*Organometallics* **2006,** *25,* 1851−1853

# *Communications*

## Reactivity of Ortho-Palladated Phenol Derivatives with Unsaturated Molecules. Carbodiimide Insertion into a C−Pd Bond and/or O−H Phenol Addition to a Carbodiimide

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*Received February 21, 2006*

*Summary: The first examples of the insertion of carbodiimides into a late-transition-metal−carbon bond and the unprecedented intramolecular addition of a phenol to a carbodiimide have allowed the synthesis of O,N and O,C six-membered palladacycles.*

Carbodiimides are important intermediates in industrial-scale syntheses. The incorporation of carbodiimides into polymeric materials accounts for the bulk of their world production. Other applications include the synthesis of nucleotides and peptides, heterocycle synthesis, biological modifications, and cycloaddition reactions.[1] The reaction products of metal complexes and carbodiimides are also of great interest. Thus, carbodiimides react with alkyl (mainly Me) or amido complexes, giving the corresponding amidininato[2−4] or guanidinato derivatives,[4−6] respectively; some of them have been used as catalysts[2,5,7] or have found industrial uses.[8] Other complexes have also been reacted with carbodiimides, giving different products after insertion of one of the C=N bonds into an M−C (M = metal)[9] or an M−H bond.[10] The metals involved in the insertion of carbodiimides into an M−C (M = metal) bond are main group, lanthanide, and early transition elements. Although carbodiimide insertion into the M−C bond of a late-transition-metal complex has been proposed as a mechanistic step, unambiguous evidence for such reactions has up until now not been available.[11] Herein we report for the first time two types of carbodiimine reactivity toward a metal complex. The first involves insertion of one of the C=N groups into the M−C bond and protonation of the other N. This process is related to one that we have just reported between a related palladium complex and nitriles,[12] except that protonation in the present case occurs at the uncoordinated nitrogen and that an additional different reaction also occurs. This involves addition of an OH to one of the C=N groups and coordination of the other N to the metal. This process is similar to that in the reaction of $[\mathrm{PdX_2}(\kappa^1 N\text{-}\mathrm{RN{=}C{=}NR'})_2]$ (X = Cl, Br, R = $^t$Bu, R′ = $^t$Bu, Me) with MeOH, giving $[\mathrm{PdX_2(RNH{-}C(OMe){=}NR')_2}]$, although this is an intermolecular process and the mode of bonding of the isourea ligand was not unambiguously established.[13]

Equimolecular amounts of $[\mathrm{Pd(C_6H_4OH\text{-}2)I(bpy)}]$ (bpy = 2,2′-bipyridine),[14] ToN=C=NTo (To = *p*-tolyl), and TlTfO (TfO = $\mathrm{CF_3SO_3}$) react to give after 3 h at room temperature $[\mathrm{Pd}\{\kappa^2 O,N\text{-}\mathrm{O}\{\mathrm{C_6H_4}\{\mathrm{C(NHTo){=}NTo}\}\text{-}2\}\}(\mathrm{bpy})]\mathrm{OTf}$ (**1a**; Scheme 1) in 86% yield. When CyN=C=NCy (Cy = cyclohexyl) was used, a mixture of the corresponding insertion, [Pd{$\kappa^2$*O,N*-

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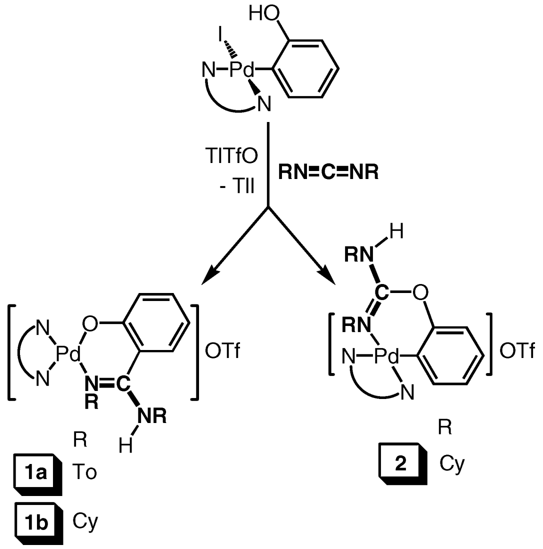
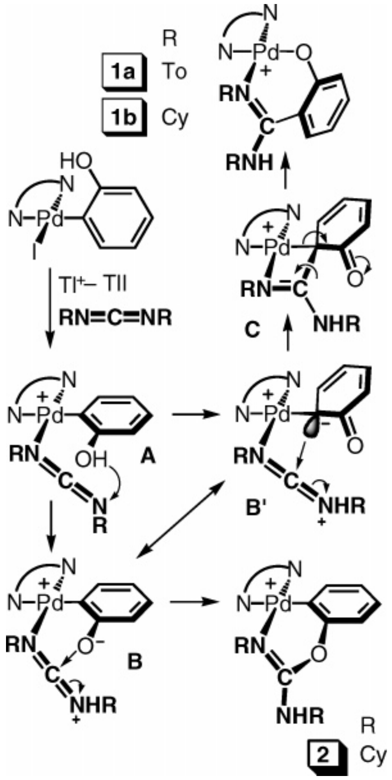
**Scheme 1. Synthesis of Complexes**



O{$C_6H_4${C(=NCy)NHCy}-2}}(bpy)]OTf (**1b**), and addition products, [Pd{$\kappa^2$*C*,*N*-{$C_6H_4${OC(=NCy)}NHCy-2}}(bpy)]OTf (**2**), was obtained. A study of the influence of the reaction conditions (molar ratio of reagents, reaction time, and temperature) allowed us to isolate pure **1b** or **2**. The best results were obtained by refluxing the reaction mixture in 1,2-dichloroethane or by using a large excess of the carbodiimide (20:1) at room temperature, respectively.

It can be postulated that the first steps in these processes are the replacement of iodine by triflate and then of the triflato ligand by the carbodiimide, which, in agreement with the structure of [$PdCl_2${N($^t$Bu)=C=N$^t$Bu}$_2$],[15] should be N-coordinated (**A** in Scheme 2). This step seems to be important, because in the absence of TlTfO, ToN=C=NTo gives a complex mixture of products and CyN=C=NCy does not react. In the reaction between the related *N,N,N′,N′*-tetramethylethylenediamine (tmeda) complex and various nitriles, the subsequent step was the protonation of the coordinated nitrogen atom of the nitrile.[12] In the present case, the protonation also occurs, but on the more basic uncoordinated nitrogen. The electronic structure of this intermediate can be formulated using the two extreme resonance forms **B** and **B′**, as proposed for the insertion of nitriles.[12] The partial negative charge at the phenolic oxygen atom can explain the nucleophilic attack at the carbodiimide central carbon atom to give the addition product **2**. This attack was not observed in the reaction with nitriles.[12] Because carbodiimides add phenols only at relatively high temperatures,[16] the formation of **2** at room temperature proves that it is an intramolecular and metal-assisted process. On the other hand, the positively charged metal center and the electron-releasing nature of the negatively charged oxygen atom favor the location of a partial negative charge on the ipso carbon atom of the aryl ligand (form **B′**). This can explain the formation of the insertion products through nucleophilic attack at the central carbon atom of the carbodiimide by the ipso carbon to give the four-membered metallacycle **C**. Cleavage of the C−Pd bond and rotation of the aryl ligand around the newly formed C−C bond allows the coordination of the oxygen atom to give **1a** or **1b**. However, while the 1:1:1 (Pd:RN=C=NR:TlOTf) room-temperature reaction gives only the insertion product for R = To

**Scheme 2. Proposed Reaction Pathway for the Synthesis of Complexes**



(**1a**), a 1:1 mixture of the insertion (**1b)** and addition (**2**) products was obtained for R = Cy. The more basic character of CyN=C=NCy could be responsible for a decrease in the formal charge at palladium, reducing the contribution of the resonance form **B′**. This would disfavor the insertion and allow the addition process. Consistently, a large excess of this ligand (20:1) that can lead to a pentacoordinated species, reducing the formal charge at palladium even further, fully suppresses the insertion at room temperature, giving only the addition product **2**. However, heating the 1:1:1 reaction mixture (refluxing in 1,2-dichloroethane) leads to an increase in the proportion of the insertion product (**1b**:**2** = 3:1), probably because the last step **C** → **1b**, requiring Pd−C bond cleavage, is favored on heating. In this reaction, thermal conversion of complex **2** into **1b** must be ruled out, because **2** remains unaltered after refluxing in 1,2-dichloroethane. The less basic character of nitriles compared to carbodiimides could also explain why they only insert into the C−Pd bond of the related tmeda complex.[12] A room-temperature reaction with a large excess (20:1) of ToN=C=NTo leads to a complex mixture of products. Preliminary results with other aryl palladium complexes and carbodiimides show that the above results are general.

The crystal structures of complexes **1a** and **2** have been solved by X-ray diffraction studies (Figures 1 and 2).[17] They show a distorted-square-planar geometry at palladium, with normal bond distances and angles. For **1a** the expected classical N−H···O contact from cation to anion is surprisingly long (H···O = 2.57(2) Å) and is accompanied by four C−H···O contacts that could be classified as hydrogen bonds. For **2**, the N−H···O contact is of normal length (H···O = 2.22(2) Å) but the anion is slightly disordered (minor site ca. 11% occupied); there are also several C−H···O contacts (for details, see the Supporting Information).

The structure of **1b** was unequivocally determined by comparing the chemical shifts of the aryl carbon nuclei with those of **1a** and **2**. The phenolate aryl group in the insertion

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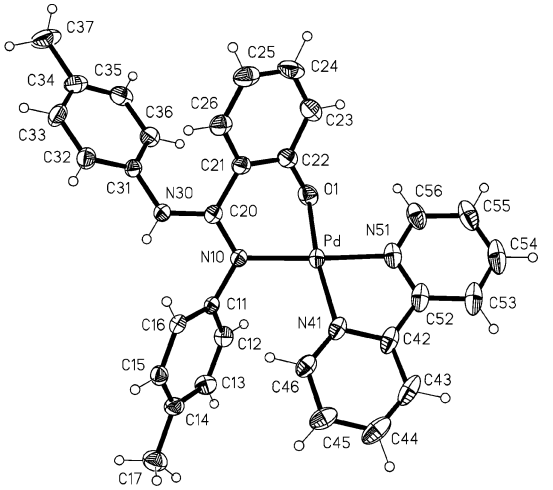

**Figure 1.** Thermal ellipsoid plot (50% probability) of the cation of **1a**.

products **1a** and **1b** gives resonances (from C(1) to C(6), values ±1 ppm) at 123 (not observed in **1b**), 167, 121, 134, 117, and 131 ppm, while **2** shows these resonances at 136, 153, 115, 125, 126, and 134 ppm.

In conclusion, we have reported the insertion of carbodiimides RN=C=NR (R = To, Cy) into a Pd−C bond. The process is assisted by three factors: the protonation of the nonbonded nitrogen by the ortho hydroxyl group, the positive charge of the metal center, and the +M effect of the phenolate oxygen. Our results represent (i) the first isolation of a product of carbodiimide insertion into a C−M bond, where M is a late transition element, and (ii) a rare insertion of a carbodiimide into an aryl−M bond.[3a,18] In addition to the insertion product, the more basic CyN=C=NCy gives the product of OH addition to the C=N bond, N being the noncoordinated nitrogen. Heating or using a large excess of the ligand favors the insertion or the addition product, respectively. This is the first report of such a dual behavior of a cumulene.

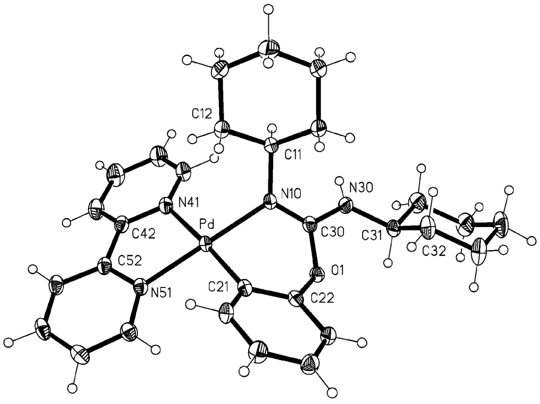

**Figure 2.** Thermal ellipsoid plot (50% probability) of the cation of **2**.

**Acknowledgment.** This work was supported by the Ministerio de Educación y Ciencia (MEC, Spain) and FEDER (EU) by Contract No. CTQ2004-05396. M.-J.L.-S. is grateful to the MEC for a grant, and we gratefully acknowledge Dr. E. Martínez-Viviente for some NMR studies.

**Supporting Information Available:** Text giving experimental details for the preparation of complexes and spectroscopic and analytical data and listings of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for complexes **1a** and **2**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) CCDC-287822 (**1a**) and CCDC-287823 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Data were recorded at −140 °C on a Bruker SMART 1000 CCD diffractometer in $\omega$ and $\varphi$ scan modes to $2\vartheta_{max} = 60°$, using monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Absorption corrections were based on indexed faces (**2**) or multiple scans (**1a**). Structures were refined on $F^2$ using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were refined using rigid methyl groups or a riding model, except for NH hydrogens, which were refined freely. The triflate group of **1a** is disordered over two positions in the ratio 8:1. Crystal data for **1a**: $C_{32}H_{27}F_3N_4O_4PdS$, monoclinic, $a = 13.8541(11)$ Å, $b = 12.0079(11)$ Å, $c = 18.6470(14)$ Å, $\beta = 100.035(4)°$, $U = 3054.6$ Å$^3$, space group $P2_1/n$, $Z = 4$, $\mu$(Mo Kα) = 0.74 mm$^{-1}$, 56 753 reflections measured, 8924 unique ($R_{int} = 0.055$). Refinement proceeded to $R_w(F^2) = 0.084$ (all data) and $R(F) = 0.034$ for 412 parameters; maximum $\Delta\rho$ 1.1 e Å$^{-3}$. Crystal data for **2**: $C_{30}H_{35}F_3N_4O_4PdS$, monoclinic, $a = 25.677(2)$ Å, $b = 13.7723(11)$ Å, $c = 20.4054(16)$ Å, $\beta = 122.774(4)°$, $U = 6067.4$ Å$^3$, space group $C2/c$, $Z = 8$, $\mu$(Mo Kα) = 0.74 mm$^{-1}$, 57 320 reflections measured, 8890 unique ($R_{int} = 0.047$). Refinement proceeded to $R_w(F^2) = 0.075$ (all data) and $R(F)$ 0.029; maximum $\Delta\rho$ 1.0 e Å$^{-3}$.

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