CO_2)$, 1730. Anal. Calcd for $C_{23}H_{34}IN_3O_5Pd$: C, 41.49; H, 5.15; N, 6.31. Found: C, 41.09; H, 5.17; N, 6.29. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion on *n*-hexane into a solution of **7*Z*** in acetone.

Synthesis of (*E*)-[PdI{C_6H_4{NHC(Me)C{C(CO_2Me)=CH-(CO_2Me)}C(O)Me}}-2}(tmeda)] (7*E*). **7*Z*** (201 mg, 0.30 mmol) was dissolved in toluene (8 mL) and stirred in a Carius tube at 95 °C for 15 h. The resulting suspension was filtered through a short pad of Celite, the solution was concentrated under vacuum to dryness, the residue was dissolved in CH_2Cl_2 (1 mL), Et_2O (12 mL) was added, and the resulting suspension was stirred at 0 °C for 10 min. The solid collected upon filtration was washed with Et_2O (3 × 1.5 mL) and dried, first by suction and then in an oven at 75 °C under vacuum for 24 h to give **7*E***·$2H_2O$ as a yellow solid. Yield: 72 mg, 36%. Mp: 168 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, two conformers: ^{M} = major, ^{m} = minor, M:m = 1.2:1): δ 1.54 (s, 4 H, H_2O), 1.84 (s, 3 H, $Me^{8,M}$), 1.86 (s, 3 H, $Me^{8,m}$), 2.00 (s, 3 H, $Me^{11,M}$), 2.08 (s, 3 H, $Me^{11,m}$), 2.40 (s, 3 H, Me, $tmeda^{M}$), 2.41 (s, 3 H, Me, $tmeda^{m}$), 2.59 (s, 3 H, Me, $tmeda^{m}$), 2.60 (s, 3 H, Me, $tmeda^{M}$), 2.68 (s, 3 H, Me, $tmeda^{M}$), 2.70 (s, 3 H, Me, $tmeda^{M+m}$), 2.75 (s, 3 H, Me, $tmeda^{m}$) 2.40−3.30 (several m, 4 H, CH_2, $tmeda^{M+m}$), 3.77 (s, 3 H, $Me^{14\ or\ 17,\ m}$), 3.81 (s, 3 H, $Me^{14\ or\ 17,\ M}$), 3.82 (s, 3 H, $Me^{14\ or\ 17,\ m}$), 3.85 (s, 3 H, $Me^{14\ or\ 17,\ M}$), 6.76 (dd, 1 H, $H^{6,\ m}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 6.80 (dd, 1 H, $H^{6,\ M}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 6.85−6.90 (various overlapped td, 4 H, $H^{4,\ M+m}$ + $H^{5,M+m)}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.06 (s, 1 H, $H^{15,\ M}$), 7.11 (s, 1 H, $H^{15,\ m}$), 7.25 (dd, 1H, $H^{3,\ M+m}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 14.05 (s, 1 H, NH^{m}), 14.10 (s, 1 H, NH^{M}); (400.9 MHz, $CDCl_3$, 90 °C) δ 1.79 (s, 3 H, Me^8), 1.92 (s, 3 H, Me^{11}), 2.25 (s, 3 H, Me, tmeda), 2.53 (s, 3 H, Me, tmeda), 2.63 (s, 6 H, Me, tmeda), 2.30−3.10 (various m, 4 H, CH_2, tmeda), 3.71 (s, 3 H, $Me^{14\ or\ 17}$), 3.78 (s, 3 H, $Me^{14\ or\ 17}$), 6.70 (m, H^6), 6.79 (m, 2 H, $H^4 + H^5$), 6.96 (s, 1 H, H^{15}), 7.17 (m, 1H, H^3), 13.81 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C): δ 18.0, 18.6 (Me^8), 27.9, 28.0 (Me^{11}), 48.2 48.6, 50.6, 50.9, 51.8, 52.4, 52.6, 52.8 (Me, tmeda), 58.58, 58.62, 61.9, 62.1 (CH_2, tmeda), 101.3, 101.5 (C^9), 122.9, 123.0 (CH, Ar), 124.7, 124.8 (CH, Ar), 124.9, 125.3 (CH, Ar), 130.1, 132.2 (C^{15}), 136.98, 137.01 (CH, Ar), 140.9, 141.0, 141.7, 142.18, 142,20, 144.4 ($C^1 + C^2 + C^{12}$), 160.6, 161.9, 165.7 (2 C), 168.21, 168.23 ($C^7 + C^{13} + C^{16}$), 191.7, 192.7 (C^{10}). IR (cm^{-1}): $\nu_{asym}(CO_2)$, 1725. Anal. Calcd for $C_{23}H_{38}IN_3O_7Pd$: C, 39.36; H, 5.46; N, 5.97. Found: C, 39.37; H, 5.13; N, 5.98. Crystals were obtained by slow diffusion of *n*-hexane into a solution of **7*E*** in CH_2Cl_2.

Synthesis of [Pd{*C,N,*O-{C(=NXy)C_6H_4{NC(Me)=C{C-(CO_2Me)=CHCO_2Me)}C(O)Me}-2}(CNXy)] (8). To a solution of **7*Z*** (400 mg, 0.60 mmol) in MeCN (16 mL) was added $AgClO_4$ (125 mg, 0.60 mmol). A suspension immediately formed, which was stirred in the dark for 20 min and filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), a solution of XyNC (158 mg, 1.20 mmol) in MeCN (5 mL) was added, and the mixture was stirred at room temperature for 1 h and concentrated under vacuum to dryness. The residue was stirred with Et_2O (80 mL), the suspension was filtered, and the solution was concentrated under vacuum to dryness. The solid residue was recrystallized from CH_2Cl_2 (ca. 0.75 mL) and *n*-pentane (20 mL), washed with *n*-pentane (3 × 3 mL), and dried by suction to give orange **8** as a 10:1 mixture of two isomers, which could not be resolved after recrystallization. Yield: 361 mg, 88%. Mp: 184 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, two isomers: ^{M} = major, ^{m} = minor, M:m = 10:1): δ 1.84 (s, 3 H, $Me^{11,M}$), 2.10 (s, 3 H, $Me^{11,m}$), 2.20 (s, 3 H, $Me^{8,M}$), 2.22 (s, 9 H, Me, $Xy^a + Xy^b$), 2.26 (s, 3 H, Me, Xy^b), 2.43 (s, 3 H, $Me^{8,m}$), 3.78 (s, 3 H, $Me^{14\ or\ 17,\ M}$), 3.80 (s, 3 H, $Me^{14\ or\ 17,\ m}$), 3.86 (s, 3 H, $Me^{14\ or\ 17,\ m}$), 3.87 (s, 3 H, $Me^{14\ or\ 17,\ M}$), 6.14 (s, 1 H, $H^{15,\ m}$), 6.29 (t, 1 H, para-$Xy^{b,\ m}$, $^3J_{HH}$ = 8 Hz), 6.30 (t, 1 H, para-$Xy^{b,\ M}$, $^3J_{HH}$ = 8 Hz), 6.71 (d, 1 H, meta-$Xy^{b,\ M+m}$, $^3J_{HH}$ = 8 Hz), 6.74 (d, 1 H, meta-$Xy^{b,\ M+m}$, $^3J_{HH}$ = 8 Hz), 6.92 (t, 1 H, $H^{4,\ M}$, $^3J_{HH}$ = 8 Hz), 6.94 (t, 1 H, $H^{4,\ m}$, $^3J_{HH}$ = 8 Hz), 6.99 (d, 2 H, meta-$Xy^{a,\ M+m}$, $^3J_{HH}$ = 8 Hz), 7.01 (d, 1 H, $H^{6,\ M+m}$, $^3J_{HH}$ = 8 Hz), 7.07 (s, 1 H, $H^{15,\ M}$), 7.14 (t, 1 H, para-$Xy^{a,\ M+m}$, $^3J_{HH}$ = 8 Hz), 7.20 (td, 1 H, $H^{5,\ M}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.21 (td, 1 H, $H^{5,\ m}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.99 (dd, 1 H, $H^{3,\ M}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.01 (d, 1 H, $H^{3,\ m}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, major isomer): δ 18.6 (Me, Xy^a), 19.3 (Me, Xy^b), 19.5 (Me, Xy^b), 22.7 (Me^8), 27.5 (Me^{11}), 52.0 ($Me^{14\ or\ 17}$), 52.9 ($Me^{14\ or\ 17}$), 106.9 (C^9), 121.4 (C^6), 122.8 (para-Xy^b), 123.3 (C^4), 125.3 (C^3), 126.7 (ortho-Xy^b), 126.9 (ortho-Xy^b), 127.3 (meta-Xy^b), 127.4 (meta-Xy^{a+b}), 128.8 (para-Xy^a), 129.7 (C^5), 131.5 (C^{15}), 134.5 (ortho-Xy^a), 142.3 (C^1), 144.4 (C^{12}), 144.7 (ipso-Xy^a), 153.0 (ipso-Xy^b), 154.9 (C^2), 163.8 (C^7), 166.0 (C^{16}), 168.1 (C^{13}), 178.2 (*C*NXy^b), 181.4 (C^{10}). ^{13}C resonances assigned to the minor isomer appear at 23.7 (Me^8), 28.2 (Me^{11}), 52.4 ($Me^{14\ or\ 17}$), 53.4 ($Me^{14\ or\ 17}$), 110.0 (C^9), 121.6, 123.6, 125.4, 128.2, 128.9, 144.7, 148.6, 152.9, 154.6, 164.3, 165.6, 169.1, 177.3 (C=N), 182.6 (C^{10}), but some could not be assigned unambiguously. IR (cm^{-1}): ν(C≡N), 2169, $\nu_{asym}(CO_2)$, 1716; ν(C=N), 1628. Anal. Calcd for $C_{35}H_{35}N_3O_5Pd$: C, 61.45; H, 5.16; N, 6.14. Found: C, 61.08; H, 5.31; N, 6.20.

Synthesis of [Pd{*C,N,O*-{C(=NXy)C_6H_4{N(dmoc)}-2](CNXy)] (9). After exposing to sunlight a solution of **8** (23 mg, 0.034 mmol) in a mixture of $CHCl_3$/*n*-pentane (1:5, 3 mL, 80 h), crystals of **9** formed along with some metallic palladium, which separated from them by adhering to the flask wall. The mother liquor was decanted, and the crystals were washed with *n*-pentane (3 × 0.5 mL) and dried under vacuum in an oven (80 °C, 15 h). Further crops of crystals grew from the mother liquor upon standing in the sunlight; these were treated as above. The procedure was repeated five times, yielding a total 18 mg (82%) after 150 h of exposure. Mp: >200 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 2.15 (s, 3 H, Me, Xy^b), 2.16 (s, 3 H, Me, Xy^b), 2.24 (s, 6 H, Me, Xy^a), 3.01, 3.28 (AB part of an ABX system, 2 H, $H^{11a+11b}$, $^2J_{AB}$ = 19.5 Hz, $^3J_{AX}$ = 7.0 Hz, $^3J_{BX}$ = 1.6 Hz), 3.73 (s, 3 H, CO_2Me), 3.75 (s, 3 H, CO_2Me), 4.19 (X part of an ABX system, 1 H, H^7), 6.21 (t, 1 H, para-Xy, $^3J_{HH}$ = 7 Hz), 6.72 (d, 1 H, meta-Xy^b, $^3J_{HH}$ = 8 Hz), 6.73 (d, 1 H, meta-Xy^b, $^3J_{HH}$ = 8 Hz), 6.99 (d, 2 H, meta-Xy^a, $^3J_{HH}$ = 7 Hz), 7.16 (dd, 1 H, para-Xy, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 8 Hz), 7.33 (m, 1 H, $H^{3\ or\ 5}$), 7.49 (m, 2 H, $H^4 + H^{3\ or\ 5}$), 8.34 (d, 1 H, H^6, Ar, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.6 (Me, Xy^a), 19.09 (Me, Xy^b), 19.10 (Me, Xy^b), 31.7 (C^{11}), 46.6 (C^7), 51.4 (CO_2*Me*), 52.3 (CO_2*Me*), 113.0 (C^{10}), 119.2 ($C^{3\ or\ 5}$), 123.4 (CH, para-Xy), 125.98 (C, ortho-Xy^b), 126.01 (C, ortho-Xy^b), 126.8 (C, ipso-Xy^a), 127.46 (C, meta-Xy^a), 127.51 (C, meta-Xy^a + meta-Xy^b), 127.7 (C^2), 129.0 ($C^{3\ or\ 5}$), 129.1 (CH, para-Xy), 131.6 (C^4), 134.5 (C, ortho-Xy^a), 141.4 (C≡N), 146.2 (C^6), 148.9 (C^1), 151.6 (C, ipso-Xy^b), 165.8 (*C*O_2Me), 166.7 (C=N), 174.6 (*C*O_2Me), 177.1 (C^9), 184.9 (C^8). IR (cm^{-1}): ν(C≡N), 2181, ν(C=N), 1618. Anal. Calcd for $C_{33}H_{31}N_3O_5Pd$: C, 60.42; H, 4.76; N, 6.40. Found: C, 60.12; H, 4.73; N, 6.37.

Synthesis of [Pd{*C,N,*O-{C(=NHXy)C_6H_4{NC(Me)=CH-{C(CO_2Me)=CH CO_2Me)}C(Me)O}-2}(CNXy)]OTf (10). To a solution of **8** (24 mg, 0.04 mmol) in CH_2Cl_2 (3 mL) was added HOTf (3 μL, 0.04 mmol). The reaction mixture was stirred for 30 min and concentrated under vacuum to 0.5 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid collected was washed with Et_2O (2 × 2 mL) and dried first by suction and then in a vacuum oven at 70 °C overnight to give **10**·$0.5H_2O$ as an orange-red solid. Yield: 21 mg, 70%. Mp: 204 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.86 (s, 3 H, Me^{11}), 2.21 (s, 6 H, Me, Xy^a), 2.22 (s, 3 H, Me, Xy^b), 2.48 (s, 3 H, Me, Me^8), 2.51 (s, 3 H, Me, Xy^b), 3.79 (s, 3 H, $Me^{14\ or\ 17}$), 3.89 (s, 3 H, $Me^{14\ or\ 17}$), 6.67 (t, 1 H, para-Xy^b, $^3J_{HH}$ = 8 Hz), 6.89 (d, 1 H, meta-Xy^b, $^3J_{HH}$ = 8 Hz), 7.01 (d, 1 H, H^3 or 6 $^3J_{HH}$ = 8 Hz), 7.08 (d, 2 H, meta-Xy^a), 7.11 (m, 1 H, $H^{4\ or\ 5}$), 7.13 (s, 1H, H^{15}), 7.25 (t, 1 H, para-Xy^a, $^3J_{HH}$ = 8 Hz), 7.45 (dt, 1 H, $H^{4\ or\ 5}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.21 (dd, 1 H, $H^{3\ or\ 6}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 12.31 (s br, 1 H, N*H*Xy^b). $^{13}C\{^1H\}$ NMR

Table 1. Crystal Data and Structure Refinement of Complexes 2, 3, and 5a

	2	**3**	**5a**
formula	$C_{30}H_{38}N_4O_4Pd_2$	$C_{24}H_{22}N_2O_4Pd_2$	$C_{48}H_{41}ClN_2O_2P_2Pd$
fw	731.44	615.24	881.62
temperature (K)	100(2)	100(2)	100(2)
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	*Fdd*2	$P2_1/n$
a (Å)	7.3382(4)	16.1086(12	9.2515(6))
b (Å)	9.4824(6)	24.6965(19)	29.745(2)
c (Å)	11.2464(7)	10.4757(8)	14.9909(11)
α (deg)	100.191(2)	90	90
β (deg)	97.345(2)	90	100.395(2)
γ (deg)	107.542(2)	90	90
volume (Å^3)	720.59(8)	4167.5(5)	4057.6(5)
Z	1	8	4
ρ_{calcd} (Mg m^{-3})	1.686	1.961	1.443
μ(Mo Kα) (mm^{-1})	1.290	1.762	0.645
F(000)	370	2432	1808
cryst size (mm)	0.28 × 0.16 × 0.13	0.32 × 0.18 × 0.14	0.18 × 0.12 × 0.07
θ range (deg)	1.88 to 28.16	2.46 to 28.43	1.94 to 28.23
no. of reflns coll	8237	6504	46 741
no. of indep reflns/R_{int}	3211/0.0130	2184/0.0127	9435/0.0265
transmissn	0.8502−0.7140	0.7905/0.6872	0.9563−0.8928
restraints/params	0/185	1/147	0/507
goodness-of-fit on F^2	1.188	1.168	1.107
R_1 ($I > 2\sigma(I)$)	0.0180	0.0158	0.0350
wR_2 (all reflns)	0.0483	0.0412	0.0868
largest diff peak/hole (e·Å^{-3})	0.351/−0.774	0.304/−0.647	0.886/−0.295

Table 2. Crystal Data and Structure Refinement of Complexes 6b, 6c, and 6e

	6b	**6c**	**6e**
formula	$C_{21}H_{20}N_2O_2Pd$	$C_{30}H_{26}NO_2PPd$	$C_{12}H_{14}N_2O_2Pd$
fw	438.79	569.89	324.65
temperature (K)	100(2)	100(2)	100(2)
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	*Pca*2(1)	*P*2(1)2(1)2(1)
a (Å)	15.3130(11)	28.719(4)	4.5852(3)
b (Å)	7.7347(5)	10.7837(14)	14.8783(11)
c (Å)	15.3771(11)	8.0015(11)	16.8496(12)
α (deg)	90	90	90
β (deg)	98.874(2)	90	90
γ (deg)	90	90	90
volume (Å^3)	1799.5(2)	2478.1(6)	1149.48(14)
Z	4	4	4
ρ_{calcd} (Mg m^{-3})	1.620	1.528	1.876
μ(Mo Kα) (mm^{-1})	1.049	0.842	1.605
F(000)	888	1160	648
cryst size (mm)	0.18 × 0.14 × 0.10	0.18 × 0.06 × 0.05	0.20 × 0.07 × 0.03
θ range (deg)	2.68 to 28.22	1.89 to 28.22	1.83 to 28.16
no. of rflns coll	20 006	15 175	13 219
no. of indep rflns/R_{int}	4168/0.0190	5483/0.0681	2652/0.0463
transmissn	0.9024−0.8337	0.9591−0.8632	0.9534−0.7397
restraints/params	0/239	9/318	6/168
goodness-of-fit on F^2	1.087	1.044	1.128
R_1 ($I > 2\sigma(I)$)	0.0218	0.0570	0.0371
wR_2 (all reflns)	0.0520	0.1071	0.0862
largest diff peak/hole (e·Å^{-3})	0.389/−0.306	0.837/−1.012	1.764/−0.648

(100 MHz, $CDCl_3$, 25 °C): *δ* 18.4 (Me, Xy^a), 18.9 (Me, Xy^b), 19.0 (Me, Xy^b), 22.6 (Me^8), 26.4 (Me^{11}), 52.1 (Me$^{14\ or\ 17}$), 53.2 (Me$^{14\ or\ 17}$), 109.2 (C^9), 120.3 (q, $^1J_{CF}$ = 320.1 Hz, CF_3) 122.1 (C$^{3\ or\ 6}$), 125.3 (C$^{4\ or\ 5}$), 125.5 (C≡N or ipso-C, Xy^a), 125.9 (C$^{3\ or\ 6}$), 128.0 (meta-CH, Xy^a), 128.2 (meta-CH,Xy^b), 128.3 (meta-CH, Xy^b), 129.7 (para-CH, Xy^b), 130.3 (para-CH, Xy^a), 132.1 (C^{15}), 131.5 (C^{15}), 134.52 (ortho-C, Xy^b), 134.53 (ortho-C, Xy^b), 134.7 (ortho-C, Xy^a), 135.8 (C^4 or C^5), 136.7 (C^1 or C^2), 137.9 (br s, C),140.8 (ipso-C, Xy^b), 143.2 (C^{12}), 158.4 (C$^{1\ or\ 2}$), 164.0 (C^7), 165.2 (C$^{13\ or\ 16}$), 167.0 (C$^{13\ or\ 16}$), 181.7 (C^{10}), 216.2 (*C*NHXy^b). IR (cm^{-1}): *ν*(NH) 3144, *ν*(C≡N), 2195, $\nu_{asym}(CO_2)$, 1722; *ν*(C═N), 1634. Anal. Calcd for $C_{36}H_{37}F_3N_3O_{8.5}PdS$: C, 51.28; H, 4.42; N, 4.98; S, 3.80. Found: C, 51.26; H, 4.38; N, 5.05; S, 3.76. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **10** in CH_2Cl_2.

Synthesis of [Pd{*C,N,O*-{C(═NXy)C_6H_4}{N(dmoc)}-2](CNXy)]·Hpic (11). To a solution of **9** (60 mg, 0.09 mmol) in $CHCl_3$ (10 mL) was added picric acid (Hpic = $HOC_6H_3(NO_2)_3$-2,4,6, 22 mg, 0.10 mmol). The reaction mixture was stirred at room temperature for 3 h and filtered through a short pad of Celite. The solution was concentrated under vacuum to 1 mL, and Et_2O (20 mL) was added. The suspension was concentrated under vacuum to half its volume and filtered. The solid collected was washed with Et_2O (3 × 1.5 mL), recrystallized from CH_2Cl_2 and

Table 3. Crystal Data and Structure Refinement of Complexes 7*Z*, 7*E*, and 10

	7*Z*	7*E*·CH_2Cl_2	10
formula	$C_{23}H_{34}IN_3O_5Pd$	$C_{24}H_{36}Cl_2IN_3O_5Pd$	$C_{36}H_{36}F_3N_3O_8PdS$
fw	665.83	750.76	834.14
temperature (K)	100(2)	100(2)	100(2)
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pca*2(1)	*P*2(1)/*c*	$P\bar{1}$
a (Å)	16.4206(6)	12.4477(7)	8.3200(8)
b (Å)	8.4472(3)	15.4666(9)	14.7538(13)
c (Å)	38.9101(15)	15.6410(9)	15.9658(15)
α (deg)	90	90	112.747(2)
β (deg)	90	94.502(2)	91.600(4)
γ (deg)	90	90	100.430(4)
volume (Å^3)	5397.1(3)	3002.0(3)	1767.1(3)
Z	8	4	2
ρ_{calcd} (Mg m^{-3})	1.639	1.661	1.568
μ(Mo Kα) (mm^{-1})	1.867	1.861	0.657
F(000)	2656	1496	852
cryst size (mm)	0.32 × 0.18 × 0.17	0.21 × 0.18 × 0.03	0.23 × 0.11 × 0.05
θ range (deg)	2.41 to 28.18	1.64 to 28.16	2.44 to 28.64
no. of reflns coll	59 032	33 737	21 896
no. of indep reflns/R_{int}	12 520/0.0203	6943/0.0481	8292/0.0410
transmissn	0.7419−0.6451	0.9463−0.7378	0.9679/0.8029
restraints/params	2/619	7/335	2/472
goodness-of-fit on F^2	1.105	1.060	1.185
R_1 ($I > 2\sigma(I)$)	0.0230	0.0433	0.0587
wR_2 (all reflns)	0.0568	0.0955	0.1204
largest diff peak/hole (e·Å^{-3})	0.797/−0.649	1.667/−1.477	1.248/−1.676

Et_2O, and dried in a vacuum oven at 75 °C for 5 h to give **11**·0.5CH_2Cl_2 as a deep yellow solid. Yield: 77 mg (91%). Mp: 170 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ* 2.16 (s, 3 H, Me, Xy^b), 2.18 (s, 3 H, Me, Xy^b), 2.24 (s, 6 H, Me, Xy^a), 2.99, 3.25 (2 H, C^{11}H$_2$, part AB of an ABX system, $^2J_{AB}$ = 19.8 Hz, $^3J_{AX}$ = 7 Hz, $^2J_{BX}$ = 0 Hz), 3.72 (s, 3 H, CO_2Me), 3.73 (s, 3 H, CO_2Me), 4.17 (d, 1 H, H^7, part X of an ABX system), 2.5−3.2 (v br, OH), 6.21 (t, 1 H, para-Xy^b, $^3J_{HH}$ = 8 Hz), 6.71 (d, 1 H, meta-Xy^b, $^3J_{HH}$ = 8 Hz), 6.74 (d, 1 H, meta-Xy^b, $^3J_{HH}$ = 7 Hz), 6.96 (d, 2 H, meta-Xy^a, $^3J_{HH}$ = 8 Hz), 7.14 (t, 1 H, para-Xy^a, $^3J_{HH}$ = 8 Hz), 7.34 (ddd, 1 H, H$^{4\text{ or }5}$, Ar, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 8 Hz), 7.47 (m, 1 H, H$^{3\text{ or }6}$, Ar), 7.51 (td, 1 H, H$^{4\text{ or }5}$, Ar, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 8 Hz), 8.36 (dd, 1 H, H$^{3\text{ or }6}$, Ar, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 8 Hz), 8.87 (br s, 2 H, Ar, pic). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): *δ* 14.0 (Me, Xy^a), 15.2 (Me, Xy^b), 31.7 (C^{11}), 46.5 (C^7), 51.5 (CO_2*Me*), 52.4 (CO_2*Me*), 113.2 (C$^{9\text{ or }10}$), 119.3 (C$^{3,4,5\text{ or }6}$), 123.7 (CH, para-Xy^b), 126.1 (CH, picrate), 126.30 (C, ortho-Xy^b), 126.33 (C, ortho-Xy^b), 126.7 (br, C, C≡N or ipso-Xy^a), 127.5 (C, meta-Xy^a), 127.6 (C, meta-Xy^b), 127.8 (C$^{3\text{ or }6}$), 129.2 (C$^{4\text{ or }5}$ + para-Xy^a), 131.9 (C$^{3,4,5\text{ or }6}$), 134.5 (ortho-Xy^a), 141.1 (br, ortho-C, picrate), 146.2 (C$^{1\text{ or }2}$), 148.5 (C$^{1\text{ or }2}$), 151.0 (ipso-Xy^b), 165.8 (*C*O$_2$Me), 167.8 (*C*=NHXy), 174.4 (*C*O$_2$Me), 177.1 (C$^{9\text{ or }10}$), 184.7 (C^8). IR (cm^{-1}): *ν*(C≡N), 2187; *ν*(C=O), 1743; *ν*(C=N), 1689. Anal. Calcd for $C_{39.5}H_{35}ClN_6O_{12}Pd$: C, 51.15; H, 3.80; N, 9.06. Found: C, 51.13; H, 3.43; N, 9.43.

X-ray Crystallography. Complexes **2**, **3**, **5a**, **6b**, **6c**, **6e**, 7*Z*, 7*E*, and **10** were measured on a Bruker Smart APEX machine. Data were collected using monochromated Mo Kα radiation in *ω* scan mode. Absorption corrections were applied on the basis of multiscans (program SADABS). The structures were solved by direct methods. All were refined anisotropically on F^2. Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. The NH and NH_2 hydrogens were refined freely with DFIX and SADI, respectively; the ordered methyl groups were refined using rigid groups (AFIX137), and the other hydrogens were refined using a riding model. For clarity, solvent contents are omitted here, but are defined in Tables 1−3. Figures 1−7 show the ellipsoid representations of the structures. Figures 8−11 illustrate some hydrogen bond interactions. *Special features and exceptions*: For complexes **3**, **6c**, **6e**, and 7*Z*, the absolute structure parameter is 0.04(3), 0.01(4), 0.01(5), and 0.602(11), respectively.[46] Complexes **2**, **5a**, **6b**, 7*E*, and **10** crystallize in centrosymmetric space groups. For complex 7*Z* the structure was refined as a racemic twin. One methyl is disordered over two positions (ca. 57:43%). For complexes 7*E* and **10**, the $CHCl_3$ and one of the xylyl groups, respectively, are disordered over two sites (ca. 64:36% and 56:44%, respectively). Further details on crystal data, data collection, and refinements are summarized in the Supporting Information.

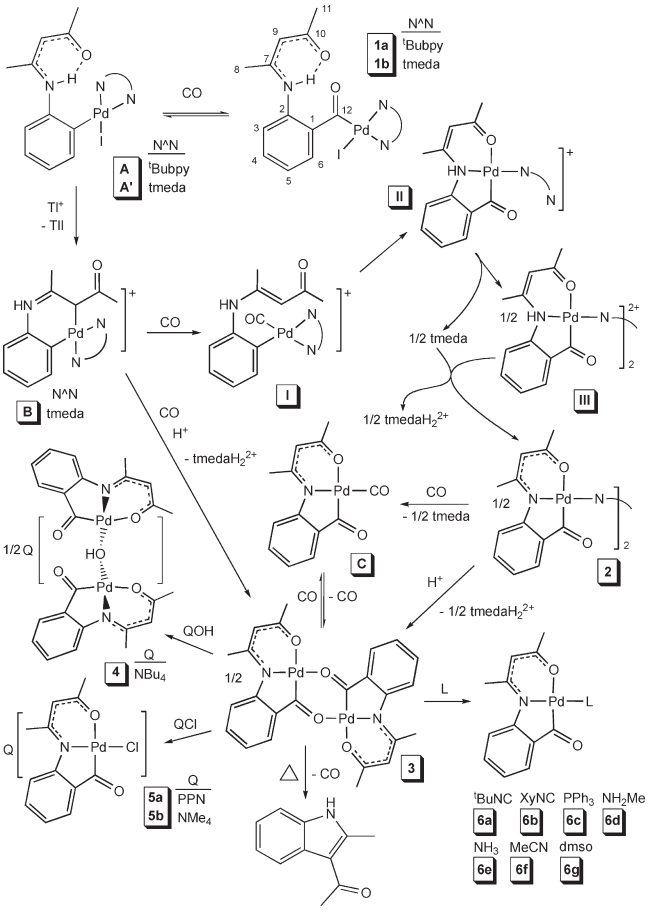
(46) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

Results and Discussion

Synthesis. We have recently reported the synthesis of complexes [PdI{C_6H_4{NHC(Me)CHC(O)Me}-2}(N^N)] [N^N = tbbpy (**A**), tmeda (**A′**); Scheme 1] and their reaction with TlOTf to give [Pd{*C,C*-C_6H_4{NH=C(Me)CHC(O)Me}-2}(N^N)]OTf [N^N = tbbpy (**B**), tmeda (**B′**)].[8] When these aryl palladium complexes were reacted with isocyanides [RNC, R = ^{t}Bu, $C_6H_3Me_2$-2,6 (Xy)] under different reaction conditions, insertion of the isocyanide into the Pd−C_{aryl} bond led to a variety of complexes including bridging iminoacyl, C,N,O-pincer, and 1,2-dihydroquinazolin-4-yl derivatives. These results prompted us to study the reactivity of the same starting materials toward CO and alkynes.

After bubbling CO through a solution of **A** or **A′** in a small volume of CH_2Cl_2 for 5 min and keeping the reaction mixture under CO atmosphere for 16−18 h, a color change from yellow to orange was observed. Addition of cold Et_2O caused the precipitation of the benzoyl complexes [PdI{C(O)-C_6H_4{NHC(Me)CHC(O)Me}-2}(N^N)] [N^N = ^{t}Bubpy (**1a**), tmeda (**1b**)], resulting from the insertion of CO into the Pd−C_{aryl} bond, which were isolated in more than 80% yield. Complex **1b** needs to be precipitated and stored under CO atmosphere because otherwise it undergoes CO deinsertion even in the solid state (at an approximate rate of 8% mol·h^{-1} or 3.5% mol·min^{-1} at 70 or 100 °C, respectively, by TGA). The process is faster in solution ($CDCl_3$, 35% mol h^{-1} at room temperature, by ^{1}H NMR). **1a** is rather more stable; it can be stored indefinitely in the solid state and decomposes

Scheme 1



in solution at room temperature at an approximate rate of 5% mol·h^{-1}. CO deinsertion in acyl or benzoyl metal complexes, achieved by thermal or photochemical means, was reported[32] long ago to afford aryl or perfluoroalkyl complexes that were not accessible through more conventional ways. Additionally, CO-releasing molecules (CORMs) are species of increasing interest since the versatile properties of CO and its participation in important biological processes have been recently recognized. In fact, mammals produce CO at a 1−6 μmol kg^{-1} day^{-1} rate, which has been shown to have antioxidative, vasodilator, anti-inflammatory, antiapoptotic, and antiproliferative effects.[30]

When CO was bubbled through a suspension of [Pd{*C,C*-C_6H_4{NH=C(Me)CHC(O)Me}-2}(tmeda)]OTf[8] (**B**, Scheme 1) in acetone, a mixture formed containing [{Pd{*C,N,O*-{C(O)C_6H_4{NC(Me)CHC(O)Me}-2}$_2$(μ-tmeda)] (**2**), the carbonyl complex [{Pd{*C,N,O*-{C(O)C_6H_4{NC(Me)CHC(O)Me}-2}(CO)] (**C**), and the dinuclear benzoyl-C,N,O-pincer complex [Pd$_2${μ-*O,C,N,O*′-{O=CC_6H_4{NC(Me)CHC(O)Me}-2}$_2$}] (**3**). Complex **2** probably forms through (1) the cleavage of the CH−Pd bond in **B** and CO coordination to give **I** (Scheme 1), (2) migratory insertion of CO followed by coordination of NH and O and monocoordination of tmeda to afford **II**, (3) formation of the dinuclear complex **III** and tmeda, and (4) deprotonation of **III** by tmeda to give **2**. This complex could be better obtained when the same reaction was carried out in the presence of 1 equiv of tmeda, which prevents the formation of the carbonyl complex **C**. In this case, the solution initially formed converted gradually into a suspension from which complex **2** was isolated in 76% yield after adding water and filtering. The mother liquor was shown to contain the byproduct [tmedaH$_2$](OTf)$_2$ (^{1}H NMR and elemental analysis). A search of the Cambridge Crystallographic Database reveals that among the very small number of dinuclear complexes with bridging tmeda ligands previously characterized by X-ray diffraction, only one is of palladium;[41] a few derivatives of representative (Li, Be, Al, Ga, Zn, Sn) and transition (Mn, Co) metals are also known.[34]

Various attempts to isolate the monomeric carbonyl complex **C** by using different solvents (acetone, CH_2Cl_2) and longer reaction times led always to **2** + **C** mixtures in which we could identify **C** by both NMR and IR spectroscopy.[47] The best **C**:**2** molar ratio (2.3:1) was achieved after 24 h of stirring **B** in acetone under a CO atmosphere. The carbonyl complex formed also when CO was bubbled through CH_2Cl_2 solutions of **6f** or **6g**. However, all attempts to isolate it failed since in the absence of a CO atmosphere it is unstable and decomposes readily to give **3**. We have also obtained **3** by reacting **2** with HOTf, but it was best prepared (90% isolated yield) by reacting **B** with CO (15 min of bubbling and 1 h of stirring under CO atmosphere) and 1 equiv of HOTf in acetone, where **3** precipitates and [tmedaH$_2$](OTf)$_2$ remains dissolved. Among the many acyl complexes of Pd previously known, some of them reported by us,[1,3,5,9,11,14,15] none bears, as **3**, a symmetric double acyl bridge. Of the few similar isolated complexes (Al,[39] Ga,[36] Re,[37,48] Ru,[38] or Ir[35]), six X-ray crystal structures have been reported, only three of them corresponding to benzoyl derivatives.[34]

Since demetalation of organometallic palladium complexes has opened the way to interesting organic products resulting from different coupling processes,[3,5,6,9,10,12−14,17,24] we heated complex **3** in toluene with the hope of obtaining 2-methyl-3-acetyl-4-oxo-1*H*-*1*,4-dihydroquinoline. However, after 24 h of heating at 120 °C in a Carius tube, not only depalladation but also decarbonylation occurred to give the previously known[49] indole derivative 2-methyl-3-acetyl-1*H*-indole, which was isolated in 50% yield and identified by its NMR and mass spectra.[50] The same compound was obtained when the complex homologue of **B** with N^N = ^{t}Bubpy[8] (Scheme 1) was refluxed in toluene for 10 h.

Complex **3** is far more reactive than its homologous iminobenzoyl derivative [{Pd$_2${*C,N,O*-{C(=NXy)C_6H_4{NC(Me)CHC(O)Me}-2}$_2$}],[8] in which the iminoacyl bridges do not split unless it is refluxed in $CHCl_3$ with phosphine or isocyanide ligands for more than 9 h, and it does not react with (PPN)Cl under the same reaction conditions. However, when a suspension of **3** in CH_2Cl_2 was treated with (Bu_4N)OH (1:1), a solution formed from which the dinuclear complex Bu$_4$N[{Pd{*C,N,O*-{C(O)C_6H_4{NC(Me)CHC(O)Me}-2}$_2$(μ-OH)] (**4**) was isolated in 69% yield. The same complex was isolated, though in lower yield, when **3** was reacted with

(47) ^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ 2.03 (s, 3 H, C(O)Me), 2.34 (s, 3 H, MeCN), 5.10 (s, 1 H, CH), 6.88 (t, 1 H, $^3J_{HH}$ = 7 Hz), 7.14−7.43 (various m obscured by the resonances of **2** in the same region). IR (cm^{-1}): ν(C≡O) 2107, ν(C=O) 1680.

(48) Lippmann, E.; Robl, C.; Berke, H.; Kaesz, H. D.; Beck, W. *Chem. Ber.* **1993**, *126*, 933.

(49) Sakamoto, T.; Nagano, T.; Kondo, Y.; Yamanaka, H. *Synthesis* **1990**, 215.

(50) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 3 H, Me), 2.75 (s, 3H, Me), 7.19−7.27 (m, 2H), 7.33 (d, 1H, $^3J_{HH}$ = 7.6 Hz), 8.02 (d, 1 H, $^3J_{HH}$ = 7.6 Hz), 8.86 (s br, 1H, NH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 15.5 (Me), 31.3 (Me), 110.8 (CH), 114.6 (C), 120.8 (CH), 122.0 (CH), 122.4 (CH) 126.9 (C), 134.5 (C), 143.7 (C), 194.8 (*C*(O)Me). EI-MS [*m*/*z*, %]: [M$^+$] 173.1, 41; [M$^+$ − Me] 158.0, 100.

$(Bu_4N)F$ in an attempt to obtain the corresponding fluoro complex. All attempts to grow single crystals of **4** by the liquid diffusion method failed, and when we used CH_2Cl_2 and Et_2O, a few crystals of Bu_4N[Pd{*C,N,O*-{C(O)C_6H_4-{NC(Me)CHC(O)Me}-2}}Cl] (homologue of complexes **5**, see below) grew instead, probably arising from the presence of traces of HCl in the chlorinated solvent. Although the atomic connectivity in the anion could be unambiguously established, the structure could not be refined because of disorder in the cation. However, we succeeded with one of its homologues (**5a**, see below).

In most complexes bearing the Pd(II)$_2$(μ-OH) moiety both metal atoms are additionally connected by a second bridging ligand. Only two complexes similar to **4** have been characterized by X-ray diffraction, namely, [{PdMe(1,5-cyclooctadiene)}$_2$(μ-OH)]SbF_6[51] and [{Pd{bis(2-pyridylmethyl)amine}}$_2$-(μ-OH)](OTf)$_3$.[52] Crystals of the former were obtained from the decomposition of [Pd(Me)(OH)(1,5-cyclooctadiene)], and its synthesis could not be reproduced. The tricationic derivative, which bears, like **4**, a pincer ligand, formed in low yield by reacting [{Pd(Me){bis(2-pyridylmethyl)amine}}]OTf with $B(C_6F_5)_3$ in CF_3CH_2OH/CH_2Cl_2.

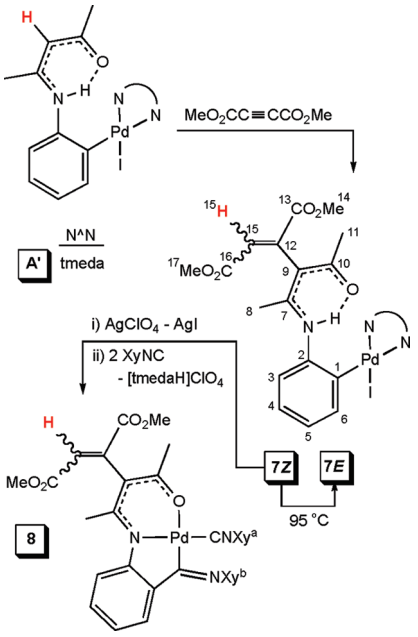
In contrast with the fluoro complex mentioned above, the homologous chloro derivatives Q[Pd{*C,N,O*-{C(O)C_6H_4-{NC(Me)CHC(O)Me}-2}}Cl] (Q = PPN (**5a**), NMe_4 (**5b**)) are stable and could be isolated in good yield from the reactions of **3** with the appropriate chlorides. An attempt to prepare the bromo complex by reacting **5b** with NaBr (1:5, in acetone, 3 h at room temperature) failed, and the starting material was quantitatively recovered.

The acyl bridges in **3** were also split by reacting it with different neutral ligands, under very mild reaction conditions, in stoichiometric amounts (^{t}BuNC, XyNC, PPh_3) or in excess (NH_2Me, NH_3, MeCN, dmso) to give [{Pd{*C,N,O*-{C(O)C_6H_4{NC(Me)CHC(O)Me}-2}L] (L = CN^{t}Bu (**6a**), CNXy (**6b**), PPh_3 (**6c**), NH_3 (**6d**), NH_2Me (**6e**), MeCN (**6f**), dmso (**6g**)) (70−90% isolated yields). They are stable in the solid state, but when we attempted to grow single crystals of **6f**, complex **3** crystallized instead. As far as we are aware, complexes **2**−**6** are the first complexes of any metal bearing an acyl-pincer ligand.

We are also interested in studying the insertion reactions of alkynes into Pd−C_{aryl} bonds, to which field we have made some contributions.[3−6,11,12,17−19] Attempts to react the palladium complex **A** or **A′** with PhC≡CPh under different reaction conditions (1:1 or with excess alkyne, in the presence or not of TlOTf) failed at room temperature or, upon refluxing in $CHCl_3$, gave mixtures, which we could not separate.

However, the reaction of **A′** with dimethylacetylenedicarboxylate (DMAD, 1:1, 10 h at room temperature in $CHCl_3$) allowed us to isolate the complex resulting from the insertion of the alkyne into the activated CH bond of the β-enaminone ligand, affording (*Z*)-[PdI{C_6H_4{NHC(Me)C{C(CO_2Me)=CH(CO_2Me)}{C(O)Me}-2}}(tmeda)] (**7*Z***, Scheme 2) instead of the product of insertion into the Pd−C bond. The yield was very good, but **7*Z*** formed along with traces of its *E* isomer, which we could not remove after repeated recrystallizations or by chromatography. Heating the reaction mixture in toluene gave a mixture of [PdI_2(tmeda)], Pd metal,

Scheme 2



and **7*E***. This complex could be isolated from the mixture in 36% yield. According to NMR data, complex **7*E*** forms as a mixture of two conformers (see the NMR Spectra section). Attempts to react DMAD with complex **A** under various reaction conditions produced mixtures of oily materials, from which we could not isolate any pure species even after repeated recrystallization or chromatography. However, their ^{1}H NMR spectra show the homologues of **7** to form along with some impurities and also that the *Z* isomer, which forms first, transforms into the *E* isomer much faster than in the case of **7**.

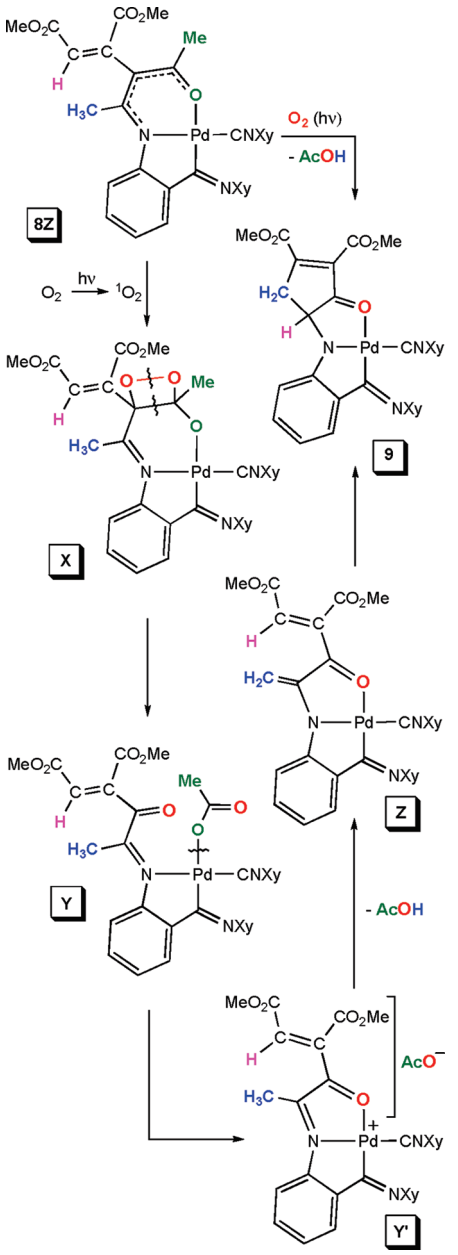
The insertion of dimethylacetylenedicarboxylate into aliphatic C(sp^2)−H bonds has been previously found to occur in β-enaminones, affording the corresponding esters instead of the expected [4+2] cycloaddition products.[43] More recently this reaction, which is said to take several days at room temperature, has proved to be general.[42] We found the reaction of DMAD with the β-enaminone MeC(O)CH=C(Me)NHPh (1:1, in $CHCl_3$ at room temperature) to be less stereospecific and much slower than that with **A′**. Conversion of only 30%, 50%, or 60% of the starting products was achieved after 12, 24, or 48 h, respectively, giving mixtures with *Z*:*E* = 10−15:1 molar ratios. *Z* to *E* conversion is very slow, and even after 4 days refluxing in chloroform a *Z*:*E* = 1:5 molar ratio is attained.

Complex **7*E*** reacted with $AgClO_4$ and XyNC to give the pincer complex [Pd{*C,N*,O-{C(=NXy)C_6H_4{NC(Me)C{C(CO_2Me)=CHCO_2Me)}C(O)Me}-2}(CNXy)] (**8**; Scheme 2) in excellent yield. The reaction was carried out in MeCN in two steps. The iodo ligand was first removed with $AgClO_4$, and then addition of 2 equiv of XyNC afforded complex **8**. In this second step, the replaced tmeda ligand deprotonates the NH group, favoring the N-coordination of the resulting imino ligand, while the insertion of XyNC leaves a free coordination position that allows the coordination of the carbonyl oxygen atom, giving a C,N,O-pincer complex. This process is similar to that giving **C** from **B** (Scheme 1) and has also been observed to occur upon the insertion of XyNC.[8]

An attempt to grow single crystals of **8** produced instead, very slowly, crystals that IR, NMR spectra, and elemental

(51) Klein, A.; Dogan, A.; Feth, M.; Bertagnolli, H. *Inorg. Chim. Acta* **2003**, *343*, 189.
(52) Cao, L.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2009**, 5171.

Scheme 3

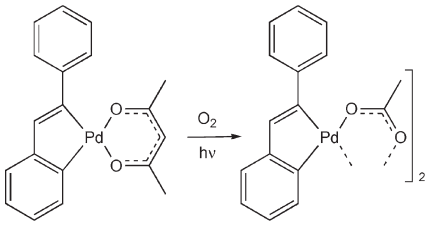


analyses proved to be of [Pd{*C,N,O*-[C(=NXy)C_6H_4{N-(dmoc)}-2](CNXy)]·2$CHCl_3$ (**9**; Scheme 3), where the imino substituent dmoc is the cycle 1,2-di(methoxycarbonyl)-3-oxocyclopent-1-en-4-yl. The conversion of **8** into **9** needs sunlight or visible-light lamp irradiation, occurs in $CHCl_3$ or CH_2Cl_2 but not in toluene, and is accompanied by some decomposition to Pd(0). Under these conditions, the best yield (82%) was obtained after 150 h since decomposition increased when the reaction time was further extended.

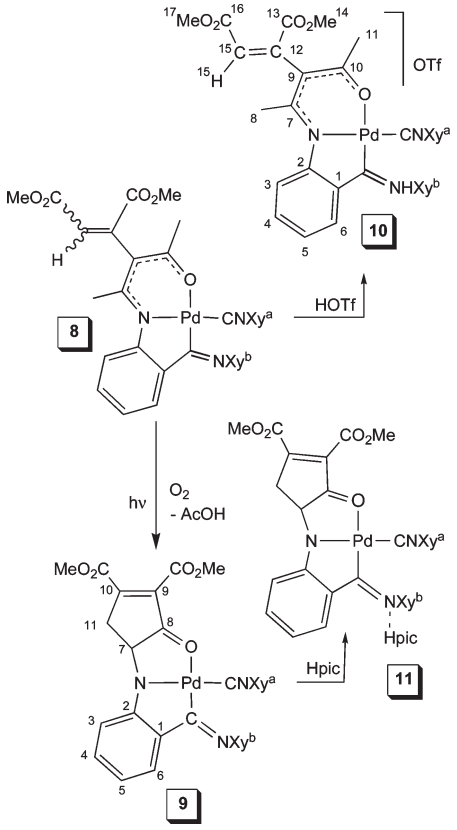
Scheme 3 shows our proposal for the reaction pathway of this process, which involves (1) formation of an 1,2-dioxetane (**X**) through the formal [2+2] cycloaddition of singlet dioxygen ($^1O_2$),[53] (2) O−O and C−C bond cleavage[54] to afford the acetato complex **Y**, (3) isomerization of **Y** to form the pincer complex **Y′**, (4) deprotonation of the N=C(Me) methyl group by the acetate counterion to give acetic acid and complex **Z**, and (5) cyclization to afford **9** through the hydrocarbonation of the C=CH_2 olefinic bond. In the mother liquor where **9** formed, trace amounts of **8*E*** were observed, which suggests that only the main isomer **8*Z*** is responsible for the formation of **9**, in agreement with the proposed reaction pathway (Scheme 3), which would not apply to the *E* isomer. To check this proposal, we carried out a reaction by bubbling dry air through an irradiated solution of **8** in $CHCl_3$ and collected the effluents in a trap cooled with liquid nitrogen. Under these reaction conditions the conversion **8** → **9** is much faster and a 63% or 90% yield was achieved after 10 or 18 h, respectively. In the effluent the presence of AcOH was detected by IR (two absorptions at 1714 and 1758 cm^{-1}) and ^1H NMR (δ 2.10 ppm) spectroscopies.

Complex **9** is the first complex of any metal with this ligand. We have reported a similar photooxygenation reaction involving the transformation of an acetylacetonato into an acetato ligand (Scheme 4).[55] However, these results differ in that, in the present case, replacement of the acetato ligand

Scheme 4



Scheme 5



(53) Adam, W.; Reinhardt, D.; Saha-Möller, C. R. *Analyst* **1996**, *121*, 1527. Mayer, A.; Neuenhofer, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1044.

(54) Matsumoto, M.; Tanimura, M.; Akimoto, T.; Watanabe, N.; Ijuin, H. K. *Tetrahedron Lett.* **2008**, *49*, 4170.

to give the pincer complex **Y′** is preferred to the formation of the acetato-bridged complex obtained when the cleaved ligand is acetylacetonato.

By reacting complex **8** or **9** with the stoichiometric amount of triflic or picric acid, complex Pd{*C,N,*O-{C(=NHXy)C_6H_4\{NC(Me)C\{C(CO_2Me)=CHCO_2Me)\}C(O)Me}-2}(CNXy)]OTf (**10**) or [Pd{*C,N,O*-{C(=NXy)C_6H_4\{N(dmoc)\}-2]-(CNXy)]·Hpic (**11**, Scheme 5, Hpic = picric acid) was obtained, respectively. Complexes **10** and **11** were prepared with the purpose of measuring their X-ray crystal structures, which we could not get for their precursors. We succeeded with complex **10**. In the case of **11** the connectivity of the atoms could be located (see SI), in spite of the refinement being far from satisfactory, which can be attributed to low diffraction, the presence of a very badly disordered triflic acid (possibly over three positions), and a region of disordered solvent (probably dichloromethane), which could not be modelled. NMR studies prove their structures in solution, showing that while **10** is a cationic complex in which the imino N atom is protonated, in agreement with the X-ray diffraction study, **11** behaves as an adduct formed between **9** and picric acid through a hydrogen bond (see NMR Spectra section).

X-ray Crystal Structures. The crystal structures of complexes **2** (Figure 1), **3** (Figure 2), **5a** (Figure 3), **6b** (Figure 4), **6c**, **6e**, **7*Z*** (Figure 5), **7*E*** (Figure 6), and **10** (Figure 7) have been determined by X-ray diffraction. The figures corresponding to the structures of **6c** and **6e** are included in the Supporting Information. In all of them, the palladium atom is in a distorted square, perfectly planar, environment. Complexes **2** and **6** and the anion in **5a**, bearing the same C,N,O-acyl-pincer ligand, display many commonalities. Thus, the C−Pd−N bond angle in the five-membered ring is always narrower (83.18(16)−84.67(18)°) than the N−Pd−O angle (89.65(6)−95.47(15)°) in the more flexible six-membered ring. The C−C, C−N, and C−O bond distances within the pincer skeleton are very similar, but the Pd−N one is sensitive to the nature of the ligand in trans position, suggesting the trans influence to decrease in the series PPh_3 > XyNC > tmeda ≈ NH_3 > Cl > O (μ-acyl). The Pd(1)−C(1) bond distance (1.923(2)−1.9646(18) Å) is somewhat shorter than that found in other palladium complexes having, trans to the benzoyl group, other ligands of low trans influence (Cl, I, N, or O donor, 1.959−2.011 Å),[34] probably because of the pincer nature of our complexes. The Pd−N_{tmeda} bond distance in **2** (2.0296(13) Å) is shorter than that found in the only other palladium complex bearing a bridging tmeda ligand[41] (2.1428(14) vs 2.228(13) Å) because of the greater trans influence of P- with respect to N-donor ligands. The acetyl PdO(1)=C(10) bond distances in **2**, **3**, **5a**, **6b**, **6c**, **6e**, and **10** (1.284(6)−1.262(6) Å) and the benzoyl PdO(2)=C(1) distance in **3** (1.240(3) Å) are longer than the benzoyl PdC(1)=O(2) lengths (1.210(2)−1.220(7) Å) because of the weakening of the C=O bond caused by coordination in the former complexes. In **3**, the Pd(1)−O(1) bond distance (2.0812(17) Å) is longer than Pd(1)−O(02A) (2.0535(14) Å) because of the greater trans influence of C- than N-donor ligands.

The crystal structures of complexes **7*Z*** and **7*E*** show that the reaction between [PdI{C_6H_4\{NHC(Me)CHC(O)Me\}-2}(tmeda)][8] and DMAD produces the insertion of one molecule of the alkyne into the C(sp^2)−H bond of the β-ketoiminato ligand. The palladium atom is in a distorted square-planar environment with narrow N−Pd−N angles (84.13(15)−84.75(10)°) caused by the small bite of the tmeda ligand. The bond distances and angles in **7*E*** and the two different molecules present in the asymmetric unit of **7*Z*** are not significantly different with the exception of the Pd−I bond distance, which is somewhat shorter in **7*E*** (2.5793(4) vs 2.5828(3) and 2.5844(3) Å). The longer Pd−N bond distances trans to aryl (**7*Z***: Pd(1)−N(1) 2.186(2), Pd(2)−N(4)

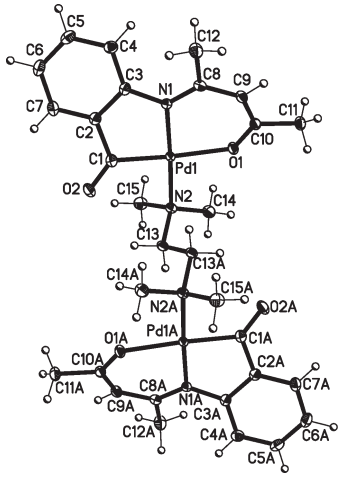


Figure 1. Thermal ellipsoid representation plot (50% probability) of complex **2**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.9594(17), Pd(1)−N(1) 2.0296(13), Pd(1)−O(1) 2.1197(12), Pd(1)−N(2) 2.1428(14), C(1)−C(2) 1.500(2), C(2)−C(3) 1.405(2), N(1)−C(3) 1.412(2), N(1)−C(8) 1.334(2), C(8)−C(9) 1.403(2), C(9)−C(10) 1.398(2), O(1)−C(10) 1.278(2), O(2)−C(1) 1.213(2); C(1)−Pd(1)−N(1) 83.18(6), N(1)−Pd(1)−O(1) 91.87(5), C(1)−Pd(1)−N(2) 94.74(6), O(1)−Pd(1)−N(2) 90.26(5).

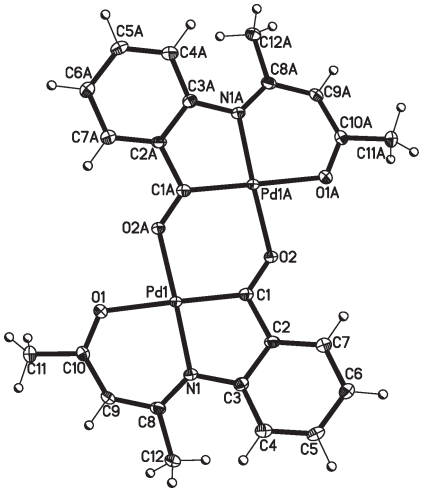


Figure 2. Thermal ellipsoid representation plot (50% probability) of complex **3**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.923(2), Pd(1)−N(1) 2.0095(17), Pd(1)−O(1) 2.0812(17), Pd(1)−O(2)#1 2.0535(14), C(1)−C(2) 1.480(3), C(2)−C(3) 1.406(3), N(1)−C(3) 1.413(3), N(1)−C(8) 1.333(3), C(8)−C(9) 1.411(3), C(9)−C(10) 1.393(3), O(1)−C(10) 1.274(3), O(2)−C(1) 1.240(3); C(1)−Pd(1)−N(1) 84.07(8), C(1)−Pd(1)−O(2)#1 97.47(7), N(1)−Pd(1)−O(1) 94.83(7), O(2)#1−Pd(1)−O(1) 83.90(6),C(1)−O(2)−Pd(1)#1 132.87(14), O(2)−C(1)−Pd(1) 129.14(17).

(55) Vicente, J.; Arcas, A.; Bautista, D.; Shul'pin, G. B. *J. Chem. Soc., Dalton Trans.* **1994**, 1505.

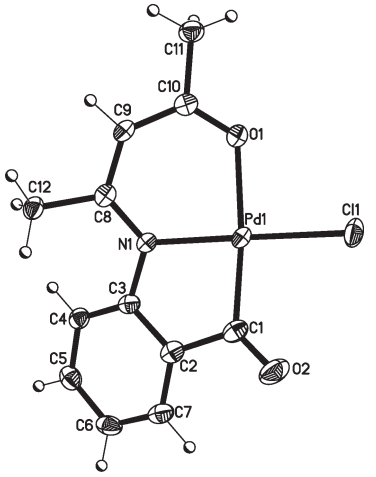


Figure 3. Thermal ellipsoid representation plot (50% probability) of the anion in complex **5a**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.948(2), Pd(1)−N(1) 2.0210(18), Pd(1)−O(1) 2.1464(15), Pd(1)−Cl(1)2.3245(6), C(1)−C(2) 1.518(3), C(2)−C(3) 1.403(3), N(1)−C(3) 1.411(3), N(1)−C(8) 1.337(3), C(8)−C(9) 1.401(3), C(9)−C(10) 1.408(3), O(1)−C(10) 1.269(3), O(2)−C(1) 1.211(3); C(1)−Pd(1)−N(1) 84.12(8), N(1)−Pd(1)−O(1) 89.65(6), C(1)−Pd(1)−Cl(1) 95.29(7), O(1)−Pd(1)−Cl(1) 90.94(4).

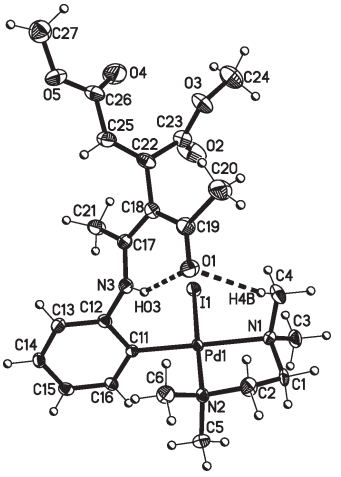


Figure 5. Thermal ellipsoid representation plot (50% probability) of complex **7*Z***. Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) 1.995(3), Pd(1)−N(2) 2.124(2), Pd(1)−N(1), 2.186(2), Pd(1)−I(1) 2.5828(3), N(3)−C(17) 1.332(4), O(1)−C(19) 1.243(4), C(17)−C(18) 1.411(4), C(18)−C(22), 1.491(5), C(22)−C(25) 1.332(5); C(11)−Pd(1)−N(2) 91.93(10), N(2)−Pd(1)−N(1) 84.38(9), C(11)−Pd(1)−I(1) 89.11(8), N(1)−Pd(1)−I(1) 94.59(7), C(25)−C(22)−C(18) 120.4(3), C(25)−C(22)−C(23) 121.4(3), C(18)−C(22)−C(23) 117.7(3), C(22)−C(25)−C(26) 124.7(3).

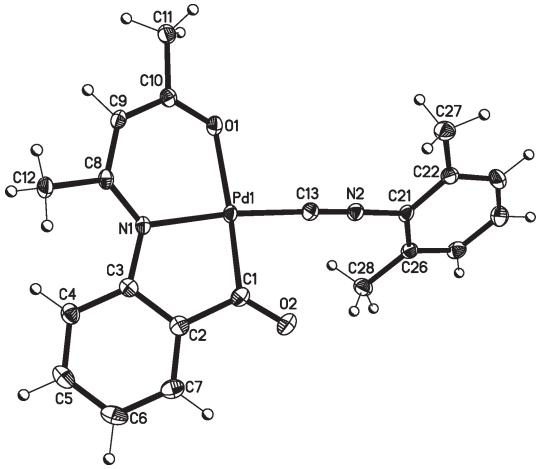


Figure 4. Thermal ellipsoid representation plot (50% probability) of complex **6b**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.9646(18), Pd(1)−N(1) 2.0422(14), Pd(1)−O(1) 2.1228(12), Pd(1)−C(13) 1.9543(17), C(1)−C(2) 1.500(2), C(2)−C(3) 1.401(2), N(1)−C(3) 1.417(2), N(1)−C(8) 1.334(2), C(8)−C(9) 1.404(2), C(9)−C(10) 1.403(2), O(1)−C(10) 1.275(2), O(2)−C(1) 1.210(2); C(1)−Pd(1)−N(1) 83.89(6), N(1)−Pd(1)−O(1) 91.96(5), C(13)−Pd(1)−C(1) 91.02(7), C(13)−Pd(1)−O(1) 93.28(6).

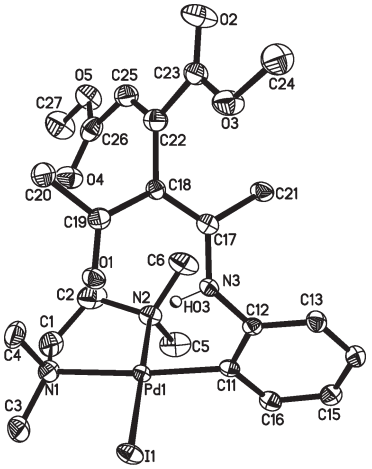


Figure 6. Thermal ellipsoid representation plot (50% probability) of complex **7*E***. Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) 2.004(4), Pd(1)−N(1) 2.182(4), Pd(1)−N(2) 2.111(3), Pd(1)−I(1) 2.5793(4), N(3)−C(12) 1.429(5), N(3)−C(17) 1.344(5), O(1)−C(19) 1.239(5), C(17)−C(18) 1.385(6), C(18)−C(19) 1.454(6), C(18)−C(22) 1.493(6), C(22)−C(23) 1.521(6), C(22)−C(25) 1.322(6), C(25)−C(26) 1.473(7); C(11)−Pd(1)−N(2) 92.21(15), N(2)−Pd(1)−N(1) 84.13(15), C(11)−Pd(1)−I(1) 88.08(11), N(1)−Pd(1)−I(1) 95.63(10), C(25)−C(22)−C(18) 125.1(4), C(25)−C(22)−C(23) 115.9(4), C(18)−C(22)−C(23) 119.0(4), C(22)−C(25)−C(26) 125.5(4).

2.173(2); **7*E***: Pd(1)−N(1) 2.182(4) Å) compared to those trans to iodo (**7*Z***: Pd(1)−N(2) 2.124(2), Pd(2)−N(5) 2.132(3); **7*E***: Pd(1)−N(2) 2.111(3) Å) are attributable to the greater trans influence of the aryl ligand.

In the crystal structure of **10** the bond distances and angles within the five- and six-membered rings constituting the pincer fragment are almost equal to those in the complex [Pd{*C,N,*O-{C(=NHXy)C_6H_4{NC(Me)CHC(Me)O}-2}(CNXy)]OTf previously reported by us,[8] while the structural parameters regarding the alkenyl fragment do not differ significantly from those found in complexes **7*E*** and **7*Z***.

Nonclassical C−H···O, C−H···Cl, or C−H···I hydrogen bonds are also observed. Thus, in **5a** two C−H···Cl interactions make the molecules arrange into chains parallel to the *a* axis (Figure 8). Classical N−H···O hydrogen bonds are observed in complexes **7*Z*** and **7*E*** (intramolecular, Figures 9 and 10, respectively). In **7*Z*** the two independent molecules in the asymmetric unit are connected by two C−H···O interactions, giving dimers; additionally, two C−H···I interactions connect one of the two independent

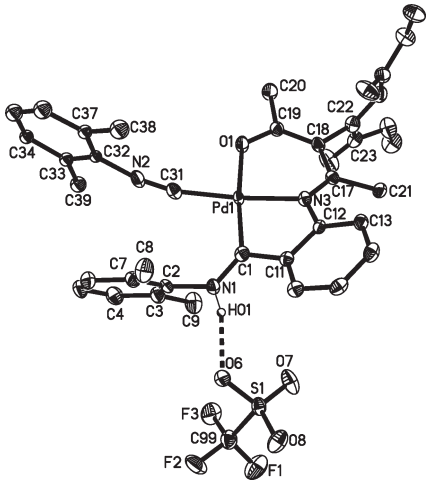


Figure 7. Thermal ellipsoid representation plot (50% probability) of complex **10**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.965(4), Pd(1)−C(31) 1.967(4), Pd(1)−N(3) 2.005(3), Pd(1)−O(1) 2.037(3), O(1)−C(19) 1.279(4), C(1)−N(1) 1.295(5), C(31)−N(2) 1.154(5), C(1)−C(11) 1.471(5), C(11)−C(12) 1.401(5), C(12)−N(3) 1.418(5), N(3)−C(17) 1.341(5), C(17)−C(18) 1.417(5), C(18)−C(19) 1.394(5), C(18)−C(22) 1.508(5), C(22)−C(23) 1.516(5), C(22)−C(25) 1.319(6), C(25)−C(26) 1.493(6), C(23)−O(2) 1.197(5), C(23)−O(3) 1.325(5), O(3)−C(24) 1.444(5), C(26)−O(4) 1.195(5); C(1)−Pd(1)−C(31) 98.34(16), C(1)−Pd(1)−N(3) 82.63(14), C(31)−Pd(1)−O(1) 87.82(13), N(3)−Pd(1)−O(1) 91.63(12).

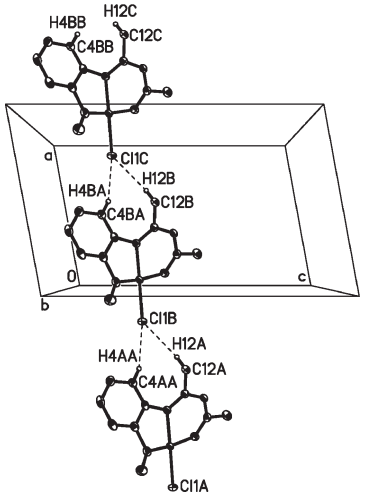


Figure 8. C−H···Cl interactions in **5a** resulting in chains parallel to the *a* axis.

molecules with its homologues to give chains along the *b* axis, which, along with other C−H···O interactions, result in a rather complex three-dimensional packing. In **7*E*** C−H···I interactions arrange the molecules into chains along the *c* axis (Figure 10). In complex **10** the xylyliminium moiety participates in N−H···O and C−H···F hydrogen bonds with the oxygen and fluorine atoms of two different triflate anions, giving rise to dimers (Figure 11).

NMR Spectra. The *Me*CN (Me[8]), *Me*C(O) (Me[11]), and CH (H[9]) (Scheme 1) resonances in the ^{1}H NMR spectra of benzoyl complexes appear in the same ranges (1.91−2.36, 1.74−2.25, and 4.79−5.31 ppm, respectively) regardless of the monocoordinated (**1**) or pincer (**2**−**6**) nature of the benzoyl ligand. The ^{13}C NMR spectra show that deprotonation of the enamine NH group in complexes **1** and the coordination to palladium of both nitrogen and oxygen atoms to give the pincer derivatives **2**−**6** cause the deshielding of the *Me*CN (Me[8]) and CH (C[9]) carbon nuclei (Me: 21.2 (**1a**), 21.0 (**1b**), 24.2−25.5 (**2**−**6**); CH: 96.5 (**1a**), 99.7 (**1b**), 102.2−103.9 (**2**−**6**); CN: 160.6 (**1a**), 160.0 (**1b**), 162.2−164.2 (**2**−**6**) ppm) and the shielding of the benzoyl carbon (C[12]: 224.1 (**1a**), 222.3 (**1b**), 211.5−217.4 (**2**-**6**) ppm). This can be attributable to an electronic flow from the nitrogen to the oxygen caused by deprotonation and coordination of nitrogen and oxygen to palladium. However, other effects regarding the displacement of the iodo and nitrogen donor ligands cannot be ruled out. The Ar*C*(O)Pd resonance in complexes **1**−**6** is 30−40 ppm deshielded with respect to the homologous Ar*C*(NR)Pd one in related iminoacyl derivatives because of the greater electronegativity of the oxygen atom.[8] The NMR show also the ^{1}H, ^{13}C, and ^{31}P resonances expected for the remaining ligands or cations except that of the μ-OH proton, which is not observed in the ^{1}H NMR spectrum of **4**, probably because of its participation in hydrogen bonds. The spectra of complexes **2** and **3** measured in d_6-dmso are

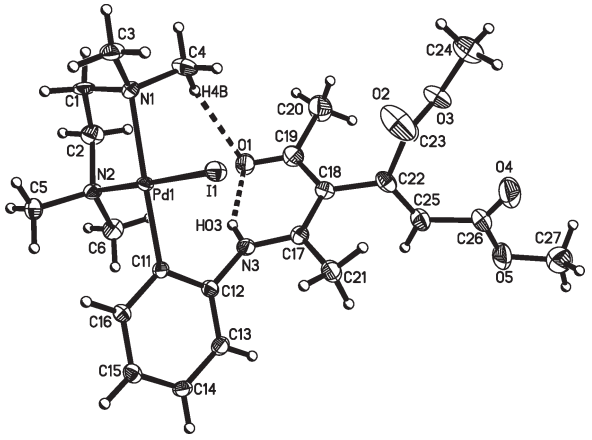


Figure 9. Intramolecular N−H···O and C−H···O interactions in **7*Z***.

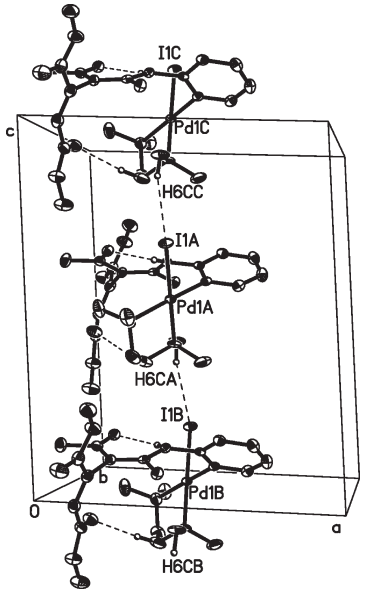


Figure 10. Chains along the *c* axis in **7*E*** resulting from C−H···I interactions.

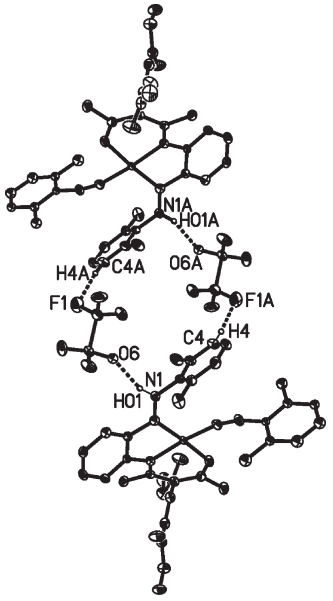


Figure 11. N−H···O and C−H···F bonds in **10** resulting in dimers.

identical to those of complex **6g**, showing that both dinuclear complexes dissolve in dmso upon bridge splitting and solvent coordination.

While a unique set of resonances is present in the ^{1}H NMR spectrum of **7*Z***, duplication is observed in that of **7*E*** at room temperature, indicating the presence of two isomers in solution, in 1.2:1 molar ratio. We think that in the *E* isomer the close vicinity of Me[8] and Me[11] to both CO_2Me groups prevents the free rotation around the C[9]−C[12] bond (Scheme 2), giving rise to two conformers. The activation energy for this rotation is overcome at 90 °C, at which temperature the ^{1}H NMR spectrum of **7*E*** gives a single set of resonances. The homologous resonances show only very small differences within the two conformers in the ^{13}C NMR spectrum of **7*E*** at room temperature, indicating their close similarity and making it impossible to assign unequivocally some of them. Most ^{1}H NMR and ^{13}C NMR resonances are also similar to those in the *Z* isomer; the main differences are those of the C[9] and H[15] nuclei (Scheme 2) (C[9]: 104.5 (**7*Z***), 101.3, 101.5 (**7*E***); H[15]: 6.15 (**7*Z***), 7.06, 7.11 (**7*E***) ppm).

The NMR spectra of complex **8** show also the presence of two isomers in solution, in 1:10 molar ratio, which must be the *E* and *Z* isomers because only one conformer is possible for each isomer. The major and minor isomers show the H[15] resonance (Scheme 2) at 7.07 and 6.14 ppm, respectively, which suggests the major isomer of **8** to be **8*E*** by comparison with the homologous resonance in **7*E*** (7.06, 7.11 ppm) and **7*Z*** (6.15 ppm). In both isomers of **8** and in **9**, the two halves of the Xy[b] group are inequivalent because of restricted rotation around the N−Xy bond, while the Xy[a] group rotates freely, as we have previously observed in similar complexes.[8] The NMR spectra of complex **9** are in agreement with the X-ray diffraction study.

When complex **8** is protonated with triflic acid, the resulting complex **10** shows a new NH proton resonance at 12.31 ppm and a highly deshielded *C*=NHXy carbon nucleus (216.2 vs 178.2 ppm in **8**; in complexes related to **10**, it is observed at 190−200 ppm[7,8]). However, complex **9** reacts with triflic acid to afford a complex of which the ^{1}H NMR spectrum does not show the expected highly deshielded NH proton resonance but a broad resonance at around 4.5 ppm, too far from that expected for the N*H*Xy proton (12.31 ppm in **10** or 9−12.5 ppm in similar complexes[7,8]). This complex decomposes in solution and in the solid state. Thus, during the acquisition time for the ^{13}C NMR spectrum, it partly decomposes back to **9** and its elemental analysis shows triflic acid loss. These data suggest that this species is probably an adduct formed through a TfOH···N(Xy)=C (**9**·HOTf) hydrogen bond between **9** and triflic acid. The picrate complex **11** seems to be similar to **9**·HOTf, although the corresponding hydrogen bond seems to be stronger because the complex is stable in solution and in the solid state. Thus, the *C*=NXy carbon resonance of **11** (167.8 ppm) appears almost at the same chemical shift as in its parent complex **9** (166.7 ppm). In addition, because of the picH···N(Xy)=C hydrogen bond, the OH proton resonance of Hpic (11.94 ppm in $CHCl_3$) is shown in **11** as a very wide resonance at around 3 ppm (1 H).

IR Spectra. The expected ν_{NH} band is not observed in the spectra of complexes **1a**, **1b**, **7*Z***, and **7*E*** probably because of the participation of the NH group in N−H···O hydrogen bonds, as shown in the crystal structures of **7*Z*** and **7*E*.** Bands assigned to $\nu_{C=O}$(acyl) in complexes **1**−**6** and to $\nu_{asym}(CO_2)$ in complexes **7** and **8** are observed in the 1620−1670 and 1715−1730 cm^{-1} regions, respectively. A ν(OH) band at 2925 cm^{-1} in the IR spectrum of **11** compared to that at 3101 cm^{-1} in the spectrum of Hpic (both measured in hexachlorobutadiene mull on KBr plates) supports the existence in **11** of the picH···N(Xy)=C hydrogen bond mentioned above. The spectra show also the expected bands attributable to the different ligands or counterions. A band at 1101 cm^{-1} in the spectrum of **6g**, assignable to the S=O stretching mode, is indicative of S-coordination of the dmso ligand.[45]

Conclusion

Carbon monoxide and dimethylacetylenedicarboxylate react differently toward aryl palladium(II) complexes containing an ortho β-enaminone substituent. While the first inserts into the Pd−C bond, affording benzoyl complexes, the second inserts into the C−H bond of the ortho substituent. Two types of complexes derived from the insertion of CO have been prepared, those with the benzoyl ligand acting as monocoordinate, which slowly lose CO, and stable C,N,O-pincer complexes that result from deprotonation of the NH group in the benzoyl ligand. Some of these complexes are of unusual types. The insertion of the alkyne affords mainly the *Z* isomer, which isomerizes upon heating to the *E* isomer and transforms by reaction with Ag^+ and an isocyanide into a pincer complex, which, in turn, is photooxygenated by atmospheric oxygen to afford a new pincer complex after AcOH loss.

Acknowledgment. We thank Ministerio de Educación y Ciencia (Spain), FEDER (CTQ2007-60808/BQU), and Fundación Séneca (04539/GERM/06 and 03059/PI/05) for financial support and for grants to A.J.M.M. and A. A.L., respectively.

Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, bond lengths and angles, thermal ellipsoid representation plots, and hydrogen bonds of complexes **6c** and **6e** and CIF files for complexes **2**, **3**, **5a**, **6b**, **6c**, **6e**, **7*Z***, **7*E***, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.