Insertion Reactions

DOI: 10.1002/ange.200501202

Reactivity of *ortho*-Palladated Phenol Derivatives with Unsaturated Molecules: Insertion of Nitriles into a Late-Transition-Metal–Carbon Bond**

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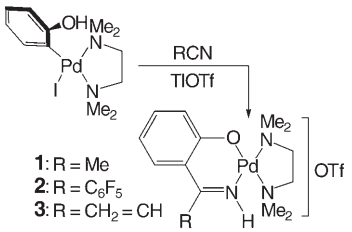
Nitriles have a very rich coordination chemistry because they are activated by some metals towards nucleophilic or electrophilic attack.[1,2] Based on this reactivity, stoichiometric and catalytic metal-mediated conversions of organonitriles into important organic compounds are currently being developed.[1,3] In contrast to other unsaturated molecules, such as alkynes, alkenes, CO, or RNC, nitriles insert less easily into metal–carbon bonds. Most of the known examples involve nitriles RCN and early-transition or actinide metal organocomplexes [M]−R′ to give azaalkenylidene complexes [M]−N=CRR′ upon insertion.[4,5] In a few cases, the azaalkenylidene ligand in [M]−N=C(R)CH_2R′ rearranges by a 1,3-H shift to the corresponding enamide [M]−NHC(R)=CHR′.[5] Some special cases involve low-valent transition-metal organocomplexes [M]−CH_2C(O)R′ that react at high temperature with a nitrile RCN and PPh_3 to give a κ^2-C,O-cyclometalated imino complex [M]−NHC(R)CHC(O)R′.[6] Another unusual case is the reaction between the extremely reactive Fe_2Mes_4 (Mes = 2,4,6-$Me_3C_6H_2$) and PhCN to give the dimer [{(PhCN)(Mes)Fe}$_2$(μ-N=CPhMes)$_2$].[7] Herein, we report a new type of nitrile insertion that also represents the first example of the insertion of a nitrile into a C−M bond (in which M is a late-transition element).

[Pd{2-(OH)C_6H_4}I(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) reacts at room temperature with excess RCN and 1 equivalent of TlOTf (OTf = CF_3SO_3) to give [Pd{1-O-2-[C(R)=NH]C_6H_4-κ^2-*O*,*N*}(tmeda)]OTf [R = Me (**1**), C_6F_5 (**2**), CH_2=CH (**3**)] (Scheme 1). As many known stable alkyl– and aryl–palladium complexes contain a *cis*-coordinated nitrile ligand,[8] we can assume that the *ortho*-hydroxy group plays a crucial role in the process and that after substitution of the iodo ligand by RCN (**A** in Scheme 2), the following step **B** is the protonation of the nitrogen atom of the nitrile. Unexpectedly, however, the usual nucleophilic attack at the nitrile carbon atom by the oxygen function[1,2] to give the addition product **C** does not occur. In our opinion, the resonance form **B**′ contributes significantly to the electronic structure of the protonated intermediate because of the electron-withdrawing character of the positively charged metal center and the electron-releasing nature of the negatively charged oxygen substituent. Both favor the location of a partial negative charge on the *ipso* carbon atom of the aryl ligand. Therefore, our results can be explained through the nucleophilic attack at the nitrile carbon by the *ipso* carbon atom, probably via the four-membered metallacycle **D**. Consequently, this insertion process differs from those reported previously with other unsaturated molecules in the role played by the *ortho*-hydroxy group, first in the proto-



Scheme 1. Reaction of [Pd{2-(OH)C_6H_4}I(tmeda)], excess nitrile, and TlOTf (1 equiv).

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[**] This work was supported by the Ministerio de Educación y Ciencia (MEC, Spain) and the FEDER (EU) by contract CTQ2004–05396. M.-J.L.S. is grateful to the MEC for a grant.

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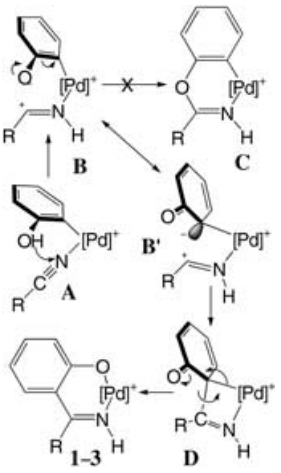

Scheme 2. Proposed mechanism for the reaction of [Pd{2-(OH)C_6H_4}I(tmeda)] with nitriles.

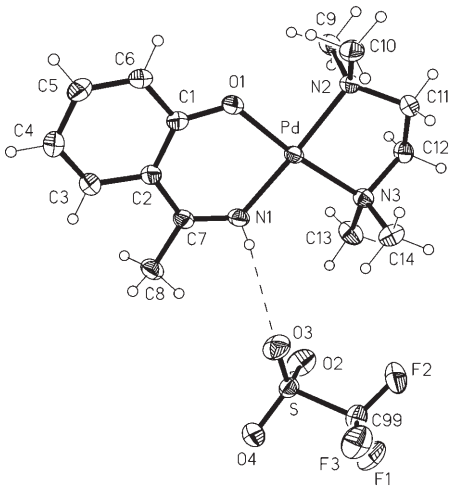

Figure 1. Thermal ellipsoid plot (50% probability) of **1**. Selected bond lengths [Å] and angles [°]: Pd–O1 1.9655(14), Pd–N1 1.9800(16), Pd–N2 2.0685(16), Pd–N3 2.0710(16), N1–C7 1.297(3), O1–C1 1.313(2); O1-Pd-N1 91.58(6), O1-Pd-N2 87.55(6), N1-Pd-N3 95.55(7), N2-Pd-N3 85.62(6), C7-N1-Pd 128.74(14), C1-O1-Pd 126.31(12), N1-C7-C2 123.24(17), N1-C7-C8 117.75(18), C2-C7-C8 118.95(17).

nation of the nitrile ligand and then in the generation of a partial negative charge on the *ipso* carbon atom of the aryl ligand.

Recently, the reaction of acrylonitrile with [PdMe-(NMe_2Ph)L_2]$^+$, [{PdMe(L_2)}$_2$(μ-Cl)]$^+$ (L_2 = various bidentate N-donor ligands),[9] and [Pd(O,N)Me(NCMe)] (O,N = Grubbs salicylaldiminato and related diazene ligands)[10] were reported to give α-cyanopropyl derivatives, that is, the insertion products of the olefinic part of the nitrile into the Pd–Me bond. In all cases, the first step was, as we propose in our case, the N-coordination of the nitrile but the difference from our result (complex **3**) proves to be the crucial role played by the hydroxy group in our reactions. We have reported that CO and olefins insert into the C–Pd bond of [Pd{2-(OH)C_6H_4}I(tmeda)] without intervention of the hydroxy group.[11]

The insertion of a nitrile group into an aryl–Pd bond has been postulated as a step in the mechanism of the synthesis of aryl ketones by the Pd-catalyzed reaction of arenes with nitriles at 75–100 °C.[12] The proposed subsequent step is the protonation of the resulting imido complex to give an imine. Our results suggest that these two steps could occur in the reverse order.

Complexes similar to **1**–**3** were prepared by the reaction of 1) [Ru(L_2)$_2$(CO_3)] (L_2 = bpy (2,2′-bipyridyl), phen (1,10-phenanthroline)) with *p*-{CH_2N=C(Me)(2-OHC_6H_4)}$_2$$C_6H_4$,[13] 2) [Ru($PPh_3$)$_3$$Cl_2$] with oximes of salicylaldehyde, 2-hydroxyacetophenone, or 2-hydroxynaphthylaldehyde,[14] and 3) aqueous ammonia, 2-hydroxo-4-methoxyacetophenone, and copper(II) salts.[15] Therefore, in the known complexes the main skeleton of the ligand is preformed in the organic reagent. Complexes **1**–**3** contain ligands of the same family as that present in Grubbs nickel catalysts.[16]

The crystal structures of the three complexes were solved by X-ray diffraction studies (Figures 1–3).[17] They show a distorted square-planar geometry at the palladium center, with normal bond lengths and angles. The chelate ring involving N1 and O1 is essentially planar in **1** but becomes less planar for **2** and **3** (mean deviations 0.03, 0.08, 0.11 Å).

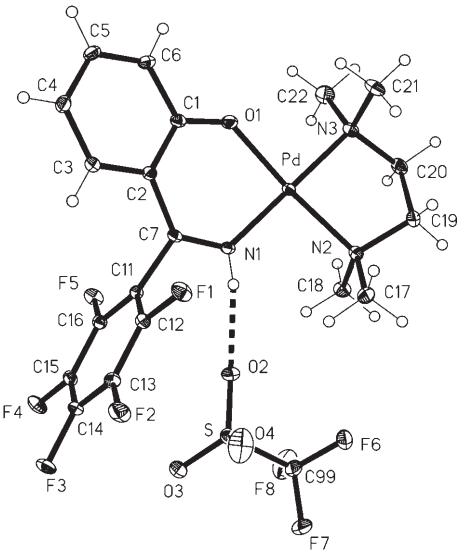

Figure 2. Thermal ellipsoid plot (30% probability) of **2**. Selected bond lengths [Å] and angles [°]: Pd–N1 1.9769(13), Pd–O1 1.9804(12), Pd–N2 2.0636(15), Pd–N3 2.0698(14), O1–C1 1.308(2), N1–C7 1.288(2); N1-Pd-O1 90.91(5), N1-Pd-N2 94.21(6), O1-Pd-N3 89.00(5), N2-Pd-N3 85.88(6), C1-O1-Pd 125.59(10), C7-N1-Pd 127.26(11), N1-C7-C2 125.08(15), N1-C7-C11 115.63(14), C2-C7-C11 119.29(14).

Cation/anion N–H···O(O_2)SCF_3 hydrogen bonds are observed.

In conclusion, we have reported the first examples of the insertion of nitriles into a late-transition-metal–carbon bond. The process involves the insertion of an alkyl (Me), aryl (C_6F_5), or vinyl nitrile into an aryl–palladium bond. The insertion is assisted by the protonation of the nitrile nitrogen atom by the *ortho*-hydroxy group present in the aryl ligand and thus represents a new type of insertion reaction.

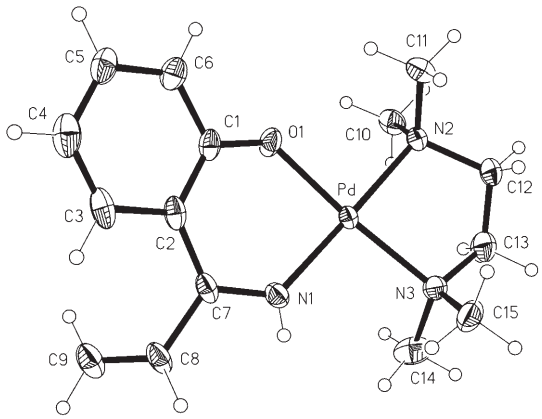

Figure 3. Thermal ellipsoid plot (30% probability) of **3**. The anion has been omitted. Selected bond lengths [Å] and angles [°]: Pd–O1 1.966(2), Pd–N1 1.983(2), Pd–N3 2.054(2), Pd–N2 2.060(2), O1–C1 1.319(3), N1–C7 1.287(4), C8–C9 1.310(4); O1-Pd-N1 90.11(11), N1-Pd-N3 95.10(11), O1-Pd-N2 88.65(9), N3-Pd-N2 86.12(10), C1-O1-Pd 123.44(18), C7-N1-Pd 128.7(2), N1-C7-C2 121.4(3), N1-C7-C8 116.8(3), C2-C7-C8 121.8(3).

Preliminary results allow us to state that the process also occurs with other alkyl and aryl nitriles.

Experimental Section

General procedure: The nitrile (1.15 mmol) and TlOTf (81 mg, 0.23 mmol) was added to a solution of [Pd{2-(OH)C_6H_4}I(tmeda)][11] (100 mg, 0.23 mmol) in CH_2Cl_2 (15 mL). The resulting mixture was stirred for 4 h at room temperature, the suspension was filtered over celite, the yellow solution was concentrated (3 mL), and Et_2O (10 mL) was added, which resulted in the precipitation of a solid. The precipitate was filtered, washed with Et_2O (3 × 5 mL), and dried to give the corresponding complex as a yellow solid.

1: Yield: 90 mg, 78%; m.p. 164°C; $\Lambda_M = 143\ \Omega^{-1}cm^2mol^{-1}$. IR: $\tilde{\nu} = 3275\ \nu$(NH), 1605 cm^{-1} ν(C=N); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.71 (s, 1H; NH), 7.47 (dd, 1H, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 1.5$ Hz; C_6H_4), 7.27 (ddd, 1H, $^3J_{HH} = 6.9$ Hz, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1.6$ Hz; C_6H_4), 6.91 (dd, 1H, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1$ Hz; C_6H_4), 6.64 (ddd, 1H, $^3J_{HH} =$ 6.9 Hz, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.6$ Hz; C_6H_4), 2.92 (s, 6H; Me (tmeda)), 2.85 (s, 4H; CH_2), 2.74 (s, 6H; Me (tmeda)), 2.68 ppm (s, 3H; Me (MeCN)); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 172.11$ (C), 163.24 (C), 134.30 (CH), 130.93 (CH), 121.04 (CH), 120.92 (C), 115.93 (CH), 63.30 (CH_2), 60.39 (CH_2), 50.92 (Me (tmeda)), 48.99 (Me (tmeda)), 24.53 ppm (Me (MeCN)); elemental analysis: calcd for $C_{15}H_{24}N_3O_4SF_3Pd$: C 35.62, H 4.78, N 8.31, S 6.34; found: C 35.31, H 4.67, N 8.21, S 6.09; single crystals were grown by slow diffusion of *n*-hexane into a solution of **1** in CH_2Cl_2.

2: Yield: 125 mg, 83%; m.p. 218°C (decomp.); $\Lambda_M =$ $125\ \Omega^{-1}cm^2mol^{-1}$; IR: $\tilde{\nu} = 3193\ \nu$(NH), 1601 cm^{-1} ν(C=N); ^{1}H NMR (400 MHz, [D_6]acetone): $\delta = 9.75$ (s, 1H; NH), 7.39 (ddd, 1H, $^3J_{HH} = 6.9$ Hz, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 1.7$ Hz; C_6H_4), 7.11 (dd, 1H, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 1$ Hz; C_6H_4), 7.04 (dd, 1H, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} =$ 1 Hz; C_6H_4), 6.58 (ddd, 1H, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 8.30$ Hz, $^4J_{HH} =$ 1.1 Hz; C_6H_4), 3.14 (s, 4H; CH_2), 2.96 (s, 6H; Me), 2.91 ppm (s, 6H; Me); ^{13}C{^{1}H} NMR (100 MHz, [D_6]acetone): $\delta = 166.65$ (C), 161.16 (C), 136.80 (CH), 133.27 (CH), 122.64 (CH), 120.70 (C), 117.15 (CH), 64.15 (CH_2), 61.45 (CH_2), 51.31 (Me), 49.67 ppm (Me); elemental analysis: calcd for $C_{20}H_{21}N_3O_4SF_8Pd$: C 36.52, H 3.22, N 6.39, S 4.87; found: C 36.41, H 3.20, N 6.43, S 4.80; single crystals were grown by slow diffusion of *n*-hexane into a solution of **2** in acetone.

3: Yield: 100 mg, 84%; m.p. 169°C (decomp.); $\Lambda_M =$ $100\ \Omega^{-1}cm^2mol^{-1}$; IR: $\tilde{\nu} = 3293\ \nu$(NH), 1603 cm^{-1} ν(C=N); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.38$ (s, 1H; NH), 7.46 (dd, 1H, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.6$ Hz; C_6H_4), 7.29 (ddd, 1H, $^3J_{HH} = 6.8$ Hz, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 1.7$ Hz; C_6H_4), 6.96–6.89 (m, 2H; C_6H_4, CH_2=CH), 6.64 (ddd, 1H, $^3J_{HH} = 7.0$ Hz, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.1$ Hz, C_6H_4), 5.83 (m, 2H; CH_2=C*H*, CH_2=CH), 2.91 (s, 6H; Me), 2.89 (s, 4H; CH_2 (tmeda)), 2.75 ppm (s, 6H; Me); ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): $\delta = 171.05$ (C), 164.64 (C), 134.77 (CH (C_6H_4)), 133.32 (CH_2= *C*H), 132.34 (CH (C_6H_4)), 126.73 (*C*H_2=CH), 121.10 (CH (C_6H_4)), 115.85 (CH (C_6H_4)), 120.58 (C), 115.85 (CH (C_6H_4)), 63.30 (CH_2 (tmeda)), 60.46 (CH_2 (tmeda)), 50.91 (Me), 49.36 ppm (Me); elemental analysis: calcd for $C_{16}H_{24}N_3O_4F_3SPd$: C 37.11, H 4.67, N 8.11, S 6.19; found: C 36.86, H 4.78, N 8.11, S 6.03; single crystals were grown by slow diffusion of Et_2O into a solution of **3** in CH_2Cl_2.

Received: April 5, 2005
Published online: August 22, 2005

Keywords: insertion · N ligands · neighboring-group effects · nitriles · palladium

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[17] CCDC-267823 (**1**), -267824 (**2**), and -267825 (**3**) 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 ω and ϕ scan modes to $2\theta_{max}$ 60° with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were based on multiple scans. Structures were refined on F^2 by 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 hydrogen atoms, which were refined freely. The triflate group of **3** is disordered over two positions in the ratio 4:1. Crystal data for **1**: $C_{15}H_{24}F_3N_3O_4PdS$, monoclinic, $a = 8.4900(6)$, $b = 12.0785(8)$, $c = 19.4179(14)$ Å, $\beta = 95.648(4)$°, $U = 1981.6$ Å^3, space group $P2_1/n$, $Z = 4$, $\mu(Mo_{K\alpha}) = 1.10$ mm^{-1}, 36424 reflections measured, 5789 unique ($R_{int} = 0.026$); refinement proceeded to $wR(F^2)$ 0.073 (all data), $R(F)$ 0.027 for 253 parameters; max. $\Delta\rho$ 1.3 e Å^{-3}. Crystal data for **2**: $C_{20}H_{21}F_8N_3O_4PdS$, orthorhombic, $a = 8.9198(6)$, $b = 11.4033(8)$, $c = 23.1269(14)$ Å, $U = 2352.4$ Å^3, space group $P2_12_12_1$, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.98$ mm^{-1}, 49530 reflections measured, 6890 unique ($R_{int} = 0.027$); refinement proceeded to $wR(F^2)$ 0.047 (all data), $R(F)$ 0.019, Flack parameter −0.009(11) for 342 parameters; max. $\Delta\rho$ 0.7 e Å^{-3}. Crystal data for **3**: $C_{16}H_{24}F_3N_3O_4PdS$, orthorhombic, $a = 8.0816(11)$, $b = 13.332(2)$, $c = 19.339(3)$ Å, $U = 2083.6$ Å^3, space group $P2_12_12_1$, $Z = 4$, $\mu(Mo_{K\alpha}) = 1.04$ mm^{-1}, 44074 reflections measured, 6095 unique ($R_{int} = 0.047$); refinement proceeded to $wR(F^2)$ 0.063 (all data), $R(F)$ 0.029, Flack parameter −0.01(2) for 334 parameters and 307 restraints; max. $\Delta\rho$ 1.0 e Å^{-3}. The Supporting Information for this article contains a listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for complexes **1**–**3**.

