Reactivity of [Pd{$CH_2C(O)Me$}Cl]$_n$ toward Isocyanides

José Vicente,* Aurelia Arcas, and Jesús M. Fernández-Hernández

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

Delia Bautista‡

S.A.C.E. Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

Peter G. Jones§

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

Received December 16, 2004

[Pd{$CH_2C(O)Me$}Cl]$_n$ (**1**) reacts at low temperature with RNC (RNC:Pd = 1 or 2) to give [Pd$_2$\{$CH_2C(O)Me$\}$_2$(μ-Cl)$_2$(CNR)$_2$] [R = ^{t}Bu (**2a**), Xy (**2b**)] or *trans*-[Pd{$CH_2C(O)Me$}Cl(CNR)$_2$] [R = ^{t}Bu (**5a**), Xy (**5b**)], respectively. These complexes decompose at room or higher temperature to give [Pd$_2$\{κ^2-*C,O*-C(NHR)CHC(O)Me\}$_2$(μ-Cl)$_2$] [R = ^{t}Bu (**3a**), Xy (**3b**)] or [Pd\{κ^2-*C,O*-C(NHR)CHC(O)Me\}Cl(CNR)] [R = ^{t}Bu (**6a**), Xy (**6b**)], respectively, via insertion of the isocyanide into the Pd−C bond plus a tautomerization process from β-ketoimine to β-ketoenamine. The complex [Pd\{κ^2-*C,O*-C(NHXy)CHC(O)Me\}Cl(NCMe)] (**4b**) can be obtained by reacting **1** with XyNC (Pd:XyNC = 1) in MeCN or complex **3b** in $CHCl_3$ with excess MeCN. Complexes *trans*-[Pd{C(NHR)=CHC(O)Me}Cl(CNR)$_2$] [R = ^{t}Bu (**8a**), Xy (**8b**)] can be obtained (i) by reacting **1** with RNC (RNC:Pd = 3) or better (ii) by reacting **6** with 1 equiv of RNC at low temperature. The Pd(I) complexes [Pd$_2$Cl$_2$(CNR)$_4$] [R = ^{t}Bu (**7a**), Xy (**7b**)] are decomposition products obtained by heating **1** with RNC (RNC:Pd = 4−5), but they are detected in trace amounts in the reaction of **1** with RNC (RNC:Pd = 2−3). Addition of RNC and KTfO to a cooled suspension of **1** (Pd:RNC:KTfO = 1:3:1) gives complexes [Pd{$CH_2C(O)Me$}(CNR)$_3$]TfO [R = ^{t}Bu (**9a**), Xy (**9b**)], which decompose at room temperature. The decomposition of **9b** gives [Pd\{κ^2-*C,O*-C(NHXy)CHC(O)Me\}(CNXy)$_2$]TfO (**10b**), which can be obtained, as can the corresponding **10a**, by reacting complexes **6** with 1 equiv of TlTfO and RNC. The reactions of the dimers **3** with PPh_3 (Pd:PPh_3 = 1) gives [Pd\{κ^2-*C,O*-C(NHR)CHC(O)Me\}Cl(PPh_3)] [R = ^{t}Bu (**11a**), Xy (**11b**)], with PEt_3 (PEt_3:Pd = 2), *trans*-[Pd{C(NHR)=CHC(O)Me}Cl(PEt_3)$_2$] [R = ^{t}Bu (**12a**), Xy (**12b**)], and with Tl(acac) (Pd:acac = 1), [Pd\{κ^2-*C,O*-C(NHR)CHC(O)Me\}(κ-*O,O*-acac)] [R = ^{t}Bu (**13a**), Xy (**13b**)]. The crystal structures of **6a**, **9b**, **10a**, and **10b** have been determined. In complex **10b** there are intermolecular $\pi-\pi$ stacking and C−H···Pd agostic interactions giving dimers.

Introduction

Palladium(II) enolates play an important role in organic synthesis.[1] However, most of the isolated species are actually ketonyl complexes ([Pd]CRR′C(O)R″)[2−9] (sometimes wrongly called C-enolates). The few genuine palladium(II) enolates ([Pd]OCR=CR′R″) adopt this coordination mode because of (i) the strong *transphobia*[10,11] between C-donor/C-donor and C-donor/P-donor ligands,[8,12] (ii) steric effects,[8,13] or (iii) the preferred coordination of the ligand as a chelate (e.g., *O,O*-acetylacetonato complexes, *O,P*-carbonyl-functionalized phosphines,[14] *O,N*-oxopropionaldehyde phenylhydrazones[15]). In this paper, we report a family of palladium complexes containing a new O,C-chelating enolato ligand.

Among the known ketonyl complexes, only a few are acetonyls. The established synthetic procedures for

* Corresponding author regarding the synthesis of complexes. E-mail: jvs1@um.es.

‡ Corresponding author regarding the X-ray diffraction study of complexes **9b**, **10a**, and **10b**. E-mail: dbc@um.es.

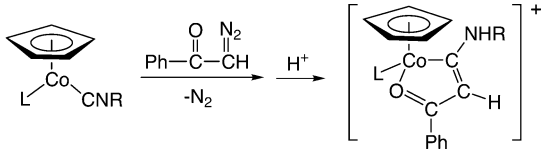
§ Corresponding author regarding the X-ray diffraction study of complex **6a**. E-mail: p.jones@tu-bs.de.

(1) See for example: Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. Mitsudo, T.; Kadokura, M.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 3186. Sodeoka, M.; Ohrai, K.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 2648. Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450. Sodeoka, M.; Tokunoh, R.; Miyazaki, F.; Hagiwara, E.; Shibasaki, M. *Synlett* **1997**, *463*. Nokami, J.; Mandai, T.; Watanabe, H.; Ohyama, H.; Tsuji, J. *J. Am. Chem. Soc.* **1989**, *111*, 4126. Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108. Sole, D.; Peidro, E.; Bonjoch, J. *Org. Lett.* **2000**, *2*, 2225. Fox, J. M.; Huang, X. H.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360. Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1473. Shaughnessy, K. H.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1998**, *63*, 6546. Sugiura, M.; Nakai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2366. Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382. Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1740. Hamada, T.; Chieffi, A.; Åhman, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1261. Culkin, D. A.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234.

10.1021/om048999c CCC: $30.25
Publication on Web 04/14/2005

these complexes invariably involve the presence of other strongly coordinated ligands, such as PPh_3,[2,5] *N,N,N′,N′*-tetramethylethylenediamine,[6] C_6F_5, $AsPh_3$,[7] or *o*-$C_6H_4CH_2NMe_2$.[7] However, we have previously reported the synthesis of the simple acetonylpalladium(II) complex [Pd{$CH_2C(O)Me$}Cl]$_n$ (**1**), obtained by transmetalation reactions employing [Hg{$CH_2C(O)Me$}$_2$] and [$PdCl_2(MeCN)_2$] or (NMe_4)[Pd_2Cl_6].[9] Complex **1** has the potential, after cleaving the acetonyl and/or chloro bridges,[16] or by subsequent chloro replacement, to prepare any chloro-monoacetonyl or monoacetonyl palladium(II) complex, whereby the other two or three ligands can be chosen freely. In this paper we illustrate both possibilities by reacting **1** with isocyanides, which leads to complexes of the types [Pd{$CH_2C(O)Me$}Cl(CNR)$_n$] (n = 1, 2) and [Pd{$CH_2C(O)Me$}(CNR)$_3$]$^+$. In addition, these are slowly converted to the first complexes containing the chelating κ^2-*C,O*-C(NHR)=CHC(O)Me (R = ^{t}Bu, Xy) ligand, resulting from insertion of the isocyanide into the Pd−$CH_2C(O)Me$ bond and a subsequent β-ketoimine to β-ketoenamine tautomerization process. This chelating mode of coordination has not been observed previously in the chemistry of palladium because, as mentioned above, the known precursors do not have the required *cis* coordination position available to allow a chelating coordination, or they do not insert the isocyanide. Thus, *trans*-[Pd{$CH_2C(O)R$}Cl(PPh_3)$_2$] reacts with isocyanides to give *trans*-[Pd{C(NHR)=CHC(O)R′}Cl(PPh_3)$_2$] (R = Me, *p*-C_6H_4OMe, R′ = Me;[2] R = ^{t}Bu, R′ = Ph[4]). In the proposed mechanism,[4] the first step was coordination of the isocyanide followed by an insertion/tautomerization process, but the intermediate adduct was not isolated. In contrast, the reaction of some aryl acetonyl palladium(II) complexes with ^{t}BuNC has been reported to give the corresponding adducts, but no insertion products were obtained.[7] Therefore, we report here for the first time the isolation of both types, adducts and insertion/tautomerization products of isocyanides into the Pd−$CH_2C(O)R$ bond. A search of the Cambridge Structural Database of metallacycles M{κ^2-*C,O*-C(NH(C)CHC(O)Me)} (M = any metal) reveals only one crystal structure, corresponding to a cobalt complex (R CH(Ph)Me, R′ = Ph; Scheme 1) obtained through a carbene attack on a coordinated isocyanide ligand, followed by a reaction with HBF_4.[17]

Scheme 1



The β-ketoenamines, also called enaminones, are important organic intermediates[18] having interesting biological activity.[19] Although *O*-[20] and *N,O*-β-ketoenamine[21] complexes are well-known, the only organometallic derivatives fully characterized (R_2N−C(M)=C(R)−C(=O)R or R_2N−C(R)=C(M)−C(=O)R, R = H, any organic group; M = any metal) are the above-mentioned complex [Pd{C(NHR)=CHC(O)R′}Cl(PPh_3)$_2$] (R = ^{t}Bu, R′ = Ph)[4] and the Co complex shown in Scheme 1.[17]

Experimental Section

Unless otherwise stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were

(2) Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15.
(3) Wanat, R. A.; Collum, D. B. *Organometallics* **1986**, *5*, 120. Yoshimura, N.; Murahashi, S.; Moritani, I. *J. Organomet. Chem.* **1973**, *52*, C58. Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30. Byers, P. K.; Canty, A. J.; Skelton, B. W.; Traill, P. R.; Watson, A. A.; White, A. H. *Organometallics* **1992**, *11*, 3085. Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Bautista, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3093. Tian, G.; Boyle, P. D.; Novak, B. M. *Organometallics* **2002**, *21*, 1462. Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **2001**, *20*, 995. Suzaki, Y.; Yagyu, T.; Yamamura, Y.; Mori, A.; Osakada, K. *Organometallics* **2002**, *21*, 5254.
(4) Veya, P.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.
(5) Suzuki, K.; Yamamoto, H. *Inorg. Chim. Acta* **1993**, *208*, 225. Albeniz, A. C.; Catalina, N. M.; Espinet, P.; Redon, R. *Organometallics* **1999**, *18*, 5571.
(6) Vicente, J.; Abad, J. A.; Chicote, M. T.; Abrisqueta, M.-D.; Lorca, J.-A.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 1564.
(7) Ruiz, J.; Rodríguez, V.; Cutillas, N.; Pardo, M.; Pérez, J.; López, G.; Chaloner, P.; Hitchcock, P. B. *Organometallics* **2001**, *20*, 1973.
(8) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398.
(9) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2001**, *20*, 2767.
(10) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066. Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848.
(11) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454.
(12) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *J. Am. Chem. Soc.* **1981**, *103*, 4945. Ooi, S.; Matsushita, T.; Nishimoto, K.; Nakamura, Y.; Kawaguchi, S.; Okeya, S. *Inorg. Chim. Acta* **1983**, *76*, L55. Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chem.* **1996**, *35*, 3064.
(13) Kujime, M.; Hikichi, S.; Akita, M. *Organometallics* **2001**, *20*, 4049.
(14) Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 799. Andrieu, J.; Braunstein, P.; Dusausoy, Y.; Ghermani, N. E. *Inorg. Chem.* **1996**, *35*, 7174. Balegroune, F.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 3320. Matt, D.; Ingold, F.; Balegroune, F.; Grandjean, D. *J. Organomet. Chem.* **1990**, *399*, 349.
(15) Albert, J.; González, A.; Granell, J.; Moragas, R.; Puerta, C.; Valerga, P. *Organometallics* **1997**, *16*, 3775.
(16) Masciocchi, N.; Ragaini, F.; Sironi, A. *Organometallics* **2002**, *21*, 3489.
(17) Strecker, B.; Zeier, B.; Schulz, M.; Wolf, J.; Werner, H. *Chem. Ber.* **1990**, *123*, 1787.
(18) Greenhill, J. V. *Chem. Soc. Rev.* **1977**, *6*, 277. Rappoport, Z. *The Chemistry of Enamines*; Wiley: Chichester, 1994.
(19) Edafiogho, I. O.; Hinko, C. N.; Chang, H. J.; Moore, J. A.; Mulzac, D.; Nicholson, J. M.; Scott, K. R. *J. Med. Chem.* **1992**, *35*, 2798. Scott, K. R.; Edafiogho, I. O.; Richardson, E. L.; Farrar, V. A.; Moore, J. A.; Tietz, E. I.; Hinko, C. N.; Chang, H. J.; Elassadi, A.; Nicholson, J. M. *J. Med. Chem.* **1993**, *36*, 1947. Kesten, S. J.; Degnan, M. J.; Hung, J. L.; McNamara, D. J.; Ortwine, D. F.; Uhlendorf, S. E.; Werbel, L. M. *J. Med. Chem.* **1992**, *35*, 3429.
(20) Rodgers, A. L.; Nassimbeni, L. R.; Pauptit, R. A.; Orpen, G.; Haigh, J. M. *Acta Crystallogr., Sect. B* **1977**, *33*, 3110. Popovic, Z.; Roje, V.; Pavlovic, G.; Matkovic-Calogovic, D.; Rajic, M.; Giester, G. *Inorg. Chim. Acta* **2001**, *322*, 65. Bresciani-Pahor, N.; Randaccio, L.; Libertini, E. *Inorg. Chim. Acta* **1980**, *45*, L11. Richardson, M. F.; Corfield, P. W. R.; Sands, D. E.; Sievers, R. E. *Inorg. Chem.* **1970**, *9*, 1632. Nassimbeni, L. R.; Orpen, G.; Pauptit, R.; Rodgers, A. L.; Haigh, J. M. *Acta Crystallogr., Sect. B* **1977**, *33*, 959. Kakaliou, L.; Scanlon, W. J., IV; Qian, B.; Baek, S. W.; Smith, M. R., III; Motry, D. H. *Inorg. Chem.* **1999**, *38*, 5964. Kim, J.; Hwang, J.-W.; Kim, Y.; Lee, M. H.; Han, Y.; Do, Y. *J. Organomet. Chem.* **2001**, *620*, 1. Haigh, J. M.; Nassimbeni, L. R.; Pauptit, R. A.; Rodgers, A. L.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1976**, *32*, 1398. Kuhn, F. E.; Lopes, A. D.; Santos, A. M.; Herdtweck, E.; Haider, J. J.; Romao, C. C.; Santos, A. G. *J. Mol. Catal. A* **2000**, *151*, 147. Jones, D.; Roberts, A.; Cavell, K.; Keim, W.; Englert, U.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 255.
(21) Nagata, T.; Imagawa, K.; Yamada, T.; Mukaiyama, T. *Inorg. Chim. Acta* **1994**, *220*, 283. Jager, E. G.; Schuhmann, K.; Gorls, H. *Inorg. Chim. Acta* **1997**, *255*, 295. Veya, P.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4892. Stack, J. G.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 453.

carried out with a Carlo Erba 1106 microanalyzer. Molar conductivities were measured on a ca. 5×10^{-4} M acetone solution with a Crison Micro CM2200 conductimeter. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets or KBr pellets. NMR spectra were recorded in a Bruker AC 200, Avance 300 or 400 or a Varian Unity 300 spectrometer at room temperature unless otherwise stated. Chemical shifts were referred to TMS, $CFCl_3$ (^{19}F) or H_3PO_4 ($^{31}P\{^1H\}$). The NMR probe temperature was calibrated using ethylene glycol ^1H NMR standard methods. When needed, NMR assignments were performed with the help of DEPT, COSY, and NOESY 1D or 2D experiments and HETCOR techniques. The synthesis of $[Pd\{CH_2C(O)Me\}Cl]_n$ (**1**) was reported previously.[9]

Synthesis of $[Pd_2\{CH_2C(O)Me\}_2(\mu\text{-}Cl)_2(CN^tBu)_2]$ (2a). To a cooled solution (0 °C) of **1** (150 mg, 0.75 mmol) in MeCN (4 mL) was added ^{t}BuNC (85.1 μL, 0.75 mmol). The solution was concentrated until a yellow solid precipitated. Et_2O (10 mL) and *n*-pentane (10 mL) were added, and the suspension was stirred for 20 min at 0 °C. The suspension was filtered off, washed with *n*-pentane, and air-dried to give **2a** as a yellow solid. Yield: 154 mg, 74%. Mp: 114 °C. IR (Nujol, cm^{-1}): ν(CN) 2216; ν(CO) 1660; ν(PdCl) 296, 252. ^1H NMR (300 MHz, $CDCl_3$): δ 2.83 (s, 4 H, CH_2), 2.24 (s, 6 H, Me), 1.52 (s, 18 H, ^{t}Bu). Anal. Calcd for $C_{16}H_{28}Cl_2N_2O_2Pd_2$: C, 34.07; H, 5.00; N, 4.97. Found: C, 34.35; H, 5.27; N, 5.29.

Synthesis of $[Pd_2\{CH_2C(O)Me\}_2(\mu\text{-}Cl)_2(CNXy)_2]$ (2b). To a cooled solution (0 °C) of **1** (100 mg, 0.50 mmol) in MeCN (5 mL) was added XyNC (66 mg, 0.50 mmol). The reaction mixture was stirred for 5 min at 0 °C, then was concentrated (ca. 2 mL) and Et_2O (15 mL) was added. The suspension was stirred for 10 min at 0 °C, filtered off, washed with Et_2O (5 mL), and air-dried, to give a yellow solid. Yield: 134 mg, 81%. Mp: 140 °C (dec). IR (Nujol, cm^{-1}): ν(CN) 2198; ν(CO) 1661; ν(PdCl) 296, 254. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 2 H, Xy), 7.11 (m, 4 H, Xy), 3.04 (s, 4 H, CH_2), 2.46 (s, 12 H, Me, Xy), 2.32 (s, 6 H, Me). Anal. Calcd for $C_{24}H_{28}Cl_2N_2O_2Pd_2$: C, 43.66; H, 4.27; N, 4.24. Found: C, 43.96; H, 4.18; N, 4.35.

Synthesis of $[Pd_2\{\kappa^2\text{-}C,O\text{-}C(NH^tBu)CHC(O)Me\}_2(\mu\text{-}Cl)_2]$ (3a). Method a. A solution of **2a** (170 mg, 0.30 mmol) in $CHCl_3$ (5 mL) was stirred at 40 °C protected from light. After 13 h the suspension was filtered through Celite, and the filtrate was concentrated to dryness. The resulting brown oil was triturated with *n*-pentane (10 mL) and air-dried to give **3a** as an orange solid. Yield: 115 mg, 68%.

Method b. To a solution of **1** (150 mg, 0.75 mmol) in MeCN (3 mL) was added ^{t}BuNC (85.1 μL, 0.75 mmol). The reaction mixture was concentrated to dryness, and the yellow residue was dissolved in $CHCl_3$ (3 mL) and filtered through Celite. The filtrate was stirred at 45 °C for 15 h protected from light and then was filtered through Celite. *n*-Pentane (15 mL) was added to the filtrate to give a solid, which was stirred at 0 °C for 30 min and was isolated by filtration to give **3a**. Yield: 150 mg, 70%. Mp: 156 °C (dec). IR (Nujol, cm^{-1}): ν(NH) 3258; ν(CO) 1536. ^1H NMR (300 MHz, $CDCl_3$): δ 6.51 (br, 2 H, NH), 4.57 (s, 2 H, CH), 2.03 (s, 6 H, Me), 1.31 (s, 18 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 203.0 (CO), 180.0 (CPd), 104.3 (CH), 55.5 (*C*(Me)$_3$), 28.9 (C(*Me*)$_3$), 21.6 (Me). Anal. Calcd for $C_{16}H_{28}Cl_2N_2O_2Pd_2$: C, 34.07; H, 5.00; N, 4.97. Found: C, 34.06; H, 5.03; N, 5.36.

Synthesis of $[Pd_2\{\kappa^2\text{-}C,O\text{-}C(NHXy)CHC(O)Me\}_2(\mu\text{-}Cl)_2]$ (3b). Method a. A solution of **2b** (171 mg, 0.26 mmol) in $CHCl_3$ (5 mL) was stirred at 45 °C for 1 h and then was filtered through Celite. The filtrate was concentrated (ca. 1 mL) and Et_2O (3 mL) added to give a solid, which was filtered off, and the filtrate was concentrated to dryness. The residue was stirred with *n*-pentane (20 mL) for 1 h at −10 °C, then filtered and air-dried to give **3b** as a yellow solid. Yield: 122 mg, 71%.

Method b. A suspension of **2b** (127 mg, 0.38 mmol) in toluene (7 mL) was stirred at 45 °C for 1 h and then filtered through Celite. The filtrate was concentrated, *n*-hexane (20 mL) was added, and the suspension was filtered. The solid was washed with *n*-pentane (5 mL) and air-dried to give **3b**. Yield: 90 mg, 70%. Mp: 144 °C. IR (Nujol, cm^{-1}): ν(NH) 3300, 3280; ν(CO) 1506; ν(Pd) 282, 246. ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (br, 2 H, NH), 7.18−7.06 (m, 6 H, Xy), 4.12 (s, 2 H, CH), 2.25 (s, 12 H, Me, Xy), 1.96 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 205.1 (CO), 182.6 (CPd), 135.0 (C, Xy), 134.3 (C, Xy), 128.4 (CH, Xy), 128.3 (CH, Xy), 103.7 (CH), 21.8 (Me), 18.1 (Me, Xy). Anal. Calcd for $C_{24}H_{28}Cl_2N_2O_2Pd_2$: C, 43.66; H, 4.27; N, 4.24. Found: C, 43.65; H, 4.38; N, 3.89

Synthesis of $[Pd\{\kappa^2\text{-}C,O\text{-}C(NHXy)CHC(O)Me\}Cl(NCMe)]$ (4b). Method a. To a solution of **3b** (50.7 mg, 0.076 mmol) in $CHCl_3$ (2 mL) was added MeCN (0.1 mL). After 15 min the suspension was filtered through Celite and the filtrate was concentrated until a solid started to precipitate. Addition of *n*-pentane (15 mL) gave a suspension that was filtered off and air-dried to give **4b** as a yellow solid. Yield: 38 mg, 67%.

Method b. To a solution of **1** (202 mg, 1.01 mmol) in MeCN (5 mL) was added XyNC (132 mg, 1.01 mmol), and the resulting yellow solution was concentrated to dryness. The residue was dissolved in $CHCl_3$ (5 mL) and then was heated at 40 °C for 1 h. The resulting suspension was filtered through Celite, the filtrate was concentrated (ca. 1 mL), and *n*-pentane (10 mL) was added. The suspension was stirred at 0 °C and filtered off, and the yellow solid obtained was air-dried to give **4b**. Yield: 205 mg, 63%. Mp: 180 °C. IR (Nujol, cm^{-1}): ν(NH) 3272; ν(CN) 2320, 2292. IR (KBr, cm^{-1}) ν(NH) 3273; ν(CN) 2320, 2292; ν(CO) 1494. ^1H NMR (300 MHz, $CDCl_3$): δ 8.24 (br, 1 H, NH), 7.17−7.08 (m, 3 H, Xy), 4.15 (s, 1 H, CH), 2.24 (s, 6 H, Me, Xy), 2.12 (s, 3 H, MeCN), 1.95 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 204.4 (CO), 183.8 (br, CPd), 134.8 (C, Xy), 128.5 (CH, Xy), 128.1 (CH, Xy), 117.6 (br, Me*C*N), 103.6 (CH), 21.7 (Me), 18.0 (Me, Xy), 2.6 (*Me*CN). Anal. Calcd for $C_{14}H_{17}ClN_2OPd$: C, 45.30; H, 4.62; N, 7.55. Found: C, 45.06; H, 4.43; N, 7.53

Synthesis of *trans*-$[Pd\{CH_2C(O)Me\}Cl(CN^tBu)_2]$ (5a). To a cooled (−10 °C) suspension of **1** (101 mg, 0.51 mmol) in CH_2Cl_2 (4 mL) was added ^{t}BuNC (115 μL, 1.01 mmol). The suspension was stirred until the solid had dissolved, then filtered through Celite. The resulting solution was concentrated to dryness, and addition of *n*-pentane (10 mL) and vigorous stirring in an acetone/N_2(l) bath gave a solid that was filtered off, washed with *n*-pentane (5 mL), and air-dried to give **5a** as a colorless solid. Yield: 150 mg, 81%. Mp: 82 °C. IR (Nujol, cm^{-1}): ν(CN) 2208; ν(CO) 1658; ν(PdCl) 278. ^1H NMR (400 MHz, $CDCl_3$): δ 2.61 (s, 2 H, CH_2), 2.14 (s, 3 H, Me), 1.55 (s, 18 H, ^{t}Bu). Anal. Calcd for $C_{13}H_{23}ClN_2OPd$: C, 42.76; H, 6.35; N, 7.67. Found: C, 42.85; H, 6.27; N, 7.63.

Synthesis of *trans*-$[Pd\{CH_2C(O)Me\}Cl(CNXy)_2]$ (5b). To a cooled (−78 °C) suspension of **1** (91 mg, 0.46 mmol) in CH_2Cl_2 (6 mL) was added XyNC (130 mg, 0.91 mmol), and the mixture was stirred until all solids had dissolved, then filtered through Celite to a cooled flask. The filtrate was concentrated (ca. 3 mL) in a cooled bath (0 °C) and *n*-pentane (20 mL) added to give a solid, which was stirred at −40 °C for 20 min. Then, the solid was filtered off, washed with *n*-pentane (5 mL), and air-dried to give **5b** as a colorless solid. Yield: 166 mg, 78%. Mp: 110 °C (dec). IR (Nujol, cm^{-1}): ν(CN) 2192; ν(CO) 1660; ν(PdCl) 296. ^1H NMR (300 MHz, $CDCl_3$, 263 K): δ 7.23−7.09 (m, 6 H, Xy), 2.98 (s, 2 H, CH_2), 2.45 (s, 12 H, Me, Xy), 2.26 (s, 3 H, Me). Anal. Calcd for $C_{21}H_{23}ClN_2OPd$: C, 54.68; H, 5.03; N, 6.07. Found: C, 54.33; H, 4.94; N, 6.15.

Synthesis of $[Pd\{\kappa^2\text{-}C,O\text{-}C(NH^tBu)CHC(O)Me\}Cl(CN^tBu)]$ (6a). Method a. A solution of **5a** (85 mg, 0.23 mmol) in $CHCl_3$ (3 mL) was heated at 40 °C for 14.5 h, and the resulting pale yellow solution was filtered through Celite. The filtrate was concentrated (ca. 0.5 mL) to give a solid, which

was filtered off and washed with Et_2O (5 mL) and then with *n*-pentane (5 mL) to give **6a** as a pale yellow solid. Yield: 52 mg, 61%.

Method b. To a cooled suspension (0 °C) of **1** (83.5 mg, 0.42 mmol) in $CHCl_3$ (6 mL) was added ^{t}BuNC (95 μL, 0.84 mmol). When complex **1** was dissolved, the solution was heated at 40 °C for 14 h, and the resulting orange solution was filtered through Celite. The filtrate was concentrated (ca. 2 mL), Et_2O (2 mL) was slowly added, and the resulting suspension was stirred for 15 min to give a solid that was filtered off and washed with Et_2O (5 mL) to give **6a** as a pale yellow solid. Yield: 115 mg, 75%. Mp: 145−147 °C (dec). IR (Nujol, cm^{-1}): ν(NH) 3418; ν(CN) 2208, ν(PdCl) 262. IR (KBr, cm^{-1}): ν(NH) 3367; ν(CN) 2218; ν(CO) 1505. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (br, 1 H, NH), 5.08 (d, 1 H, CH, $^4J_{HH}$ = 0.9 Hz), 2.04 (s, 3 H, Me), 1.58 (br, 9 H, ^{t}BuNC), 1.40 (s, 9 H, ^{t}BuNH). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 205.5 (CO), 190.0 (C(Pd)-NH), 127.5 (t, {1:1:1}, CN, $^1J_{CN}$ = 20 Hz), 106.0 (CH), 59.0 (t, {1:1:1}, CN*C*(Me)$_3$, $^1J_{CN}$ = 4.3 Hz), 55.9 (CNH*C*(Me)$_3$), 30.0 (CNHC(*Me*)$_3$), 29.0 (CNC(*Me*)$_3$), 22.5 (Me). Anal. Calcd for $C_{13}H_{23}ClN_2OPd$: C, 42.76; H, 6.35; N, 7.67. Found: C, 42.73; H, 6.62; N, 7.67. Single crystals of **6a** were obtained by slow diffusion of Et_2O into an acetone solution of **6a**.

Synthesis of [Pd{κ^2-*C,O*-C(NHXy)CHC(O)Me}Cl-(CNXy)] (6b). Method a. A solution of **5b** (54 mg, 0.12 mmol) in $CHCl_3$ (3 mL) was heated at 40 °C for 5 h and then filtered through Celite. The filtrate was concentrated (0.5 mL), and Et_2O (5 mL) was slowly added to give a suspension, which was filtered off, washed with Et_2O (5 mL), and air-dried to give **6b** as a pale yellow solid. Yield: 44 mg, 81%.

Method b. To a cooled suspension (−10 °C) of **1** (85.5 mg, 0.43 mmol) in $CHCl_3$ (6 mL) was added XyNC (112.7 mg, 0.86 mmol). When complex **1** was dissolved, the reaction mixture was filtered through Celite, and the filtrate was heated at 40 °C for 4 h and then was filtered through Celite. The filtrate was concentrated (ca. 2 mL), Et_2O (5 mL) was slowly added, and the resulting suspension was stirred for 15 min to give a suspension, which was filtered off, washed with Et_2O (10 mL), and air-dried to give **6b**. Yield: 158 mg, 80%. Mp: 150−156 °C (dec). IR (Nujol, cm^{-1}): ν(NH) 3202; ν(CN) 2198; ν(PdCl) 274. IR (KBr, cm^{-1}): ν(NH) 3274; ν(CN) 2197; ν(CO) 1497. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.12 (m, 6 H, Xy), 6.90 (br, 1 H, NH), 4.61 (d, 1 H, CH, $^4J_{HH}$ = 0.9 Hz), 2.49 (s, 6 H, Me, XyNC), 2.27 (s, 6 H, Me, XyNHC), 2.03 (s, 3 H, Me). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 208.8 (CO), 192.4 (C(Pd)-NH), 135.7 (C, Xy), 135.0 (C, Xy), 130.4 (CH, Xy), 128.7 (CH, Xy), 128.6 (CH, Xy), 128.3 (CH, Xy), 125.8 (C, Xy), 106.0 (CH), 22.9 (Me), 18.9 (Me, Xy), 18.1 (Me, Xy). Anal. Calcd for $C_{21}H_{23}ClN_2OPd$: C, 54.68; H, 5.03; N, 6.07. Found: C, 54.22; H, 5.01; N, 5.82

Synthesis of [Pd$_2$Cl$_2$(CN^{t}Bu)$_4$] (7a). To a suspension of **1** (100 mg, 0.50 mmol) in toluene (3 mL) was added ^{t}BuNC (284 μL, 2.51 mmol) under N_2. The resulting solution was heated (60 °C) in a water bath for 5 h and then was filtered to give solid **7a** contaminated with Pd. The filtrate was concentrated to dryness, and the residue was triturated with *n*-pentane (5 mL) and filtered off to get a second crop of **7a**. Both crude mixtures were recrystallized from CH_2Cl_2/Et_2O to give **7a** as a yellow solid, which has previously been described.[11,22] Yield: 122 mg, 80%. Anal. Calcd for $C_{20}H_{36}Cl_2N_4Pd_2$: C, 38.98; H, 5.89; N, 9.09. Found: C, 39.10; H, 6.10; N, 9.06.

Synthesis of [Pd$_2$Cl$_2$(CNXy)$_4$] (7b). To a suspension of **1** (75 mg, 0.38 mmol) in toluene (3 mL) was added XyNC (247 mg, 1.88 mmol) under N_2. The mixture was heated (60 °C) in a water bath for 5 h and then was filtered to give a solid that was recrystallized from CH_2Cl_2/Et_2O to give **7b** as a yellow solid. Yield: 65 mg, 42%. IR (Nujol, cm^{-1}): ν(CN) 2154; ν(PdCl) 256. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26−7.20 (m, 4 H, Xy), 7.12−7.09 (m, 8 H, Xy), 2.51 (s, 24 H, Me). Anal. Calcd for $C_{36}H_{36}Cl_2N_4Pd_2$: C, 53.48; H, 4.49; N, 6.93. Found: C, 53.51; H, 4.66; N, 6.96.

Synthesis of *trans*-[Pd{C(NH^{t}Bu)=CHC(O)Me}Cl-(CN^{t}Bu)$_2$] (8a). A solution of complex **6a** (82.2 mg, 0.23 mmol) in CH_2Cl_2 (2 mL) was cooled (0 °C), and ^{t}BuNC (26 μL, 0.23 mmol) was added. The solution was stirred for 5 min and concentrated to dryness. The residue was triturated with *n*-pentane (20 mL) at −10 °C to give a solid, which was filtered, washed with *n*-pentane (5 mL), and air-dried to give **8a** as a pale yellow solid. Yield: 70 mg, 70%. IR (Nujol, cm^{-1}): ν(CN) 2232 (sh), 2208; ν(CO) 1556; ν(PdCl) 288. (KBr, cm^{-1}): ν(NH) 2980; ν(CN) 2208; ν(CO) 1560. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.16 (br, 1 H, NH), 5.39 (s, 1 H, CH), 1.93 (s, 3 H Me), 1.54 (s, 9 H ^{t}Bu), 1.48 (s, 18 H, ^{t}Bu). Anal. Calcd for $C_{18}H_{32}ClN_3OPd$: C, 48.22; H, 7.19; N, 9.37. Found: C, 48.42; H, 7.55; N, 9.40

Synthesis of *trans*-[Pd{C(NHXy)=CHC(O)Me}Cl-(CNXy)$_2$] (8b). A solution of complex **6b** (73 mg, 0.16 mmol) in CH_2Cl_2 (2 mL) was cooled (0 °C), and then, XyNC (21 mg, 0.16 mmol) was added. The mixture reaction was quickly filtered, and the filtrate was collected in a cooled flask and concentrated. Then *n*-pentane (5 mL) was added, and the cooled mixture was stirred to give a pale yellow solid, which was filtered, washed with *n*-pentane (10 mL), and air-dried. Yield: 75 mg, 80%. IR (Nujol, cm^{-1}): ν(CN) 2192, 2160; ν(CO) 1570; ν(PdCl) 290. (KBr, cm^{-1}): ν(NH) 3028; ν(CN) 2188, 2160; ν(CO) 1570. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.90 (br, 1 H, NH), 7.29−7.25 (m, 2 H, Xy), 7.13−7.11 (m, 4 H, Xy), 7.04−7.00 (m, 1 H, Xy), 6.94−6.93 (m, 2 H, Xy), 5.68 (s, 1 H, CH), 2.36 (s, 12 H, Me, Xy), 2.30 (s, 6 H, Me, Xy), 2.08 (s, 3 H, Me). Because of its instability, an analytically pure sample could not be isolated. See discussion.

Synthesis of [Pd{CH$_2$C(O)Me}(CN^{t}Bu)$_3$]TfO (9a). A suspension of **1** (100 mg, 0.50 mmol) in acetone (5 mL) was cooled (−10 °C) for 15 min. Then ^{t}BuNC (175 μL, 1.54 mmol) was added. When **1** dissolved, KTfO (95 mg, 0.51 mmol) was added and the mixture was stirred for 10 min in a cold bath and concentrated to dryness. The residue was extracted with CH_2Cl_2 (5 mL) and filtered through Celite, and the filtrate was evaporated to dryness. The residue was triturated with *n*-pentane (10 mL), and the mixture was vigorously stirred at −10 °C for 30 min. The solid was filtered off, washed with *n*-pentane (5 mL), and air-dried to give **9a** as a colorless solid. Yield: 253 mg, 90%. Mp: 163 °C (dec). Λ_M (acetone, 6.97 × 10^{-4} M): 122 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(CN) 2254, 2228; ν(CO) 1668. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.66 (s, 2 H, CH_2), 2.13 (s, 3 H, Me), 1.64 (s, 18 H, ^{t}Bu), 1.61 (s, 9 H, ^{t}Bu). ^{19}F NMR (282.20 MHz, $CDCl_3$): δ 78.0. Anal. Calcd for $C_{19}H_{32}F_3N_3O_4PdS$: C, 40.61; H, 5.74; N, 7.48; S, 5.71. Found: C, 40.61; H, 6.06; N, 7.50; S, 5.54.

Synthesis of [Pd{CH$_2$C(O)Me}(CNXy)$_3$]TfO (9b). A suspension of **1** (100 mg, 0.50 mmol) in acetone (3 mL) was cooled (−10 °C) for 15 min. Then, XyNC (199 mg, 1.51 mmol) was added, and when the suspension dissolved, KTfO (97 mg, 0.51 mmol) was added. The suspension was stirred for 10 min in a cold bath and then concentrated to dryness. The residue was extracted with CH_2Cl_2 (5 mL) and filtered through Celite, and the filtrate was evaporated to dryness. The residue was vigorously stirred with *n*-pentane (10 mL) for 30 min at −10 °C, and the solid was filtered off, washed with *n*-pentane (5 mL), and air-dried to give **9b** as a colorless solid. Yield: 309 mg, 88%. Mp: 87 °C. Λ_M (acetone, 5.7 × 10^{-4} M): 122 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(CN) 2200; ν(CO) 1666. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.32 (m, 3 H, Xy), 7.21−7.18 (m, 6 H, Xy), 3.18 (s, 2 H, CH_2), 2.54 (s, 12 H, Me, Xy), 2.48 (s, 6 H, Me, Xy), 2.30 (s, 3 H, Me). ^{19}F NMR (282.20 MHz, $CDCl_3$): δ 78.14. Anal. Calcd for $C_{31}H_{32}F_3N_3O_4PdS$: C, 52.73; H, 4.57; N, 5.95; S, 4.54. Found: C, 52.68; H, 4.58; N, 5.90; S, 4.26. Single crystals of **9b**·$CHCl_3$ were obtained by slow diffusion of *n*-pentane into a solution of **9b** in $CHCl_3$.

(22) Duravila, V.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2000**, *600*, 198.

Synthesis of [Pd{κ²-*C,O*-C(NH^{t}Bu)CHC(O)Me}(CN^{t}Bu)$_2$]TfO (10a). To a solution of **6a** (41 mg, 0.11 mmol) in acetone (2 mL) were added TlTfO (35 mg, 0.11 mmol) and ^{t}BuNC (12.7 μL, 0.11 mmol). The reaction mixture was concentrated to dryness, and the residue was extracted with CH_2Cl_2 (4 mL) and filtered through Celite. The filtrate was concentrated to dryness. The residue was dissolved in acetone (1 mL) and cooled at 0 °C, and *n*-pentane (10 mL) was added to give a precipitate, which was filtered and vacuum-dried to give **10a**·H_2O as a hygroscopic pale yellow solid. Yield: 31 mg, 50%. Λ_M (acetone, 4.55×10^{-4} M): 108 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(NH) 3388; ν(CN) 2232 (sh), 2218; ν(CO) 1514. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (br, 1 H, NH), 5.16 (s, 1 H, CH), 2.07 (s, 3 H, Me), 1.63 (s, 9 H, ^{t}Bu), 1.58 (s, 9 H, ^{t}Bu), 1.42 (s, 9 H, ^{t}Bu). ^{19}F NMR (282.20 MHz, $CDCl_3$): δ 78.1. Anal. Calcd for $C_{19}H_{34}F_3N_3O_5PdS$: C, 39.35; H, 5.91; N, 7.25, S, 5.53. Found: C, 39.72; H, 5.75; N, 7.20; S, 5.46. Single crystals of **10a**·Me_2CO were obtained by slow diffusion of *n*-pentane into a solution of **10a** in acetone.

Synthesis of [Pd{κ²-*C,O*-C(NHXy)CHC(O)Me}(CNXy)$_2$]TfO (10b). To a solution of **6b** (38 mg, 0.08 mmol) in acetone (2 mL) were added TlTfO (30 mg, 0.08 mmol) and XyNC (10.8 mg, 0.082 mmol). The reaction mixture was concentrated to dryness, and the residue was extracted with CH_2Cl_2 (3 mL) and filtered through Celite. The yellow filtrate was concentrated to dryness to give an oil, which was triturated with *n*-pentane (20 mL) in a cool bath (−10 °C) to give a solid, which was filtered, washed with *n*-pentane, and air-dried to give **10b** as a yellow solid. Yield: 48 mg, 83%. Mp: 197 °C. Λ_M (acetone, 4.50×10^{-4} M): 119 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν(NH) 3204 (br); ν(CN) 2210, 2190. IR (KBr, cm^{-1}): ν(NH) 3216 (br); ν(CN) 2211, 2191; ν(CO) 1490. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.70 (br, 1 H, NH), 7.37−7.06 (m, 9 H, Xy), 4.60 (s, 1 H, CH), 2.51 (s, 6 H, Me, XyN≡C), 2.49 (s, 6 H, Me, XyN≡C), 2.29 (s, 6 H, Me, XyNH), 2.01 (s, 3 H, Me). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ 78.8. Anal. Calcd for $C_{31}H_{32}F_3N_3O_4PdS$: C, 52.73; H, 4.57; N, 5.95; S, 4.54. Found: C, 52.97; H, 4.45; N, 6.03; S, 4.38. Single crystals of **10b** were obtained by a CH_2Cl_2/*n*-pentane solution of **10b**.

Synthesis of [Pd{κ²-*C,O*-C(NH^{t}Bu)CHC(O)Me}Cl(PPh$_3$)] (11a). To a suspension of **3a** (30 mg, 0.053 mmol) in dry THF (4 mL), under N_2 atmosphere, was added PPh_3 (27.8 mg, 0.11 mmol). The orange solution was concentrated (ca. 1 mL) and *n*-pentane (10 mL) was added, yielding a solid, which was filtered and air-dried to give **11a** as an orange solid. Yield: 31 mg, 54%. Mp: 113 °C. IR (Nujol, cm^{-1}): ν(NH) 3265. IR (KBr, cm^{-1}): ν(NH) 3265. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74−7.68 (m, 6 H, Ph), 7.51−7.42 (m, 9 H, Ph), 5.17 (s, 1 H, CH), 4.85 (br, 1 H, NH), 2.16 (s, 3 H, Me), 0.79 (s, 9 H, ^{t}Bu). ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$): δ 42.30 (br). Anal. Calcd for $C_{26}H_{29}ClNOPPd$: C, 57.37; H, 5.37; N, 2.57. Found: C, 57.29; H, 5.44; N, 2.57.

Synthesis of [Pd{κ²-*C,O*-C(NHXy)CHC(O)Me}Cl(PPh$_3$)] (11b). To a suspension of **3b** (53.7 mg, 0.081 mmol) in dry THF (6 mL), under N_2 atmosphere, was added PPh_3 (85.3 mg, 0.33 mmol). The pale orange solution was concentrated (ca. 0.5 mL) and Et_2O (15 mL) was added. The mixture was stirred for 30 min at 0 °C, and then, the suspension was filtered off, washed with Et_2O (15 mL), and air-dried to give **11b** as a yellow solid. Yield: 78 mg, 81%. Mp: 166 °C (dec). IR (Nujol, cm^{-1}): ν(NH) 3340; ν(PdCl) 291. IR (KBr, cm^{-1}): ν(NH) 3340; ν(CO) 1479. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85−7.80 (m, 12 H, Ph), 7.49−7.42 (m, 18 H, Ph), 7.00 (m, 1 H, Xy), 6.90 (m, 2 H, Xy), 5.68 (br, 1 H, NH), 4.53 (s, 1 H, CH), 2.03 (s, 3 H, Me), 1.76 (s, 9 H, Me, Xy). ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$): δ 39.02 (s). Anal. Calcd for $C_{30}H_{29}ClNOPPd$: C, 60.82; H, 4.93; N, 2.36. Found: C, 60.83; H, 5.15; N, 2.36.

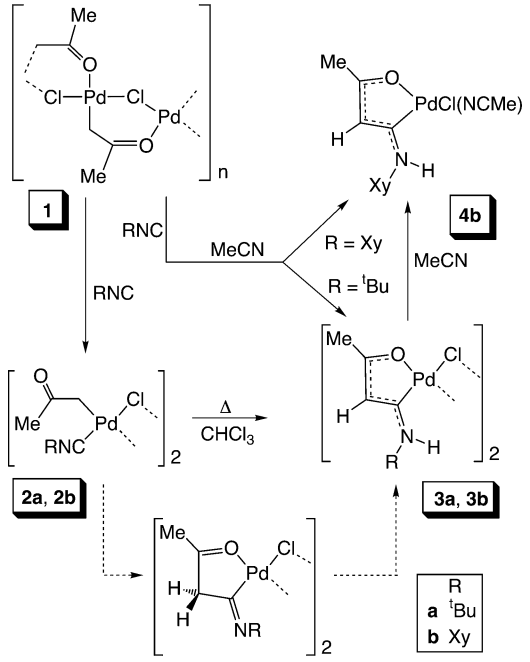
Synthesis of *trans*-[Pd{C(NH^{t}Bu)=CHC(O)Me}Cl(PEt$_3$)$_2$] (12a). To a suspension of **3a** (40.6 mg, 0.072 mmol) in dry THF (3 mL) was added PEt_3 (43 μL, 0.29 mmol) under N_2. The resulting pale yellow solution was concentrated to dryness, and the residue was stirred (30 min) with *n*-hexane (15 mL) at 0 °C to obtain a solid, which was filtered and dried under N_2 to give **12a** as a yellow solid. Yield: 38 mg, 51%. IR (Nujol, cm^{-1}): ν(CO) 1567; ν(PdCl) 299. IR (KBr, cm^{-1}): ν(NH) 2964; ν(CO) 1572. ^{1}H NMR (300 MHz, C_6D_6): δ 13.15 (br, 1 H, NH), 5.50 (d, 1 H, CH, $^2J_{HP}$ = 1.4 Hz), 2.12 (s, 3 H, Me), 1.82−1.69 (m, 12 H, P(C*H*$_2$Me)$_3$), 1.44 (s, 9 H, ^{t}Bu), 0.98 (t, 18 H, P(CH$_2$*Me*)$_3$, $^3J_{HH}$ = 7.8 Hz). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): δ 186.8 (t, CO, $^4J_{CP}$ = 3.8 Hz), 184.6 (t, CPd, $^2J_{CP}$ = 1.1 Hz), 102.5 (t, CH, $^3J_{CP}$ = 3.3 Hz), 52.5 (*C*(Me)$_3$), 31.1 (P(CH$_2$*Me*)$_3$), 27.8 (Me), 15.4 ('t', P(*C*H$_2$Me)$_3$, $|^1J_{CP} + {}^3J_{CP}|$ = 41 Hz), 8.4 (C(*Me*)$_3$). ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$): 8.62 (s). Anal. Calcd for $C_{20}H_{44}ClNOP_2Pd$: C, 46.34; H, 8.56; N, 2.70. Found: C, 46.00; H, 8.50; N, 2.63.

Synthesis of [Pd{κ²-*C,O*-C(NH^{t}Bu)CHC(O)Me}(acac)] (13a). To a solution of **3a** (55 mg, 0.10 mmol) in CH_2Cl_2 (3 mL) was added Tl(acac) (59 mg, 0.20 mmol), and a colorless precipitate appeared that within 10 min turned gray. The suspension was filtered through Celite to give a yellow solution, which was concentrated to dryness, and the residue was extracted with *n*-pentane (10 mL), filtered through Celite, and concentrated to dryness to give **13a** as a yellow solid. Yield: 54 mg, 80%. Mp: 115−119 °C. IR (Nujol, cm^{-1}): ν(NH) 3315; ν(CO) 1589, 1545, 1514. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.69 (br, 1 H, NH), 5.31 (s, 1 H, CH, acac), 4.97 (d, 1 H, CH, $^4J_{HH}$ = 1 Hz), 2.06 (s, 3 H, Me), 2.01 (s, 3 H, Me, acac), 1.96 (s, 3 H, Me, acac), 1.37 (s, 3 H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 202.8 (CO), 190.2 (CO, acac), 185.7 (CPd), 184.6 (CO, acac), 103.9 (CH), 100.8 (CH, acac), 53.7 (*C*(Me)$_3$), 29.0 (C(*Me*)$_3$), 27.6 (Me, acac), 27.2 (Me, acac), 21.8 (Me). Anal. Calcd for $C_{13}H_{21}NO_3Pd$: C, 45.21; H, 6.13; N, 4.05. Found: C, 45.43; H, 6.14; N, 4.19.

Synthesis of [Pd{κ²-*C,O*-C(NHXy)CHC(O)Me}(acac)] (13b). To a solution of **3b** (30 mg, 0.045 mmol) in CH_2Cl_2 (3 mL) was added Tl(acac) (28 mg, 0.09 mmol), and the reaction mixture was stirred for 6 h. The gray suspension was filtered through Celite, the solution was concentrated to dryness, and the residue was extracted with Et_2O (10 mL), filtered through Celite, concentrated to dryness, and dried for 1 day under vacuum to give **13b** as a yellow solid. Yield: 30 mg, 84%. Mp: 110−115 °C (dec). IR (Nujol, cm^{-1}): ν(NH) 3315; ν(CO) 1584, 1514. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (br, 1 H, NH), 7.17−7.09 (s, 3 H, Xy), 5.37 (s, 1 H, CH, acac), 4.47 (d, 1 H, CH, $^4J_{HH}$ = 1 Hz), 2.25 (s, 3 H, Me, Xy), 2.06 (s, 3 H, Me, acac), 2.00 (s, 3 H, Me), 1.99 (s, Me, acac). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 205.1 (CO), 190.1 (CO, acac), 188.7 (CPd), 185.0 (CO, acac), 135.0 (C, Xy), 134.6 (C, Xy), 128.3 (CH, Xy), 127.8 (CH, Xy), 103.7 (CH), 100.9 (CH, acac), 27.7 (Me, acac), 27.1 (Me, acac), 22.0 (Me), 18.2 (Me, Xy). Anal. Calcd for $C_{17}H_{21}NO_3Pd$: C, 51.85; H, 5.38; N, 3.56. Found: C, 52.14; H, 5.51; N, 3.89.

Crystal Structures of 6a, 9b, 10a, and 10b. The crystal structures of **6a**, **9b**, **10a**, and **10b** were determined by single-crystal X-ray diffraction. Measurements were recorded for **6a** on a Bruker SMART 1000 CCD, and otherwise on a Siemens P4 diffractometer using monochromated Mo Kα radiation in ω-scan mode (for **6a** also φ-scans). The structures were solved by the heavy-atom method and refined anisotropically on F^2 with the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using a riding model or rigid methyl groups. Special features of the refinement are as follows. The polar axis direction of **6a** was determined by the Flack parameter of −0.020(16). Compound **9b** crystallizes with one molecule of chloroform, and the hydrogen atoms at C3 are disordered over two positions. For compounds **6a**, **10a**, and **10b** the hydrogen on N was located in the Fourier difference map and refined freely (with DFIX). Compound **10a** crystallizes with one molecule of acetone, which is disordered over two positions; its hydrogen atoms were not included in the refinement. The fluorine atoms of its triflate

Scheme 2



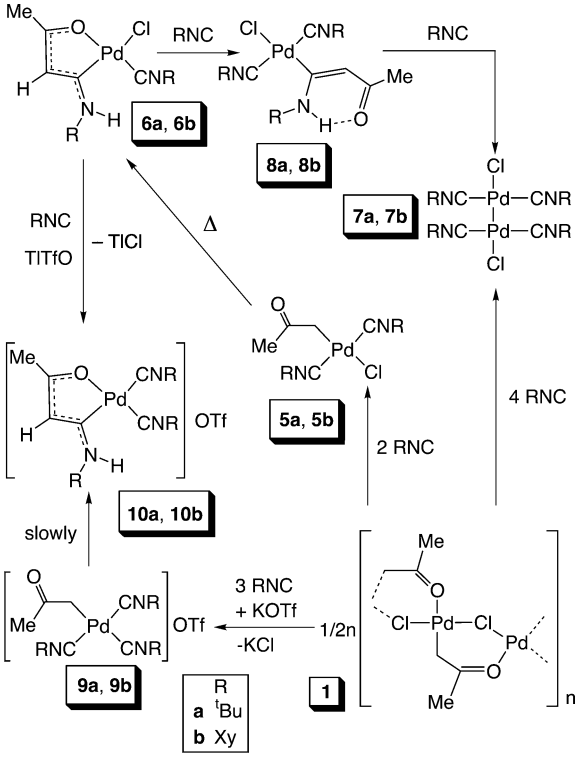
anion are disordered over two positions. The triflate anion in **10b** is disordered over two positions.

Results and Discussion

Reactions of [Pd{CH$_2$C(O)Me}Cl]$_n$ (1) with Isocyanides. The 1:1 Reactions. [Pd{CH$_2$C(O)Me}Cl]$_n$ (**1**) and isocyanides (RNC:Pd = 1) at 0 °C react to give complexes [Pd$_2$\{CH$_2$C(O)Me\}$_2$(μ-Cl)$_2$(CNR)$_2$] [R = ^{t}Bu (**2a**), Xy (**2b**); Scheme 2]. Complexes **2** are stable at temperatures ≤ 4 °C, but at room temperature, their solutions in organic solvents are not stable and an insertion of the isocyanide into the Pd−C bond plus a tautomerization process from β-ketoimine to β-ketoenamine occurs to give [Pd$_2$\{κ^2-*C,O*-C(NHR)CHC(O)Me\}$_2$(μ-Cl)$_2$] [R = ^{t}Bu (**3a**), Xy (**3b**); Scheme 2]. Imine−enamine tautomeric equilibria in palladium imidoyl complexes have been studied by Carmona et al.[23] In our case, the tautomerization process is driven to the enamine form by the formation of the stable palladacycle in complexes **3**. Therefore, when complexes **2** were synthesized at room temperature, they were always contaminated with the corresponding complexes **3**. Pure complexes **3** could be obtained by heating solutions of complexes **2** to 40−45 °C in organic solvents (CHCl$_3$, THF, toluene).

Kinetics of conversion of **2** to **3** was conveniently followed by ^{1}H NMR in CDCl$_3$ at 317 K (see Supporting Information). The reactions follow a first-order rate law with respect to **2**. The rate of disappearance of **2a** (k_{obs} = (8.1 ± 0.3) × 10^{-5} s^{-1}) is much lower than that of **2b** (k_{obs} = (4.1 ± 0.1) × 10^{-4} s^{-1}). These results agree with those reported for the insertion of the same isocyanides into a Pd−Me bond.[24] Complex **3a** can also be obtained

Scheme 3



by reacting ^{t}BuNC and **1** (^{t}BuNC:Pd = 1) in MeCN. However, under the same conditions, XyNC reacts with **1** to give [Pd\{κ^2-*C,O*-C(NHR)CHC(O)Me\}Cl(NCMe)] (**4b**), which can also be obtained by reacting **3b** in a CHCl$_3$ solution with an excess of MeCN. This difference of reactivity could be due to the greater electron-withdrawing character of the Xy group that makes the palladium atom harder. Complexes **3** and **4b** are stable in the solid state and in organic solvents at room temperature (acetone, CH$_2$Cl$_2$, CHCl$_3$, THF).

A few examples of these insertion−tautomerization reactions have been reported to give *trans*-[Pd\{C(NHR)=CHC(O)R′\}Cl(PPh$_3$)$_2$] (R = Me, *p*-C$_6$H$_4$OMe, R′ = Me;[2] R = ^{t}Bu, R′ = Ph[4]). In these cases the ligand is not chelating because of the presence of the two phosphines *cis* to the β-ketoenamine ligand.

The 1:2 Reactions. Low-temperature reactions of **1** with RNC (RNC:Pd = 2) give complexes *trans*-[Pd\{CH$_2$C(O)Me\}Cl(CNR)$_2$] [R = ^{t}Bu (**5a**), Xy (**5b**); Scheme 3], which are stable in the solid state below 4 °C. When these reactions were carried out at room temperature, mixtures of **5** and the corresponding complexes [Pd\{κ^2-*C,O*-C(NHR)CHC(O)Me\}Cl(CNR)] [R = ^{t}Bu (**6a**), Xy (**6b**)] were isolated. The formation of complexes **6**, which like that of complexes **3** involves an insertion−tautomerization process, can be achieved by heating solutions of complexes **5** in CHCl$_3$ to 40 °C (Scheme 3). These processes were also studied kinetically and found to follow a first-order rate law (see Supporting Information). The calculated k_{obs} of these reactions at 317 K, as for conversion of **2** into **3**, was lower for R = ^{t}Bu (**6a** k_{obs} = (1.8 ± 0.1) × 10^{-4} s^{-1}) than for R = Xy (**6b** k_{obs} = (1.1 ± 0.2) × 10^{-3} s^{-1}). The one-pot synthesis of complexes **6** from **1**, heating CHCl$_3$ solutions of **1** with the corresponding isocyanides (RNC:Pd = 2), gave also trace amounts of the corresponding Pd(I) complexes [Pd$_2$Cl$_2$(CNR)$_4$] [R = ^{t}Bu (**7a**), Xy (**7b**)]. Complex **7a**[25]

(23) Campora, J.; Hudson, S. A.; Massiot, P.; Maya, C. M.; Palma, P.; Carmona, E.; Martinez Cruz, L. A.; Vegas, A. *Organometallics* **1999**, *18*, 5225. Alias, F. M.; Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1997**, *16*, 301.

(24) Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; van Leeuwen, P.; Veldman, N.; Spek, A. L.; van Neer, F. J. R. *Organometallics* **1997**, *16*, 2948.

and complexes related to **7b**, $[Pd_2X_2(CNXy)_4]$ (X = Br,[11,22] I[22]), have been reported. Complexes **7** were not detected in solutions of complexes **6** or when they were prepared from **5**. Therefore, the one-pot synthesis of **6** from **1** is better achieved in two steps, the first involving the low-temperature formation of **5** and then its thermal transformation to **6**.

The 1:3, 1:4, and 1:5 Reactions. The room-temperature reaction between **1** and XyNC (XyNC:Pd = 3) was followed by ^{1}H NMR in $CDCl_3$. Initially, **5b** and traces of *trans*-[Pd{C(NHXy)=CHC(O)Me}Cl(CNXy)$_2$] (**8b**) were observed. After 3 h no signals of **5b** were detected and the major product was **8b** with traces of **7b**. When the reaction was carried out in XyNC:Pd = 4, the proportion of **7b** increased. The ^{t}BuNC:Pd = 5 reaction at 50 °C in C_6D_6 gave, after 5 h, **7a** and unidentified products. Complexes *trans*-[Pd{C(NHR)=CHC(O)Me}Cl(CNR)$_2$] [R = ^{t}Bu (**8a**), Xy (**8b**); Scheme 3] are better synthesized by reacting **6** with 1 equiv of RNC at low temperature because the one-pot reaction of **1** with isocyanides (RNC:Pd = 3) gave **8** contaminated with **7**. Pure complex **8a** could be isolated at 0 °C after 5 min of reaction and concentration to dryness of the reaction mixture; however, analytically pure **8b** could not be isolated because it decomposes faster.

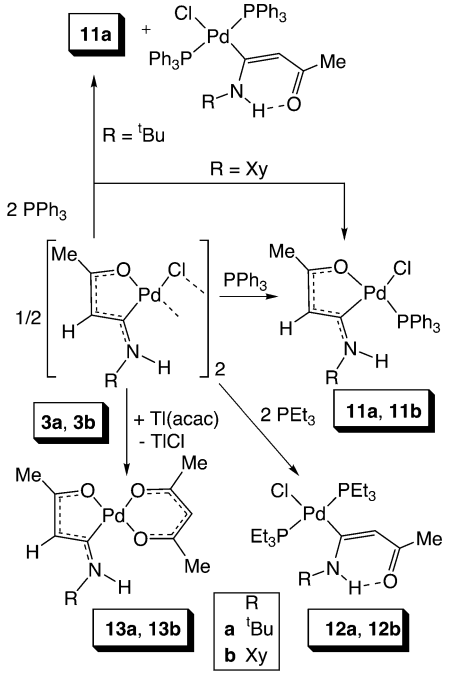
Complexes **6** and **7** were identified by ^{1}H NMR as the decomposition products of **8** in $CDCl_3$ after 1 h at 50 °C. On the other hand, ^{1}H NMR spectra of mixtures of **8** and 1 equiv of isocyanide gave **7** and other products that could not be identified. The decomposition process of **8** could be associated with a C−Pd homolytic cleavage generating complex **7** and organic products; a similar mechanism was proposed by Floriani et al. to explain the reaction of *trans*-[Pd{C(NH^{t}Bu)=CHC(O)Ph}Cl(PPh$_3$)$_2$] with ^{t}BuNC.[4]

Addition of isocyanide to a cooled (−10 °C) suspension of **1** in Me_2CO (XyNC:Pd = 3) led to a solution containing **5** (Scheme 3). Addition of 1 equiv of KTfO to this reaction mixture led to the precipitation of KCl and a solution from which complexes [Pd{CH_2C(O)Me}(CNR)$_3$]TfO [R = ^{t}Bu (**9a**), Xy (**9b**)] could be isolated if the low temperature was maintained to avoid insertion processes. These complexes are stable in the solid state at 4 °C and decompose in solution at room temperature. The room-temperature ^{1}H NMR spectrum of **9b** in $CDCl_3$ shows its transformation into the product of the insertion−tautomerization reaction [Pd{κ^2-*C,O*-C(NHXy)CHC(O)Me}(CNXy)$_2$]TfO (**10b**) along with other byproducts that could not be separated. This and the analogous ^{t}BuNC complex **10a** could be isolated pure by reaction of acetone solutions of **6** with TlTfO and addition of the corresponding isocyanide in a 1:1:1 molar ratio. Organic solutions of complexes **10** are unstable, but both complexes are stable in the solid state if stored at 4 °C.

Reactivity of Complexes 3. Complexes **3** are suitable precursors for the synthesis of other complexes containing the C(NHR)CHC(O)Me ligand. Thus, we have shown above that MeCN cleaves the bridge in **3b**, giving **4b** (Scheme 2). Similarly, the reactions of the dimers **3** with PPh_3 (PPh_3:Pd = 1) gave the corresponding complexes [Pd{κ^2-*C,O*-C(NHR)CHC(O)Me}Cl(PPh$_3$)] [R = ^{t}Bu (**11a**), Xy (**11b**); Scheme 4]. The proposed structure is based on the strong *transphobia* between C- and P-donor ligands.[10,11] Both complexes are stable at room temperature in the solid state, but ^{1}H NMR spectra in chlorinated (CD_2Cl_2, $CDCl_3$) or nonchlorinated (d_8-THF) solvents show that they decompose slowly into $[PdCl_2(PPh_3)_2]$ and other unidentified compounds. Complex **11b** was obtained, with even better yield (81 vs 65%), when **3b** was reacted with PPh_3 (PPh_3:Pd = 2). However, the reaction of complex **3a** with PPh_3 using PPh_3:Pd = 2 or 4 led to a mixture, which could not be separated, of **11a** and a product that, in agreement with its ^{1}H and ^{31}P{^{1}H} NMR (see Supporting Information), is *trans*-[Pd{C(NH^{t}Bu)=CHC(O)Me}Cl(PPh$_3$)$_2$] (1.1:2) (Scheme 4). By reacting **3** with the more basic PEt_3 (PPh_3:Pd = 2), we have been able to obtain the complexes *trans*-[Pd{C(NHR)=CHC(O)Me}Cl(PEt$_3$)$_2$] [R = ^{t}Bu (**12a**), Xy (**12b**); Scheme 4]. Complex **12a** was obtained in moderate yield (65%) due to its extreme solubility in most organic solvents (acetone, $CHCl_3$, CH_2Cl_2, Et_2O, THF; partially soluble in *n*-hexane). However, **12b** could not be obtained analytically pure because it is more soluble in *n*-hexane and *n*-pentane (see Supporting Information). Complexes **12** have to be stored under N_2. The ^{1}H NMR spectra of complexes **12** prove that their structures are like those of the related complexes *trans*-[Pd{C(NHR)=CHC(O)R′}Cl(PPh$_3$)$_2$] (R = Me, *p*-C_6H_4OMe, R′ = Me;[2] R = ^{t}Bu, R′ = Ph[4]).

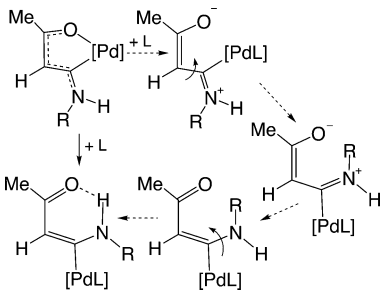
As shown below, the geometry around the PdC−NHR bond in the palladacyclic complexes is *trans*, while that of complexes **8** and **12** is *cis*. This isomerization occurs because the cleavage of the O−Pd bond allows the rotation around the CH−CNHR bond (Scheme 5) and decreases the enolato character of the β-ketoenamine ligand, favoring the resonance form Me(C=O)-CH=C(Pd)−NHR, the free rotation around the C(Pd)−NHR bond, and the formation of the hydrogen bond that leads

Scheme 4



(25) Otsuka, S.; Tatsuno, Y.; Ataka, K. *J. Am. Chem. Soc.* **1971**, *93*, 6705. Rettig, M. F.; Kirk, E. A.; Maitlis, P. M. *J. Organomet. Chem.* **1976**, *111*, 113. Yamamoto, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1987**, *58*, 1843. Marsh, R. E.; Schaefer, W. P.; Lyon, D. K.; Labinger, J. A.; Bercaw, J. E. *Acta Crystallogr., Sect. B* **1992**, *53*, 317.

Scheme 5



to complexes **8** and **12**. This conformation is the most important in secondary β-ketoenamines, probably due to the strong intramolecular hydrogen bond.[26]

Reaction of **3** with Tl(acac) (acac:Pd = 2) gives complexes [Pd{κ^2-*C,O*-C(NHR)CHC(O)Me}(κ-*O,O*-acac)] [R = ^{t}Bu (**13a**), Xy (**13b**); Scheme 4]. The transformation of **3a** into **13a** occurs quickly, but complete conversion of **3b** into **13b** requires 6 h. Both complexes **13** are soluble in common precipitating organic solvents (*n*-hexane, *n*-pentane, Et$_2$O). To isolate these complexes, it was necessary to concentrate an *n*-pentane or Et$_2$O solution, respectively, and dry the residue under vacuum over 1−2 days. At room temperature both compounds are air-stable in the solid state and in solution.

Crystal Structures. The crystal structures of complexes **6a** (Figure 1), **9b** (Figure 2), **10a** (Figure 3), and **10b** (Figure 4) have been solved. All of them show an aproximately square-planar coordination around the palladium atom. The *trans* influences of ^{t}BuNC and XyNC ligands are similar because in complexes **10** analogous Pd−C(NHR) [**10a** 2.019(4) Å, **10b** 2.003(4) Å] and Pd−O [**10a** 2.024(3) Å, **10b** 2.021(3) Å] distances are observed. Complexes **10** show the Pd−CNR bond distance *trans* to C [**10a** 2.057(4) Å, **10b** 2.042(4) Å] longer than that *trans* to O [**10a** 1.937(4) Å, **10b** 1.932(4) Å] as a consequence of the stronger *trans* influence of the C-donor ligand. Similarly, in **9b** the Pd−CNXy bond *trans* to the acetonyl group [2.090(2) Å] is longer than those corresponding to the two mutually *trans* Pd−CNXy bond distances [1.973(3) and 1.980(3) Å] due to the greater *trans* influence of acetonyl than the XyNC ligand. The cationic nature of complex **10a** causes the shortening of the Pd−O bond [2.024(3) Å] with respect to that in the neutral complex **6a** [2.038(1) Å], despite being *trans* to the same ligand. In contrast, the Pd−C(NHR) bond distance is longer in complex **10a** [2.019(4) Å] than in complex **6a** [1.9931(14) Å] due to the greater *trans* influence of the ^{t}BuNC ligand than that of Cl, and the Pd−CN^{t}Bu bond *trans* to oxygen is also longer in **10a** [1.937(4) Å] than that in **6a** [1.9207(15) Å], probably due to the greater Pd to ^{t}BuNC π-back-bonding in the neutral than in the cationic complex. The geometry of **6a** is in agreement with the greater *transphobia* of the pair C-donor ligand/C-donor ligand than that of the pair C-donor ligand/Cl.[10,11] For this reason, and because of its similar nature, we propose the same geometry for **6b**.

(26) Sandström, J. Chapter 6: Static and Dynamic Stereochemistry of Acceptor-Substituted Enamines. In *The Chemistry of Enamines*; Rappoport, Z., Ed.; Wiley: Chichester, 1994; p 406. Zhuo, J. C. *Magn. Reson. Chem.* **1996**, *34*, 595. Zhuo, J. C. *Magn. Reson. Chem.* **1997**, *35*, 21. Zhuo, J. C. *Magn. Reson. Chem.* **1997**, *35*, 311. Chiara, J. L.; Gómez-Sánchez, A. Chapter 5: NMR Spectra. In *The Chemistry of Enamines*; Rappoport, Z., Ed.; Wiley: Chichester, 1994; p 280.

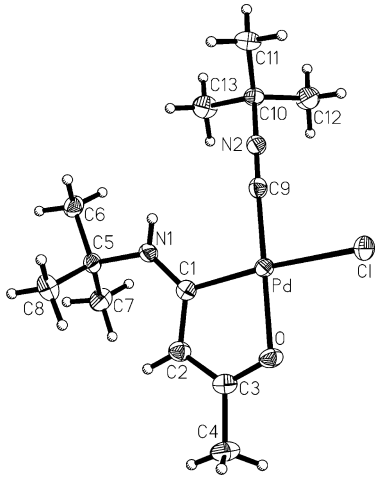


Figure 1. Thermal ellipsoid plot (50% probability) of **6a**. Selected bond lengths (Å) and angles (deg): Pd−C(9) = 1.9207(15), Pd−C(1) = 1.9931(14), Pd−O = 2.0380(10), Pd−Cl = 2.3738(4), O−C(3) = 1.2929(18), C(1)−N(1) = 1.3258(19), C(1)−C(2) = 1.413(2), C(2)−C(3) = 1.383(2), C(3)−C(4) = 1.503(2), N(1)−C(5) = 1.4948(19), N(2)−C(9) = 1.150(2), N(2)−C(10) = 1.4661(18), C(9)−Pd−C(1) = 94.08(6), C(1)−Pd−O = 82.33(5), C(9)−Pd−Cl = 90.83(4), O−Pd−Cl = 92.72(3), C(3)−O−Pd = 110.68(9), N(1)−C(1)−C(2) = 125.32(14), N(1)−C(1)−Pd = 124.07(11), C(2)−C(1)−Pd = 110.61(10), C(3)−C(2)−C(1) = 115.12(14), O−C(3)−C(2) = 120.98(13), O−C(3)−C(4) = 116.44(14), C(2)−C(3)−C(4) = 122.58(15), C(1)−N(1)−C(5) = 129.98(12), C(9)−N(2)−C(10) = 173.02(14), N(2)−C(9)−Pd = 171.28(12).

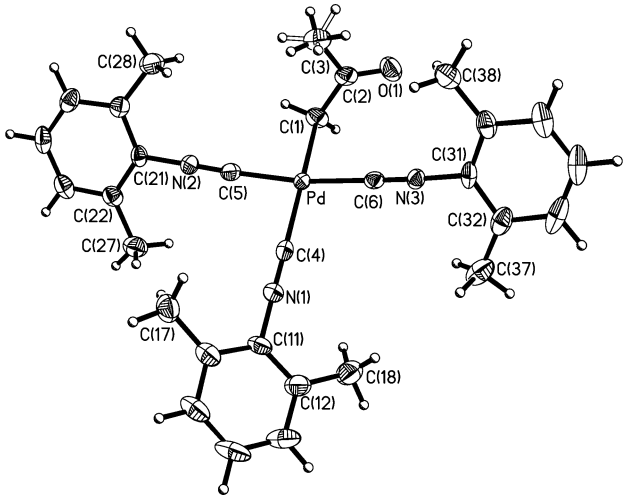


Figure 2. Thermal ellipsoid plot (50% probability) of the cation of complex **9b**. Selected bond lengths (Å) and angles (deg): Pd−C(5) = 1.972(3), Pd−C(6) = 1.979(3), Pd−C(4) = 2.027(3), Pd−C(1) = 2.090(2), O(1)−C(2) = 1.218(3), N(1)−C(4) = 1.148(3), N(1)−C(11) = 1.408(3), N(2)−C(5) = 1.146(3), N(2)−C(21) = 1.408(3), N(3)−C(6) = 1.152(3), N(3)−C(31) = 1.407(3), C(1)−C(2) = 1.475(4), C(2)−C(3) = 1.505(4), C(5)−Pd−C(4) = 91.20(10), C(6)−Pd−C(4) = 93.05(10), C(5)−Pd−C(1) = 86.36(11), C(6)−Pd−C(1) = 90.30(10), C(4)−N(1)−C(11) = 179.2(3), C(5)−N(2)−C(21) = 178.5(3), C(6)−N(3)−C(31) = 177.1(2), C(2)−C(1)−Pd = 114.57(18), O(1)−C(2)−C(1) = 122.4(3), O(1)−C(2)−C(3) = 120.9(3), C(1)−C(2)−C(3) = 116.7(3), N(1)−C(4)−Pd = 173.8(2), N(2)−C(5)−Pd = 175.4(2), N(3)−C(6)−Pd = 173.7(2).

The palladacycles in complexes **6a**, **10a**, and **10b** show a high degree of electron delocalization over the

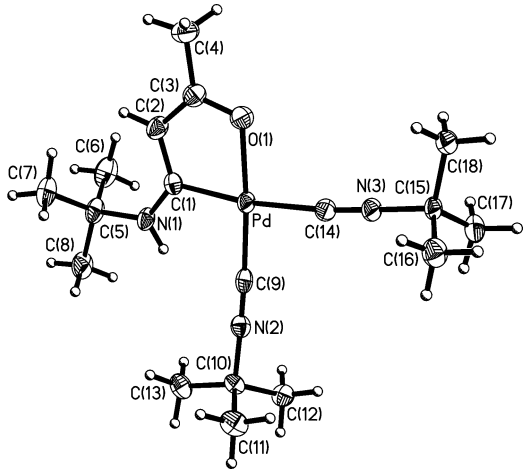


Figure 3. Thermal ellipsoid plot (50% probability) of the cation of complex **10a**. Selected bond lengths (Å) and angles (deg): Pd−C(9) = 1.937(4), Pd−C(1) = 2.019(4), Pd−O(1) = 2.024(3), Pd−C(14) = 2.057(4), O(1)−C(3) = 1.296(5), N(1)−C(1) = 1.328(5), N(1)−C(5) = 1.503(5), N(2)−C(9) = 1.146(5), N(2)−C(10) = 1.471(5), N(3)−C(14) = 1.145(5), N(3)−C(15) = 1.474(5), C(1)−C(2) = 1.400(5), C(2)−C(3) = 1.378(6), C(3)−C(4) = 1.502(6), C(9)−Pd−C(1) = 93.69-(15), C(1)−Pd−O(1) = 82.39(13), C(9)−Pd−C(14) = 94.28-(15), O(1)−Pd−C(14) = 89.67(13), C(3)−O(1)−Pd = 110.9-(2), C(1)−N(1)−C(5) = 129.5(3), C(9)−N(2)−C(10) = 177.9(4), C(14)−N(3)−C(15) = 179.0(4), N(1)−C(1)−C(2) = 126.0-(4), N(1)−C(1)−Pd = 124.4(3), C(2)−C(1)−Pd = 109.7(3), C(3)−C(2)−C(1) = 116.0(4), O(1)−C(3)−C(2) = 121.0(4), O(1)−C(3)−C(4) = 115.1(4), C(2)−C(3)−C(4) = 123.9(4), N(1)−C(5)−C(8) = 104.6(3), N(2)−C(9)−Pd = 177.0(3), N(3)−C(14)−Pd = 174.8(4).

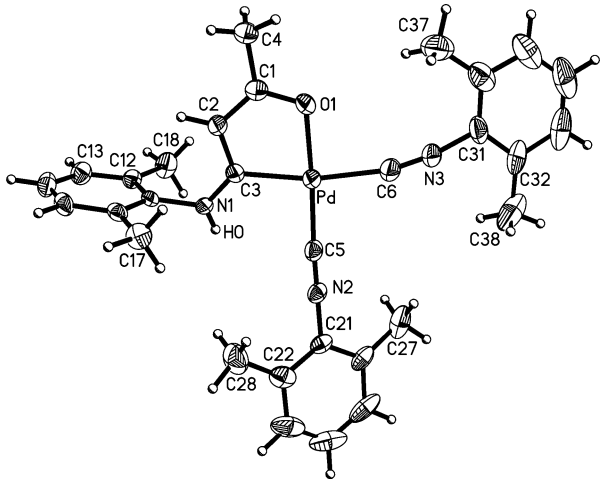
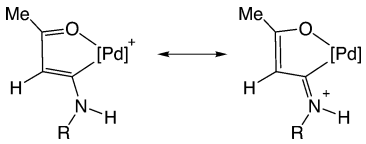


Figure 4. Thermal ellipsoid plot (50% probability) of the cation of complex **10b**. Selected bond lengths (Å) and angles (deg): Pd−C(5) = 1.932(4), Pd−C(3) = 2.003(4), Pd−O(1) = 2.021(3), Pd−C(6) = 2.042(4), O(1)−C(1) = 1.294(5), N(1)−C(3) = 1.322(4), N(1)−C(11) = 1.443(4), N(2)−C(5) = 1.144(5), N(2)−C(21) = 1.400(5), N(3)−C(6) = 1.147(5), N(3)−C(31) = 1.409(5), C(1)−C(2) = 1.381(5), C(1)−C(4) = 1.498(5), C(2)−C(3) = 1.399(5), C(5)−Pd−C(3) = 95.20-(15), C(3)−Pd−O(1) = 82.29(12), C(5)−Pd−C(6) = 95.23-(15), O(1)−Pd−C(6) = 87.75(13), C(1)−O(1)−Pd = 111.1(2), C(3)−N(1)−C(11) = 123.0(3), C(5)−N(2)−C(21) = 178.9-(4), C(6)−N(3)−C(31) = 170.8(4), O(1)−C(1)−C(2) = 120.5-(3), O(1)−C(1)−C(4) = 115.9(3), C(2)−C(1)−C(4) = 123.7(4), C(1)−C(2)−C(3) = 115.6(3), N(1)−C(3)−C(2) = 122.8(3), N(1)−C(3)−Pd = 127.1(3), C(2)−C(3)−Pd = 110.0(3), N(2)−C(5)−Pd = 173.9(3), N(3)−C(6)−Pd = 165.7(4).

OCCCNC group, as shown in Schemes 1−4. Chart 1 shows the two canonical forms of the chelating β-ketoenamine ligand. The structural parameters that support this electron delocalization are as follows. (i) The five-membered rings adopt an essentially planar geometry (mean deviation of the five atoms from the mean plane: **6a** 0.026 Å, **10a** 0.020 Å, **10b** 0.029 Å). (ii) The PdOC−C [**6a** 1.383(2) Å, **10a** 1.378(6) Å, **10b** 1.381(5) Å] and PdC−C [**6a** 1.413(2) Å, **10a** 1.400(5) Å, **10b** 1.399(5) Å] bond distances are intermediate between that of a single (O)*C*−*C*═C bond [1.464 Å] and a double (O)C−*C*═*C* bond [1.340 Å].[27] (iii) The C−O bond distances [**6a** 1.2929(18) Å, **10a** 1.296(5) Å, **10b** 1.294(5) Å] are intermediate between that of a single C−O(Pd-CNR-*trans*) bond [1.337−1.356 Å][28] and a double Me_2C═O(PdC-*trans*) bond [mean value 1.225 Å].[29] They are also longer than the C−O bond distance in terminal (e.g., 1.220(4) Å in **9**) or bridging (e.g., 1.263(4) Å in $[Pd_2\{CH_2C(O)Me\}\{\mu\text{-}\kappa^2\text{-}C,O\text{-}CH_2C(O)Me\}(\mu\text{-}Cl)Cl(dmso)_2]$[9]) acetonyl ligands, which shows that the β-ketoenamine ligands have greater enolato character than bridging acetonyl ligands. (iv) The exocyclic C−N distances [**6a** 1.3258(19) Å, **10a** 1.328(5) Å, **10b** 1.322(4) Å] are much shorter than that of a single R_2N-CH_2Pd bond (mean value, 1.450 Å)[30] and intermediate between a double XyNH═C(Me)Pd bond (ca. 1.30 Å)[31] and the C−N bond distances in pyridine (1.337 Å).[27] The geometry around the PdC−NHR bond in complexes **6a** and **10a** is *trans*; the same was observed in solution for all the palladacycles studied (see below). (v) The OCCCN(H)C systems are planar. In the only other described complex with this metallacycle, $[Co(\eta^5\text{-}C_5H_5)\{\kappa^2\text{-}C,O\text{-}C(NHCPhMe)CHC(O)Ph\}(PMe_3)]BF_4$, the CoC−C [1.406(6) Å], C−O [1.292(5) Å], CoOC−C [1.384-(6) Å], and the exocyclic C−N distances [1.325(6) Å] are not significantly different.[17] In complex *trans*-$[Pd\{C(NH^tBu)═CHC(O)Ph\}Cl(PPh_3)_2]$, where the same ligand adopts a monocoordinate bonding, as in complexes **8** and **12**, a high degree of π delocalization over the ligand has also been proposed.[4] However, comparing their X-ray structural data with those in the κ^2-*C,O*-$C(NH^tBu)CHC(O)Me$ ligand in complex **6a**, there are

Chart 1



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

(28) Modinos, A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2065. Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fischer, A. *Organometallics* **2001**, *20*, 2704.

(29) Falvello, L. R.; Fornies, J.; Navarro, R.; Sicilia, V.; Tomas, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3143. Hashmi, A. S. K.; Grundl, M. A.; Bats, J. W.; Bolte, M. *Eur. J. Org. Chem.* **2002**, 1263. Hashmi, A. S. K.; Naumann, F.; Bats, J. W. *Chem. Ber.* **1997**, *130*, 1457. Hashmi, A. S. K.; Naumann, F.; Nass, A. R.; Bolte, M. *J. Prakt. Chem.* **1998**, *340*, 240. Canty, A. J.; Patel, J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *607*, 194. Vicente, J.; Arcas, A.; Bautista, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *New J. Chem.* **1996**, *20*, 345.

(30) 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 Crystallogr., Sect. B* **1981**, *37*, 447.

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

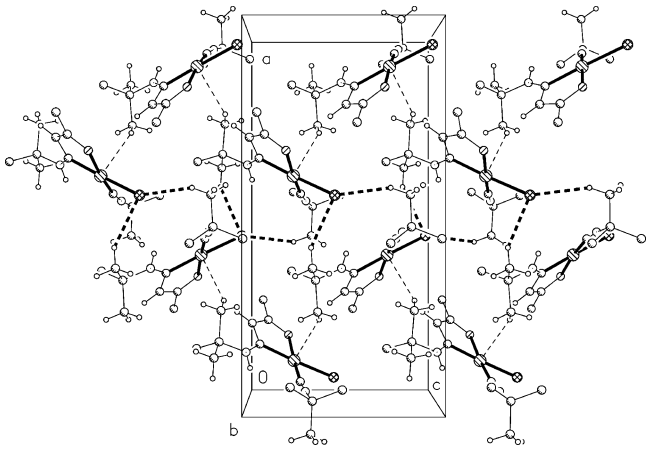


Figure 5. View of the H···Pd and H···Cl interactions in **6a**.

some analogies, for example, in the Pd−C [1.992(4), 1.9931(14) Å, respectively] PdC−N [1.325(4), 1.3258(19)Å, respectively], and PdC−C [1.399(4), 1.413(2) Å, respectively] distances, but significant differences, in PdCC−C [1.409(6) and 1.383(2) Å, respectively] and C−O [1.262(4), 1.2929(18) Å, respectively] bond distances, probably because of the presence of different substituents (Ph, Me, respectively), the hydrogen bond in the complex with the monocoordinate ligand, and the greater enolato character of the chelating ligand.

The Pd−C(NHR) distances [**6a** 1.9931(14) Å, **10a** 2.019(4) Å, **10b** 2.003(2) Å] are significantly shorter than the Pd−CH$_2$C(O)Me bond distance in complex **9b** [2.090(2) Å], despite being *trans* to an isocyanide ligand in **10** and **9**. In addition, the Pd−C(NHR) distance in **10b** [2.003(2) Å] is shorter than the Pd−C(NXy) *trans* to the same ligand in the complex *cis*-[Pd{κ^2-*C,N*-C(=NXy)-C$_6$H$_4$NH$_2$-2}(CNXy)$_2$]TfO [2.034(3) Å].[32] The Pd−CH$_2$C(O)Me bond distance is longer in **9b** [2.090(2) Å] than in the two other reported acetonyl palladium complexes, [Pd$_2$\{CH$_2$C(O)Me\}\{μ-κ^2-*C,O*-CH$_2$C(O)Me\}(μ-Cl)-Cl-(dmso)$_2$] [2.050(3) Å] and [Pd$_2$\{CH$_2$C(O)Me\}$_2$(μ-Cl)$_2$-(tht)$_2$], [2.053(3) Å],[9] due to the greater *trans* influence of the XyNC ligand with respect to Cl.

In **6a** there are no hydrogen bonds involving the NH group, but one H···Pd and two H···Cl weak interactions (Figure 5) lead to layers of molecules parallel to the *xz* plane. In complexes **9b** and **10a** the cationic units are connected to the anion through hydrogen bonds (Figures 6 and 7). In addition, in **9b** there is also a C−H···Cl interaction with the molecule of CHCl$_3$ (Figure 6). In complex **10b** there are intermolecular $\pi-\pi$ stacking and C−H···Pd agostic interactions giving dimers (Figure 8). The first interactions are between the π electron densities of the C≡N group of one molecule and the aryl group of the other molecule of the dimer. The segment between the centroids is 3.72 Å in length, and its angle with the aryl plane is 85.5°. Whereas $\pi-\pi$ stacking interactions are well established for organic and biological systems,[33] their role in organometallic compounds is scarcely recognized.[34] The parameters of the C−H···Pd agostic interactions are C(34)···Pd 3.264(6) Å, H···Pd 3.11 Å, C(34)−H(34)···Pd 92.8°, and H−C···Pd 70.5°.

Spectroscopic Properties. The ^{1}H NMR spectra of complexes show the MeC(O), CH$_2$, and CH protons as

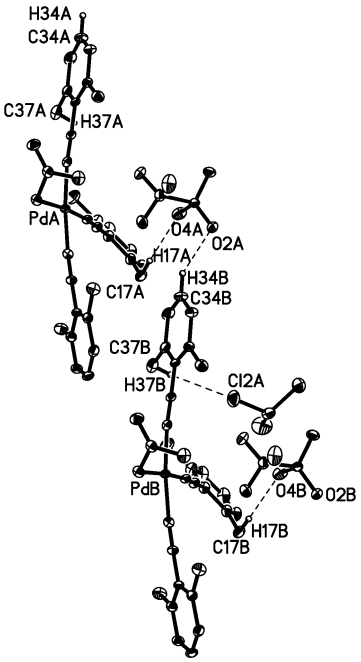


Figure 6. View of the hydrogen bond interactions in **9b**. All hydrogen atoms, except those involved in hydrogen bond interactions, have been omitted.

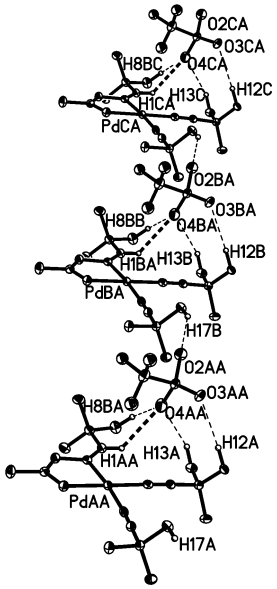


Figure 7. View of the hydrogen bond interactions in **10a**. All hydrogen atoms, except those involved in hydrogen bond interactions, have been omitted.

singlets in the ranges δ 1.93−2.32, 2.61−3.18, and 4.12−5.73, respectively. As expected, the CH$_2$ protons are more shielded for ^{t}BuNC than XyNC complexes ($\Delta\delta$ = 0.52−0.21 ppm). The NH proton in the palladacyclic complexes appears as a broad resonance

(32) Vicente, J.; Abad, J. A.; Frankland, A. D.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272.

(33) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210.

(34) Magistrato, A.; Pregosin, P. S.; Albinati, A.; Rothlisberger, U. *Organometallics* **2001**, *20*, 4178, and references therein. Gibson, D. H.; Mashuta, M. S.; Yin, X. L. *Acta Crystallogr., Sect. C* **2004**, *60*, M366. Gladiali, S.; Taras, R.; Ceder, R. M.; Rocamora, M.; Muller, G.; Solans, X.; Font-Bardia, M. *Tetrahedron Asymm.* **2004**, *15*, 1477. Dotta, P.; Magistrato, A.; Rothlisberger, U.; Pregosin, P. S.; Albinati, A. *Organometallics* **2002**, *21*, 3033.

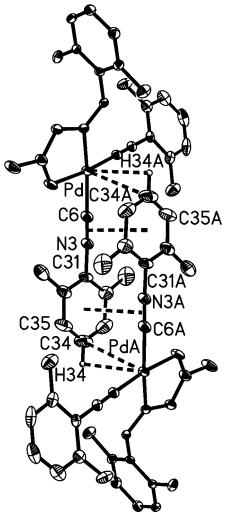


Figure 8. View of the $\pi-\pi$ and agostic interactions in **10b**. All hydrogen atoms, except those involved in the C−H···Pd interactions, have been omitted.

in the wide range 4.85−9.70 ppm, shielded with respect to that in complexes with the monocoordinate C(NHR)=CHC(O)Me ligand (12.16−14.08 ppm), which supports the proposal of an intramolecular hydrogen bond in the latter (Scheme 4). In the ^{1}H NMR of complexes *trans*-[Pd{C(NHR)=CHC(O)Me}Cl(PPh_3)$_2$] (R = Me, *p*-C_6H_4OMe), containing hydrogen-bonded heterocycles, the NH proton appears as a broad resonance at 10.0 and 11.6 ppm, respectively.[2] As expected, the ^{t}BuNH proton is more shielded ($\Delta\delta$ = 2.9−0.83 ppm) than the XyNH proton. This effect is also observed for the protons of the group C*H*C(O)Me of the nonpalladacyclic complexes **8** and **12** ($\Delta\delta$ = 0.29−0.23 ppm) and the carbon nucleus of CO ($\Delta\delta$ = 3.3−2.1 ppm) and Pd*C*NHR ($\Delta\delta$ = 3−2.4 ppm) groups. These effects are a consequence of the electron delocalization over the β-ketoenamine ligands, which have also been reported in related organic compounds.[26] However, the C*H*C(O)Me proton of the carbacyclic complexes undergoes an important shielding due to the ring current effect of the Xy group, which determines a smaller δ(CH) in complexes with R = Xy than with ^{t}Bu ($\Delta\delta$ = 0.64−0.45 ppm). This effect proves the *trans* geometry of the PdC−NXy group in these complexes, as we also show below.

NOE experiments were conducted to elucidate the geometry around the PdC−NHR bond. For complexes **3**, **4b**, **6**, **10b**, and **13**, NOESY 1D or 2D experiments reveal a NOE between the CH of the β-ketoenamine moiety and the protons of the Me and R group (^{t}Bu or Xy). No effect exists between this CH and NH protons. The ^{t}Bu and Xy groups of the β-ketoenamine ligand have a strong NOE with the NH in all cases. The NH proton also has a NOE in complexes **6** with the R group of the coordinated isonitrile and in **13** with the closer Me group of the acac ligand. All this proves the *trans* PdC−NHR bond conformation of these complexes in solution, which is the same as that found in the crystal structures of **6a**, **10a**, and **10b** (Figures 1, 3, 4 and Schemes 2−4). All ketoenamine complexes, except **13**, showed at various temperatures small signals that could be due to other isomers containing a different conformation of the PdC−NHR bond or to a *cis*−*trans* isomerization in the case of complexes **3**, **4b**, and **6**. Unfortunately, it was not possible to characterize them because they were present at very low concentrations. In the case of complex **4b**, no NOE effects were observed between the Me protons of the MeCN ligand and other protons of the molecule. This prevents assigning the geometry of this complex (see Scheme 2).

Only the ^{13}C NMR spectra of the most stable complexes, **3**, **4b**, **6**, **12a** and **13**, could be recorded. The CO carbon nucleus in the chelating β-ketoenamine ligands is deshielded (202.8−208.8 ppm) with respect to that in the monocoordinate ligand in **12a** (186.8 ppm) as a consequence of the greater enolato character of the chelating ligands.

The IR spectra of complexes with ^{t}BuNC show the ν(CN) absortion in the region 2254−2208 cm^{-1} and those with XyNC in the region 2200−2160 cm^{-1}, showing, as usual, an increase with respect to ν(CN) in the free ligands (2134 and 2109 cm^{-1}, respectively).

The acetonyl complexes **2**, **5**, and **9** show the ν(CO) band in the narrow range 1658−1668 cm^{-1}. In the palladacyclic complexes (**3**, **4b**, **6**, **10**, and **11**) the ν(CO) appears at lower frequency, 1479−1536 cm^{-1}, showing the reduction of the C=O bond order found in the X-ray diffraction studies of complexes **6a** and **10**. In complexes **8** and **12**, the ν(CO) band appears in the range 1556−1570 cm^{-1}, i.e. slightly above that in the palladacyclic complexes, in agreement with the lower enolato character of the monocoordinate C(NHR)=CHC(O)Me ligand with respect to that in the chelating ligand. We have previously reported[9] that terminal and *C,O*-bridging acetonyl ligands can be distinguished by IR spectroscopy because they show the ν(CO) band in the ranges 1685−1628 and 1565−1534 cm^{-1}, respectively.[35] The present IR data suggest that the enolato character of the chelating or monocoordinate β-ketoenamine ligands is greater than or similar to, respectively, that in the *C,O*-bridging acetonyl ligand.

The IR spectra of the nonpalladacyclic complexes **8** and **12** show the band due to the ν(NH) mode (3028−2964 cm^{-1}) ca. 400−200 cm^{-1} below that corresponding to the palladacyclic complexes (3418−3202 cm^{-1}). This can be attributed to the intramolecular hydrogen bond present in the former such as it has also been reported in related organic compounds.[36]

The position of the bands from the ν(PdCl) modes has been tentatively assigned in agreement with the coordination type of the chloro ligand, bridging [ν_b(PdCl)] or terminal [ν_t(PdCl)], and on the *trans* influence of the ligand L *trans* to the chloro ligand [ν(PdCl)$_L$]. Thus, in complexes **2a** (296, 252 cm^{-1}) and **2b** (296, 254 cm^{-1}), those at higher wavenumbers must be assigned to ν_b(PdCl)$_{CNR}$ (R = ^{t}Bu, Xy) and the others to ν_b(PdCl)$_{CH2R'}$ (R′ = C(O)Me) in agreement with previous asignments[9] and the above observation of a stronger *trans* influence of the acetonyl group than the isocyanide ligand. Complex **3b** shows two bands at 282 and 246 cm^{-1} that can be assigned to ν_b(PdCl)$_O$ and ν_b(PdCl)$_{CNHR}$, respectively. As expected, ν_t(PdCl)$_L$

(35) Failing to reference this observation, Ruiz et al. (Ruiz, J.; Martínez, M. T.; Rodríguez, V.; López, G.; Pérez, J.; Chaloner, P. A.; Hitchcock, P. B. *Dalton Trans.* **2004**, 3521) have recently discovered that "the carbonyl stretching band...may be used...for distinguishing terminal C-bound enolate from bridging C,O bound enolate".

(36) Dudek, G. O. *J. Org. Chem.* **1965**, *30*, 548.

Table 1. Crystal Data for Complexes 6a, 9b·CHCl$_3$, 10a·Me$_2$CO, and 10b

	6a	**9b**·$CHCl_3$	**10a**·Me_2CO	**10b**
formula	$C_{13}H_{23}ClN_2OPd$	$C_{32}H_{33}Cl_3F_3N_3O4PdS$	$C_{22}H_{38}F_3N_3O_5PdS$	$C_{31}H_{32}F_3N_3O_4PdS$
M_r	365.18	25.42	620.01	706.06
cryst size (mm)	0.35 × 0.35 × 0.09	0.46 × 0.32 × 0.17	0.49 × 0.34 × 0.24	0.50 × 0.30 × 0.14
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
space group	$Pca2_1$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
cell constants				
a, Å	18.2636(11)	8.6505(5)	12.8580(8)	8.3651(6)
b, Å	9.3501(4)	11.8001(6)	17.0414(11)	22.9882(15)
c, Å	9.2895(4)	18.7442(14)	13.3978(8)	17.1156(9)
α, deg	90	83.546(5)	90	90
β, deg	90	87.742(5)	95.509(5)	103.680(6)
γ, deg	90	70.234(4)	90	90
volume, (Å^3), Z	1586.34(14), 4	1789.20(19), 2	2922.1(3), 4	3197.9(4), 4
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ(calc) (Mg m^{-3})	1.330	1.532	1.409	1.466
F(000)	744	836	1280	1400
T (K)	133	173	173	173
μ, mm^{-1}	1.53	0.856	0.759	0.702
transmissions	0.642−0.880	0.910−0.743	0.746−0.740	0.839−0.763
θ, range (deg)	2.2−30.0	3.01−25.0	3.05−25.0	3.02−25.0
limiting indices	$-25 \le h \le 25$	$0 \le h \le 10$	$-15 \le h \le 0$	$-9 \le h \le 2$
	$-13 \le k \le 13$	$-13 \le k \le 13$	$-20 \le k \le 1$	$-27 \le k \le 0$
	$-13 \le l \le 13$	$-22 \le l \le 22$	$-15 \le l \le 15$	$-20 \le l \le 20$
no. of reflns				
measd	31977	6735	5603	6984
indep	4637	6278	5132	5607
R_{int}	0.029	0.0181	0.0172	0.0349
abs corr	SADABS	ψ-scans	ψ-scans	ψ-scans
refinement method	full-matrix least squares on F^2			
no. data/rest/params	4637/2/174	6278/39/455	5132/7/318	5607/363/393
S (F^2)	1.044	1.041	1.075	0.977
R1	0.015	0.029	0.039	0.039
wR2	0.039	0.070	0.100	0.094
largest $\Delta\rho$ (e Å^{-3})	0.387,−0.201	0.693,−0.554	0.721,−0.861	0.775,−0.678

> ν_b(PdCl)$_L$. Thus, the bands assignable to the ν_t(PdCl)$_{CNHR}$ mode appear in the range 262−299 cm^{-1} with ν_t(PdCl)$_{CNHt_{Bu}}$ < ν_t(PdCl)$_{CNHXy}$. In some cases, ν(PdCl) could not be assigned (**3a**, **11a**, **12b**). In the IR spectrum of complex **4b** there are three bands at 361, 326, and 292 cm^{-1} that could be due to the ν(PdCl) mode. Therefore, we cannot use these data to propose a geometry for this complex.

Conclusions

To illustrate the capacity of [Pd{CH$_2$C(O)Me}Cl]$_n$ to prepare chloro-monoacetonyl or monoacetonyl palladium(II) complexes, we have isolated complexes of the types [Pd{CH$_2$C(O)Me}Cl(CNR)$_n$] (n = 1, 2) and [Pd{CH$_2$C(O)Me}(CNR)$_3$]$^+$. We have studied the thermal transformation of these compounds into C-palladated β-ketoenamine complexes resulting from insertion of one molecule of the isocyanide followed by a β-ketoimine to β-ketoenamine tautomerization process. The resulting complexes are the first palladium compounds containing such ligands acting as a chelate. We report here for the first time the isolation of both types, adducts and insertion/tautomerization products of isocyanides into the Pd−CH$_2$C(O)R bond.

Acknowledgment. We thank the financial support of Ministerio de Ciencia y Tecnología, FEDER (BQU2001-0133) and Fundación Séneca (Comunidad Autónoma de la Región de Murcia, Spain) for a grant to J.M.F.-H.

Supporting Information Available: Experimental details of the preparation of **12b** and *trans*-[Pd{C(NH^{t}Bu)=CHC(O)Me}Cl(PPh$_3$)$_2$]. Experimental procedure, kinetic data for the conversion of **2** into **3** and **5** into **6**, and plots of these data. Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **6a**, **9b**, **10a**, and **10b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM048999C