Palladium-Assisted Formation of Carbon−Carbon Bonds. 7.[1] Reactions of (2,3,4-Trimethoxy-6-X-phenyl)palladium Complexes with Alkynes (X = C(O)NHBu^t) and Isocyanides (X = C(O)NHBu^t, C(O)Me, CHO): Crystal and Molecular Structures of [Pd{C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}(bpy)](CF$_3$SO$_3$), [Pd{C(CO$_2$Me)=C(CO$_2$Me)C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4)}Cl(PPh$_3$)], [Pd{C(=NXy)C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}(bpy)](CF$_3$SO$_3$), and the Ketenimine 2-(2,6-Dimethylphenyl)-1-(((2,6-dimethylphenyl)imino)methylene)-5,6,7-trimethoxy-3-oxoisoindoline

José Vicente,*,† José-Antonio Abad,*,‡ Kenneth F. Shaw, Juan Gil-Rubio, and M. Carmen Ramírez de Arellano

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

Peter G. Jones*,||

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Received May 23, 1997[⊗]

The mercuriation of 3,4,5-trimethoxy(*N*-*tert*-butylcarbamoyl)benzene with mercury(II) acetate and subsequent reaction with KCl leads to the formation of [Hg{C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}Cl] (**1**), which is symmetrized with [NMe$_4$]Cl to give [Hg{C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}$_2$] (**2**). The reaction of **2** with [PdCl$_2$(MeCN)$_2$] and 2,2′-bipyridine (bpy) affords [Pd(C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4)Cl(bpy)] (**3**), which reacts with Tl(CF$_3$SO$_3$) giving [Pd{C_6H{C(O)NHBu^t}}(bpy)](CF$_3$SO$_3$) (**4**). Complex **2** reacts with [PdCl$_2$(MeCN)$_2$] and acetylenes RC≡CR to give metallic palladium and the spirocyclic compound 10-(*N*-*tert*-butylcarbamoyl)-6,7-dimethoxy-1,2,3,4-tetraphenylspiro[4.5]-1,3,6,9-decatetraen-8-one (**5**) when R = Ph or the monoinserted palladium complex [Pd{C(CO$_2$Me)=C(CO$_2$Me)C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}(μ-Cl)]$_2$ (**6**) when R = CO$_2$Me. By reaction of **6** with L (1:2) or PPh$_3$ and Tl(CF$_3$SO$_3$) (1:4:2), the complexes [Pd{C(CO$_2$Me)=C(CO$_2$Me)C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}Cl(L)] (L = PPh$_3$ (**7**), CNXy (**8**) (Xy = 2,6-dimethylphenyl)) or [Pd{C(CO$_2$Me)=C(CO$_2$Me)C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}(PPh$_3$)$_2$](CF$_3$SO$_3$) (**9**) are obtained respectively. The reactions of **4** and of the related complexes [Pd{C_6H{C(O)Me}-6-(OMe)$_3$-2,3,4}(bpy)](CF$_3$SO$_3$) (**10**) or [Pd{C_6H{C(O)H}-6-(OMe)$_3$-2,3,4}(NCMe)(bpy)](CF$_3$SO$_3$) (**11**) with CNXy have also been studied, the following compounds being isolated: [Pd{C(=NXy)C_6H{C(O)NHBu^t}-6-(OMe)$_3$-2,3,4}(bpy)](CF$_3$SO$_3$) (**12**) [Pd{C_6H{C(O)Me}-6-(OMe)$_3$-2,3,4}(CNXy)(bpy)](CF$_3$SO$_3$) (**13**), [Pd{C_6H{C(O)H}-6-(OMe)$_3$-2,3,4}(CNXy)(bpy)](CF$_3$SO$_3$) (**14**), and the ketenimine 2-(2,6-dimethylphenyl)-1-(((2,6-dimethylphenyl)imino)methylene)-5,6,7-trimethoxy-3-oxoisoindoline (**15**). The structures of **4**, **7**, **12**, and **15** have been determined by X-ray crystallography.

Introduction

The use of organopalladium complexes in organic syntheses constitutes a topic of current interest;[2] in particular, reactions involving arylpalladium complexes and alkynes have proved to be useful for the synthesis of various types of organic compounds.[3−9] In this paper, we report a new example of this type of reaction that gives a highly functionalized spirocyclic compound. However, although reactions of isocyanides with alkyl-,[10−13] alkynyl-,[14−16] aryl-,[5,17−22] and other[23,24] organopalladium derivatives are known to give insertion

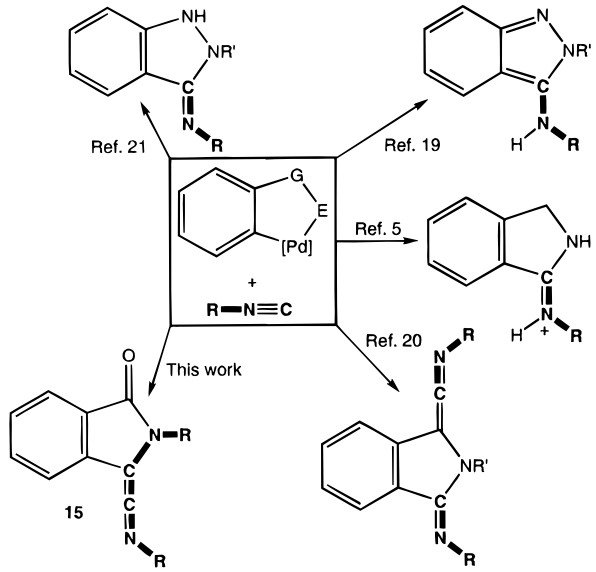
† E-mail: jvs@fcu.um.es.
‡ E-mail: jaab@fcu.um.es.
§ WWW: http://www.scc.um.es/gi/gqo/.
|| E-mail: jones@xray36.anchem.nat.tu-bs.de.
⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1997.

(1) Part 6: Vicente, J.; Abad, J. A.; Gil-Rubio, J. *Organometallics* **1996**, *15*, 3509.

S0276-7333(97)00426-3 CCC: $14.00

products, only a few such reactions lead directly[11,12,19−21] or after reaction with other reagents[13,18] to organic products. Some heterocyclic compounds are among the more interesting of these organic products (see Scheme 1).[19−21] We report in this paper a member of a new family of ketenimines that is formed by a new type of head-to-head coupling of two isocyanide molecules (see Scheme 1). Ketenimines are useful as dehydrating agents for peptide syntheses, as coreagents in oxidations, and as building blocks in the synthesis of carbo- and *N*-heterocyclic rings.[25,26] They are usually prepared using classical organic methods[25] or *via* metal complexes.[11,20,27]

Scheme 1



Weak molecular interactions are at present attracting general interest.[28] The directional interactions resulting from hydrogen bonding are being exploited for the synthesis of different assemblies.[29,30] In particular, C−H···O interactions are currently one of the main topics of hydrogen-bond research.[31−35] In this paper, we report a new example of such an interaction between identical molecules. This type of interaction is a much less common phenomenon.[35,36]

We are currently investigating the synthesis and reactivity of (2,3,4-trimethoxyaryl)palladium complexes bearing different substituents at the 6 position.[1,37−44] Given the nature of the functional substituents attached to the aryl ring, which are often incompatible with the use of lithium or Grignard reagents, such complexes

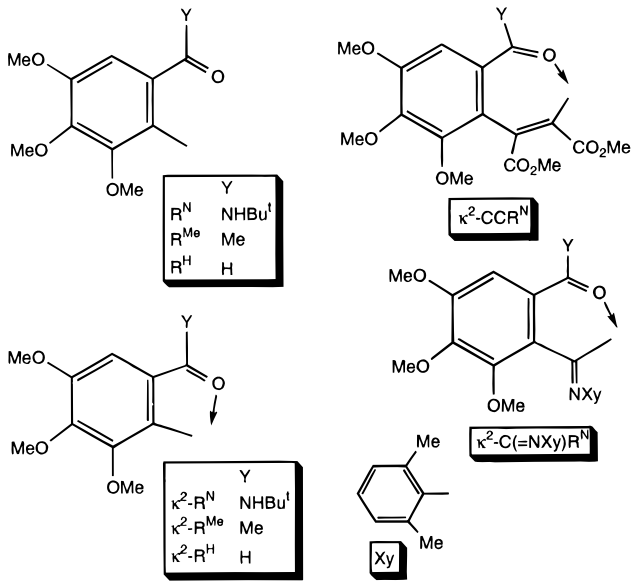
(2) Heck, R. F. *Palladium Reagents in Organic Synthesis*. Academic Press: New York, 1985. Tsuji, J. *Palladium Reagents and Catalysts*. John Wiley: Chichester, U.K., 1995.
(3) Ryabov, A. D. *Synthesis* **1985**, 233. Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335. Spencer, J.; Pfeffer, M. *Tetrahedron: Asymmetry* **1995**, *6*, 419. Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214. Pfeffer, M.; Sutter, J. P.; Rotteveel, M. A.; Decian, A.; Fischer, J. *Tetrahedron* **1992**, *48*, 2427. Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550. Nguefack, J. F.; Bolitt, V.; Sinou, D. *Tetrahedron Lett.* **1996**, *37*, 5527. Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1996**, *118*, 6305. Larock, R. C.; Yum, E. K. *J. Am. Chem. Soc.* **1991**, *113*, 6689. Pfeffer, M.; Rotteveel, M. A.; Le Borgne, G.; Fischer, J. *J. Org. Chem.* **1992**, *57*, 2147. Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029. Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535. Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116. Beydoun, N.; Pfeffer, M. *Synthesis* **1990**, 729. Liao, H. Y.; Cheng, C. H. *J. Org. Chem.* **1995**, *60*, 3711. Dupont, J.; Pfeffer, M. *J. Organomet. Chem.* **1987**, *321*, C13. Pfeffer, M.; Rotteveel, M. A.; Sutter, J.-P.; De Cian, A.; Fisher, J. *J. Organomet. Chem.* **1989**, *371*, C21. Larock, R. C.; Doty, M. J.; Cacchi, S. J. *J. Org. Chem.* **1995**, *60*, 3270. Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2043. Pfeffer, M.; Sutter, J. P.; De Cian, A.; Fischer, J. *Organometallics* **1993**, *12*, 1167. Catellani, M.; Marmiroli, B.; Fagnola, M. C.; Acquotti, D. *J. Organomet. Chem.* **1996**, *507*, 157.
(4) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567.
(5) O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1165.
(6) Maassarani, F.; Pfeffer, M.; Spencer, J.; Wehman, E. *J. Organomet. Chem.* **1994**, *466*, 265.
(7) Dupont, J.; Pfeffer, M.; Theurel, L.; Rotteveel, M. A.; Decian, A.; Fischer, J. *New J. Chem.* **1991**, *15*, 551.
(8) Beydoun, N.; Pfeffer, M.; Decian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3693.
(9) Spencer, J.; Pfeffer, M.; Decian, A.; Fischer, J. *J. Org. Chem.* **1995**, *60*, 1005.
(10) Yamamoto, Y. *Coord. Chem. Rev* **1980**, *32*, 193. Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196. Ito, Y.; Hirao, T.; Ohta, N.; Saegusa, T. *Tetrahedron Lett.* **1977**. Yamamoto, Y.; Tanase, T.; Yanai, T.; Asano, T.; Kobayashi, K. *J. Organomet. Chem.* **1993**, *456*, 287. Delis, J. G. P.; Aubel, P. G.; Vanleeuwen, P.; Vrieze, K.; Veldman, N.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1995**, 2233. Campora, J.; Hudson, S. A.; Carmona, E. *Organometallics* **1995**, *14*, 2151. Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15.
(11) Tanase, T.; Fukushima, T.; Nomura, T.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1994**, *33*, 32.
(12) Veya, P.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.
(13) Veya, P.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 441.
(14) Onitsuka, K.; Joh, T.; Takahashi, S. *J. Organomet. Chem.* **1994**, *464*, 247.
(15) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. *Organometallics* **1994**, *13*, 3862.
(16) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531.
(17) Dupont, J.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3193.
(18) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1980**, *41*, 229.
(19) Gehrig, K.; Klaus, A. J.; Rys, P. *Helv. Chim. Acta* **1983**, *66*, 2603.
(20) Albinati, A.; Pregosin, P. S.; Rüedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046.
(21) Yamamoto, Y.; Yamazaki, H. *Synthesis* **1976**, 750.
(22) van Baar, J. F.; Klerks, J. M.; Overbosch, P.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1976**, *112*, 95.
(23) Wouters, J. M. A.; Klein, R. A.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Organometallics* **1993**, *12*, 3864.
(24) Crociani, B.; Sala, M.; Polo, A.; Bombieri, G. *Organometallics* **1986**, *5*, 1369.
(25) Row, G. K. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435.
(26) Aumann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456. Merlic, C. A.; Burns, E. E. *Tetrahedron Lett.* **1993**, *34*, 5401. Dennehy, R. D.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1992**, 35.
(27) Dennehy, R. D.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1992**, 35. Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108. Merlic, C. A.; Burns, E. E. *Tetrahedron Lett.* **1993**, *34*, 5401. Aumann, R.; Jasper, B.; Lage, M.; Krebs, B. *Organometallics* **1994**, *13*, 3502. Aumann, R.; Jasper, B.; Frohlich, R. *Organometallics* **1995**, *14*, 231.
(28) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 90. Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155. Tamiaki, H.; Miyatake, T.; Tanikaga, R.; Holzwarth, A. R.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 772. Philp, D.; Stodart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1155. Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312. Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229.
(29) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320. Burrows, A. D.; Chan, C.-W.; Chowdhry, M. M.; McGrady, J. E.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, *24*, 329. Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397. MacDonald, J. C.; Whitsides, G. M. *Chem. Rev.* **1994**, *94*, 2383.
(30) Burrows, A. D.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 97.
(31) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.
(32) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222. Steiner, T.; Tamm, M.; Lutz, B.; Maas, J. v. d. *Chem. Commun.* **1996**, 1127.
(33) Munakata, M.; Wu, L. P.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Am. Chem. Soc.* **1996**, *118*, 3117.
(34) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.
(35) Metzger, S.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1228.
(36) Turi, L.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1994**, *116*, 8714. Schmalle, H. W.; Jarchow, O. H.; Adiwidjaja, G.; König, W. A.; Heitsch, H.; Rathmann, R.; Hausen, B. M.; Schulz, K.-H. *Acta Crystallogr.* **1988**, *C44*, 693.

have been synthesized by a route, widely exploited by us, using the corresponding diarylmercurials as transmetalating agents.[45] Starting from these arylpalladium compounds, we have recently prepared indenones, indenols,[1,44] benzofulvenes,[39] and spirocyclic compounds.[1,38−40] Most of these compounds bear a trimethoxyaryl moiety, which is also present in many organic molecules of pharmaceutical interest.[46] In this paper, we report on the synthesis of 2,3,4-trimethoxy-6-(*N-tert*-butylcarbamoyl)phenylpalladium complexes and their reactivity with alkynes and the reactions of (2,3,4-trimethoxyaryl)palladium complexes, bearing the groups −C(O)NHBu^t, −C(O)Me, and CHO at the ortho position, with 2,6-dimethylphenyl isocyanide. We also report the first palladium complexes containing a carbamoylaryl group.[47]

Experimental Section

C, H, and N analyses, melting point determinations, conductance measurements, and NMR spectra were performed as described elsewhere.[39] Infrared spectra were recorded in the range 4000−200 cm^{-1} on a FT-IR Perkin-Elmer U-2000 spectrophotometer using Nujol mulls between polyethylene sheets or KBr pellets. Mass spectra were carried out on a Hewlett-Packard 5993 spectrometer. The exact molecular weight of **15** was determined on a Fisons VG-AutoSpec 8000 instrument. Special group symbols: the groups $C_6H\{C(O)NHBu^t\}$-6-$(OMe)_3$-2,3,4, $C(CO_2Me)$═$(CO_2Me)[C_6H\{C(O)NHBu^t\}$-6-$(OMe)_3$-2,3,4], $C_6H\{C(O)Me\}$-6-$(OMe)_3$-2,3,4 and $C_6H(CHO)$-6-$(OMe)_3$-2,3,4 are represented as R^N, CCR^N, R^{Me}, and R^H, respectively (when these groups are bonded to palladium through carbon and the carbonyl oxygen we use the notations κ^2-R^N, κ^2-CCR^N, κ^2-R^{Me}, and κ^2-R^H, see Chart 1); bpy is the ligand 2,2′-bipyridine, and Xy is the group 2,6-dimethylphenyl. The palladium compounds **10**, **11**, and **16** were prepared following previously described procedures.[41,42] All reactions were carried out without exclusion of atmospheric air or moisture and at ambient temperature, unless otherwise indicated. Chromatographic separations were carried out by TLC on silica gel (70−230 mesh).

Chart 1



Synthesis of [Hg(R^N)Cl] (1). R^NH (8.63 g, 32.3 mmol), $Hg(OAc)_2$ (10.3 g, 32.3 mmol), and HOAc (8 cm^3) were dissolved in EtOH (180 cm^3) and refluxed for 5 h. After the mixture was cooled, it was stirred overnight and then poured into a solution of KCl (9.64 g, 130 mmol) in water (250 cm^3) to afford a copious white precipitate. After the reaction mixture was stirred for 10 min, the precipitate was isolated by filtration, washed with water, and dried in the oven at 70 °C to yield **1** as a white powder in quantitative yield. Mp: 162 °C. IR (cm^{-1}): ν(NH) 3428, ν(CO) 1630, ν(HgCl) 338. ^{1}H NMR ($CDCl_3$): 6.89 (s, 1H, C_6H), 6.08 (br s, 1H, NH), 3.93, 3.88, 3.87 (all s, 3H, MeO), 1.46 (s, 9H, $C(Me)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): 168.73 (C═O), 156.28, 154.63, 145.78, 136.67, 134.82 (quaternary C in C_6H), 108.66 (CH in C_6H), 61.21, 60.77, 56.76 (3MeO), 52.43 (CMe_3), 28.71 ($C(Me)_3$). Anal. Calcd for $C_{14}H_{20}ClHgNO_4$: C, 33.5; H, 4.0; N, 2.8. Found: C, 33.5; H, 4.1; N, 2.8.

Synthesis of [Hg(R^N)$_2$] (2). **1** (0.61 g, 1.22 mmol) and $(Me_4N)Cl$ (0.14 g, 1.32 mmol) were stirred in acetone (55 cm^3) for 24 h and then filtered through $MgSO_4$ to give a gray deposit and a colorless solution. After the solid was washed with acetone (4 × 5 cm^3), the combined filtrate and washings were evaporated to dryness *in vacuo* to yield a dry solid foam, **2**, in essentially quantitative yield. At this stage, the purity was generally checked by ^{1}H NMR and found to be >95%, which was considered pure enough for synthetic use. If desired, the crude product could be further purified by several recrystallizations from Et_2O/hexane. Mp: 102 °C. IR (cm^{-1}): ν(NH) 3324, ν(CO) 1632. ^{1}H NMR ($CDCl_3$, ppm): 7.01 (s, 1H, C_6H), 6.03 (br s, 1H, NH), 3.91 (br s, 6H, 2OMe), 3.90 (s, 3H, OMe), 1.41 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: 170.36 (C═O), 157.98, 152.84, 152.12, 144.94, 138.30 (quaternary C in C_6H), 107.53 (CH in C_6H), 61.00, 60.73, 56.52 (3MeO), 51.67 (CMe_3), 28.74 ($C(Me)_3$). Anal. Calcd for $C_{28}H_{40}HgN_2O_8$: C, 45.9; H, 5.5; N, 3.8. Found: C, 45.7; H, 5.4; N, 3.6.

Synthesis of [Pd(R^N)Cl(bpy)] (3). The diarylmercurial **2** (306 mg, 0.42 mmol) and $[PdCl_2(MeCN)_2]$ (103 mg, 0.40 mmol) were stirred in acetone (12 cm^3) at 0 °C for 1 h, during which time the orange suspension changed to an olive brown solution, which we assume to contain the intermediate $[Pd(\kappa^2\text{-}R^N)(\mu\text{-}Cl)]_2$ (**A**). Then bpy (60 mg, 0.40 mmol) was added, whereby the solution instantly became paler in color. The mixture was allowed to warm to room temperature and then filtered and washed (2 × 5 cm^3 washings) through $MgSO_4$ to give a yellow filtrate. The filtrate was evaporated to dryness

(37) Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 1422. Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Bautista, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3093.
(38) Vicente, J.; Abad, J. A.; Fernández de Bobadilla, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 24.
(39) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *Organometallics* **1995**, *14*, 2677.
(40) Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G. *Inorg. Chim. Acta* **1994**, *222*, 1.
(41) Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G.; Bembenek, E. *Organometallics* **1993**, *12*, 4151.
(42) Vicente, J.; Abad, J. A.; Jones, P. G. *Organometallics* **1992**, *11*, 3512.
(43) Vicente, J.; Abad, J. A.; Stiakaki, M. A.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 137.
(44) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *J. Organomet. Chem.* **1992**, *436*, C9.
(45) (a) Vicente, J.; Bermúdez, M. D.; Carrión, F. J.; Jones, P. G. *Chem. Ber.* **1996**, *129*, 1395. (b) Vicente, J.; Chicote, M. T.; Ramírez de Arellano, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1992**, 1839. (c) Vicente, J.; Abad, J. A.; Lahoz, F. J.; Plou, F. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1459. (d) Vicente, J.; Abad, J. A.; Gutierrez-Jugo, J. F.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1989**, 2241. (e) Vicente, J.; Abad, J. A.; Teruel, F.; García, J. *J. Organomet. Chem.* **1988**, *345*, 233. (f) Bonnardel, P. A.; Parish, R. V. *J. Organomet. Chem.* **1996**, *515*, 221. (g) Bonnardel, P. A.; Parish, R. V.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1996**, 3185.
(46) Ziegler, F. E.; Chliwner, I.; Fowler, K. W.; Kanfer, S. J.; Kuo, S. J.; Sinha, N. D. *J. Am. Chem. Soc.* **1980**, *102*, 790. Tomioka, K.; Ishiguro, T.; Mizuguchi, H.; Komeshima, N.; Koga, K.; Tsukogoshi, G.; Tsuruo, T.; Tashiro, T.; Tanida, S.; Kishi, T. *J. Med. Chem.* **1991**, *34*, 54. Gupta, S. P. *Chem. Rev.* **1994**, *94*, 1507. Chan, J. H.; Roth, B. *J. Med. Chem.* **1991**, *34*, 550. Ringel, I.; Jaffe, D.; Alerhand, S.; Boye, O.; Muzafar, A.; Brossi, A. *J. Med. Chem.* **1991**, *34*, 3334. Hitotsuyanagi, Y.; Naka, Y.; Yamagami, K.; Akihiro, F.; Tahara, T. *J. Chem. Soc., Chem. Commun.* **1995**, 49.
(47) Omae, I. *Organometallic Intramolecular-Coordination Compounds*; Elsevier: Amsterdam, The Netherlands, 1986.

in vacuo, the resultant yellow solid was redissolved in CH_2Cl_2 (5 cm^3) and filtered though Celite, the solution was concentrated (1 cm^3), and excess diethyl ether was added, which precipitated a pale yellow solid. At this stage, we could not obtain analytically pure samples of **3**, probably because of the presence of water (by NMR). For further purification, the solid was redissolved in acetone (20 cm^3), anhydrous $MgSO_4$ and Na_2CO_3 were added, and the mixture was stirred for 1 day. The solution was then filtered to give a yellow filtrate, which was evaporated to dryness *in vacuo*, redissolved in the minimum volume of CH_2Cl_2, and excess ether added to precipitate **3**, which was isolated as a pale yellow powder. Yield: 110 mg, 49%. Mp: 259 °C dec. Λ_M: 0. IR (cm^{-1}): ν(NH) 3332, ν(CO) 1646. ^{1}H NMR ($CDCl_3$, ppm): 9.30 (m, 1H, bpy), 8.47 (br s, 1H, NH), 8.07 (m, 2H, bpy), 8.05 (m, 1H, bpy), 7.97 (m, 1H, bpy), 7.65 (m, 2H, bpy), 7.64 (m, 1H, bpy), 7.20 (s, 1H, C_6H), 4.01, 3.93, 3.89 (all s, 3H, MeO), 1.31 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: 169.62 (CO), 155.75, 154.00, 153.69, 151.73, 151.23, 149.08, 143.43, 139.44, 138.87, 136.54, 129.25, 127.12, 126.58, 122.26, 121.62, 109.04 (CH of C_6H), 60.74, 60.59, 55.99 (all MeO), 51.60 (CMe_3), 28.91 (CMe_3). Anal. Calcd for $C_{24}H_{28}ClN_3O_4Pd$: C, 51.1; H, 5.0; N, 7.45. Found: C, 50.5; H, 4.8; N, 7.4.

Synthesis of [Pd(κ^2-R^N)(bpy)](CF_3SO_3) (4). Complex **3** (72 mg, 0.12 mmol) and $Tl(CF_3SO_3)$(43 mg, 0.12 mmol) were stirred together in acetone (15 cm^3) for 30 min, the mixture was filtered through Celite to give a bright green-yellow filtrate, which was evaporated to dryness, and the resultant yellow powder was recrystallized from CH_2Cl_2/Et_2O to produce **4** as diffraction-quality green-yellow crystals. Yield: 68 mg, 82%. Mp: 254 °C. Λ_M: 107 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(NH) 3252, ν(CO) 1575. ^{1}H NMR ($CDCl_3$, ppm): 9.41−7.37 (several m, 9H, bpy + C_6H), 3.97, 3.95, 3.73 (all s, 3H, MeO), 1.54 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: 179.44 (CO), 157.67, 156.94, 156.43, 154.15, 151.89, 148.08, 145.45, 141.12, 140.39, 137.36, 135.66, 126.99, 126.48, 123.76, 123.40, 120.79 (q, $^1J_{CF}$ = 320 Hz, CF_3), 107.87 (CH of C_6H), 63.16, 61.36, 56.96 (all MeO), 54.13 (CMe_3), 28.88 (CMe_3). Anal. Calcd for $C_{25}H_{28}F_3N_3O_7PdS$: C, 44.3; H, 4.15; N, 6.2; S, 4.7. Found: C, 44.5; H, 3.75; N, 6.2; S, 5.2.

Synthesis of 10-(*N*-*tert*-Butylcarbamoyl)-6,7-dimethoxy-1,2,3,4-tetraphenylspiro[4.5]-1,3,6,9-decatetraen-8-one (5). A solution of the intermediate [Pd(κ^2-R^N)(μ-Cl)]$_2$ (**A**) was prepared from **2** (336 mg, 0.46 mmol) and [$PdCl_2$(MeCN)$_2$] (114 mg, 0.44 mmol) as described for **3**. Then PhC_2Ph (235 mg, 1.32 mmol) in acetone (4 cm^3) was added, and the mixture was allowed to warm to room temperature, a darkening from red to black was observed. The mixture continued to stir a further 72 h, then the mixture was filtered and washed through $MgSO_4$ to give a black residue and a green filtrate. The filtrate was evaporated to dryness, redissolved in chloroform, and chromatographed. A bright yellow band (R_f = 0.9, Et_2O: hexane 4:1) was collected, isolated, and dried to give **5** as a yellow powder. Crystals were grown by the slow diffusion of water into a methanol solution of **5**. Yield: 229 mg, 86%. Mp: 176 °C. IR: ν(NH) 3352, ν(CO) 1649 (br). ^{1}H NMR ($CDCl_3$, ppm): 7.11 (br, 16H, Ph), 6.95 (br, 2H, Ph), 6.94 (br, 2H, Ph), 6.64 (s, 1H, C_6H), 5.28 (br s, 1H, NH), 3.99 (s, 3H, MeO), 3.40 (s, 3H, MeO), 1.23 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: 183.91, 163.45, 160.23, 148.58, 148.07, 141.85, 140.64, 134.70, 133.67, 131.20, 129.76, 129.02, 127.99, 127.62, 127.44, 127.21, 68.47 (spiro C), 61.16 (MeO), 60.33 (MeO), 51.51 (CMe_3), 28.38 (CMe_3). MS (*m*/*e*): 608 (M^+, 6.6), 105 ($PhCO^+$, 100), 57 (C_4H_9, 71.1). Anal. Calcd for $C_{41}H_{37}NO_4$: C, 81.2; H, 6.0; N, 2.3. Found: C, 81.2; H, 6.2; N, 2.3.

Synthesis of [Pd_2(κ^2-CCR^N)$_2$(μ-Cl)$_2$] (6). The intermediate **A** was prepared in an acetone (11 cm^3) solution from **2** (366 mg, 0.50 mmol) and [$PdCl_2$(MeCN)$_2$] (123 mg, 0.47 mmol) as described for **3**. $MeO_2CC{\equiv}CCO_2Me$ (202 mg, 1.42 mmol) in acetone (4 cm^3) was then added, and the ice bath was removed. Within 1 min a yellow precipitate appeared. The mixture continued to stir for a further 15 min, then the mixture was filtered under gravity to give a yellow residue and a pale orange solution. The residue was washed with acetone (5 × 5 cm^3) and then removed from the sinter by slurrying with MeCN. The MeCN slurry was then heated to boiling, with further additions of solvent until the solid completely dissolved, giving a yellow solution. This solution was then filtered hot, cooled, evaporated to dryness, and removed mechanically under Et_2O to yield a dry yellow powder, **6**, soluble in DMSO and hot MeCN. Yield: 333 mg, 67%. Mp: 254−262 °C dec. IR (cm^{-1}): ν(NH) 3296, ν(CO_2) 1710, ν(CO) 1582 or 1556. ^{1}H NMR (DMSO-d_6, ppm): 9.53 (br s, 1H, NH), 6.86 (s, 1H, C_6H), 3.90, 3.82, 3.75, 3.66, 3.55 (each s, 3H, MeO), 1.28 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: decomposition over the time scale of the experiment. Anal. Calcd for $C_{20}H_{26}ClNO_8Pd$: C, 43.6; H, 4.8; N, 2.55. Found: C, 43.6; H, 4.9; N, 2.6.

Synthesis of [Pd(κ^2-CCR^N)Cl(PPh_3)] (7). PPh_3 (39 mg, 0.15 mmol) in acetone (4 cm^3) was added to a suspension of **6** (82 mg, 0.15 mmol) in acetone (8 cm^3); rapid dissolution of the solid was observed. After 5 min, the solution was filtered through $MgSO_4$ and the residue washed with acetone (2 × 5 cm^3). The yellow filtrate was evaporated to dryness and redissolved in a minimum quantity of CH_2Cl_2, and hexane added to precipitate **7** as a creamy yellow solid. Yield: 93 mg, 77%. Diffraction quality crystals were grown by slow diffusion of hexane into a CH_2Cl_2 solution of **7** at −20 °C. Mp: 218 °C dec. Λ_M (acetone): 3 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(NH) 3386, ν(CO_2) 1730, 1708, ν(CO) 1602 or 1582. ^{1}H NMR ($CDCl_3$, ppm): 7.57−7.24 (m, 15H, PPh_3), 6.87 (s, 1H, C_6H), 6.28 (br s, 1H, NH), 4.02, 5.67, 3.58, 3.57, 3.34 (each s, 3H, MeO), 1.42 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: 172.82, 169.07, 166.62, 164.48, 153.36, 151.70, 143.23, 133.12, 131.31, 134.72, 134.59, 130.56, 130.43, 127.89, 127.18, 125.23, 105.07 (CH of RCC), 60.55, 60.23, 56.54, 54.08, 52.68, 51.45 (3MeO, 2CO_2Me, and CMe_3), 28.46 (CMe_3). ^{31}P NMR: 33.3 (s). Anal. Calcd for $C_{38}H_{41}ClNO_8PPd$: C, 56.2; H, 5.1; N, 1.7. Found: C, 56.1; H, 5.2; N, 1.7.

Synthesis of [Pd(κ^2-CCR^N)Cl(CNXy)] (8). Complex **6** (101 mg, 0.18 mmol) was suspended in acetone (6 cm^3), and a solution of CNXy (24 mg, 0.18 mmol) in acetone (4 cm^3) was added. The suspension rapidly became paler in color. The mixture was stirred for 40 min and then filtered through Celite to give a pale yellow filtrate. The filtrate was evaporated to dryness to yield a yellow glassy solid. This was then redissolved in a minimum volume of CH_2Cl_2 and hexane added to precipitate **8** as a voluminous cream solid. Yield: 99 mg, 79%. Mp: 148 °C, dec. Λ_M (acetone): 2 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(NH) 3338, ν(C≡N) 2200, ν(CO_2) 1716, ν(CO) 1584 or 1560. ^{1}H NMR ($CDCl_3$, ppm): 7.3−7.0 (m, 3H, C_6H_3), 6.77 (s, 1H, C_6H), 6.50 (br s, 1H, NH), 3.94, 3.90, 3.83, 3.74, 3.67 (each s, 3H, MeO), 2.41 (s, 6H, $C_6H_3Me_2$), 1.44 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: decomposition over the time scale of the experiment. Anal. Calcd for $C_{29}H_{35}ClN_2O_8Pd$: C, 51.1; H, 5.2; N, 4.1. Found: C, 51.1; H, 5.5; N, 4.1.

Synthesis of [Pd(κ^2-CCR^N)(PPh_3)$_2$](CF_3SO_3) (9). Complex **6** (82 mg, 0.15 mmol), $TlCF_3SO_3$ (53 mg, 0.15 mmol) and PPh_3 (157 mg, 0.60 mmol) were reacted in CH_2Cl_2 (14 cm^3) for 10 min, giving almost instantaneously a yellow solution and a flocculent white precipitate. The mixture was filtered through Celite to give an orange filtrate, which was evaporated to dryness to give an orange oil. The mixture was stirred with hexane (20 cm^3), yielding a bright orange solid, **9**, which was isolated by filtration and repeated washings with hexane. Yield: 134 mg, 76%. **9** could also be synthesized by the addition of $TlCF_3SO_3$ and PPh_3 to **7**, but the overall yield was lower. Mp: 116 °C. Λ_M (acetone): 129 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(NH) 3246, ν(CO_2) 1712, ν(CO) 1580 or 1556. ^{1}H NMR ($CDCl_3$, ppm): 7.71 (br s, 1H, NH), 7.4−7.0 (m, 30H, 2PPh_3), 6.92 (s, 1H, C_6H), 4.23, 3.85, 3.69, 3.59, 3.54 (all s, 3H, 3MeO and 3CO_2Me), 0.98 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: 172.98, 169.04, 153.95, 151.52, 143.22, 134.25, 134.10, 133.93, 133.77, 132.28, 131.36, 131.33, 131.06, 131.03, 129.17, 128.43,

128.72, 128.68, 128.43, 128.28, 106.61 (CH of C_6H), 60.73, 60.29, 57.31, 54.15, 51.74, 51.63 (3*Me*O, 2CO_2*Me*, *C*Me_3), 27.54 (C*Me*$_3$). ^{31}P NMR: 32.91 (d, $^2J_{PP}$ = 32 Hz), 16.41 (d, $^2J_{PP}$ = 32 Hz). Anal. Calcd for $C_{57}H_{56}F_3NO_{11}P_2PdS$: C, 57.6; H, 4.75; N, 1.2; S 2.7. Found: C, 57.7; H, 5.05; N, 1.3; S, 2.1.

Synthesis of [Pd{κ^2-C(=NXy)R^N}(bpy)](CF$_3$SO$_3$) (12). Tl(CF_3SO_3) (63 mg, 0.18 mmol) was added to a solution of complex **3** (100 mg, 0.18 mmol) in acetone (10 mL). The mixture was stirred for 30 min and filtered through Celite, and CNXy (24 mg, 0.18 mmol) was added. The solution was stirred for 30 min and evaporated to dryness. CH_2Cl_2 was added to the residue, and it was filtered through Celite. The yellow-orange solution was evaporated to *ca*. 3 mL. Addition of diethyl ether (20 cm^3) gave **12** as a yellow-orange solid. Diffraction quality crystals were grown by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **12**. Yield: 120 mg, 82%. Mp: 140 °C. IR (cm^{-1}): ν(NH) 3262, ν(C=N) 1634, ν(CO) 1598, 1574, or 1546. ^{1}H NMR ($CDCl_3$, ppm): 8.50−7.97 (m, bpy + NH, 7H), 7.59 (t, bpy, 1H, $^3J_{HH}$ = 6 Hz), 7.36 (t, 1H, bpy, $^3J_{HH}$ = 6 Hz), 7.29 (s, 1H, H6 of R^N group), 6.91−6.72 (m, 3H, ArH of Xy group), 4.07, 3.93, 3.90 (3 s, 9H, 3MeO), 2.48 (s, 6H, 2Me), 1.60 (s, 9H, CMe_3). ^{13}C{^{1}H} NMR: 170.9 (C=O), 155.0 (quaternary carbon), 153.2 (CH), 153.0, 152.7 (quaternary carbons), 147.6 (CH), 146.7, 146.5, 146.2 (quaternary carbons), 140.6, 140.1 (CH), 128.5 (CH br), 127.2 (quaternary carbon), 126.9, 125.9, 123.8, 123.5, 123.0 (CH), 122.8 (quaternary carbon), 108.4 (C5 of R^N group), 65.9 (Me$_3$*C*), 62.0, 61.0, 56.9 (3MeO), 54.9 (2Me), 29.0 (*Me*$_3$C). Anal. Calcd for $C_{34}H_{37}F_3N_4O_7PdS$: C, 50.5; H, 4.6; N, 6.9; S, 3.95. Found: C, 50.3; H, 4.65; N, 6.95; S, 3.75.

Synthesis of [Pd(R^{Me})(CNXy)(bpy)](CF$_3$SO$_3$) (13). CNXy (32 mg, 0.24 mmol) was added to a suspension of [Pd(η^2-R^{Me})(bpy)]CF_3SO_3 (**10**) (150 mg, 0.24 mmol) in CH_2Cl_2 (10 cm^3), and the resultant mixture was stirred for 40 min. The yellow-orange solution was filtered through Celite and evaporated up to *ca*. 2 mL. Addition of diethyl ether (25 cm^3) gave **13** as a beige solid. Yield: 164 mg, 91%. Mp: 126 °C. IR (cm^{-1}): ν(C≡N) 2188, ν(CO) 1652. ^{1}H NMR ($CDCl_3$, ppm): 8.70 (d, 2H, bpy), 8.42−8.22 (m, 2H, br, bpy), 7.55−7.34 (very broad m, 4H, bpy), 7.40 (s, H5 of R^{Me} group, 1H), 7.31−7.11 (2m, 3H, ArH of CNXy), 3.99 (s, 3H, MeO), 3.98 (s, 3H, MeO), 3.86 (s, 3H, MeO), 2.65 (s, 3H, *Me*CO), 2.26 (s, 6H, 2Me of Xy group). ^{13}C{^{1}H} NMR: 199.4 (C=O), 155.2, 152.0, 150.4 (br), 146.5 (quaternary carbons), 141.7 (CH), 137.0, 135.6, 133.0 (quaternary carbons), 130.7 (CH), 128.5 (CH), 128.3 (quaternary carbon), 127.7 (CH), 124.6 (CH), 112.3 (CH), 61.0 (MeO), 60.5 (MeO), 56.5 (MeO), 28.2 (MeCO), 18.5 (2Me of Xy group). Anal. Calcd for $C_{31}H_{30}F_3N_3O_7PdS$: C, 49.5; H, 4.0; N, 5.6; S, 4.25. Found: C, 49.7; H, 4.0; N, 5.6; S, 4.2.

Synthesis of [Pd(R^H)(CNXy)(bpy)](CF$_3$SO$_3$) (14). CNXy (12 mg, 0.093 mmol) was added to a solution of [Pd(R^H)(bpy)(NCMe)]CF_3SO_3 (**11**) (60 mg, 0.093 mmol) in CH_2Cl_2 (8 cm^3), and the resultant mixture was stirred for 20 min. The yellow-orange solution was filtered through Celite and evaporated up to *ca*. 4 mL. Addition of diethyl ether (10 cm^3) gave **14** as a yellow-orange solid. Yield: 52 mg, 76%. Mp: 140 °C. IR (cm^{-1}): ν(C≡N) 2194, ν(CO) 1674. ^{1}H NMR ($CDCl_3$, ppm): 10.36 (s, 1H, CHO), 8.80−8.73 (m, 2H, bpy), 8.42−8.23 (m, 2H, bpy), 7.87−7.80 (m, 1H, bpy), 7.55−7.41 (m, 2H, bpy), 7.35 (s, 1H, H5 of R^H group), 7.29−7.11 (m, 4H, ArH of Xy−NC and a proton of bpy). ^{13}C{^{1}H} NMR: decomposition over the time scale of the experiment. Anal. Calcd for $C_{30}H_{28}F_3N_3O_7PdS$: C, 48.8; H, 3.8; N, 5.7; S, 4.35. Found: C, 48.2; H, 3.8; N, 5.95; S, 4.4.

Synthesis of 2-(2,6-Dimethylphenyl)-1-(((2,6-dimethylphenyl)imino)methylene)-5,6,7-trimethoxy-3-oxoisoindoline (15). CNXy (134 mg, 1.02 mmol) was added to a solution of [Pd(R^H)Cl(bpy)] (**16**) (168 mg, 0.34 mmol) in CH_2Cl_2 (10 cm^3), and the resultant mixture was stirred for 25 h. The brown suspension was filtered to yield a beige solid identified as [Pd(bpy)Cl_2] (27 mg, 24%). The resultant solution was evaporated to *ca*. 1 mL. Addition of diethyl ether (25 cm^3) gave [Pd_2Cl_2(CNXy)$_4$] (70 mg, 25%). The ether solution was chromatographed (silica gel, Et_2O/hexane 1:1) to get a first fraction (R_f = 0.3) containing a mixture of bpy and a colorless organic compound (25 mg). From the second fraction (R_f = 0.1) the ketenimine **15** could be isolated as a yellow solid. Single crystals were obtained by vapor diffusion of *n*-hexane into 1,2-dichloroethane solutions of **15**. Yield: 61 mg, 39%. Mp: 173 °C. IR (cm^{-1}): ν(C=C=N) 2028, ν(C=O) 1682. ^{1}H NMR ($CDCl_3$, ppm): 7.35 (s, 1H, ArH), 7.21−6.96 (m, 6H, ArH from Xy groups), 3.970, 3.966, 3.955 (3s, 9H, MeO), 2.21 (s, 6H, Me of Xy group), 2.08 (s, 6H, Me of Xy group). ^{13}C{^{1}H} NMR: 184.5 (C=*C*=N), 161.7 (C=O), 154.3, 146.6, 144.8, 137.4, 136.8, 133.6, 132.0 (quaternary carbons), 129.0, 128.52, 128.48, 127.2 (Ar CH of Xy groups), 123.1, 121.6 (quaternary carbons), 102.4 (CH), 86.0 (*C*=C=N), 61.3 (MeO), 61.2 (MeO), 56.5 (MeO), 18.4 (2Me of Xy group), 18.1 (2Me of Xy group). MS *m*/*z*: 456 (M$^+$, 8), 220 (3), 196 (10), 168 (20), 132 (18), 131 (13), 130 (22), 117 (11), 116 (15), 106 (15), 105 (84), 104 (17), 103 (69), 93 (10), 91 (16), 79 (76), 78 (33), 77 (100). Mol wt calcd for $C_{28}H_{28}N_2O_4$: 456.204908. Found: 456.206322.

Crystal Structure Analyses. Crystal data are presented in Table 1. Data collection and reduction: Monochromated Mo Kα radiation (λ = 0.710 73 Å); cell constants refined from (**4**, **7**) $\pm\omega$ values of *ca*. 50 reflections to $2\theta_{max}$= 23°, (**12**, **15**) *ca*. 60 reflections to $2\theta_{max}$ = 23°; (**7**, **12**) absorption correction by ψ-scans. Structure solution: Heavy-atom (**4**, **7**) or direct (**12**, **15**) methods. Structure refinement: Full-matrix least-squares on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen) (exception, for **12** the refinement was blocked); H atoms as rigid methyls or with riding model (exception, for **12** not all solvent H were located, and for **7** no solvent H). Ideally staggered H positions for **15**.

Results and Discussion

Synthesis of Arylmercurials and Arylpalladium(II) Complexes. The arene 3,4,5-trimethoxy(*N*-*tert*-butylcarbamoyl)benzene is mercuriated by Hg(OAc)$_2$ in boiling ethanol giving a solution which, after pouring into aqueous KCl, affords [Hg(R^N)Cl] (**1**). 2-Chloromercury benzamide and mono- and diethylbenzamides have been reported.[45f] Compound **1** can be symmetrized with [NMe_4]Cl to give [Hg(R^N)$_2$] (**2**) (Scheme 2).

The reaction of **2** with [$PdCl_2$(MeCN)$_2$] gives an olive-brown solution which must contain the complex [Pd(κ^2-R^N)(μ-Cl)]$_2$ (**A**); this seems to be reasonably stable in solution but decomposes on attempts to isolate it. However, after addition of bpy (2,2′-bipyridine), the solution color changes to light yellow and it is possible to isolate the stable compound [Pd(R^N)Cl(bpy)] (**3**). The byproduct **1** is easily removed since it is quite soluble in Et_2O, in contrast to **3**. This reaction constitutes another example of the utility of the organomercury derivatives as transmetalating agents for the synthesis of new organometallic compounds containing highly functionalized aryl ligands not easily accessible by the normal routes, viz. organolithium or magnesium reagents.[45]

Complex **3** reacts with Tl(CF_3SO_3) forming insoluble TlCl and the cyclopalladated compound [Pd(κ^2-R^N)(bpy)](CF_3SO_3) (**4**) in which the aryl group is also coordinated to the palladium atom by the oxygen of the *tert*-butylcarbamoyl substituent (Scheme 2), as shown by IR and confirmed by X-ray studies.

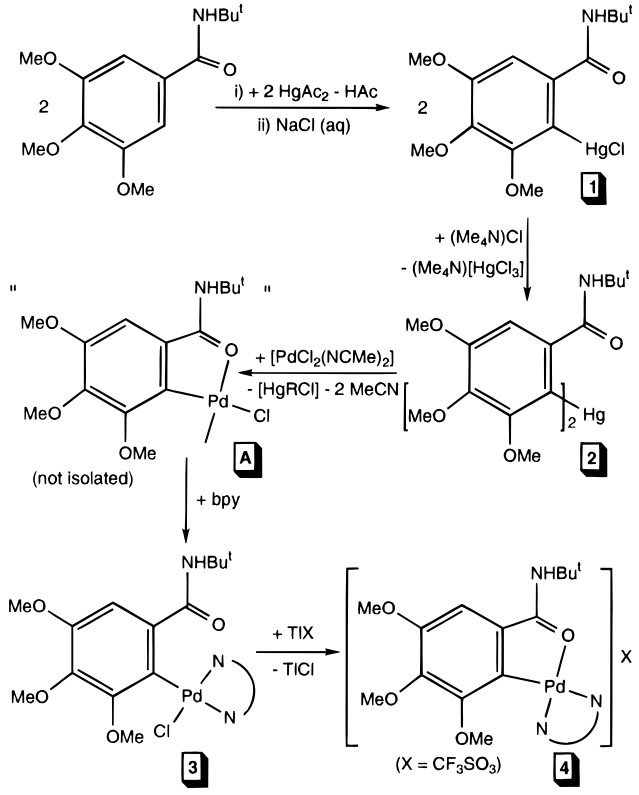
We have previously reported similar cyclometalated complexes containing the 3,4,5-trimethoxy-6-formylphenyl and 3,4,5-trimethoxy-6-acetylphenyl ligands.[41,42] When the *ortho* group was formylaryl, a rearrangement took place in which the formyl substituent and the

Table 1. Crystal Data for Compounds 4, 7, 12, and 15

compound	**4**	**7**·H_2O	**12**·$^1/_3C_3H_6O$	**15**
mol formula	$C_{25}H_{28}F_3N_3O_7PdS$	$C_{38}H_{43}ClNO_9PPd$	$C_{35}H_{39}F_3N_4O_{7.3}PdS$	$C_{28}H_{28}N_2O_4$
mol wt	677.96	830.55	828.50	456.52
description	tablet	prism	tablet	tablet
color	yellow	pale yellow	orange	yellow
cryst size, mm	0.35 × 0.35 × 0.15	0.75 × 0.25 × 0.15	0.60 × 0.35 × 0.35	0.60 × 0.44 × 0.14
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.359(3)	9.345(3)	13.241(2)	8.003(2)
b, Å	11.293(3)	11.619(3)	18.728(2)	11.451(2)
c, Å	12.924(3)	19.076(5)	23.258(3)	13.796(2)
α, deg	107.29(2)	78.47(2)	72.406(8)	98.69(2)
β, deg	103.18(2)	79.19(2)	89.433(8)	103.360(10)
γ, deg	102.08(2)	66.47(2)	88.567(10)	95.77(2)
V, Å^3	1341.6(6)	1847.2(9)	5495.8(12)	1203.8(4)
Z	2	2	6	2
temperature, K	143(2)	143(2)	173(2)	298(2)
μ, mm^{-1}	0.840	0.674	0.632	0.085
trans. %		0.78−0.87	0.76−0.90	
diffractometer	Stoe STADI-4	Stoe STADI-4	Siemens P4	Siemens P4
scan method	*ω*/*θ*	*ω*/*θ*	*ω*	*ω*
2*θ* range, min−max, deg	6.0−55.1	6.1−55.1	6.0−50.0	6.2−50.0
no. of reflns measd	5642	9851	20560	10456
no. of independent reflns	5382	8519	19075	4240
parameters/restraints	367/93	467/389	1407/1320	308/4238
R_{int}	0.017	0.0475	0.0464	0.0429
R1[a]	0.0350	0.0475	0.0940	0.0429
wR2[b]	0.0792	0.1187	0.0940	0.1206
$S(F^2)$	1.08	1.19	0.81	1.008
Δ*ρ*, e/Å	0.83	1.10	1.16	0.17

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

Scheme 2



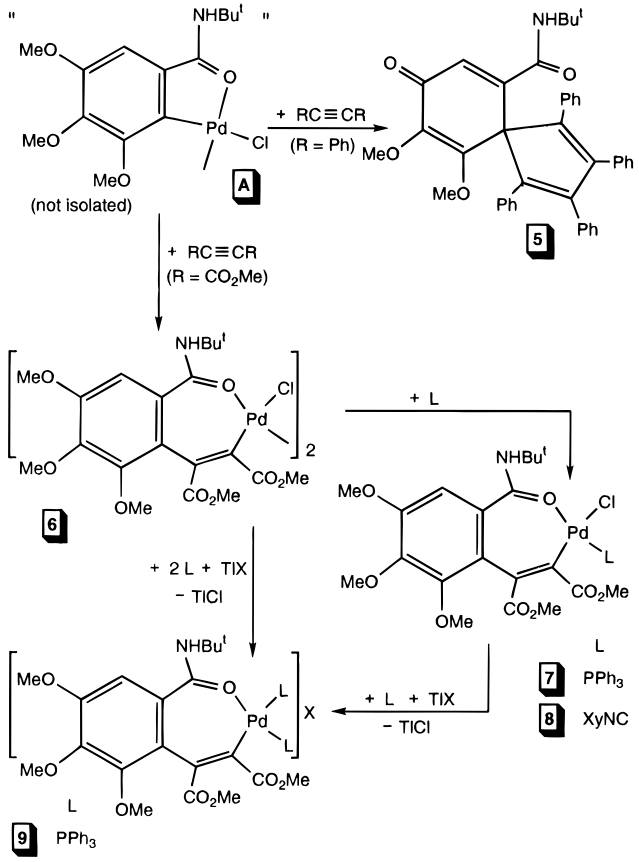
palladium moiety exchanged positions; however, in the case of the acetylaryl complex, no such rearrangement was observed. We proposed that the greater electron-releasing capacity of the Me group in the acetyl substituent (compared to the H atom of the formyl group) was responsible for this different behavior. In the present example, no isomerization of the aryl ligand is observed (X-ray crystal structure, see below), consistent with the above explanation since the NHBu^t group is more electron-releasing than Me or H.

Reactions with Alkynes. When acetone solutions containing the intermediate [Pd(κ^2-R^N)(μ-Cl)]$_2$ (**A**) are reacted with diphenylacetylene at room temperature, a slow precipitation of metallic palladium is observed. From the resulting solution, the spirocycle 10-(*N*-*tert*-butylcarbamoyl)-6,7-dimethoxy-1,2,3,4-tetraphenylspiro-[4.5]-1,3,6,9-decatetraen-8-one (**5**, see Scheme 3) was isolated in excellent yield. Reaction of **A** with PhC≡CCO$_2$Me gave a mixture whose ^{1}H and ^{13}C NMR spectra indicate the presence of two isomeric spiro compounds (head-to-tail and one of the two other isomers, head-to-head or tail-to-tail) in a *ca*. 1:1 molar ratio. We were not able to obtain a pure isomer from this mixture. These results are similar to those observed in the reactions of [Pd(κ^2-R^{Me})(μ-Cl)]$_2$, the 6-acetylaryl complex analogous to **A**, with several arylalkynes.[39] These reactions are rare examples of a stoichiometric, palladium-assisted formation of spirocyclic compounds. The pathway to **5** must be similar to that proposed previously, with the participation of a π-allyl intermediate.[39]

When **A** is reacted with MeO$_2$CC≡CCO$_2$Me, no decomposition to metallic palladium is observed and the complex [Pd(κ^2-CCR^N)(μ-Cl)]$_2$ (**6**) (Scheme 3), resulting from the insertion of an alkyne molecule into the carbon−palladium bond, is isolated. Monoinserted cyclopalladated compounds of this type are well documented,[4,7−9] although very few examples are known with oxygen as the heteroatom bonded to palladium.[38,48] Complex **6** is isolated even when an excess of alkyne is used. This is the normal behavior with alkynes substituted with electron-withdrawing substituents such as CF$_3$ or CO$_2$R. With other alkynes, the insertion of the first alkyne molecule is usually the rate-determining

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

Scheme 3



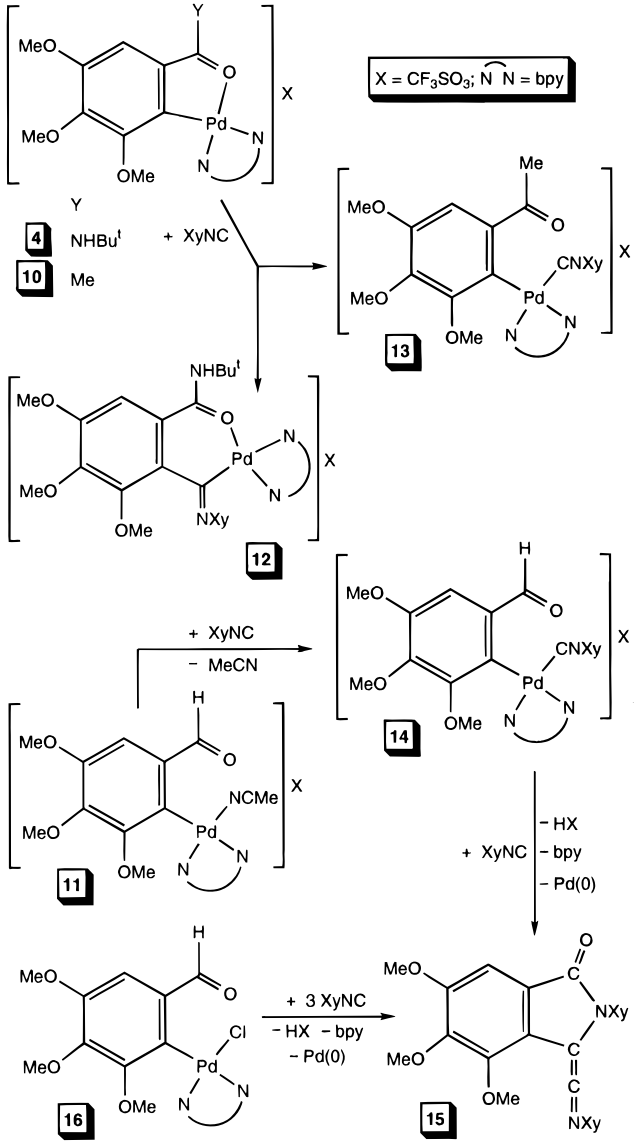
step and, therefore, in most cases, only the di-inserted compound is obtained.[49]

It is possible to prepare derivatives of **6** by reacting it with PPh_3 or XyNC (Xy = $C_6H_3Me_2$-2,6) to give [Pd(κ^2-CCR^N)Cl(PPh_3)] (**7**) or [Pd(κ^2-CCR^N)Cl(CNXy)] (**8**), resulting from rupture of the chloro bridge. The reaction of **6** or **7** with 2 or 1 equiv of PPh_3, respectively, in the presence of Tl(CF_3SO_3) yields the cationic compound [Pd(κ^2-CCR^N)(PPh_3)$_2$](CF_3SO_3) (**9**) (Scheme 3). The coordination of the carbamoyl substituent in complexes **6**−**9** is based on the IR data. Thus, complexes **6**−**9** show bands at 1550−90 cm^{-1}, strongly suggesting coordination through the O atom (see above). This has also been confirmed by X-ray diffraction for **7** (see below).

Reactions with CNXy. Complex **4**, formed *in situ*, reacts with CNXy to give [Pd{κ^2-C(=NXy)R^N}(bpy)](CF_3SO_3) (**12**), the result of the insertion of an isocyanide molecule into the carbon−palladium bond (Scheme 4). As shown by an X-ray crystallographic study (see below), the −C(O)NHBu^t substituent is O-coordinated to the palladium atom forming a six-membered chelate ring.

In order to establish comparisons, we have studied similar reactions of related trimethoxyarylpalladium complexes previously prepared by us. Thus, the reaction of [Pd(κ^2-R^{Me})(bpy)](CF_3SO_3) (**10**) or [Pd(R^H)(NCMe)(bpy)](CF_3SO_3) (**11**) with CNXy affords [Pd(R^{Me})(CNXy)(bpy)](CF_3SO_3) (**13**) or [Pd(R^H)(CNXy)(bpy)] (CF_3SO_3) (**14**), respectively, instead of an inserted complex. The greater electron releasing ability of the NHBu^t group than that of Me must induce a stronger Pd−O bond in **4** than in **10**. This could explain the different behavior

Scheme 4



of these complexes when reacted with XyNC. Concerning the strength of the Pd−O bond in **4**, see the discussion of its crystal structure below.

Complexes such as **13** or **14** are considered to be intermediates in the formation of inserted compounds such as **12**.[14,18,21,22,24] When **12** or **13** is reacted with another equivalent of the isocyanide, mixtures were obtained that we were not able to separate. However, from the complex mixture obtained by reacting **14** with another CNXy, the highly functionalized, stable ketenimine **15** (see Scheme 3) could be isolated. It is also possible to obtain **15** by reaction of [Pd(R^H)Cl(bpy)] (**16**) with 3 equiv of CNXy; in this case, we have identified some of the other components of the mixture as [$PdCl_2$(bpy)$_2$] (24%), the palladium(I) complex [Pd_2Cl_2(CNXy)$_4$] (25%),[50] bpy, and an unknown organic product. **15** was isolated in 39% yield. The IR spectrum of this compound exhibits a characteristic cumulene absorption at 2028 cm^{-1} typical of ketenimines;[25] however, due to the complexity of **15**, determination of its structure by X-ray diffraction methods was necessary (see below). **15**

(49) Ryabov, A. D.; Vaneldik, R.; Leborgne, G.; Pfeffer, M. *Organometallics* **1993**, *12*, 1386.

(50) Rettig, M. F.; Kirk, E. A.; Maitlis, P. M. *J. Organomet. Chem.* **1976**, *111*, 113. Rutherford, N. M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1984**, *23*, 2833.

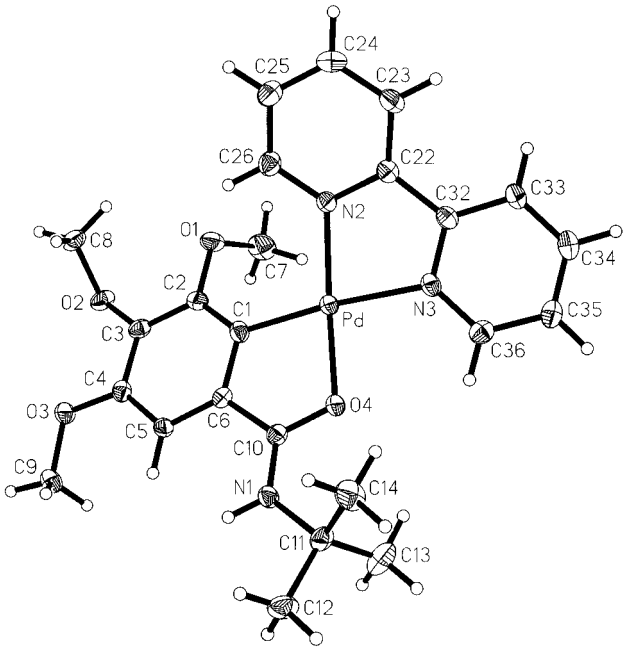


Figure 1. ORTEP plot of **4** with the labeling scheme (50% probability ellipsoids).

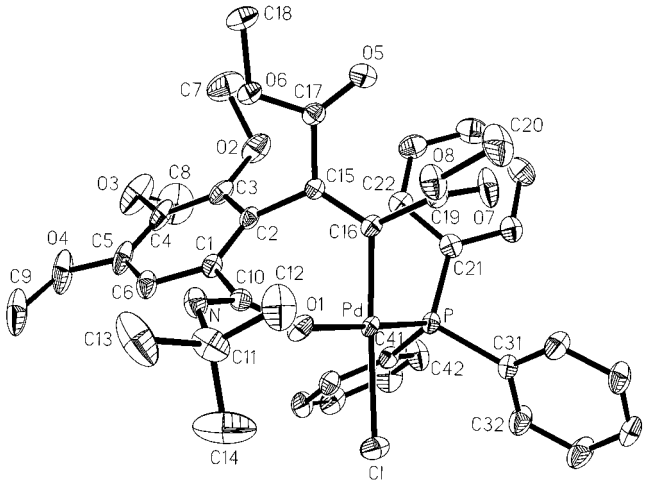
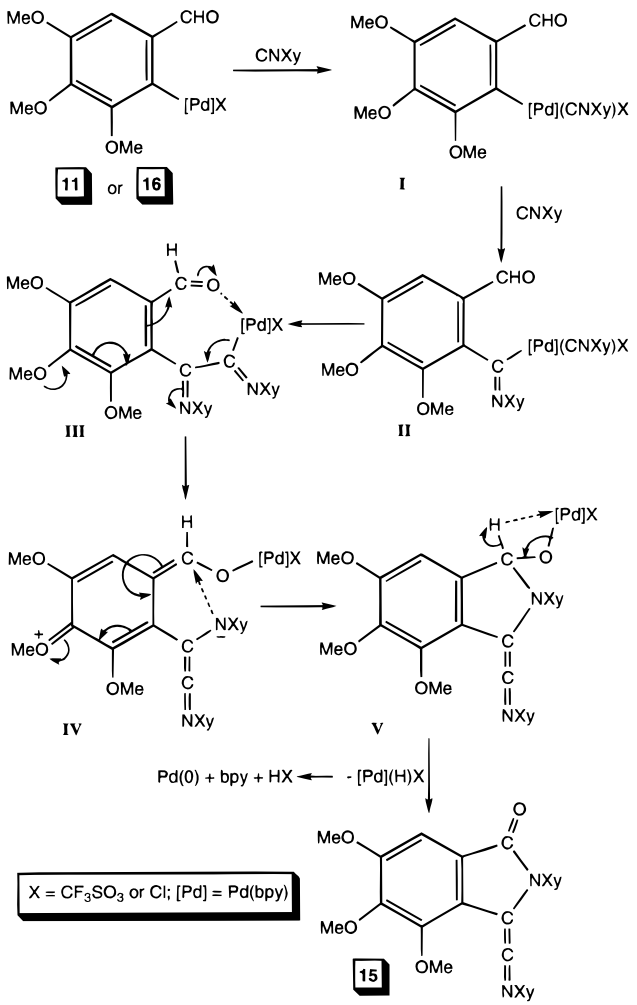


Figure 2. ORTEP plot of **7** with the labeling scheme (50% probability ellipsoids).

is the first member of a new family of ketenimine compounds.

We propose in Scheme 5 a reasonable pathway to explain the formation of **15**. The first product **I** is a result of the coordination of the isocyanide. When the starting product is **11**, this intermediate is the isolated complex **14**. The intermediate **II** is the unstable product we mentioned above. The di-insertion of isocyanides into the Pd−C bond to give **III** is a known process.[14,16,22] Formation of the enolato complex **IV** is electronically favored (**III**), and similar compounds have been isolated[6] or postulated[51,52] in alkyne insertions into the Pd−C bond of complexes related to **16**. The nucleophilic character of the nitrogen atom of the first inserted isocyanide (**IV**), its attack at the carbonyl carbon atom, and a β-hydrogen elimination causes the formation of the ketenimine **15**. The β-hydrogen elimination is a

Scheme 5



common feature in most depalladation reactions,[1,2] and in particular, it occurs in the depalladation of some of the products of the insertion of isocyanides into the Pd−C bond.[11,20] As far as we are aware, there is no precedent for the synthesis of heterocyclic ketenimines resulting from the insertion of two isonitrile molecules into a carbon−metal bond (see Scheme 1).

Crystal Structure of Complexes 4, 7·H_2O, and 12·0.33Me_2CO. The structures are shown in Figures 1−3 with selected bond lengths and angles in Tables 2−4. Compound **12** crystallizes with three independent molecules, for which reason average values are generally used in the discussion.

The structure determinations confirm in all cases coordination of the carbamoyl substituent through the oxygen atom and furthermore the monoinsertion of the alkyne in **7** and of the isocyanide in **12**. The coordination at the palladium atoms is planar as expected; for **7**, the mean deviation of the central five atoms is 0.10 Å and for **12** 0.05, 0.05, 0.03 Å in the three molecules. However, the deviation from an ideal geometry in **4** is much greater; the four atoms Pd, C1, O4, and N3 are coplanar to within 0.04 Å, but N2 lies 0.56 Å out of the plane so defined, presumably to minimize steric pressure between C26−H26 and O1 (the C···O and H···O distances are only 2.96, 2.31Å). Associated with this effect, the interplanar angle of the bpy ligand in **4** is 19°.

The Pd−C bond distances (2.001(3) (**4**), 1.983(3) (**7**), average 1.975 (**12**) Å) are within the observed range in

(51) Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977**, 157.
(52) Tamaru, Y.; Yamada, Y.; Inoue, K.; Yamamoto, Y.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 1286.

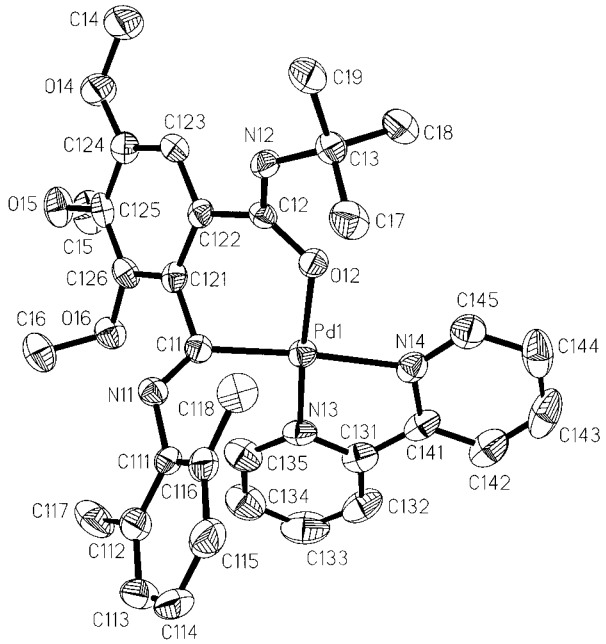


Figure 3. ORTEP plot of **12** with the labeling scheme (50% probability ellipsoids).

related complexes (2.027(5)−1.986(3) Å).[38,41−43] From the Pd−N bond lengths *trans* to carbon (2.081(3) (**4**), average 2.130 (**12**) Å) and those *trans* to oxygen (2.033-(3) (**4**), average 2.034 (**12**) Å), it can be established that the order of the *trans* influence is imine carbon > aryl >> carbamoyl oxygen. The increase in the Pd−O bond distance from complex **4** (2.009(2) Å) to **12** (average 2.053 Å) could be attributed to the increase in the size of the O−Pd−C_n ring from five to six. The longer Pd−O bond in **7** (2.097(3) Å) can be attributed to the greater *trans* influence of PPh_3 than bpy, although the increase in the size of the O−Pd−C_n ring to seven in complex **7** may also be important. The order **7** > **12** > **4** in the Pd−O bond lengths is reversed for the C−O bond distance (**4** (1.276(4) Å) > **12** (average 1.264 Å) > **7** (1.245(4) Å)), whereas the carbamoyl C−N bond distances are not significantly different (**7** (1.325(4) Å) > **12** (average 1.317 Å) > **4** (1.315(4) Å)). All of these C−O and C−N distances in the carbamoyl substituent are longer and shorter, respectively (marginally in the case of **7**), than those usually observed in acyclic amides, 1.231 and 1.334 Å.[53] This implies, as expected, a greater importance of the resonance form Bu^tHN^+=(aryl)C−O^- than Bu^tHN−(Aryl)C=O in these complexes [**4** > **12** >> **7**] than in amides. The stronger Pd−O bond in **4** than that in **10** could explain why **4** reacts with XyNC to give the insertion product **12** while **10** gives the adduct **13**.

Compounds **4** and **12** exhibit N−H···O hydrogen bonding. In **4**, N1−H1···O7, with N···O of 3.009 Å and N−H···O of 158°, connects the molecules in pairs across inversion centers. In **12**, there are three such H bonds: N12−H12···O3 (2.924 Å, 161°) and N22−H22···O9 (2.981 Å, 164°) involve triflate anions and N32−H32···O99 (2.940 Å, 159°) involves the acetone of solvation.

Crystal Structure of the Ketenimine 15. The molecule of **15** is shown in Figure 4 with a packing diagram in Figure 5; Table 5 gives selected bond lengths and angles. The most interesting feature of the crystal structure of **15** is that it adopts a self-assembled supramolecular structure. Dimers are formed through intermolecular hydrogen bonding between a methyl hydrogen at C12 and the keto oxygen (see Figures 4 and 5). After a long controversy concerning the validity of hydrogen bonds of the type C−H···O, the phenomenon is now well-established and is becoming increasingly important for the understanding of molecular packing in crystals.[30−32,34,36,54] In **15**, the C···O (3.362(3) Å) and H···O (2.50 Å) distances and the C−H···O angle (150°)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Bond Lengths			
Pd−O(4)	2.009(2)	Pd−C(1)	2.001(3)
Pd−N(2)	2.033(3)	Pd−N(3)	2.081(3)
C(6)−C(10)	1.481(4)	C(10)−O(4)	1.276(4)
C(10)−N(1)	1.315(4)	C(11)−N(1)	1.492(4)

Bond Angles			
O(4)−Pd−C(1)	81.41(11)	C(1)−Pd−N(2)	105.55(11)
O(4)−Pd−N(3)	94.60(10)	N(2)−Pd−N(3)	79.68(10)
C(6)−C(1)−Pd	111.9(2)	C(1)−C(6)−C(10)	113.0(3)
O(4)−C(10)−N(1)	120.2(3)	O(4)−C(10)−C(6)	116.8(3)
N(1)−C(10)−C(6)	123.0(3)	C(10)−O(4)−Pd	113.1(2)
C(10)−N(1)−C(11)	126.3(3)	C(22)−N(2)−Pd	114.6(2)
C(32)−N(3)−Pd	113.6(2)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 7

Bond Lengths			
Pd−C(16)	1.983(3)	Pd−O(1)	2.097(3)
Pd−P	2.2239(11)	Pd−Cl	2.3768(12)
N−C(10)	1.325(4)	N−C(11)	1.482(5)
O(1)−C(10)	1.245(4)	C(1)−C(2)	1.389(5)
C(1)−C(10)	1.499(5)	C(15)−C(16)	1.339(4)

Bond Angles			
C(16)−Pd−O(1)	84.20(12)	C(16)−Pd−P	95.26(10)
O(1)−Pd−Cl	90.32(8)	P−Pd−Cl	90.85(4)
C(10)−N−C(11)	124.6(3)	C(10)−O(1)−Pd	126.8(2)
O(1)−C(10)−N	121.3(3)	O(1)−C(10)−C(1)	122.6(3)
N−C(10)−C(1)	116.0(3)	C(16)−C(15)−C(2)	123.2(3)
C(15)−C(16)−Pd	122.0(2)		

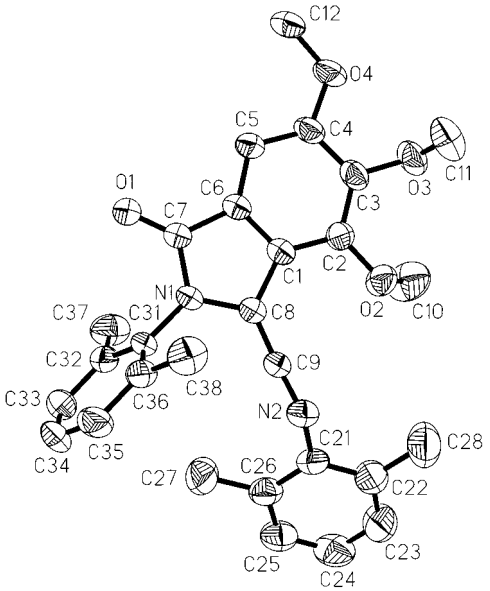


Figure 4. ORTEP plot of **15** with the labeling scheme (50% probability ellipsoids).

(53) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, S1.

(54) Cardullo, F.; Giuffrida, D.; Kohnke, F. H.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 339.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 12

Bond Lengths			
Pd(1)−C(11)	1.973(5)	Pd(1)−N(13)	2.029(4)
Pd(1)−O(12)	2.058(3)	Pd(1)−N(14)	2.136(4)
O(12)−C(12)	1.269(5)	N(12)−C(12)	1.312(5)
N(11)−C(11)	1.263(6)	N(12)−C(13)	1.484(6)
Pd(2)−C(21)	1.984(5)	Pd(2)−N(23)	2.040(4)
Pd(2)−O(22)	2.046(3)	Pd(2)−N(24)	2.127(4)
O(22)−C(22)	1.261(5)	N(22)−C(22)	1.320(6)
N(21)−C(21)	1.266(6)	N(22)−C(23)	1.487(6)
Pd(3)−C(31)	1.967(5)	Pd(3)−N(33)	2.033(4)
Pd(3)−O(32)	2.055(3)	Pd(3)−N(34)	2.128(4)
O(32)−C(32)	1.262(5)	N(32)−C(32)	1.318(6)
N(31)−C(31)	1.267(6)	N(32)−C(33)	1.484(6)
Bond Angles			
C(11)−Pd(1)−N(13)	97.7(2)	C(11)−Pd(1)−O(12)	86.8(2)
N(13)−Pd(1)−N(14)	78.8(2)	O(12)−Pd(1)−N(14)	96.8(2)
C(12)−O(12)−Pd(1)	123.8(3)	C(11)−N(11)−C(111)	126.9(4)
C(12)−N(12)−C(13)	126.5(4)	C(121)−C(11)−Pd(1)	107.5(3)
C(121)−C(11)−N(11)	119.4(4)	Pd(1)−C(11)−N(11)	133.0(4)
O(12)−C(12)−N(12)	120.5(4)	O(12)−C(12)−C(122)	120.9(4)
N(12)−C(12)−C(122)	118.5(4)	C(21)−Pd(2)−N(23)	100.8(2)
C(21)−Pd(2)−O(22)	86.4(2)	N(23)−Pd(2)−N(24)	79.2(2)
O(22)−Pd(2)−N(24)	93.71(14)	C(22)−O(22)−Pd(2)	122.2(3)
C(21)−N(21)−C(211)	124.5(4)	C(22)−N(22)−C(23)	126.4(4)
C(221)−C(21)−Pd(2)	108.0(3)	C(221)−C(21)−N(21)	119.2(4)
Pd(2)−C(21)−N(21)	132.7(4)	O(22)−C(22)−N(22)	122.0(5)
O(22)−C(22)−C(222)	121.9(4)	N(22)−C(22)−C(222)	116.1(4)
C(31)−Pd(3)−N(33)	99.7(2)	C(31)−Pd(3)−O(32)	85.6(2)
N(33)−Pd(3)−N(34)	78.8(2)	O(32)−Pd(3)−N(34)	95.9(2)
C(32)−O(32)−Pd(3)	122.9(3)	C(31)−N(31)−C(311)	125.2(5)
C(32)−N(32)−C(33)	127.1(4)	C(321)−C(31)−Pd(3)	108.7(3)
C(321)−C(31)−N(31)	119.5(5)	Pd(3)−C(31)−N(31)	131.5(4)
O(32)−C(32)−N(32)	120.2(5)	O(32)−C(32)−C(322)	122.1(4)
N(32)−C(32)−C(322)	117.7(4)		

are values considered normal for C−H···O hydrogen bonds. The dimers stack along the *a* axis forming a tubular cavity in the space between the hydrogen bonding interactions (Figure 5a). The mean distance between dimers is approximately 5.15 Å (Figure 5b).

Spectroscopic Data of Compounds. The IR spectra of compounds containing the $NHBu^t$ group show a band at 3428−3246 cm^{-1} corresponding to the ν(NH) mode. The arene, R^NH, the spirocyclic compound **5**, and complexes **1**, **2**, **3**, **13**, and **14** exhibit a band assignable to the ν(CO) mode at 1674−1630 cm^{-1}, while in **4** the only band appearing in this region is observed at 1575 cm^{-1}, which can be assigned to a ν(CO) mode of a coordinated carbonyl group.[41,42] In complexes **6**−**9**, one or two bands corresponding to the $\nu_a(CO_2)$ mode appear at 1730−1708 cm^{-1} while two bands in the 1602−1556 cm^{-1} region make it difficult to assign the ν(CO) mode. Complex **12** exhibits the band assignable to the ν(C═N) mode at 1634 cm^{-1}, while three bands are observed in the region expected for the band assignable to the ν(CO) mode. The ν(C≡N) mode in **8**, **13**, and **14** appears at 2200−2188 cm^{-1}. The ketenimine **15** exhibits bands assignable to the ν(C═C═N) and ν(CO) modes at 2028 and 1682 cm^{-1}, respectively. A band assignable to ν(HgCl) is observed in **1** at 338 cm^{-1}.

The O-coordination of the carbonyl group in **4** or **12** causes, in their ^{13}C NMR spectra, a deshielding of the carbonyl carbon atom (δ 179.44 and 170.9 ppm) when compared with other species without such coordination (*e.g.*, **1**−**3** 170.36−168.73 ppm).

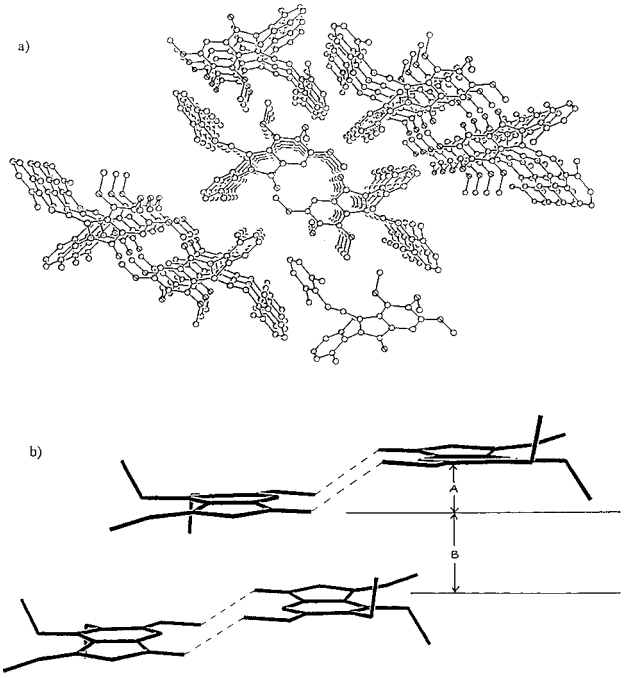


Figure 5. (a) Packing diagram along the *a* axis of compound **15** in the solid state. (b) Another perspective showing the hydrogen bond interactions and interplanar distances; A = 1.23 Å, B = 3.92 Å.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex 15

Bond Lengths			
O(1)−C(7)	1.223(2)	N(1)−C(7)	1.387(2)
N(1)−C(8)	1.423(2)	N(2)−C(9)	1.218(2)
N(2)−C(21)	1.443(2)	C(8)−C(9)	1.315(2)
Bond Angles			
C(2)−O(2)−C(10)	116.3(2)	C(7)−N(1)−C(8)	111.44(13)
C(7)−N(1)−C(31)	124.58(14)	C(8)−N(1)−C(31)	123.98(13)
C(9)−N(2)−C(21)	129.5(2)	O(1)−C(7)−N(1)	125.0(2)
O(1)−C(7)−C(6)	129.3(2)	N(1)−C(7)−C(6)	105.64(14)
C(9)−C(8)−N(1)	124.8(2)	C(9)−C(8)−C(1)	129.2(2)
N(1)−C(8)−C(1)	105.91(13)	N(2)−C(9)−C(8)	168.9(2)

Acknowledgment. We thank Dirección General de Investigación Científica y Técnica (Grant No. PB92-0982-C) and the Fonds der Chemischen Industrie for financial support. K.F.S. is grateful to the Human Capital and Mobility Research Program of the Commission of the European Communities for a research training fellowship (Contract No. ERBCHBGCT920143). J.G.-R. and M.C.R.A. are grateful to the Ministerio de Educación y Ciencia (Spain) for a grant and a contract, respectively.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **4**, **7**, **12** and **15** (30 pages). Ordering information is given on any current masthead page.

OM970426V