## **Observation of a Non-H-Bond-Stabilized Tautomeric** Imine-Enamine Equilibrium in Iminoacyl-Palladium Complexes

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Summary: Iminoacyl complexes of the type trans-Pd- $(C(=NBu^{t})(CH_{2}C_{6}H_{4}-p-X))Cl(PR_{3})_{2}$  exist in solution as equilibrium mixtures of their imine and enamine forms. The position of the equilibria can be tuned by varying the X substituent of the aryl ring and the phosphine ligands, allowing in some cases the isolation of compounds that exist as the less common enamine form, both in solution and in the solid state.

Prototropic tautomerism is an important process that is involved in many organic transformations.<sup>1</sup> Of the different kinds, keto-enol and imine-enamine tautomerism have been the subject of numerous investigations due to their importance not only in organic but also in biological processes.<sup>2</sup> Although organometallic acyl and iminoacyl complexes are widespread and their chemical behavior has been thoroughly studied,<sup>3</sup> they are almost invariably encountered in their keto and imine forms, respectively.<sup>4</sup> In transition-metal-iminoacyl chemistry, imine-to-enamine tautomerism has been invoked to account for the nature of the product of the reaction of the iminoacyl trans- $Pd(C(=NC_6H_4-p-Me)Me)Cl(PEt_3)_2$ with  $MeO_2CC \equiv CCO_2Me^{5}$  but tautomerization to a stable enamine structure is uncommon and requires stabilization by hydrogen bonding,<sup>6</sup> extensive electron delocalization,<sup>7a</sup> or formation of more complex structures.<sup>7b,c</sup> A similar situation is found for organic imines and enamines, where the imine form usually predominates.<sup>1a,2,8</sup> In this communication we wish to report the first observation of a quantifiable imine-enamine equilibrium in the system arising from the insertion of CNBu<sup>t</sup> into the Pd-C bond of complexes of the type Pd- $(CH_2C_6H_4-p-X)Cl(PR_3)_2$ . The position of this equilibrium can be varied by modifying the nature of the X group and the phosphine ligands, thereby allowing the study of the factors that affect the equilibrium constant and of the complexes that exist as the more uncommon enamine tautomer.

Reaction of the benzylpalladium derivative 1al with tert-butyl isocyanide yields a yellow product, 1im,9 whose NMR and IR spectra<sup>5</sup> display features typical for a  $\eta^1$ -iminoacyl complex.<sup>10</sup> However, NMR spectra also show a second set of signals associated with a minor product, 1en,<sup>9</sup> which amounts to ca. 8% of the overall mixture and could not be separated by recrystallization. Careful examination of the <sup>1</sup>H NMR spectrum of 1en (acetone- $d_6$ , 20 °C) revealed the presence of resonances at  $\delta$  5.65 (t,  $J_{\text{HP}} = 2.8 \text{ Hz}$ ) and 4.82 (br s) attributable to an olefinic and an NH proton, respectively. These signals strongly suggest that **len** has the enamine structure shown in Scheme 1. Since the low concentration of 1en in solution prevented the observation, under ordinary conditions, of the <sup>13</sup>C resonance corresponding

(11) The cationic carbene complex formed upon protonation of compound 3im/3en by triflic acid has been isolated and characterized.

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<sup>(1) (</sup>a) March, J. Advanced Organic Chemistry: Reactions, Mechanisms and Structure; Wiley: New York, 1992. (b) Lowry, M. T.; Richardson, K. S. Mechanism and Theory in Organic Chemistry; Harper and Row: New York, 1987.

<sup>(2)</sup> Lammersma, K.; Pasad, B. V. J. Am. Chem. Soc. 1994, 116, 642 and references therein.

<sup>(3) (</sup>a) Durfee, L. D.; Rothwell, I. P. Chem. Rev. 1988, 88, 1059. (b) Crociani, B. In Reactions of Coordinated Ligands; Braterman, P., Ed.; Plenum Press: New York, 1986; Chapter 9. (c) Alexander, J. J. In The Chemistry of the Metal-Carbon Bond; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, Chapter 5.

<sup>(4)</sup> We are not aware of any well-documented example of M-C(O)- $CHR \Rightarrow M-C(OH)=CR_2$  tautomerism. However, transition-metal enolates are an important and synthetically useful class of organometallic compounds. For some examples see: (a) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. J. Am. Chem. Soc. 1989, 111, 2550. (b) Heah, P. C.; Patton, A. T.; Gladysz, J. A. J. Am. Chem. Soc. 1986, 108, 1185. (c) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. J. Am. Chem. Soc. 1986, 108, 6328. (d) Davies, S. G.; Walker, J. C. J. Chem. Soc., Chem. Commun. 1985, 209. (e) Theopold, K. H.; Becker, P. N.; Bergman, R. G. J. Am. Chem. Soc. **1982**, 104, 5250. (f) Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. J. Am. Chem. Soc. **1984**, 106, 2210.

<sup>(5)</sup> Clark, H. C.; Milne, C. R. C.; Payne, N. C. J. Am. Chem. Soc. 1978, 100, 1164.

<sup>(6) (</sup>a) Veya, P.; Floriani, C. Organometallics 1993, 12, 4899. (b) Bertani, R.; Castellani, C. B.; Crociani, B. J. Organomet. Chem. 1984, 269. C15.

<sup>(7) (</sup>a) Belderrain, T. R.; Paneque, M.; Carmona, E., to be submitted for publication. (b) Bellachioma, G.; Cardaci, G.; Zanazzi, P. Inorg. Chem. 1987, 26, 84. (c) Werner, H.; Heiser, B.; Kühn, A. Angew. Chem., Int. Ed. Engl. 1981, 20, 300.

<sup>(8)</sup> de Jeso, B.; Pommier, J. C. J. Chem. Soc., Chem. Commun. 1977, 565.

<sup>(9)</sup> Procedure, analytical and selected spectroscopic data for compounds 1im/1en, 2im/2en, and 3im/3en are as follows. 1im/1en: To a stirred solution of  $Pd(CP_6H_5)Cl(PM_{e3})_2$  (0.2 g, 0.57 mmol) in THF (40 mL) at room temperature was added CNBu<sup>t</sup> (0.6 mL, 1 M solution in THF). There was an immediate color change from dark yellow to light yellow. The mixture was stirred at room temperature for 4 h light yellow. The mixture was stirred at room temperature for 4 h and then evaporated *in vacuo*. The solid residue was crystallized from diethyl ether (20 mL) at -20 °C, giving a yellow crystalline material in 71% yield. **2im/2en** and **3im/3en** were prepared in the same manner, also giving yellow crystalline products in 71% and 73% yields, respectively. **1im**: IR (cm<sup>-1</sup>, Nujol)  $v_{C-N}$  1637; <sup>1</sup>H NMR (20 °C, acetone- $d_6$ )  $\delta$  3.84 (s, 2 H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, acetone- $d_6$ )  $\delta$  -18.3. **1en**: <sup>1</sup>H NMR (20 °C, acetone- $d_6$ )  $\delta$  -18.3. **1en**: <sup>1</sup>H NMR (20 °C, acetone- $d_6$ )  $\delta$  -6.7 (by  $d_{C-N} = 28$  Hz =CCH); <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C) 

K. J. Chem. Soc., Dalton Trans. 1976, 327.



to the enaminic  $Pd-C(NHBu^t)$  carbon atom as well as the IR NH absorption, we sought a means of increasing the equilibrium concentration of the enamine form. The use of various solvents was of little help, since only a small difference in the tautomer ratio was observed when compound **lim/len** was dissolved in benzene or chloroform as compared to more polar solvents such as acetone, the enamine form being slightly more favored in the latter.

The ground state of organic enamines has been described as a resonance hybrid of the neutral enamine form  $\mathbf{A}$  and the 1,3-dipolar iminium salt form  $\mathbf{B}$ .<sup>1</sup> For



compounds **1en**-**3en**, a dipolar carbene form, **C**, could also be taken into account. From this picture, it can be readily understood that the presence of electron-releasing substituents on the nitrogen or palladium atoms, or of electron-withdrawing substituents on the aryl ring, should increase the relative stability of the enamine form. In agreement with these expectations, the concentration of the enamine tautomer is markedly increased for complexes **2**, which bear a *p*-trifluoromethyl fragment. NMR spectra for these tautomers, recorded in acetone-*d*<sub>6</sub> at 20 °C, showed a 3:4 equilibrium mixture of **2im** and **2en**.<sup>9</sup>

Although the structural and spectroscopic properties of late-transition-metal iminoacyl complexes do not suggest an important contribution of the amidocarbene resonance form to the electronic ground-state structure of these compounds,<sup>12</sup> the participation of such a dipolar carbene form C, particularly in the case of the enamines **2en** and **3en**, cannot be disregarded. Accordingly, compound **3im/3en**, in which the more basic ligand triethylphosphine replaces the trimethylphosphine of compound **2im/2en**, shows an even stronger preference for the enaminic form, **3en**, lowering the concentration

Scheme 2



of the imine form 3im to undetectable levels. This observation is in accord with the stabilizing effect exerted by electron-releasing ligands on resonance form C.

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the enamine isomer 2en displays resonances at 166.3 and 100.7 ppm, attributable respectively to the Pd-C and Pd-C=CHatoms; corresponding resonances can be found for compound **3en** at  $\delta$  164.4 and 102.2 ppm. This assignation has been confirmed by gated-decoupling and HET-COR spectroscopy  $({}^{1}H-{}^{13}C)$  and is consistent with the chemical shifts expected for such derivatives. Whereas the crystallized mixtures of 1im = 1en and 2im = 2en display a prominent IR band at 1640 cm<sup>-1</sup> which is characteristic of  $\eta^1$ -iminoacyl ligands, this absorption is absent in the spectrum of  $\mathbf{3}$  and is replaced by new bands at 3450 and 1540  $cm^{-1}$ , associated with the N–H and C=C bonds, respectively. The imine form **3im** has not been detected for this system; thus, pure enamine **3en** exists in the solid state.

Although we still do not have enough data to confirm a mechanism for the proton exchange, we have observed that these iminoacyl complexes are readily protonated to the corresponding cationic products (Scheme 2).<sup>11</sup> This behavior has previously been observed in related iminoacyl complexes,<sup>6a,12</sup> and is in accord with the expected basicity of the nitrogen atom. Even though tautomer exchange may occur by an intramolecular hydrogen shift, as has been proposed for other prototropies involving the iminoacyl functionality,<sup>13</sup> it seems more likely that it is promoted by trace quantities of an acid catalyst such as water present in the solvent, as shown in Scheme 2. Supporting this hypothesis. exchange of the NH, =CH, and CH<sub>2</sub> protons with deuterium occurs when D<sub>2</sub>O is added to solutions of 2im  $\Rightarrow$  **2en** in acetone- $d_6$ .

In summary, we have demonstrated that the enamine structure of simple Pd-iminoacyl complexes can be stabilized by appropriately modifying the electronic characteristics of the metal center and the alkyl ligand.

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<sup>(12)</sup> Carmona, E.; Palma, P.; Poveda, M. L. Polyhedron 1989, 12, 1447.

<sup>(13)</sup> Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. Organometallics **1990**, *9*, 2375.