3066 *Organometallics* **2010,** *29,* 3066–3076
DOI: 10.1021/om100079x

ORGANOMETALLICS
Article

Organometallic Complexes of Palladium(II) Derived from 2,6-Diacetylpyridine Dimethylketal

José Vicente,* Aurelia Arcas,* and Francisco Juliá-Hernández

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

Delia Bautista[‡]

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

Peter G. Jones[§]

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. [‡] *To whom correspondence regarding the X-ray diffraction studies of complexes* ***2***, ***5b***, ***6a***, *and* ***7a*** *should be addressed. E-mail: dbc@um.es.* [§] *To whom correspondence regarding the X-ray diffraction studies of complex* ***1*** *should be addressed. E-mail: p.jones@tu-bs.de.*

Received February 1, 2010

$PdCl_2$ reacts with 2,6-diacetylpyridine (dap) (1:1) in refluxing MeOH to give the pincer complex [Pd(O^1,N^1,C^1-L)Cl] (**1**) and $(QH)_2[\{PdCl_2(\mu\text{-}Cl)\}]_2$ (**2**), where L is the monoanionic ligand resulting from deprotonation of the acetyl methyl group of the monoketal of dap and QH is $C_5H_3NH\{C(OMe)_2Me\}_2$-2,6, the diketal of $Hdap^+$. Reaction of **2** with NEt_3 (1:2) in MeOH affords Q = $C_5H_3N\{C(OMe)_2Me\}_2$-2,6 (**3**). Complex **1** reacts with 2 equiv of RNC at 0 °C to give *trans*-[Pd(C^1-L)Cl(CNR)$_2$] (R = Xy = 2,6-dimethylphenyl (**4a**), ^{t}Bu (**4b**)) but at room temperature affords [Pd(O^2,C^2-L_R)Cl(CNR)] (R = Xy (**5a**), ^{t}Bu (**5b**)). The ligand L_R results from the insertion of one isocyanide into the Pd−C bond plus a tautomerization process from β-ketoimine to β-ketoenamine and coordinates in **5** through the carbonyl oxygen atom (O^2) and the inserted isocyanide carbon atom (C^2). The reaction of **1** with 1 equiv of RNC at 0 °C leads to a mixture of [Pd(N^1,C^1-L)Cl(CNR)] (R = Xy (**6a**), ^{t}Bu (**6b**); 85−90%), **1**, and **4**, but at room temperature gives the pincer complex [Pd(O^1,N^1,C^2-L_R)Cl] (R = Xy (**7a**), ^{t}Bu (**7b**)), resulting from insertion/tautomerization processes similar to that leading to **5**. Complex **7** reacts at 0 °C (1) with 2 equiv of RNC to give *trans*-[Pd(C^2-L_R)Cl(CNXy)$_2$] (R = Xy (**8a**), ^{t}Bu (**8b**)) or (2) with 1 equiv of ^{t}BuNC to afford **5b**. The reaction of **1** (1) with [Tl(acac)] gives [Pd(N^1,C^1-L)(acac)] (**9**); (2) with chelating ligands N^N affords [Pd(C^1-L)Cl(N^N)] (N^N = 2,2′-bipyridine = bpy (**10**), 4,4′-di-*tert*-butyl-2,2′-bipyridine = dbbpy (**11**)); (3) with 1 equiv of PPh_3 gives, in the same way as with isocyanides, an equilibrium mixture of [Pd(N^1,C^1-L)Cl(PPh_3)] (**12**), **1**, and *trans*-[Pd(C^1-L)Cl(PPh_3)$_2$] (**13**), which is the only product when 2 equiv of PPh_3 is added to the reaction mixture; and (4) with excess PPh_3 affords the monoketal of dap, $C_5H_3N\{C(O)Me\text{-}2\}\{C(OMe)_2Me\text{-}6\}$ (**14**), and [Pd(PPh_3)$_4$]. The crystal structures of complexes **1**, **2**, **5b**, **6a**, and **7a** have been determined.

Introduction

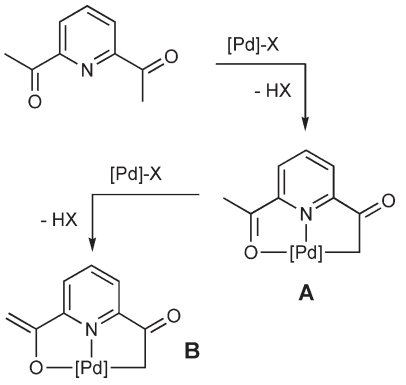
We are currently involved in the synthesis of ketonyl metal complexes $[M]CH_2C(O)R$ (M = Pd, Pt, Au, Hg, Tl) because of the great stability that this alkyl ligand confers to their complexes, their interesting reactivity,[1−4] and their roles as intermediates in organic synthesis.[2,5] Recently, we have reported the synthesis and reactivity of $[Pd\{CH_2C(O)Me\}Cl]_n$, $[Pt\{CH_2C(O)Me\}Cl_2(\eta^2\text{-}C_2H_4)]$, and $[Pt_2\{CH_2C(O)Me\}_6(\mu\text{-}Cl)_3]^-$, studies that have allowed us to prepare unprecedented types of metal complexes.[3,6]

We report here our attempts to prepare ketonyl palladium complexes derived from 2,6-diacetylpyridine (dap). Our interest centered on the possibility that this ligand would allow us to prepare complexes with mono- and dianionic ligands resulting from deprotonation reactions like those shown in Scheme 1. The reactivity of complexes of type **A** is expected to be similar to that of other palladium ketonyl complexes, although it could be modified by the coordination of the pyridine moiety. Cyclometalation of 2-acetylpyridine has been reported only for Rh(III) and Au(III),[7] and one Pd(II) complex has been prepared (but not isolated) by using a silyl enol ether of 2-acetylpyridine,[8] while [Te(O^1,N^1,C^1-L)Cl_3], obtained by reacting dap with $TeCl_4$, is the only reported complex with the ligand present in **A**.[9] However, the reactivity of these species has not been studied. Formation of mixed enolato/ketonyl *O,N,C*-complexes (**B**) is expected in those containing the dianionic ligand because the strong C/C[10] transphobia[11] would destabilize the *C,N,C* pincer

*Corresponding authors. E-mail: jvs1@um.es (J.V.); aurelia@um.es (A.A.). Web: http://www.um.es/gqo/.

 Published on Web 06/28/2010

Scheme 1



isomer. This second functionality would confer on these complexes the expected reactivity of enolato metal complexes (aldol reactions, for example), but, more interestingly, the dual and unprecedented nature of these complexes could lead to novel patterns of reactivity.

The study of the synthesis and reactivity of dap metal complexes has additional relevance because complexes of Fe(II) and Co(II) with bis(imino) derivatives of dap (PDI) are highly active catalysts for polymerization and oligomerization of olefins.[12] It has been reported that some of these PDI ligands prepared with two different amines have important effects on the catalytic perfomance of their complexes.[13,14] One additional reason for preparing complexes **A** is their potential use as catalysts or for the synthesis of complexes with nonsymmetrical PDI-related monoanionic ligands.

Pincer complexes have attracted great interest because of their important applications in organic synthesis, homogeneous catalysis, bond activation, and design of new materials.[15] In spite of the great number of reported Pd(II) pincer complexes, those of type **A** (C,N,O-pincer) are represented only by two families derived from 2-alkyl-substituted 8-quinolinols[16] or $C_6H_4\{NHC(Me)CHC(Me)O\}$-2 derivatives[4] and one complex derived from 8-alkylquinoline-2-carboxylic acid.[17]

Attempts to prepare complexes of type **A** were initially unsuccessful; instead we isolated a family of [*C,N,O*]-pincer ketonyl complexes derived from 2,6-diacetylpyridine dimethylketal when methanol was used as solvent. However, while studying their reactivity, we found that some of their

(1) Vicente, J.; Bermúdez, M. D.; Chicote, M. T.; Sánchez-Santano, M. J. *J. Chem. Soc., Chem. Commun.* **1989**, 141. Vicente, J.; Abad, J. A.; Cara, G.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1125. Vicente, J.; Bermúdez, M. D.; Chicote, M. T.; Sánchez-Santano, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1945. Vicente, J.; Abad, J. A.; Cara, G.; F., G.-J. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2481. Vicente, J.; Bermúdez, M. D.; Carrillo, M. P.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1992**, 1975. Vicente, J.; Bermúdez, M. D.; Carrillo, M. P.; Jones, P. G. *J. Organomet. Chem.* **1993**, *456*, 305. Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Bautista, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3093. Vicente, J.; Abad, J. A.; Bergs, R.; G., J. P.; Bautista, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3093. Vicente, J.; Chicote, M. T.; Huertas, S.; Ramírez de Arellano, M. C.; Jones, P. G. *Eur. J. Inorg. Chem.* **1998**, 511. Vicente, J.; Abad, J. A.; Chicote, M. T.; Abrisqueta, M.-D.; Lorca, J.-A.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 1564. Vicente, J.; Chicote, M. T.; Rubio, C.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2750. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2001**, *20*, 2767. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Sironi, A.; Masciocchi, N. *Chem. Commun.* **2005**, 1267.

(2) Vicente, J.; Bermúdez, M. D.; Escribano, J.; Carrillo, M. P.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3083. Vicente, J.; Bermúdez, M. D.; Carrión, F. J. *Inorg. Chim. Acta* **1994**, *220*, 1.

(3) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2006**, *25*, 4404. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Aullon, G.; Bautista, D. *Organometallics* **2007**, *26*, 6155. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2008**, *27*, 3978.

(4) Vicente, J.; Chicote, M. T.; Martínez-Martínez, J. A.; Jones, P. G.; Bautista, D. *Organometallics* **2008**, *27*, 3254.

(5) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011. Carfagna, C.; Musco, A.; Sallese, G.; Santi, R.; Fiorani, T. *J. Org. Chem.* **1991**, *56*, 261. Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley: Chinchester, U.K., 1995. Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108. Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1740. Culkin, D. A.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234. Sodeoka, M.; Hamashima, Y. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 941. Chen, G. S.; Kwong, F. Y.; Chan, H. O.; Yu, W. Y.; Chan, A. S. C. *Chem. Commun.* **2006**, 1413.

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

(7) Boutadla, Y.; Al-Duaij, O.; Davies, D. L.; Griffith, G. A.; Singh, K. *Organometallics* **2009**, *28*, 433. Fan, D.; Melendez, E.; Ranford, J. D.; Lee, P. F.; Vittal, J. J. *J. Organomet. Chem.* **2004**, *689*, 2969.

(8) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450.

(9) Gysling, H. J.; Luss, H. R.; Gardner, S. A. *J. Organomet. Chem.* **1980**, *184*, 417.

(10) Vicente, J.; Arcas, A.; Gálvez-López, M.-D.; Juliá-Hernández, F.; Bautista, D.; Jones, P. G. *Organometallics* **2008**, *27*, 1582.

(11) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454. Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem.—Eur. J.* **1999**, *5*, 3066. 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.; Arcas, A.; Bautista, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *New J. Chem.* **1996**, *20*, 345. Amatore, C.; Bahsoun, A. A.; Jutand, A.; Meyer, G.; Ntepe, A. N.; Ricard, L. *J. Am. Chem. Soc.* **2003**, *125*, 4212. Crespo, M.; Granell, J.; Solans, X.; Fontbardia, M. *J. Organomet. Chem.* **2003**, *681*, 143. Huynh, H. V.; Han, Y.; Jothibasu, R.; Yang, J. A. *Organometallics* **2009**, *28*, 5395. López, C.; Caubet, A.; Pérez, S.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **2003**, *681*, 82. Ng, J. K. P.; Chen, S.; Li, Y.; Tan, G. K.; Koh, L. L.; Leung, P. H. *Inorg. Chem.* **2007**, *46*, 5100.

(12) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(13) Campora, J.; Cartes, M. A.; Rodriguez-Delgado, A.; Naz, A. M.; Palma, P.; Perez, C. M.; del Rio, D. *Inorg. Chem.* **2009**, *48*, 3679.

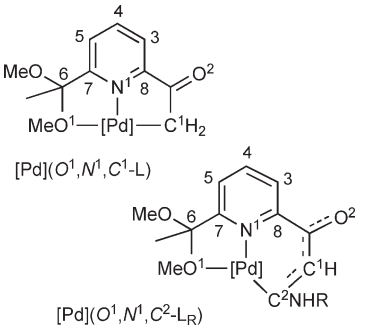
(14) Ionkin, A. S.; Marshall, W. J.; Adelman, D. J.; Fones, B. B.; Fish, B. M.; Schiffhauer, M. F. *Organometallics* **2006**, *25*, 2978. Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120.

(15) Lipke, M. C.; Woloszynek, R. A.; Ma, L.; Protasiewicz, J. D. *Organometallics* **2009**, *28*, 188. Inés, B.; Sanmartin, R.; Churruca, F.; Domínguez, E.; Urtiaga, M. K.; Arriortua, M. I. *Organometallics* **2008**, *27*, 2833. Bollinger, J. E.; Blacque, O.; Frech, C. M. *Chem.—Eur. J.* **2008**, *14*, 7969. Bollinger, J. E.; Blacque, O.; Frech, C. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6514. Gong, J. F.; Zhang, Y. H.; Song, M. P.; Xu, C. *Organometallics* **2007**, *26*, 6487. Solé, D. *Organometallics* **2006**, *25*, 1995. Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. Bolliger, J. L.; Frech, C. M. *Adv. Synth. Catal.* **2009**, *351*, 891. Gossage, R. A.; Van De Kuil, L. A.; Van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423. Gossage, R. A.; Ryabov, A. D.; Spek, A. L.; Stufkens, D. J.; van Beek, J. A. M.; van Eldik, R.; van Koten, G. *J. Am. Chem. Soc.* **1999**, *121*, 2488. Leis, W.; Mayer, H. A.; Kaska, W. C. *Coord. Chem. Rev.* **2008**, *252*, 1787. Moreno, I.; SanMartin, R.; Ines, B.; Herrero, M. T.; Dominguez, E. *Curr. Org. Chem.* **2009**, *13*, 878. Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610. Vicente, J.; Abad, J. A.; Lopez-Serrano, J.; Jones, P. G.; Najera, C.; Botella-Segura, L. *Organometallics* **2005**, *24*, 5044. Bonnet, S.; van Lenthe, J. H.; Siegler, M. A.; Spek, A. L.; van Koten, G.; Gebbink, R. *Organometallics* **2009**, *28*, 2325. Gagliardo, M.; Selander, N.; Mehendale, N. C.; van Koten, G.; Gebbink, R.; Szabo, K. J. *Chem.—Eur. J.* **2008**, *14*, 4800. Li, J.; Minnaard, A. J.; Gebbink, R.; van Koten, G. *Tetrahedron Lett.* **2009**, *50*, 2232. McDonald, A. R.; Dijkstra, H. P.; Suijkerbuijk, B. M. J. M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2009**, *28*, 4689. O'Leary, P.; van Walree, C. A.; Mehendale, N. C.; Sumerel, J.; Morse, D. E.; Kaska, W. C.; van Koten, G.; Gebbink, R. *Dalton Trans.* **2009**, 4289.

(16) Billodeaux, D. R.; Fronczek, F. R.; Yoneda, A.; Newkome, G. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *C54*, 1439. Yoneda, A.; Newkome, G. R.; Theriot, K. J. *J. Organomet. Chem.* **1991**, *401*, 217. Yoneda, A.; Ouchi, M.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Chem. Lett.* **1993**, 709. Yoneda, A.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Organometallics* **1994**, *13*, 4912.

(17) Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117.

Chart 1



derivatives decompose to give the desired complexes, which provided the necessary information for their rational synthesis. In this paper we report the synthesis of these dimethylketal derivatives and their reactivity toward isocyanides. There is only one related precedent for these complexes, 2-lithium phenyl dimethylketal, which is described as a non-isolated intermediate obtained from the dimethylketal of 2-bromoacetophenone via metal−halogen exchange.[18]

Experimental Section

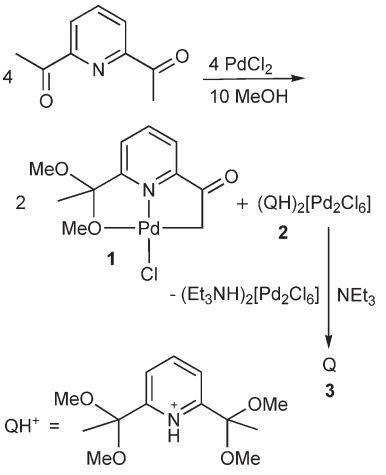
General Procedures. The reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Bruker AC 200 or Avance 300 or 400 spectrometer at room temperature. Chemical shifts were referred to TMS (^{1}H, ^{13}C) or H_3PO_4 (^{31}P). When needed, NMR assignments were performed with the help of APT, HMQC, and HMBC techniques. Chart 1 shows the atom numbering used in the NMR assignments. The R groups (Xy, ^{t}Bu) of inserted and coordinated isocyanides are distinguished by using the notation Xy^i, ^{t}Bu^1 and ^{t}Bu^c, Xy^c, respectively.

Synthesis of [Pd(O^1,N^1,C^1-L)Cl] (1) and (C_5H_3NH{C(OMe)$_2$-Me}-2,6)$_2$[{PdCl$_2$(μ-Cl)}]$_2$ (2). To a suspension of $PdCl_2$ (390.6 mg, 2.20 mmol) in MeOH (20 mL) were added 2,6-diacetylpyridine (359.3 mg, 2.20 mmol) and NEt_3 (57 μL, 0.40 mmol). The suspension was refluxed for 95 min and then filtered through Celite. The orange filtrate was concentrated (2 mL), and Et_2O (1 mL) was added. The resulting precipitate was filtered off and air-dried. The solid was extracted with $CHCl_3$ (4 × 5 mL), giving solution A (used to prepare **1**) and a solid, which was air-dried, giving orange **2**. Yield: 92.4 mg, 18% (based on the stoichiometry shown in Scheme 2). Mp: 131−132 °C. IR (cm^{-1}): ν(NH) 3248, 3217, ν(CN) 1617, ν(PdCl) 346, 334. ^{1}H NMR (300 MHz, MeCN-d_3): δ 12.55 (br, NH), 8.75 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 8.13 (d, 2 H, H3,5, $^3J_{HH}$ = 8 Hz), 3.30 (s, 12H, OMe), 1.71 (s, 6H, Me). ^{13}C{^{1}H} NMR (75.4 MHz, MeCN-d_3): δ 150.4 (C4), 126.1 (C3,5), 100.2 (C6), 50.8 (MeO), 24.7 (Me). Anal. Calcd for $C_{26}H_{44}N_2O_8Cl_6Pd_2$: C, 33.29; H, 4.72; N, 2.98. Found: C, 33.08; H, 4.92; N, 2.90. Single crystals of **2** were obtained by slow evaporation of a MeOH solution of **2**.

Solution A was concentrated (1 mL) and column chromatographed on silica gel using $CHCl_3$ as eluent. The first collected fraction was concentrated (1 mL). Addition of Et_2O (4 mL) and *n*-pentane (4 mL) gave a suspension, which was filtered off to give complex **1** as a yellow solid. Yield: 267.1 mg, 69% (based on the stoichiometry shown in Scheme 2). Mp: 137−138 °C.

(18) Morrow, G. W.; Wang, S.; Swenton, J. S. *Tetrahedron Lett.* **1988**, *29*, 3441.

Scheme 2



IR (cm^{-1}): ν(C=O) 1684, ν(CN) 1603, ν(PdCl) 321. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 7.80 (dd, 1H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.63 (dd, 1H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 3.52 (s, 2 H, CH_2), 3.42 (s, 6 H, OMe), 1.77 (s, 3 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 203.7 (CO), 158.5 (C7), 152.7 (C8), 139.8 (C4), 126.4 (C5), 123.6 (C3), 106.9 (C6), 51.5 (MeO), 30.7 (C1), 25.0 (Me). Anal. Calcd for $C_{11}H_{14}NO_3ClPd$: C, 37.74; H, 4.03; N, 4.00. Found: C, 37.63; H, 3.97; N, 3.95. Single crystals of **1** were obtained by slow evaporation of a MeOH solution of **1**.

Synthesis of C_5H_3N{C(OMe)$_2$Me}$_2$ (3). To a suspension of **2** (2466.9 mg, 2.63 mmol) in MeOH (30 mL) was added NEt_3 (733 μL, 5.26 mmol). The reaction mixture was stirred for 24 h and then concentrated to dryness. The residue was extracted with *n*-pentane (2 × 20 mL), and the solution was concentrated to dryness to give **3** as a colorless solid. Yield: 1246.0 mg, 93%. Mp: 103−104 °C. IR (cm^{-1}): ν(CN) 1582. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71−7.57 (m, 3H, py), 3.19 (s, 12H, MeO), 1.66 (s, 6H, Me). ^{13}C{^{1}H} NMR (50.30 MHz, $CDCl_3$): δ 159.7 (*o*-C), 136.2 (*p*-C), 120.4 (*m*-C), 101.8 (*C*Me), 49.1 (OMe), 23.6 (Me). Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.16; H, 8.29; N, 5.49. Found: C, 61.05; H, 8.57; N, 5.58.

Synthesis of *trans*-[Pd(C^1-L)Cl(CNXy)$_2$]·0.5H$_2$O (4a). To a cooled (0 °C) solution of **1** (23.3 mg, 0.07 mmol) in $CHCl_3$ (5 mL) was added XyNC (20.2 mg, 0.15 mmol). After 5 min of stirring the solution was concentrated to dryness. The residue was vigorously stirred in a cooled (0 °C) mixture of Et_2O (2 mL) and *n*-pentane (6 mL). The resulting suspension was filtered off, and the solid washed with *n*-pentane and air-dried to give **4a** as a pale yellow solid. Yield: 37.4 mg, 90%. Mp: 134−135 °C. IR (cm^{-1}): ν(N≡C) 2192, ν(C=O) 1647, ν(C=N) 1579, ν(PdCl) 280. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92−7.90 (m, 1H, ABC system), 7.77−7.72 (m, 2H, ABC system), 7.27−7.11 (m, 6H, Xy), 3.73 (s, 2H, CH_2), 3.08 (s, 6H, OMe), 2.49 (s, 12H, Me, Xy), 1.48 (s, 3H, Me). The ^{13}C{^{1}H} NMR spectrum could not be registered because it transforms into **5a** during the acquisition time. Anal. Calcd for $C_{29}H_{33}N_3O_{3.5}ClPd$: C, 56.05; H, 5.35; N, 6.76. Found: C, 55.91; H, 5.29; N, 6.81

Synthesis of *trans*-[Pd(C^1-L)Cl(CN^{t}Bu)$_2$] (4b). To a cooled (0 °C) solution of **1** (18.7 mg, 0.05 mmol) in CH_2Cl_2 (6 mL) was added ^{t}BuNC (11.1 mg, 0.13 mmol), and the mixture was stirred for 20 min. Concentration to dryness, addition of *n*-pentane (6 mL), and vigorous stirring led to a suspension. The solid was filtered off, washed with Et_2O, and air-dried to give **4b** as a colorless solid. Yield: 26.2 mg, 96%. Mp: 124−125 °C. IR (cm^{-1}): ν(N≡C) 2211, ν(C=O) 1651, ν(C=N) 1579, ν(PdCl) 289. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.95−7.70 (m, 3H, ABC system), 3.35 (s, 2H, CH_2), 3.22 (s, 6H, OMe), 1.72 (s, 3H, Me), 1.52 (s, 18H, ^{t}Bu). The ^{13}C{^{1}H} NMR spectrum could not be registered because it transforms into **5b** during the acquisition

time. Anal. Calcd for $C_{21}H_{32}N_3O_3ClPd$: C, 48.85; H, 6.25; N, 8.14. Found: C, 48.53; H, 6.58; N, 8.07.

Synthesis of [Pd(O^2,C^2-L_{Xy})Cl(CNXy)] (5a). To a cooled solution (0 °C) of **7a** (22.9 mg, 0.05 mmol) in CH_2Cl_2 (8 mL) was added XyNC (6.3 mg, 0.05 mmol), and the mixture was stirred for 10 min. Concentration (1 mL) and addition of *n*-pentane (9 mL) gave a suspension; the solid was filtered off, washed with *n*-pentane, and air-dried to give a mixture (26.2 mg) of **5a**, **7a**, and **8a** (81:15:4) with traces of XyNC. ^{1}H NMR (300 MHz, $CDCl_3$) of **5a**: δ 8.20 (dd, 1H, H3 or 5, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 7.75 (t, 1H, H4, $^3J_{HH}$ = 7.5 Hz), 7.67 (dd, 1H, H5 or 3, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 7.30−7.20 (m, 6H, Xy), 5.86 (d, 1H, H1, J = 1 Hz), 3.12 (s, 6H, MeO), 2.52 (s, 6H, Me, Xy^c), 2.28 (s, 6H, Me, Xy^i), 1.51 (s, 3H, Me).

Synthesis of [Pd(O^2,C^2-L_{Bu})Cl(CN^{t}Bu)] (5b). To a solution of **1** (129.4 mg, 0.37 mmol) in $CHCl_3$ (15 mL) was added ^{t}BuNC (3.43 mL, 226.2 mM solution, 0.78 mmol). The solution was stirred for 4.5 days at room temperature and then concentrated to dryness. The residue was purified by preparative TLC chromatography on silica gel (70−200 μm) using CH_2Cl_2/Et_2O (1:2) as eluent. The first fraction (R_f = 0.50) was collected and extracted with acetone (3 × 15 mL) to give a solution that was concentrated to dryness. The residue was dissolved in CH_2Cl_2, and anhydrous $MgSO_4$ was added. The resulting suspension was stirred and filtered. The filtrate was concentrated to dryness, and the residue was recrystallized from Et_2O/*n*-pentane, to give **5b** as a yellow solid. Yield: 150.9 mg, 79%. Mp: 240 °C dec. IR (cm^{-1}): ν(C≡N) 2211, ν(C=O) 1590, ν(C=N) 1513, ν(PdCl) 281. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, 1H, H3, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1 Hz), 7.75 (t, 1H, H4, $^3J_{HH}$ = 7.6 Hz), 7.69 (dd, 1H, H5, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1 Hz), 6.45 (d, 1H, H1, J = 1 Hz), 6.00 (br, 1H, NH), 3.19 (s, 6H, MeO), 1.66 (s, 3H, Me), 1.61 (br, 9H, Me, $^tBu^i$), 1.48 (s, 9H, Me, $^tBu^c$). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 196.6 (CO), 190.5 (C2), 159.1 (C7), 151.9 (C8), 136.5 (C4), 127.5 (t, *C*N^{t}Bu, $^1J_{CN}$ = 20 Hz), 123.4 (C5), 121.7 (C3), 105.1 (C1), 101.6 (C6), 59.3 (br, *C*Me_3^c), 56.5 (*C*Me_3^i), 49.2 (OMe), 30.2 (Me, $^tBu^c$), 29.4 (Me, $^tBu^i$), 23.0 (Me). Anal. Calcd for $C_{21}H_{32}N_3O_3ClPd$: C, 48.85; H, 6.25; N, 8.14. Found: C, 48.56; H, 6.25; N, 8.15. Single crystals were obtained by slow diffusion of a mixture Et_2O/*n*-hexane into a toluene solution of **5b** (1:1:1).

Synthesis of [Pd(N^1,C^1-L)Cl(CNXy)] (6a). To a cooled (0 °C) solution of **1** (44.5 mg, 0.13 mmol) in $CHCl_3$ (3 mL) was added XyNC (16.7 mg, 0.13 mmol), and the resulting pale yellow solution was stirred for 30 min and concentrated (1 mL). Addition of *n*-pentane (4 mL) gave a suspension; the solid was filtered off, washed with *n*-pentane, and air-dried to give a mixture (56.2 mg) of **6a**, **1**, and **4a** (85:9:6) with traces of XyNC that could not be separated. ^{1}H NMR (400 MHz, $CDCl_3$) of **6a**: δ 8.06 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 7.94 (dd, 1H, H3 or 5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.73 (dd, 1H, H5 or 3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.26−7.11 (m, 3H, Xy), 3.44 (s, 2H, CH_2), 3.27 (s, 6H, OMe), 2.49 (s, 6H, Me, Xy), 2.03 (s, 3H, Me).

Synthesis of [Pd(N^1,C^1-L)Cl(CN^{t}Bu)] (6b). To a cooled (0 °C) solution of **1** (30.2 mg, 0.09 mmol) in $CHCl_3$ (4 mL) was added ^{t}BuNC (400 μL of a 226.2 mM $CHCl_3$ solution, 0.09 mmol). The resulting pale yellow solution was stirred for 20 min and concentrated (1 mL). Addition of *n*-pentane (4 mL) gave a suspension; the solid was filtered off, washed with *n*-pentane, and air-dried to give a mixture (32.1 mg) of **6b**, **1**, and **4b** (84:7:9) with traces of ^{t}BuNC that could not be separated. ^{1}H NMR (400 MHz, $CDCl_3$) of **6b**: δ 8.02 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 7.90 (dd, 1H, H3 or 5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.70 (dd, 1H, H5 or 3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 3.27 (s, 2H, CH_2), 3.24 (s, 6H, OMe), 1.99 (s, 3H, Me), 1.55 (s, 9H, ^tBu).

Synthesis of [Pd(O^1,N^1,C^2-L_{Xy})Cl] (7a). To a solution of **1** (104.6 mg, 0.30 mmol) in $CHCl_3$ (15 mL) was added XyNC (47.1 mg, 0.36 mmol). The pale yellow solution was stirred for 10 days to give an orange solution, which was concentrated to dryness. The resulting solid was purified by preparative TLC chromatography using silica gel (70−200 μm) with CH_2Cl_2/Et_2O (7:1) as eluent. The yellow fraction at R_f = 0.26 was collected and extracted with acetone (3 × 20 mL) to give a solution, which was concentrated to dryness. The residue was stirred with Et_2O (2 mL) and *n*-pentane (8 mL). The suspension was filtered, and the solid was washed with *n*-pentane and air-dried to give **7a** as an orange solid. Yield: 98.3 mg, 68%. Mp: 180 °C dec. IR (cm^{-1}): ν(NH) 3321, ν(C=N, py) 1609, ν(C=O) 1566, ν(C=NH) 1504, ν(PdCl) 334. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (dd, 1H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 8.65 (br, 1H, NH), 8.15 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 7.59 (dd, 1H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.13−7.03 (m, ABC system, 3H, Xy), 4.67 (s, 1H, H1), 3.47 (s, 6H, MeO), 2.25 (s, 6H, Me, Xy) 1.92 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 181.9 (CO), 164.9 (C2), 158.2 (C7), 150.5 (C8), 140.0 (C4), 138.2 (C-N, Xy), 135.0 (*o*-*C*(Xy)), 128.3 (*m*-*C*(Xy)), 127.5 (*p*-*C*(Xy)), 126.2 (C3), 124.7 (C5), 108.5 (C6), 93.5 (C1), 52.2 (MeO), 26.3 (Me), 18.3 (Me, Xy). Anal. Calcd for $C_{20}H_{23}O_3N_2ClPd$: C, 49.91; H, 4.82; N, 5.82. Found: C, 49.91; H, 5.03; N, 5.74. Single crystals of **7a** were obtained by slow diffusion of *n*-pentane into a $CHCl_3$ solution of **7a**.

Synthesis of [Pd(O^1,N^1,C^2-L_{Bu})Cl] (7b). To a solution of **1** (69.6 mg, 0.20 mmol) in $CHCl_3$ (15 mL) was added ^{t}BuNC (924 μL, 226.2 mM $CHCl_3$ solution, 0.21 mmol). The yellow solution was refluxed for 16 h, and the resulting solution was concentrated to dryness. The resulting solid was purified by means of silica gel (70−200 μm) preparative TLC chromatography using CH_2Cl_2/Et_2O (3:1) as eluent. The yellow fraction at R_f = 0.14 was collected and extracted with acetone (3 × 20 mL), and the solution was concentrated to dryness. The residue was stirred with Et_2O (2 mL) and *n*-pentane (8 mL). The suspension was filtered and the solid washed with *n*-pentane and air-dried to give **7b** as a yellow solid. Yield: 79.8 mg, 89%. Mp: 172−173 °C. IR (cm^{-1}): ν(NH) 3334, ν(C=N, py) 1607, ν(C=O) 1560, ν(C=NH) 1534, ν(PdCl) 321. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (dd, 1H, H3, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 8.13 (t, 1H, H4, $^3J_{HH}$ = 7.6 Hz), 7.63 (br, 1H, NH), 7.55 (dd, 1H, H5, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 5.17 (br, 1H, H1), 3.41 (s, 6H, MeO), 1.88 (s, 3H, Me), 1.42 (s, 9H, ^tBu). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 180.8 (br, CO), 164.8 (br, C2), 158.0 (C7), 150.6 (C8), 139.9 (C4), 126.0 (C3), 124.5 (C5), 108.0 (C6), 94.2 (C1), 55.6 (*C*Me_3), 52.1 (MeO), 29.1 (C*Me*$_3$), 26.1 (Me). Anal. Calcd for $C_{16}H_{25}O_4N_2ClPd$: C, 42.59; H, 5.58; N, 6.20. Found: C, 42.70; H, 5.35; N, 6.35.

Synthesis of *trans*-[Pd(C^2-L_{Xy})Cl(CNXy)$_2$]·1/4$CHCl_3$ (8a). To a cooled (0 °C) solution of **7a** (50.7 mg, 0.11 mmol) in $CHCl_3$ (7 mL) was added XyNC (29.0 mg, 0.22 mmol). The solution was stirred for 5 min and concentrated to dryness. The residue was dissolved in Et_2O, and *n*-pentane was added. The suspension was filtered and the solid washed with *n*-pentane and air-dried to give **8a** as a pale yellow solid. Yield: 69.2 mg, 85%. Mp: 125−126 °C. IR (cm^{-1}): ν(N≡C) 2175, ν(C=O) 1567, ν(PdCl) 285. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.68 (br, 1H, NH), 8.12 (dd, 1H, H3, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 7.80 (t, 1H, H4, $^3J_{HH}$ = 7.6 Hz), 7.72 (dd, 1H, H5, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 7.22 (s, 1H, H1), 7.25−6.95 (m, 9H, Xy), 3.19 (s, 6H, MeO), 2.37 (s, 6H, Me, Xy^i), 2.32 (s, 12H, Me, Xy^c), 1.71 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 180.1 (C2), 178.5 (CO), 158.9 (C7), 155.5 (C8), 141.4 (br, C≡N), 141.5 (C_{ipso}, Xy^i), 136.6 (C4), 136.2 (*o*-C, Xy^c), 134.7 (*o*-C, Xy^i), 130.3 (*p*-C, Xy^c), 128.4 (*m*-C, Xy^i), 128.0 (*m*-C, Xy^c), 126.7 (*p*-C, Xy^i), 122.3 (C5), 120.9 (C3), 102.5 (C1), 101.8 (C6), 49.0 (OMe), 23.2 (Me), 19.3 (Me, Xy^i), 18.7 (Me, Xy^c). Anal. Calcd for $C_{38.25}H_{41.25}N_4O_3Cl_{1.75}Pd$: C, 59.40; H, 5.38; N, 7.24. Found: C, 59.44; H, 5.13; N, 7.50.

Synthesis of *trans*-[Pd(C^2-L_{Xy})Cl(CN^{t}Bu)$_2$]·1/4$CHCl_3$ (8b). To a cooled (0 °C) solution of **7b** (24.8 mg, 0.06 mmol) in $CHCl_3$ (6 mL) was added ^{t}BuNC (531 μL, 226.2 mM, 0.12 mmol). The solution was stirred for 5 min at 0 °C and concentrated to dryness. The residue was dissolved in Et_2O, and *n*-pentane was added. The suspension was filtered and the solid washed with *n*-pentane and air-dried to give **8b** as a pale yellow solid.

Yield: 32.6 mg, 91%. Mp: 127−128 °C. IR (cm^{-1}): ν(N≡C) 2208, ν(C═O) 1538, ν(PdCl) 290. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.96 (br, 1H, NH), 8.02 (dd, 1H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.75 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 7.65 (dd, 1H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 6.86 (s, 1H, H1), 3.21 (s, 6H, MeO), 1.75 (s, 3H, Me), 1.64 (s, 9H, ^{t}Bu^i), 1.45 (s, 18H, ^{t}Bu^c). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$): δ 178.3 (CO), 176.0 (C2), 158.6 (C7), 156.3 (C8), 136.4 (C4), 130 (m, C≡N), 121.8 (C3), 120.5 (C5), 101.9 (C6), 99.1 (C1), 58.5 (CNH), 53.0 (*C*Me$_3^c$), 49.1 (MeO), 31.3 (Me, ^{t}Bu^i), 29.8 (Me, ^{t}Bu^c), 23.3 (Me). Anal. Calcd for $C_{26.25}H_{41.25}N_4O_3Cl_{1.75}Pd$: C, 50.10; H, 6.61; N, 8.90. Found: C, 49.89; H, 6.57; N, 9.19.

Synthesis of [Pd(*N*^{1},*C*^{1}-L)(*O*,*O*-acac)] (9). To a solution of **1** (39.7 mg, 0.11 mmol) in $CHCl_3$ (8 mL) was added Tl(acac)[19] (34.3 mg; 0.11 mmol). The suspension was filtered through Celite, and the filtrate was concentrated to dryness. The residue was crystallized from Et_2O (2 mL) and *n*-pentane (7 mL). The crystals were filtered off, washed with *n*-pentane, and air-dried to give **9** as a yellow solid. Yield: 44.6 mg, 96%. Mp: 159−160 °C. IR (cm^{-1}): ν(C═O) 1673, ν(CO, acac) 1579, 1515. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.96 (t, 1H, H4, $^3J_{HH}$ = 7.6 Hz), 7.75 (dd, 1H, H3, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz), 7.64 (dd, 1H, H5, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz), 5.28 (s, 1H, CH, acac), 3.43 (s, 2H, H1), 3.25 (s, 6H, OMe), 1.92 (s, 6H, Me, acac), 1.84 (s, 3H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 192.9 (br, CO), 186.8 (br, CO, acac), 185.3 (br, CO, acac), 163.3 (C7), 160.3 (C8), 139.4 (C4), 124.8 (C5), 120.2 (C3), 101.2 (C6), 99.6 (CH, acac), 49.3 (OMe), 40.5 (C1), 27.2 (br, Me, acac), 26.7 (br, Me, acac), 24.4 (Me). Anal. Calcd for $C_{16}H_{21}NO_5Pd$: C, 46.44; H, 5.12; N, 3.39. Found: C, 46.32; H, 5.01; N, 3.44

Synthesis of [Pd(*C*^{1}-L)Cl(bpy)] (10). To a solution of **1** (17.9 mg, 0.05 mmol) in acetone (4 mL) was added bpy (8.0 mg, 0.05 mmol). After stirring for 20 min, the suspension was filtered and the resulting yellow solid was washed with acetone and air-dried to give **10**. Yield: 21.2 mg, 82%. Mp: 224−225 °C. IR (cm^{-1}): ν(C═O) 1608, ν(CN) 1580, ν(PdCl) 336. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.58 (d, 1H, bpy, $^3J_{HH}$ = 5 Hz), 9.14 (d, 1H, bpy, $^3J_{HH}$ = 5 Hz), 8.05 (m, 3H, bpy + 1H, py), 7.94 (d, 1H, py, $^3J_{HH}$ = 8 Hz), 7.76 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 7.70 (m, 2H, bpy), 7.52 (t, 1H, bpy, $^3J_{HH}$ = 5 Hz), 3.59 (s, 2H, CH_2), 3.15 (s, 6H, MeO), 1.63 (s, 3H, Me). Anal. Calcd for $C_{21}H_{22}N_3O_3ClPd$: C, 49.82; H, 4.38; N, 8.30. Found: C, 49.94; H, 4.41; N, 8.23.

Synthesis of [Pd(*C*^{1}-L)Cl(dbbpy)]·1/2H$_2$O (11). To a solution of **1** (61.8 mg, 0.18 mmol) in CH_2Cl_2 (6 mL) was added dbbpy (4,4′-di-*tert*-butyl-2,2′-bipyridine, 47.5 mg, 0.18 mmol). The resulting solution was stirred (5 min) and concentrated (1 mL). Addition of *n*-pentane (8 mL) gave a suspension, which was cooled (−4 °C) for 30 min and filtered. The solid was washed with *n*-pentane and air-dried to give **11** as a pale yellow solid. Yield: 104.1 mg, 94%. Mp: 218−219 °C. IR (cm^{-1}): ν(C═O) 1642, ν(CN) 1614, 1583, 1545, ν(PdCl) 337. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (d, 1H, dbbpy, $^3J_{HH}$ = 6 Hz), 9.04 (d, 1H, dbbpy, $^3J_{HH}$ = 6 Hz), 7.99 (dd, 1H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.90 (d, 1H, dbbpy, $^4J_{HH}$ = 2 Hz), 7.87 (d, 1H, dbbpy, $^4J_{HH}$ = 2 Hz), 7.73 (t, 1H, H4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.69 (dd, 1H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.66 (dd, 1H, dbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.43 (dd, 1H, dbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 3.69 (s, 2H, CH_2), 3.21 (s, 6H, MeO), 1.72 (s, 3H, Me), 1.45 (s, 9H, ^{t}Bu), 1.39 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 205.8 (CO), 163.6 (C, dbbpy), 163.2 (C, dbbpy), 158.7 (C7), 157.1 (C8), 156.3 (C, dbbpy), 153.9 (C, dbbpy), 151.9 (CH, dbbpy), 149.2 (CH, dbbpy), 136.4 (C4), 124.2 (CH, dbbpy), 123.2 (CH, dbbpy), 122.8 (C3), 121.3 (C5), 118.4 (CH, dbbpy), 117.6 (CH, dbbpy), 101.9 (C6), 49.2 (MeO), 35.4 (*C*Me$_3$), 30.3 (C*Me$_3$*), 30.2 (C*Me$_3$*), 23.7 (Me), 21.3 (C1). Anal. Calcd for $C_{29}H_{39}N_3O_{3.5}ClPd$: C, 55.51; H, 6.26; N, 6.70. Found: C, 55.68; H, 6.26; N, 6.63.

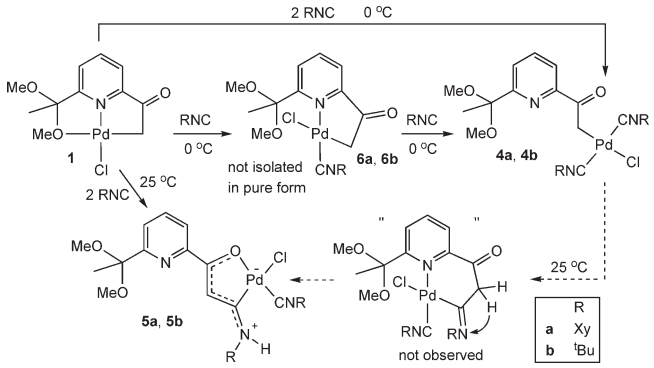
Synthesis of [Pd(*N*^{1},*C*^{1}-L)Cl(PPh$_3$)] (12). To a cooled solution (0 °C) of **1** (35.4 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) was added PPh_3 (26.5 mg, 0.10 mmol). The resulting yellow solution was stirred for 20 min and concentrated (1 mL). Addition of Et_2O (5 mL) gave a suspension; the solid was filtered off, washed with Et_2O, and air-dried to give a mixture (60.9 mg) of **12**, **1**, and **13** (90:5:5) that could not be separated. NMR data of **12**: ^{1}H (300 MHz, $CDCl_3$): δ 7.95 (t, 1H, H4, $^3J_{HH}$ = 7.8 Hz), 7.86 (dd, 1H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.76−7.41 (m, 16H, H5 or H3 + PPh_3), 3.30 (br, 6H, OMe), 2.89 (br, 2H, H1), 2.03 (s, 3H, Me). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 36.8 (s).

Synthesis of *trans*-[Pd(*C*^{1}-L)Cl(PPh$_3$)$_2$] (13). To a cooled solution (0 °C) of **1** (59.3 mg, 0.17 mmol) in CH_2Cl_2 (8 mL) was added PPh_3 (90.6 mg, 0.35 mmol). The resulting yellow solution was stirred for 10 min and concentrated (1 mL). Addition of Et_2O (2 mL) and *n*-pentane (8 mL) gave a suspension; the solid was filtered off, washed with *n*-pentane, and air-dried to give **13** (140.3 mg) contamined with a product containing PPh_3 that we could not remove. NMR data of **13**: ^{1}H (300 MHz, $CDCl_3$), δ 7.94 (t, 1H, H4, $^3J_{HH}$ = 7.8 Hz), 7.82 (dd, 1H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.80−7.40 (m, 16H, H5 or H3 + PPh_3), 3.45 (br, 2H, H1), 3.20 (br, 6H, OMe), 1.68 (s, 3H, Me). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 23.8 (s).

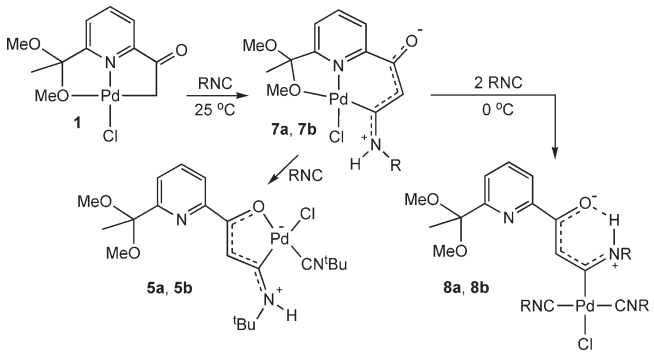
Synthesis of C$_5$H$_3$N{C(O)Me-2}{C(OMe)$_2$Me-6} (14). To a solution of **1** (15.2 mg, 0.04 mmol) in $CDCl_3$ (0.8 mL) in a NMR tube was added PPh_3 (57.7 mg, 0.22 mmol). After 5 min at room temperature, a ^{1}H NMR spectrum was recorded, showing signals that we assign to **14**. In addition, the ^{31}P{^{1}H} NMR spectrum showed resonances due to $[Pd(PPh_3)_4]$ and its dissociation products $[Pd(PPh_3)_3]$ and PPh_3. **14** could not be purified by recrystallization because of the excess of PPh_3; TLC chromatography in silica gel led to hydrolysis to give dap. ^{1}H NMR (400 MHz, $CDCl_3$) of **14**: δ 7.94 (dd, 1H, H3 or H5, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1 Hz), 7.85 (dd, 1H, H5 or H3, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1 Hz), 7.80 (t, 1H, H4, $^3J_{HH}$ = 7.4 Hz), 3.21 (s, 6H, OMe), 2.75 (s, 3H, Me), 1.71 (s, 3H, Me).

X-ray Structure Determinations. Complexes **2**, **5b**, **6a**, and **7a** were measured on a Bruker Smart APEX diffractometer and **1** on an Oxford Diffraction Nova O diffractometer. Data were collected in ω scan mode using monochromated Mo Kα radiation

Scheme 3

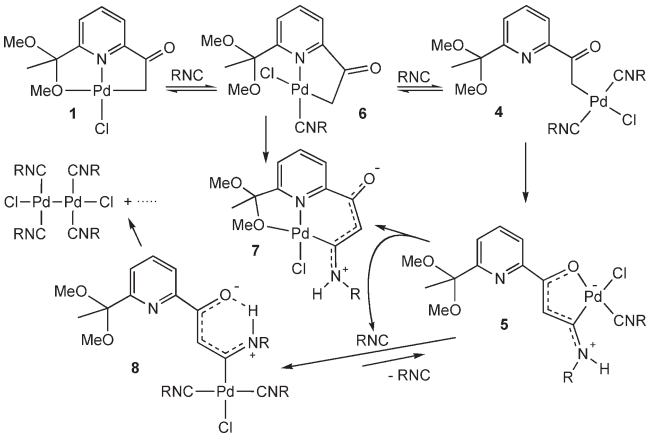


Scheme 4



(19) Vicente, J.; Chicote, M. T. *Inorg. Synth.* **1998**, *32*, 172.

Scheme 5



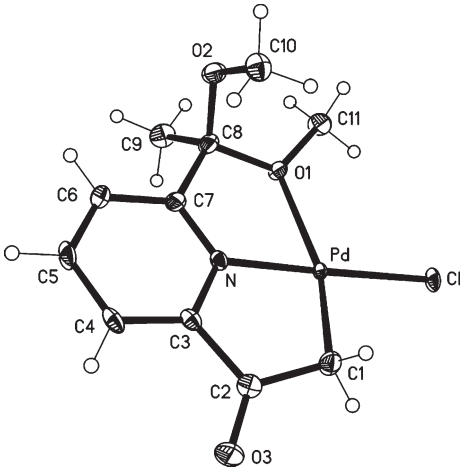


Figure 1. Ellipsoid representation of **1** (50% probability). Selected bond lengths (Å) and angles (deg): Pd−N 1.9752(19), Pd−C(1) 2.000(2), Pd−O(1) 2.2149(16), Pd−Cl 2.3040(5), Pd−Pd#1 3.3460(3), O(3)−C(2) 1.217(3), C(1)−C(2) 1.497(3), C(2)−C(3) 1.499(3), N−Pd−C(1) 83.85(9), N−Pd−O(1) 76.32(7), C(1)−Pd−Cl 96.63(7), O(1)−Pd−Cl 103.03(4).

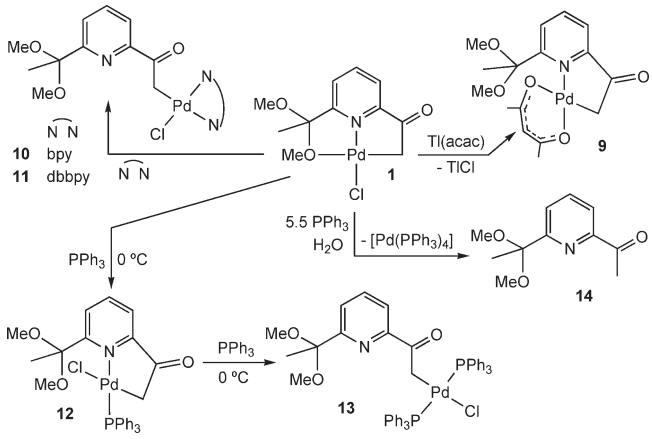
for **2**, **5b**, **6a**, and **7a** and mirror-focused Cu Kα radiation (λ = 1.54184 Å) for **1**. Absorption corrections were applied on the basis of multiscans (program SADABS for **2**, **5b**, **6a**, and **7a** and CrysAlis RED for **1**). All structures were refined anisotropically on F^2 using the program SHELXL-97.[20] NH hydrogens were refined freely, but with a DFIX restraint to the NH distance in **5b**. The ordered methyl groups were refined as rigid groups (AFIX 137), and the other hydrogens were refined using a riding model. *Special features and exceptions*: for **5b** the absolute structure parameter is −0.006(16).[21] The $C(OMe)_2Me$ group of one of the molecules is disordered over two positions (ca. 67:33%).

Results and Discussion

Reactions of 2,6-Diacetylpyridine with Palladium Compounds. Numerous attempts to prepare ketonyl palladium complexes derived from 2,6-diacetylpyridine (dap) failed. Thus, by reacting dap with the usual starting palladium(II) compounds ($[Pd(OAc)_2]$, $PdCl_2$, $[PdCl_2(NCMe)_2]$, $(NMe_4)_2[Pd_2Cl_6]$), using various solvents ($Me_2C(O)$, CH_2Cl_2, THF, MeCN) and reaction temperatures, in the absence of a base or adding Ag_2O, $Tl_2(CO_3)$, or K^tBuO, led to palladium metal and/or complex mixtures. We interpreted these negative results in terms of the low coordinative ability of dap, in turn attributable to the electron-withdrawing character of both ortho acetyl substituents. It is well-known that ligand to metal coordination assists the C−H activation required to afford a metalated complex of that ligand. Indeed, the number of dap metal complexes is very scarce,[13,22,23] and in the only reported crystal structure, $[Ag(O,N,O\text{-dap})_2]^{2+}$, the Ag−N bond distances are much longer (2.316(6) Å) than those in $[Ag(py)_2]^+$ (2.126(4) and 2.133(4) Å).[23]

Finally, the only successful result was obtained by reacting dap and $PdCl_2$ (1:1) in refluxing MeOH, which gave a mixture of the pincer complex $[Pd(O^1,N^1,C^1\text{-L})Cl]$ (**1**), where L is the monoanionic ligand resulting from deprotonation of the acetyl methyl group of the monoketal of dap (Scheme 2), and $(QH)_2[PdCl_2(\mu\text{-Cl})]_2$ (**2**) (Scheme 2), where QH is the diketal of $Hdap^+$. This mixture could be separated on the basis of the different solubility of its components in $CHCl_3$. The yield of **1** improved (69%, based on the stoichiometry shown in Scheme 2) in the presence of NEt_3 (Pd:dap:NEt_3 = 1:1:0.4). An increase in the amount of NEt_3 caused decomposition to palladium metal, decreasing the yield of **1** and increasing that of **2**. Methods for the monoketalization of dicarbonyl compounds are scarce, but some have been reported,[24] including a few giving ethyleneglycol monoketal derivatives of 2,6-diacetylpyridine.[25] Probably, $PdCl_2$ acts as an acid for the ketalization of one acetyl group. The electron-releasing capacity of the ketal group will favor the coordination of Pd to the pyridine N and, correspondingly, the

Scheme 6



(20) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
(21) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.
(22) Keypour, H.; Pritchard, R. G.; Parish, R. V. *Trans. Met. Chem.* **1998**, *23*, 609. Orrell, K. G.; Osborne, A. G.; Sik, V.; Dasilva, M. W. *Polyhedron* **1995**, *14*, 2797. Drew, M. G. B.; Nelson, J.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1678.
(23) Silong, B.; Engelhardt, L. M.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 1381.
(24) Flink, H.; Putkonen, T.; Sipos, A.; Jokel, R. *Tetrahedron* **2010**, *66*, 887. Grosu, I.; Muntean, L.; Toupet, L.; Ple, G.; Pop, M.; Balog, M.; Mager, S.; Bogdan, E. *Monatsh. Chem.* **2002**, *133*, 631. Koyanagi, J.; Yamamoto, K.; Nakayama, K.; Tanaka, A. *J. Heterocycl. Chem.* **1997**, *34*, 407. Camps, P.; Farres, X.; Mauleon, D.; Palomer, A.; Carganico, G. *Synth. Commun.* **1993**, *23*, 1739. Kym, P. R.; Carlson, K. E.; Katzenellenbogen, J. A. *J. Med. Chem.* **1993**, *36*, 1111. Schoening, A.; Debaerdemaeker, T.; Zander, M.; Friedrichsen, W. *Chem. Ber.* **1989**, *122*, 1119. Giri, V. S.; Maiti, B. C.; Pakrashi, S. C. *Heterocycles* **1985**, *23*, 71.
(25) Suh, J.; Kwon, W. J. *Bioorg. Chem.* **1998**, *26*, 103. Lama, M.; Mamula, O.; Scopelliti, R. *Synlett* **2004**, 1808.

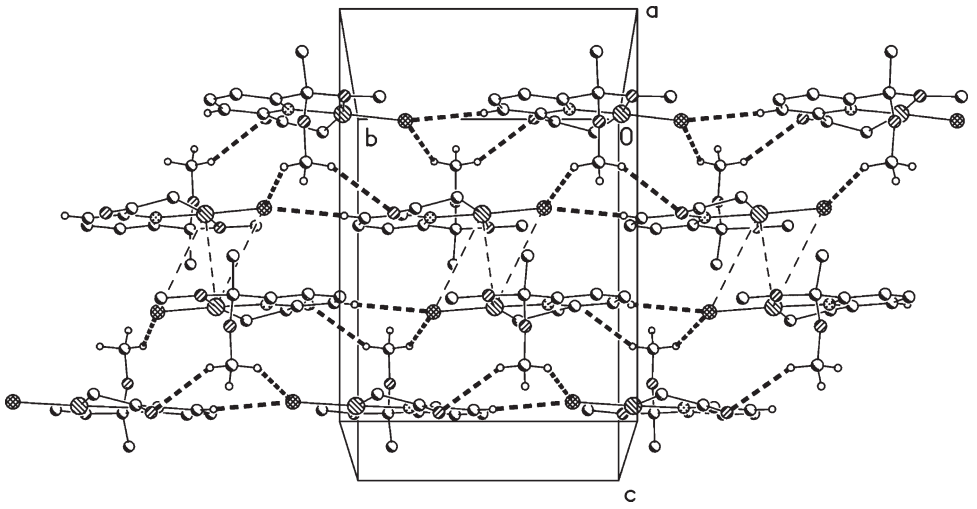


Figure 2. Packing diagram showing Pd···Pd and Pd···Cl contacts (thin dashed bonds) and C−H···Cl and C−H···O hydrogen bonds (thick dashed bonds) in complex **1**.

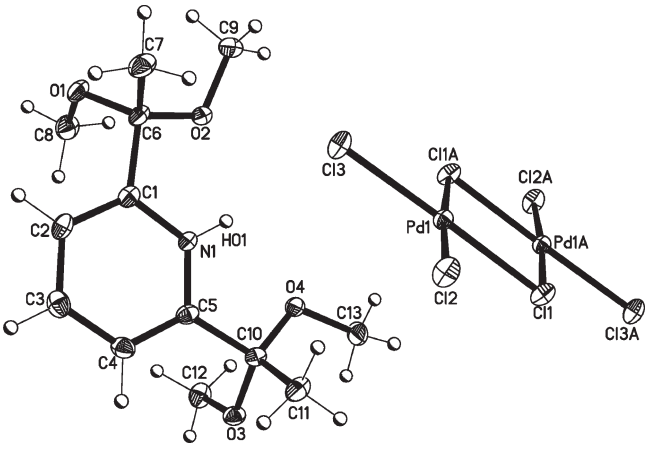


Figure 3. Ellipsoid representation of **2** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(3) = 2.2750(6), Pd(1)−Cl(2) = 2.2798(6), Pd(1)−Cl(1) = 2.3259(6), Pd(1)-Cl-(1A) = 2.3287(6), N(1)−C(5) = 1.344(3), N(1)−C(1) = 1.353(3), O(1)−C(6) = 1.410(3), O(2)−C(6) = 1.405(3), O(3)−C(10) = 1.415(2), O(4)−C(10) = 1.407(3), C(1)−C(6) = 1.526(3), C(5)−C(10) = 1.525(3), Cl(3)−Pd(1)−Cl(2) = 92.25(2), Cl(2)−Pd(1)−Cl(1) = 91.53(2), Cl(3)−Pd(1)−Cl(1A) = 91.04(2), Cl(1)−Pd(1)−Cl(1A) = 85.26(2), Pd(1)−Cl(1)−Pd(1A) = 94.735(19), N(1)−C-(1)−C(6) = 117.27(19), N(1)−C(5)−C(10) = 118.56(19), O(4)−C-(10)−C(5) = 104.23(16).

palladation of the other acetyl group. The full ketalization of dap in the presence of the formed HCl will give the corresponding pyridinium salt, which will react with $PdCl_2$ to afford complex **2**.

The reaction of **2** with 2 equiv of NEt_3 at room temperature in MeOH for 1 day gives the diketal of dap, Q = $C_5H_3N\{C(OMe)_2Me\}_2$-2,6 (**3**; Scheme 2), in 93% yield. The synthesis of this compound has not been reported, and our attempts to synthesize it using *para*-toluenesulfonic acid as catalyst were unfruitful. When the reaction was carried out using an excess of NEt_3, impure **3** was obtained. This compound is soluble in organic solvents and is stable in the solid state and in solution.

Reactions of 1 with Isocyanides. The reaction of **1** with 2 equiv of isocyanide at 0 °C (5 min for R = Xy, 20 min for R = ^{t}Bu) afforded *trans*-[Pd(C^1-L)Cl(CNR)$_2$] (R = Xy (**4a**), ^{t}Bu (**4b**); Scheme 3, solid arrow). However, at 25 °C this reaction led to the isolation of [Pd(O^2,C^2-L_R)(CNR)Cl] (R = ^{t}Bu, **5b**), whereas the corresponding product with R = Xy (**5a**) could only be isolated in impure form (see below). Complexes **5** are probably formed from **4** after insertion of one isocyanide into the Pd−C bond plus a tautomerization process from β-ketoimine to β-ketoenamine that converts the ligand C^1-L into O^2,C^2-L_R (Scheme 3, dashed arrows). The reaction of complex **1** with 1 equiv of isocyanide at 0 °C gave a mixture of [Pd(N^1,C^1-L)Cl(CNR)] (Scheme 3, R = Xy (**6a**), ^{t}Bu (**6b**)), **4**, and unreacted **1** (85:9:6 molar ratios).

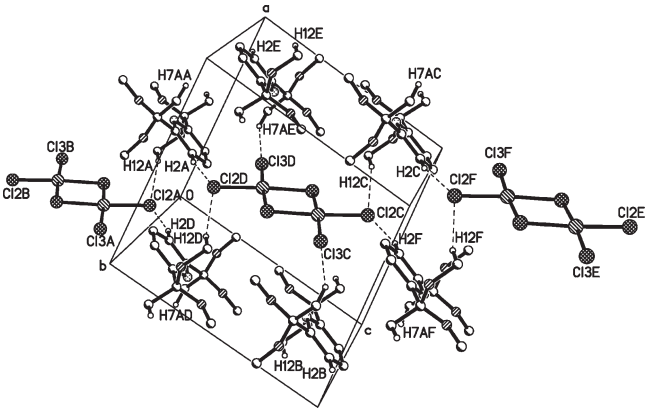


Figure 4. Packing diagram showing the hydrogen bonds between terminal Cl atoms of the anion and Me and MeO groups of cations in complex **2**.

The reaction of **1** with 1 equiv of RNC at room temperature afforded the pincer complex [Pd(O^1,N^1,C^2-L_R)Cl] (R = Xy (**7a**), ^{t}Bu (**7b**); Scheme 4) probably resulting from insertion/tautomerization processes similar to those leading to **5** from **4**. Complex **7b** was better prepared in refluxing $CHCl_3$, but **7a** had to be prepared at room temperature over 10 days because refluxing in $CHCl_3$ (1.5 h) led to mixtures, the main component of which was the Pd(I) complex $[PdCl(CNXy)_2]_2$. We have reported a similar behavior when studying the reactivity of $[Pd\{CH_2C(O)Me\}Cl]_n$ toward isocyanides.[6] Complexes **7** reacted at 0 °C (1) with 2 equiv of RNC to give

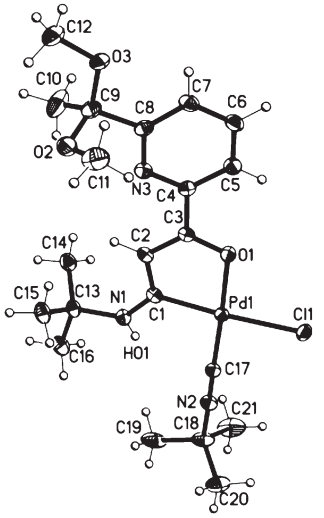


Figure 5. Ellipsoid representation of one of the two independent molecules in complex **5b** (50% probability). Selected bond lengths (Å) and angles (deg) for $\mathbf{5b_1}$: Pd(1)−C(17) = 1.914(3), Pd(1)−C(1) = 1.988(3), Pd(1)−O(1) = 2.021(2), Pd(1)−Cl(1) = 2.3846(8), Pd(1)−Pd(1′) = 3.1652(3), O(1)−C(3) = 1.293(4), C(1)−N(1) = 1.324(4), C(1)−C(2) = 1.412(4), N(1)−C(13) = 1.498(4), C(2)−C(3) = 1.386(4), C(3)−C(4) = 1.492(4), C(17)−N(2) = 1.150(4), C(17)−Pd(1)−C(1) = 95.89(12), C(1)−Pd(1)−O(1) = 82.15(10), C(17)−Pd(1)−Cl(1) = 88.92(8), O(1)−Pd(1)−Cl(1) = 93.00(6), C(17)−Pd(1)−Pd(2) = 82.29(8), C(1)−Pd(1)−Pd(1) = 81.80(8), O(1)−Pd(1)−Pd(1) = 99.98(6), Cl(1)−Pd(1)−Pd(1) = 99.87(2), C(3)−O(1)−Pd(1) = 111.24(18), C(2)−C(1)−Pd(1) = 111.2(2), C(3)−C(2)−C(1) = 114.2(3), O(1)−C(3)−C(2) = 120.9(3). $\mathbf{5b_2}$: Pd(1′)-C(17′) = 1.912(3), Pd(1′)−C(1′) = 1.978(3), Pd(1′)−O(1′) = 2.048(2), Pd(1′)−Cl(1′) = 2.3956(7), O(1′)−C(3′) = 1.289(4), C(1′)−N(1′) = 1.326(4), C(1′)−C(2′) = 1.408(4), C(2′)−C(3′) = 1.389(4), C(3′)−C(4′) = 1.487(4), C(17′)−Pd(1′)−C(1′) = 92.04(12), C(1′)−Pd(1′)−O(1′) = 82.21(11), C(17′)−Pd(1′)−Cl(1′) = 90.47(9), O(1′)−Pd(1′)−Cl(1′) = 94.58(6), C(17′)−Pd(1′)−Pd(1) = 98.63(9), C(1′)−Pd(1′)−Pd(1) = 82.68(9), O(1′)−Pd(1′)−Pd(1) = 92.18(6), Cl(1′)−Pd(1′)−Pd(1) = 100.62(2), C(3′)−O(1′)−Pd(1′) = 109.42(18), C(2′)−C(1′)−Pd(1′) = 111.1(2), C(3′)−C(2′)−C(1′) = 114.0(3), O(1′)−C(3′)−C(2′) = 121.8(3).

trans-[Pd(C^2-L_R)Cl(CNXy)$_2$] (R = Xy (**8a**), ^{t}Bu (**8b**)) or (2) with 1 equiv of RNC to afford **5**. This is a better way to prepare **5b** than the reaction **1** with 2 equiv of ^{t}BuNC. The corresponding reaction with XyNC gave **5a** contaminated with **7a** and **8a** (81:15:4), which is the same irresolvable mixture obtained by reacting **1** with 2 equiv of XyNC (see above), suggesting that complexes **7** are intermediates in the synthesis of **5** from **1** (Scheme 3).

Reaction Pathways. The reaction of **1** with 1 equiv of isocyanide was monitored by ^{1}H NMR at 0 °C (Scheme 3). The intermediate **6** was first observed, but, as it reacts with isocyanide to afford **4**, it could only be isolated mixed with **4** and **1**.

The 10-day reaction of **1** with 1 equiv of XyNC at 25 °C was monitored by ^{1}H NMR, showing the initial formation of **6a** along with minor amounts of **4a** (Scheme 5). Their concentrations' decrease was accompanied by the formation of **7a** and traces of **5a** and **8a**. Through the 10-day period the concentration of **7a** increased and that of **1** remained constant (ca. 4% of the initial concentration). These data and those mentioned above suggest that complexes **1** and **4**−**8** are related through the reactions shown in Scheme 5.

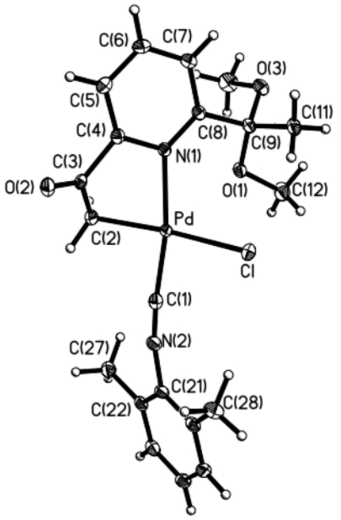


Figure 6. Ellipsoid representation of **6a** (50% probability). Selected bond lengths (Å) and angles (deg): Pd−C(1) = 1.9037(15), Pd−C(2) = 2.0558(14), Pd−N(1) = 2.1169(12), Pd−Cl = 2.4001(4), C(1)−N(2) = 1.156(2), N(2)−C(21) = 1.4044(18), C(2)−C(3) = 1.477(2), C(3)−O(2) = 1.2205(18), C(3)−C(4) = 1.505(2), C(4)−N(1) = 1.3557(18), N(1)−C(8) = 1.3462(18), C(8)−C(9) = 1.537(2), C(9)−O(1) = 1.4044(17), C(9)−O(3) = 1.4228(18), C(10)−O(3) = 1.432(2), C(12)−O(1) = 1.4358(18), C(1)−Pd−C(2) = 90.24(6), C(2)−Pd−N(1) = 79.90(5), C(1)−Pd−Cl = 87.31(5), N(2)−C(1)−Pd = 172.58(13), C(1)−N(2)−C(21) = 168.61(14), C(3)−C(2)−Pd = 94.11(9), C(2)−C(3)−C(4) = 111.86(12), N(1)−C(4)−C(3) = 112.59(12), C(8)−N(1)−Pd = 135.13(10), C(4)−N(1)−Pd = 105.73(9), N(1)−C(8)−C(9) = 120.67(13).

The ^{1}H NMR monitoring of the reactions of **1** with 2 equiv of the isocyanide at 25 °C showed the formation of **4** and its conversion into **5**, as proposed above (Scheme 3). The final product was **5**, along with minor amounts of **7**, **8**, and [PdCl(CNR)$_2$]$_2$. The reaction was faster with XyNC (Scheme 5).

A ^{1}H NMR study of the behavior of **4a** at 25 °C in $CDCl_3$ showed that it decomposes initially to **6a**, and later formation of **5a**, **7a**, and **8a** was observed. After 2 days **4a** and **6a** had disappeared, while the amounts of **5a** and **8a** increased over 48 h and 25 min, respectively, and then decreased, and the amount of **7a** increased continuously. Perhaps the transformation of **8a** into the Pd(I) complex [PdCl(CNXy)$_2$]$_2$ (a radical mechanism might reasonably be assumed) could explain the concentration decrease of **5a** and **8a**. In fact, a ^{1}H NMR study of the behavior of **8a** at 25 °C in $CDCl_3$ showed that it decomposed after 5 days to [PdCl(CNXy)$_2$]$_2$ (**8a**:[PdCl(CNXy)$_2$]$_2$ = 4; minor amounts of **5a** and traces of **7a** were also observed). This can explain why the attempt to prepare **7a** by refluxing a 1:1 mixture of **1** and XyNC gave mainly [PdCl(CNXy)$_2$]$_2$. Complex **4b** behaves similarly, but all processes were much slower. Thus, after 4 days the **4b**:**6b**:**7b**:**5b**:**8b** molar ratios are 3:0:4:88:5.

Reactions of [Pd(O^1,N^1,C^1-L)Cl] (1) with P-, N-, or O-Donor Ligands. The reaction of complex **1** with PPh_3 gave similar results to those with isocyanides. Thus, at 0 °C the equimolecular reaction led to the expected product [Pd(N^1,C^1-L)Cl(PPh_3)] (**12**) along with **1** (5%) and *trans*-[Pd(C^1-L)Cl(PPh_3)$_2$] (**13**) (5%) (Scheme 6). This prevented the isolation of pure **12**. The reaction with 2 equiv of PPh_3 gave complex **13**, but it could not be obtained analytically pure

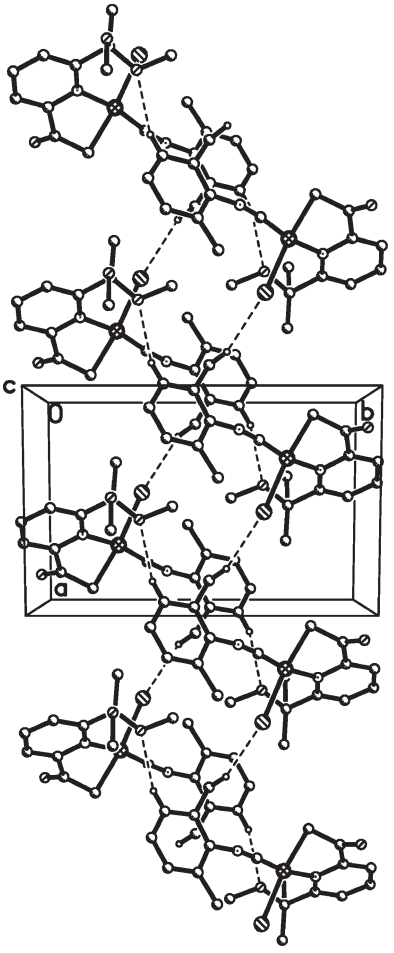


Figure 7. Packing diagram showing the hydrogen bonds in complex **6a**.

because traces of an unidentified impurity containing PPh_3 could not be separated. The ^1H NMR spectrum of the reaction mixture obtained from **1** and an excess of PPh_3 (1:5.5) showed, almost instantly, the presence of a mixture of the monoketal of dap, $C_5H_3N\{C(O)Me\text{-}2\}\{C(OMe)_2Me\text{-}6\}$ (**14**), $[Pd(PPh_3)_4]$, and its dissociation products $[Pd(PPh_3)_3]$ and PPh_3 as well as traces of dap. This was formed by hydrolysis of **14**, because the traces of water initially observed in the spectrum disappeared. Probably, the formed hydroxo Pd(II) complex is reduced by PPh_3 to $[Pd(PPh_3)_3]$. The excess of PPh_3 precluded separation of the mixture by recrystallization, and TLC chromatography using silica gel led to the hydrolysis of **14** to give dap.

Complex **1** reacted with 2,2′-bipyridine (bpy) or 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbpy) to afford the adducts $[Pd(C^1\text{-}L)Cl(N\text{^}N)]$ (N^N = bpy (**10**), dbbpy (**11**)) (Scheme 6) and with [Tl(acac)] to give [Pd(L)(acac)] (**9**).

Crystal Structures. The crystal structures of complexes **1** (Figures 1 and 2), **2** (Figures 3 and 4), **5b** (Figure 5), **6a** (Figures 6 and 7), and **7a** (Figures 8 and 9) have been determined (Table 1, SI). All show a nearly square-planar coordination around the palladium atom. Crystals apparently suitable for an X-ray crystallographic study were selected for **5a**. Although a complete crystallographic analysis was not possible, because of severely disordered methoxy groups, the position of the ligands was established with certainty to be that indicated in Scheme 3.

In complex **1** (Figure 1), the three rings of the coordinated pincer ligand are almost coplanar, the angle between the mean

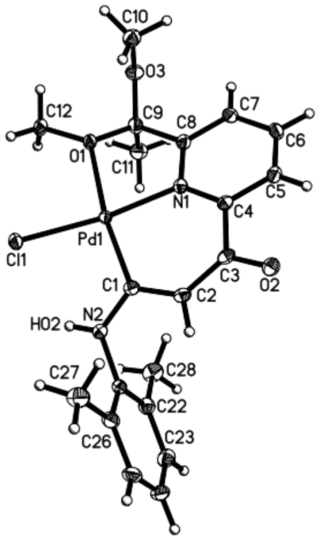


Figure 8. Ellipsoid representation of **7a** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 1.9492(17), Pd(1)−N(1) = 2.0257(15), Pd(1)−O(1) = 2.1673(12), Pd(1)−Cl(1) = 2.3022(5), O(1)−C(9) = 1.443(2), N(1)−C(4) = 1.349(2), N(1)−C(8) = 1.352(2), C(1)−N(2) = 1.351(2), C(1)−C(2) = 1.379(2), N(2)−C(21) = 1.443(2), C(2)−C(3) = 1.418(3), C(3)−O(2) = 1.242(2), C(3)−C(4) = 1.515(2), C(8)−C(9) = 1.534(2), C(9)−O(3) = 1.389(2), C(1)−Pd(1)−N(1) = 92.73(7), N(1)−Pd(1)−O(1) = 79.19(5), C(1)−Pd(1)−Cl(1) = 93.60(5), N(1)−Pd(1)−Cl(1) = 172.35(4), O(1)−Pd(1)−Cl(1) = 94.99(3), C(9)−O(1)−Pd(1) = 110.19(10), C(4)−N(1)−Pd(1) = 126.05(12), C(8)−N(1)−Pd(1) = 114.51(12), C(2)−C(1)−Pd(1) = 122.75(13), C(1)−N(2)−C(21) = 122.71(15), C(1)−C(2)−C(3) = 128.73(16), O(2)−C(3)−C(2) = 122.29(16), O(2)−C(3)−C(4) = 115.73(16), C(2)−C(3)−C(4) = 121.71(16), N(1)−C(4)−C(3) = 121.87(16), N(1)−C(8)−C(9) = 119.09(15), O(1)−C(9)−C(8) = 105.70(14), C(22)−C(21)−N(2) = 118.60(16).

planes of the py ring and the palladacycles PdNCCO and PdNCC(O)C being 3.9° and 2.6°, respectively. The molecules are connected by Pd···Pd (3.3460(3) Å) and Pd···Cl (3.9016(6) Å) contacts (van der Waals radii of Pd: 2.05 Å and Cl: 1.8 Å[26]), giving dimers that form layers via C−H···Cl and C−H···O hydrogen bonds (Figure 2).

In complex **2** (Figure 3), the $[Pd_2Cl_6]^{2-}$ anion lies across an inversion center with each palladium atom in a square-planar environment. The geometrical parameters of the anion agree with those found in other $[Pd_2Cl_6]^{2-}$ salts.[27] Anions and cations are connected by hydrogen bonds between terminal Cl atoms of the anion and Me and MeO groups of cations (Figure 4).

In **5b** (Figure 5), two crystallographically independent molecules are present in the unit cell with a strong intermolecular Pd−Pd interaction (3.1652(3) Å)[26] within the asymmetric unit. The angle between the coordination planes of these two molecules is 6.6°. In **6a** (Figure 6), the metal is in a very distorted square-planar coordination; the mean deviation from the coordination plane is 0.12 Å, with the CH_2 carbon 0.16 Å and the chlorine atom 0.13 Å out of this plane. This distortion might be attributable to the steric hindrance of the uncoordinated ortho substituent. The chlorine atom lies +1.911 Å and C(9) −0.124 Å out of the plane of the pyridyl ligand and the

(26) Batsanov, S. S. *Inorg. Mater.* **2001**, *37*, 871.
(27) Chitanda, J. M.; Quail, J. W.; Foley, S. R. *Acta Crystallogr. Sect. E* **2008**, *64*, m907. Fábry, J.; Dusek, M.; Fejfarová, K.; Krupková, R.; Vanek, P.; Nemec, I. *Acta Crystallogr. Sect. C* **2004**, *60*, m426.

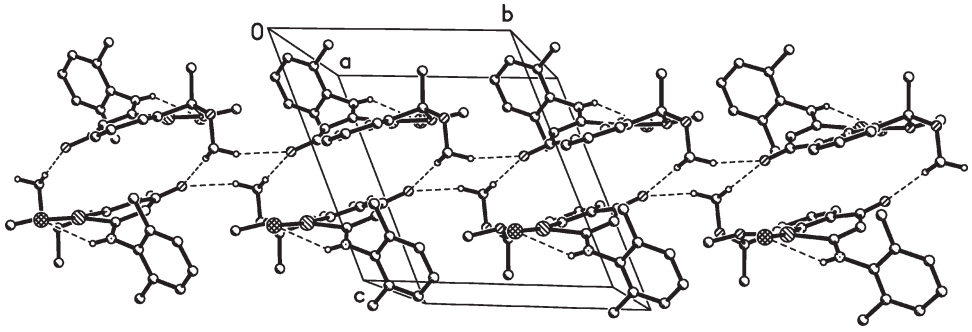


Figure 9. Packing diagram showing the hydrogen bonds in complex **7a**.

palladium atom (mean deviation 0.070 Å). The molecules of **6a** are connected through CH···OMe hydrogen bonds, giving dimers that form double chains along the *a* axis via the hydrogen bond of one Me and the chlorine atom (Figure 7).

The structure of **7a** (Figure 8) shows the metal in a slightly distorted square-planar coordination, the mean deviation from the coordination plane being 0.081 Å. The complex has two palladacycles; the five-membered ring has an envelope conformation with the sp^3 carbon out of the ring plane, and the six-membered ring has a boat conformation, with the CO carbon and the palladium atom out of the plane. Each molecule has one classical intramolecular N−H···Cl hydrogen bond and four nonclassical C−H···O hydrogen bonds, affording a double chain (Figure 9).

The structures of complexes **5b** and **7a** show that Pd and the Xy group are mutually trans, as shown in Schemes 3 and 4. Although a complete X-ray crystallographic study was not possible for **5a**, the same geometry around the PdC−NHXy bond was established with certainty, which was also observed in other β-ketoenamine complexes previously described by us.[6] In addition, both have a high degree of electron delocalization over the OCCCN group, as shown in Scheme 5 because (1) it is almost planar (mean deviation of the five atoms from the mean plane 0.034°, 0.020° (for the two molecules of **5b**) and 0.051° (**7a**), respectively), (2) the C−O bond distance is longer (**5b**: 1.293(4), 1.289(4) Å; **7a**: 1.242(2) Å) than in **1** (1.217(3) Å) or **6a** (1.2205(18) Å), (3) the C(1)−C(2) distances (**5b**: 1.412(4) Å, 1.408(4); **7a**: 1.379(3) Å) and C(2)−C(3) (**5b**: 1.386(4), 1.389(4) Å; **7a**: 1.418(2) Å) are intermediate between that of a single (O)*C*−*C*=C (1.464 Å) and a double (O)C−*C*=*C* bond (1.340 Å),[28] and (4) the C−N bond distances (**5b**: 1.324(4), 1.326(4) Å; **7a**: 1.351(2) Å) are intermediate between that of a single R_2N-CH_2Pd bond (mean value, 1.450 Å)[29] and a double XyNH=C(Me)Pd bond (ca. 1.30 Å).[30]

The Pd−CH_2 bond distance is longer in **6a** (2.0558(14) Å) than in **1** (2.000(2) Å), showing the greater trans influence of the Cl ligand than the O-donor ligand. The Pd−N bond distances decrease in the series **6a** (2.1169(12) Å), **7a** (2.0257(15) Å), **1** (1.9752(19) Å), because the angle between the coordination and pyridine planes decreases (44.3°, 18.4°, 5.8°), thus favoring the Pd to pyridine π-back-bonding and also because of the greater trans influence of the XyNC than the Cl ligand. The Pd−Cl bond distances in complexes **1** and **7a** (2.3040(5) and 2.3022(5) Å) are shorter than those in **5b** (2.3846(8), 2.3956(7) Å) and **6a** (2.4001(4) Å), attributable to the lower trans influence of a N-donor ligand than a C-donor ligand.

Spectroscopic Properties. The ^1H and $^{13}C\{^1H\}$ NMR spectra of all compounds are in agreement with the structures shown in Schemes 2−6, except for the MeO protons and the corresponding carbons, which appear as only one resonance corresponding to the six protons or the two carbons, respectively, in the ranges δ 3.08−3.47 and 49−52.2 ppm, respectively. The exchange of these MeO groups cannot be slowed down enough at −60 °C to see the expected two resonances in their spectra, but they coalesce at this temperature in complex **1**. The ^1H and $^{13}C\{^1H\}$ NMR methyl resonances of the *Me*C(OMe)$_2$ group appear as singlets in the ranges δ 1.48−2.03 and 23−26.3 ppm, respectively.

The ketonyl complexes (**1**, **4**, **6**, **9**−**11**) show the CH_2 protons as singlets in the range δ 3.73−3.35. In the case of **6**, the equivalence of the CH_2 protons can be explained assuming a fast equilibrium with the cationic [Pd(O^1,N^1,C^1-L)(CNR)]Cl. These protons are less shielded than the CH_2 of the acetonyl palladium complexes [Pd$_2${CH_2C(O)Me}$_2$(μ-Cl)$_2$(CNR)$_2$], *trans*-[Pd{CH_2C(O)Me}Cl(CNR)$_2$], and [Pd{CH_2C(O)Me}(CNR)$_3$]TfO (R = XyNC, ^{t}BuNC; range δ 3.18−2.61),[6] caused by the pyridine group. As expected, for isocyanide complexes **4** and **6**, the CH_2 protons are more shielded for ^{t}BuNC (**4b**: 3.35; **6b**: 3.27) than XyNC (**4a**: 3.73; **6a**: 3.44) complexes. The NH proton in L_R palladacyclic complexes **5** and **7** appears as a broad resonance in the range 6.00−8.65 ppm, shielded with respect to that in the monocoordinate L_R ligands (**8a**: 13.68; **8b**: 12.96), which supports the proposal of an intramolecular hydrogen bond in the latter (Scheme 4). Again, the NH proton is more shielded for R = ^{t}Bu (**7b**: 7.63; **8b**: 12.96) than for Xy (**7a**: 8.65; **8a**: 13.68). The C*H*C(O) proton is weakly coupled with the NH proton for **5a** or **5b** (6.45 or 5.86 ppm, J = 1 Hz), but it appears as a singlet for **7a**, **8a**, or **8b** (4.67, 7.22, or 6.86 ppm) or a broad signal for **7b** (5.17 ppm).

In the ^1H NMR spectrum of **9** at room temperature, the Me acac protons appear as a broad resonance, but at −40 °C this resolves into two signals, which could be associated with an equilibrium between [Pd(N^1,C^1-L)(O,O-acac)] and [Pd(O^1,N^1,C^1-L)(*C*-acac)]. However, in the $^{13}C\{^1H\}$ NMR spectrum, the two Me acac carbon nuclei resonate as two broad singlets at room temperature.

The IR spectra of chloro complexes show a band assignable to ν(PdCl) at various wavenumbers depending on the nature of the ligands in trans position. Thus, complexes with chloro trans to a N-donor ligand (**1**, **7**, **10**, **11**) show ν(PdCl) absortion in the range 337−321 cm^{-1}, while in complexes with chloro trans to a C-donor ligand (**4**, **6**, **8**, **12**, **13**) the absorption is observed in the range 290−280 cm^{-1}, in

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

(29) Enzmann, A.; Eckert, M.; Ponikwar, W.; Polborn, K.; Schneiderbauer, S.; Beller, M.; Beck, W. *Eur. J. Inorg. Chem.* **2004**, 1330. Miki, K.; Tanaka, N.; Kasai, N. *Acta Cristallogr., Sect. B* **1981**, *37*, 447.

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

agreement with the stronger trans influence of a C-donor ligand with respect to a N-donor ligand.

The ketonyl complexes **1**, **4**, and **9**−**11** show the ν(C═O) absortion in the range 1684−1608, cm^{-1}, while in complexes **5**, **7**, and **8** the ν(C═O) appears at lower frequency, 1590−1538 cm^{-1}, showing the reduction of the C−O bond order, consistent with the results of the X-ray diffraction study of complexes **5b** and **7a** and attributable to the electron delocalization over the OCCCNC group of the β-ketoenamine ligand.

The IR spectra of complexes with the ligand XyNC show the ν(N≡C) band in the region 2192−2175 cm^{-1} and those with ^{t}BuNC in the narrow range 2211−2208 cm^{-1}, showing, as usual, an increase with respect to ν(CN) in the free ligands (2109 and 2134 cm^{-1}, respectively).

Conclusion

2,6-Diacetylpyridine can be palladated using $PdCl_2$ in methanol via its transformation into its dimethylketal. The resulting complex, which contains the monoanionic pincer ligand resulting from the deprotonation of the acetyl methyl group of the monoketal of dap, reacts with isocyanides, giving complexes resulting from coordination or/and insertion of the isocyanide followed by a tautomerization process from β-ketoimine to β-ketoenamine. The reaction pathway has been studied at different molar ratios and temperatures.

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 a grant to F.J.-H.

Supporting Information Available: Listing of all crystal data, refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles and CIF files for compounds **1**, **2**, **5b**, **6a**, and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.