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Methylation of a Terdentate Schiff Base Ligand *NNO*-Coordinated to Palladium with Nitromethane

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The reaction of the complex [Pd(κ^3-NN′O)CH_3] [NN′O = 2-Py-CH=N-(*o*-C_6H_4)O^-] (**1a**) with nitromethane affords a mixture of **2a** and **2b**. In this reaction methylation of the ligand takes place. These complexes display exchange equilibrium in solution. The methylation reaction is proposed to occur through nucleophilic attack of the nitronate anion on the iminic carbon atom. DFT calculations are presented in order to support a part of the mechanism and these calculations show that the participation of water in the migration of a proton is important. The crystal structure of the derivative product after spontaneous release of methane (**3**) is presented as well. Attempts to extend the reaction to other nitroalkanes resulted in a mixture of complexes that was not easy to characterize.

Introduction

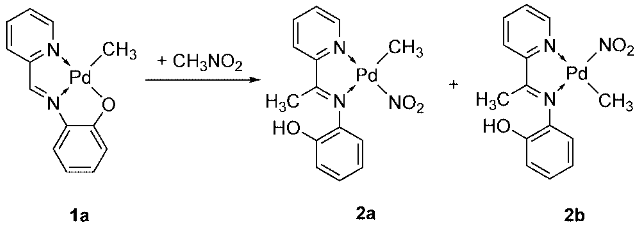
There has been increasing interest in the inorganic and organometallic chemistry of nitroalkanes. Nitroaldol (Henry) condensation is a highly versatile carbon–carbon bond formation reaction, which allows the synthesis of a huge number of interesting molecular frameworks.[1,2] In recent years considerable efforts have been devoted to developing asymmetric versions of the Henry reaction.[3] The work of Palomo et al.[3] highlights the advances in stereocontrol in these reactions that have been achieved by the use of catalysts such as cinchona alkaloids, guanidine bases, quaternary ammonium salts, or complexes of copper, zinc, or lithium/lanthanum. Recent advances on complexes of copper,[4–11] lanthanum,[12] cobalt,[13] or zinc,[11] which can act as catalysts for the asymmetric nitroaldol reaction, have been reported.

It is proposed that the metal-catalyzed nitroaldol reaction occurs through a mechanism involving *O* coordination of monodentate nitronate to the metal center.[14,15] To the best of our knowledge there are only two complexes that have a nitronate ligand coordinated to a metallic center in this way.[16] Additionally, Evans et al. reported that weakly Lewis acidic metal complexes bearing moderately basic, charged ligands may facilitate the deprotonation of nitroalkanes.[4]

In previous works of our group we have studied the dynamic behavior and the catalytic activity of palladium complexes with bi- and tridentate nitrogen donor ligands.[17,18] Those complexes have pyridine–imine donor ligands. Pelagatti et al.[19] have reported the synthesis of a palladium complex very similar to the complexes that we have studied, incorporating an additional coordination position with basic character, which could be a good candidate to catalyze the Henry reaction. In this work we report the behavior of the nitronate as a nucleophilic reagent towards this palladium complex.

Results and Discussion

The deep purple solution of complex **1a** in nitromethane at room temperature afforded a yellow precipitate that was characterized as **2** where the *N*,*N*′,*O* tridentate ligand became only *N*,*N*′ bidentate and was methylated at the iminic carbon (see Scheme 1). For complex **2** it is possible to propose two isomers, labeled in Scheme 1 as **2a** and **2b**.



Scheme 1.

The ^{1}H NMR characterization of the reaction products was carried out in [D_6]DMSO because of their low solubility in other less coordinating solvents. This NMR spectrum shows two signals belonging to methyl groups bonded to

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palladium at δ = 0.60 and 0.14 ppm, which is consistent with the presence of both isomers in solution. In the analysis of the values of the integrals, the isomer where the methyl group appears at δ = 0.14 ppm is ten times more abundant than the other isomer. The comparison of these chemical shifts with the values reported for similar palladium–methyl complexes with pyridine–imine ligands[20] indicates that the signal of the palladium–methyl group located in *cis* position to the pyridine ring appears downfield when compared with the same signal in the complex with the methyl group in *trans* position to the pyridine ring. Therefore, in this case, the values of the integrals indicate that the dominant isomer is **2b**. Furthermore, isomers **2a** and **2b** undergo a dynamic equilibrium in solution. A NOESY experiment (see Figure 1) shows that the signal appearing at δ = 0.14 ppm has peaks out of the diagonal; the signals belong to the H^6 of the pyridine ring and the *ortho*-hydrogen of the phenyl ring, which is consistent with such equilibrium. The EXSY phase of the same experiment (see Figure 2) shows peaks out of the diagonal for the signals appearing at δ = 0.14 and 0.60 ppm, also indicating the presence of the equilibrium between **2a** and **2b**.

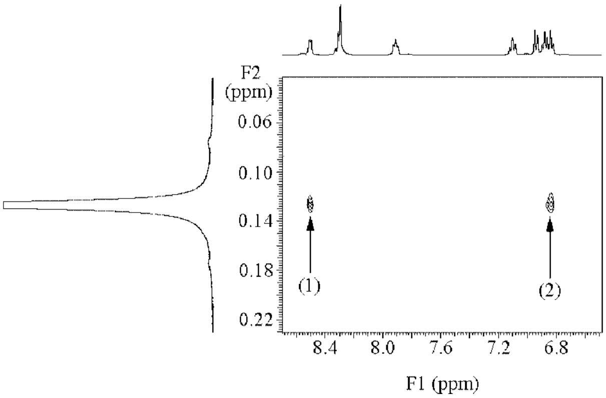


Figure 1. Expansion of the NOESY spectrum for mixture of complexes **2a** and **2b**. (1) Peak out of diagonal of the peak Pd–Me in **2b** with the H^6 signal of the pyridine ring. (2) Peak out of diagonal of the peak Pd–Me in **2b** with the *ortho*-hydrogen of the phenyl.

At first glance, the product of the reaction is similar to a Henry reaction product,[1,2] but there are some important differences. In our case, the bond between the nitrogen atom and the methyl carbon is broken, and the resulting nitro group is coordinated to the palladium atom. The other important difference is that the bond between the carbonylic carbon and the nitrogen atom remains as a double bond and is not transformed into a single bond as occurs in Henry reactions. For the process that we have found, the acid/base equilibrium of nitromethane can be taken into account.[21,22] This equilibrium generates a nitronate carbanionic nucleophile and a proton. We suggest that in the first step the proton attacks the phenoxide to generate the phenolic group, as shown in Scheme 2. The next step, which can be simultaneous to the previous step, is the attack of the nucleophile on the carbonylic carbon of the coordinated imine. Nucleophilic attacks on coordinated imines are known,[23–27] and the nucleophilic behavior of nitronates has been reported as well;[14,28,29] even the nitronate attack on an imine coordinated to cobalt has been reported.[30] In our proposed mechanism, this nucleophilic attack is followed by the breaking up of the C–N bond of the nitronate fragment in an analogous way to that described for a cobalt[23] or a nickel complex[31] (see Scheme 3).

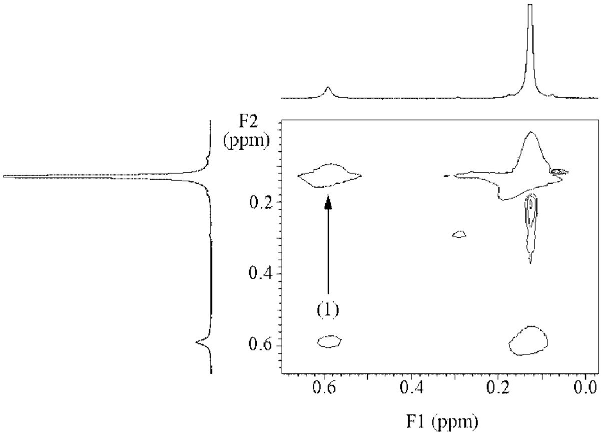
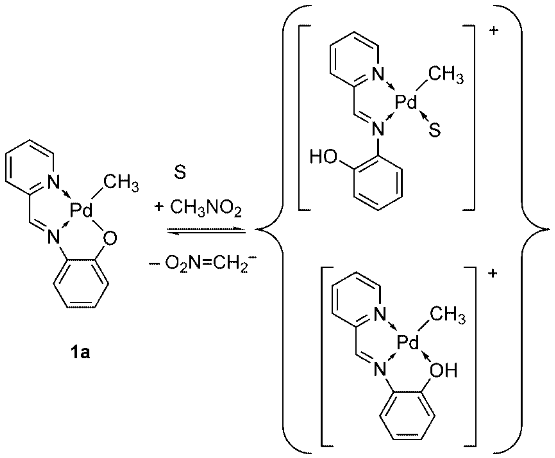


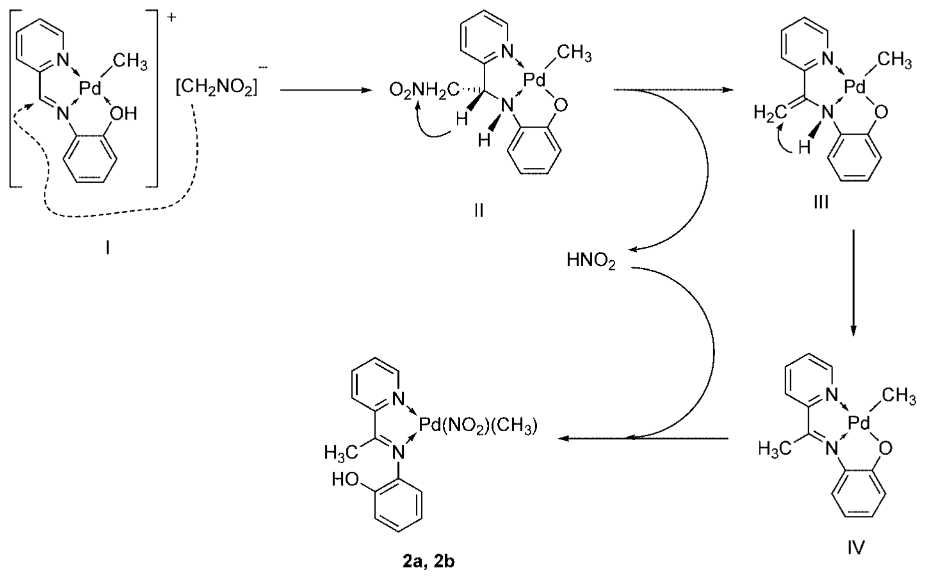
Figure 2. Expansion of the NOESY spectrum for mixture of complexes **2a** and **2b**. (1) EXSY signal out of the diagonal showing the exchange between Pd–Me groups in isomers **2a** and **2b**.



Scheme 2.

In this process, the nucleophilic attack of the carbanion on the iminic carbon atom generates the compound with structure II. This compound can release nitrous acid to afford the compound of structure III. Next, the hydrogen atom bonded to the aminic nitrogen atom “jumps” to the methylenic carbon to generate the complex with structure IV in a process of imine–enamine tautomerism. This migration of the proton has to be aided by a molecule of water, as we have found in theoretical calculations (see below). The process without water displays high activation barriers, as we will discuss later. Finally, the protonation of structure IV with the nitrous acid released earlier affords the observed products **2a** and **2b**.

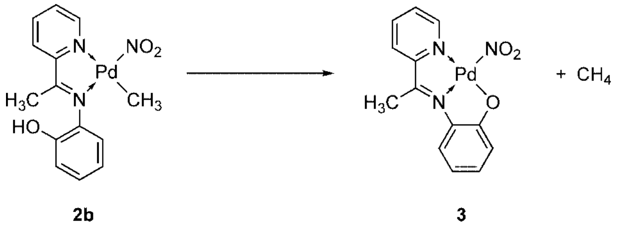
In order to support this proposed mechanism, we carried out ^1H NMR measurements of **1a** dissolved in CD_3NO_2



Scheme 3.

and in CD_3NO_2/D_2O, and ^1H NMR measurements of the products of these reactions dissolved in [D$_6$]DMSO, but they did not shed light on the proposal.

The slow evaporation of the mother liquors of the reaction for the preparation of complexes **2** afforded a crystal suitable for structural X-ray analysis, but not enough crystals for spectroscopic characterization. The structure of the crystal is not the structure proposed for complexes **2a** or **2b** but a complex **3** in which one molecule of methane has been lost by deprotonation of the phenolic proton, (see Scheme 4). The acidity of the phenolic proton seems to be sufficient to cause such slow methane elimination.[19,32]



Scheme 4.

Structure of Complex 3

The molecular structure of complex **3** is shown in Figure 3, and selected bond lengths, bond angles, and torsion angles are given in Table 1. The chelating ligand binds to the metal through a pyridyl donor N(1), secondary imine donor N(2), and aryloxide oxygen O(1). The N(1)–Pd(1)–N(2) bond angle is 81.25(13)° and the N(2)–Pd(1)–O(1) bond angle is 84.95(12)°. The pyridyl donor makes a slightly larger bond to the metal than the imine does. The torsion angles N(1)–C(5)–C(6)–N(2) and N(2)–C(8)–C(13)–O(1) are close to planarity, with values of 5.0(5)° and 0.9(5)° respectively. The nitro group is out of the coordination plane of the palladium as the torsion angle O(1)–Pd(1)–N(3)–O(3) is –136.5(3)°.

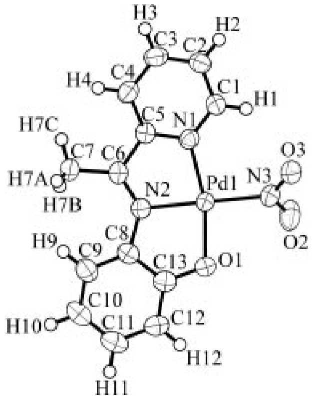


Figure 3. Molecular geometry for complex **3**.

Table 1. Selected bond lengths [Å] and angles [°] for compound **3**.

Distances [Å]		Angles [°]	
Pd(1)–N(2)	1.979(3)	N(2)–Pd(1)–O(1)	84.95(12)
Pd(1)–O(1)	1.997(3)	N(2)–Pd(1)–N(3)	178.06(11)
Pd(1)–N(3)	2.011(3)	O(1)–Pd(1)–N(3)	94.41(13)
Pd(1)–N(1)	2.013(3)	N(2)–Pd(1)–N(1)	81.25(13)
N(1)–C(5)	1.355(5)	O(1)–Pd(1)–N(1)	166.17(12)
N(2)–C(6)	1.293(5)	N(3)–Pd(1)–N(1)	99.40(13)
N(3)–O(2)	1.229(4)	O(2)–N(3)–O(3)	119.3(3)
N(3)–O(3)	1.247(4)		
O(1)–C(13)	1.321(5)	N(1)–C(5)–C(6)–N(2)	5.0(5)
C(5)–C(6)	1.489(5)	N(2)–C(8)–C(13)–O(1)	0.9(5)
		O(1)–Pd(1)–N(3)–O(3)	–136.5(3)
		N(1)–Pd(1)–N(3)–O(3)	43.1(3)

The packing of the crystal is built up through hydrogen bonds and π–π interactions. There are two weak intermolecular hydrogen bonds between the oxygen atoms of the nitro group and several hydrogen atoms of the ligand of neighbor complexes. The oxygen atom labeled as O(2) establishes bifurcated hydrogen bonds to the methyl group and arylic hydrogen atoms. The oxygen atom labeled as O(3) establishes trifurcated hydrogen bonds to the methyl group and arylic hydrogen atoms. The values of these hydrogen bonds are displayed in Table 2 and they are in good agreement with the values reported in the literature.[33–35] Additionally, there is a π–π interaction between the π systems of couples of molecules, with a separation between parallel planes (defined by the aromatics systems of the ligand) of 3.385 Å.[36] The combination of all these interactions packs the molecules in columns, as shown in Figure 4.

Table 2. Distances and angles of weak interactions in complex **3**.

Hydrogen bonds			
O(2), bifurcated		O(3), trifurcated	
O(2)–H(2)	2.603 Å	O(3)–H(1)	2.678 Å
O(2)–C(2)	3.402 Å	O(3)–C(1)	3.290 Å
O(2)–H(2)–C(2)	144.37°	O(3)–H(1)–C(1)	123.95°
O(2)–H(7)B	2.448 Å	O(3)–H(7)A	2.487 Å
O(2)–C(7)	3.384 Å	O(3)–C(7)	3.442 Å
O(2)–H(7)B–C(7)	165.01°	O(3)–H(7)A–C(7)	173.12°
		O(3)–H(3)	2.472 Å
		O(3)–C(3)	3.265 Å
		O(3)–H(3)–C(3)	143.29°
Interaction π–π			
Cj [N(1)–C(5)–C(6)–N(2)–Pd(1)]		Ci [C(8)–C(9)–C(10)–C(11)–C(12)–C(13)]	
Ci–Cj	3.515 Å	H(12)–Cj–Ci	35.74°

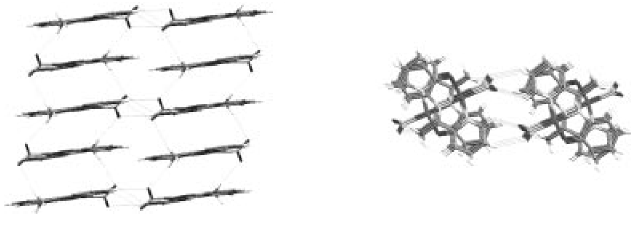
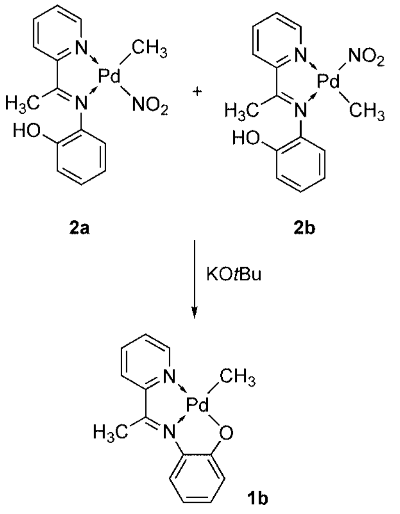


Figure 4. Packing of the molecules of complex **3** forming columns. The weak interactions are displayed.

Deprotonation of 2

The presence of the O–H group in complexes **2** encouraged us to explore its deprotonation. Thus, as shown in Scheme 5, the reaction of the mixture of compounds **2a** and **2b** with KO*t*Bu afforded the expected O–H deprotonation to yield a new compound, **1b**, which is garnet in color. This compound has been characterized by spectroscopic techniques. The ^{1}H NMR spectrum shows the presence of the two different methyl groups, a singlet at δ = 0.51 ppm (belonging to the palladium-bonded methyl) and another singlet at δ = 2.54 ppm (belonging to the carbonylic methyl).



Scheme 5.

The synthesis of complex **1b** was also attempted following an alternate pathway, like that reported for **1a**.[19] However, we were unable to synthesize the *N*,*N′*,*O* tridentate ligand through the conventional condensation of 2-acetylpyridine with 2-aminophenol using Dean–Stark equipment in the presence of a catalytic amount of *p*-toluenesulfonic acid.

DFT Calculations

In order to rationalize the observed results, DFT quantum chemical calculations were carried out on a model of complex **1a**. The positions of nucleophilic attack should display positive charge. The process starts with the protonation of complex **1a**. It is reasonable to think that the protonation occurs on the oxygen atom, as the NBO analysis[37,38] displays a negative charge on that atom (–0.67). Although the oxygen atom is not the most negatively charged atom (we have found that the methyl carbon atom bonded to the metal has a charge of –0.90), the participation of the p_z atomic orbital of the oxygen in the HOMO and the nonparticipation of any atomic orbital of the carbon atom reinforces this proposal. In addition to the protonation of the oxygen atom, there is a nucleophilic attack of the nitronate anion on the iminic carbon atom. An NBO analysis displays a positive charge on the iminic carbon (0.016). Although this value is not the most positive value (palladium atom has a value of 0.690), there is strong participation of the orbitals of the π system in the LUMO of the complex and the iminic carbon atom is a place for nucleophilic attack analogous to that observed for the Henry reaction,[1,2] accounting for the observed reaction of the nitromethane.

We have modeled the migration of the hydrogen atom from the nitrogen atom to the carbon atom, as depicted in steps III–IV in Scheme 3. This process was proposed by other authors[23,31] on similar systems. The compound with structure III comes from the compound with structure II through the loss of nitrous acid. We have found that glob-

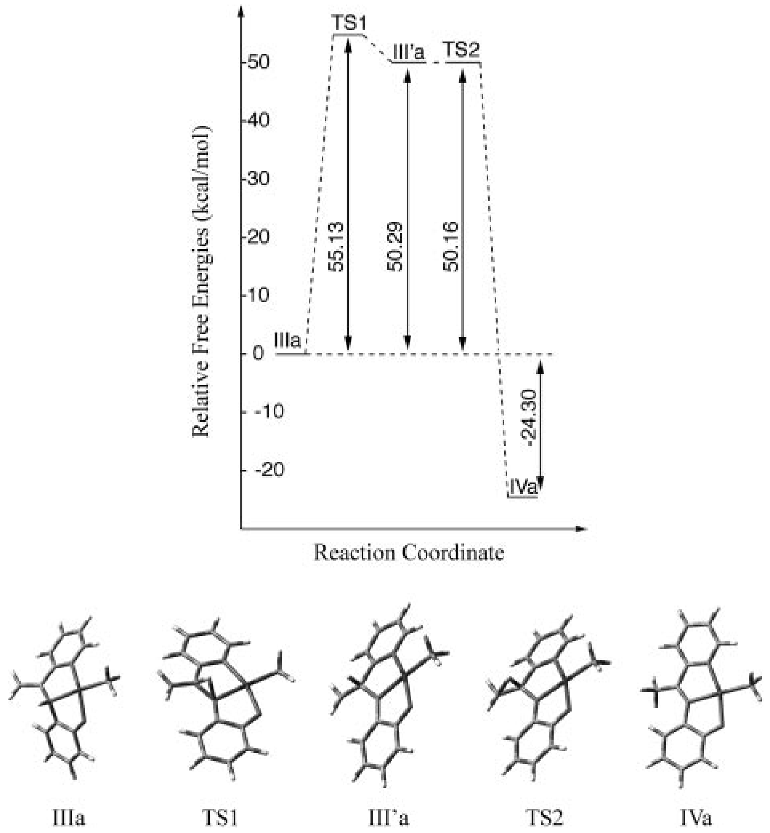
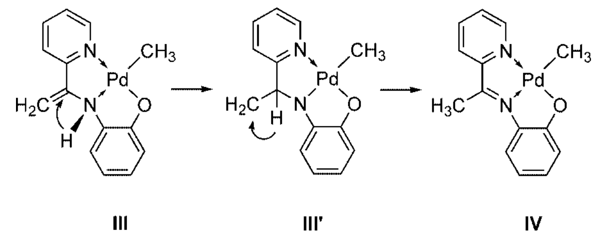


Figure 5. Calculated reaction pathway in the migration of the hydrogen atom without any molecule of water.

ally this process is an imine–enamine tautomerism through two steps. The first step is the migration of the aminic hydrogen atom from the nitrogen to the adjacent carbon atom (structure III′ in Scheme 6). This first step is highly endothermic (50.3 kcal/mol), with a high activation energy (55.1 kcal/mol). The second step of the tautomerism is a new migration of the hydrogen atom to generate the methyl and the double bond C=N (structure IV in Scheme 3; see Figure 5). This step has an activation energy very close to 0 kcal/mol, and the complete process is exothermic (–24.3 kcal/mol), taking as reference the energy of structure III.



Scheme 6.

The high value of the activation energy makes this mechanism unreliable. We thought that perhaps a molecule of water could help the migration of the proton. The addition of a molecule of water to structure III (see Scheme 3) established a hydrogen bond with the oxygen atom of the aryloxide fragment, stabilizing the structure. A second molecule of water established a hydrogen bond with the amine hydrogen atom, and this molecule is the carrier of the hydrogen atom to the carbon atom (see Figure 6). In

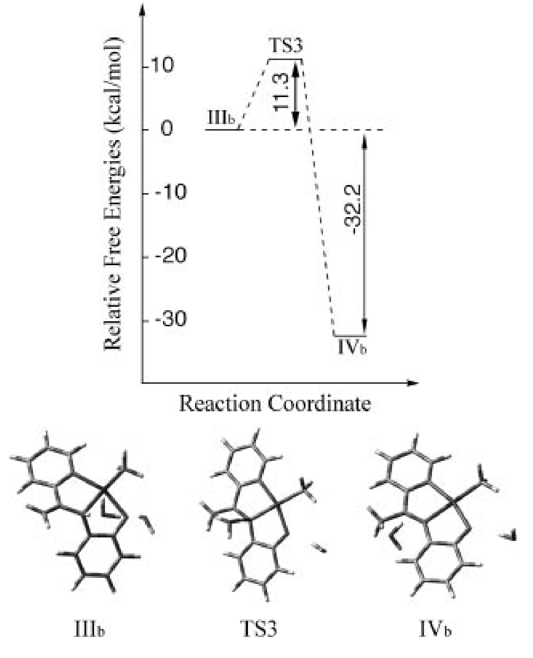


Figure 6. Calculated reaction pathway in the migration of the hydrogen atom assisted by molecules of water.

this mechanism the molecule of water takes the proton bonded to the amine nitrogen and gives another proton to the carbon. Intrinsic reaction coordinate (IRC) calculations[39] verified this process. This process is exothermic, with a free energy of –32.2 kcal/mol and activation energy of 11.3 kcal/mol.

Experimental Section

General: Elemental analyses (C,H,N) were performed with a LECO CHNS-932 apparatus. Infrared spectra were recorded with a Nicolet Impact 410 FTIR spectrophotometer in the 4000–400 cm^{-1} range, as KBr disks. ^{1}H NMR spectra were obtained on a Varian Unity Inova 400-MHz spectrometer with SiMe$_4$ as internal standard at 25 °C. Complex **1a** was synthesized as reported in the literature.[19] Nitromethane and potassium *tert*-butoxide were commercial grade and were used without further purification.

[$C_{14}H_{15}N_3O_3Pd$] (2): Complex **1a** (50 mg, 0.157 mmol) was dissolved in nitromethane (3.5 mL). The mixture was stirred for 20 h. During this time the initial purple color disappeared and a yellow precipitate was formed. The solid was filtered off, washed with diethyl ether, and then dried under vacuum. Yield: 45.4 mg (76%). ^{1}H NMR (signals of complex **2b**) (400 MHz, [D$_6$]DMSO, 20 °C): δ = 9.73 (s, 1 H, O-H), 8.52 (d, $^3J_{H,H}$ = 4.6 Hz, 1 H, 6-H py), 8.31 (m, 2 H, 4-H, 3-H py), 7.92 (m, 1 H, 5-H py), 7.13 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 7.4 Hz, 1 H, 4-H Ar), 6.95 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, 3-H Ar), 6.88 (m, 2 H, 5-H, 6-H Ar), 2.28 [s, 3 H, C**H$_3$**-C(py)=N], 0.14 (s, 3 H, C**H$_3$**-Pd) ppm. IR: $\tilde{\nu}$ = 1660 [m (C=N)] cm^{-1}. $C_{14}H_{15}N_3O_3Pd$ (379.69): calcd. C 44.28, H 3.98, N 11.07; found C 43.96, H 3.92, N 11.13.

[$C_{14}H_{14}N_2OPd$] (1b): Complex **2** (30 mg, 0.079 mmol) was dissolved in dichloromethane (10 mL), and potassium *tert*-butoxide (8.9 mg, 0.079 mmol) was added. The mixture was stirred for 45 min. The solvent of this red solution was removed under vacuum and the residue was dissolved in dichloromethane, filtered through Celite, and concentrated under vacuum. The addition of hexanes affords a purple solid that was filtered off, washed with cold diethyl ether, and then dried under vacuum. Yield: 19.2 mg (73%). ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 8.14 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, 6-H py), 7.80 (m, 1 H, 4-H py), 7.50 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, 3-H py), 7.22 (m, 1 H, 5-H py), 7.10 (m, 1 H, 6-H Ar), 6.96 (m, 1 H, 4-H Ar), 6.72 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 3-H Ar), 6.36 (m, 1 H, 5-H Ar), 2.54 [s, 3 H, C**H$_3$**-C(py)=N], 0.51 (s, 3 H, C**H$_3$**-Pd) ppm. IR: $\tilde{\nu}$ = 1627 [m (C=N)] cm^{-1}. $C_{14}H_{14}N_2OPd$: calcd. C 50.54, H 4.24, N 8.42; found C 49.80, H 4.47, N 8.82.

X-ray Structure Determination: Crystallographic data for compound **3** were collected on a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[40] Intensities were integrated[41] from several series of exposures, each exposure covering 0.3° in ω, and the total dataset being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[42] The structure was solved by direct methods and refined by least-squares on weighted F^2 values for all reflections (see Table 3).[43] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 3. Complex neutral-atom scattering factors were used.[44]

CCDC-645201 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cam-

Table 3. Crystal data for complex **3**.

Empirical formula	$C_{13}H_{11}N_3O_3Pd$
Temperature [K]	273(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	7.4316(17)
b [Å]	8.596(3)
c [Å]	10.274(4)
α [°]	76.215(17)
β [°]	76.56(3)
γ [°]	85.287(16)
V [Å^3]	619.7(4)
Z	2
D_{calcd} [Mg/m^3]	1.949
Absorption coefficient [mm^{-1}]	1.508
F(000)	360
Crystal size [mm]	$0.60 \times 0.30 \times 0.20$
θ range for data collection [°]	2.09–25.00
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 9$, $-12 \le l \le 12$
Reflections collected	3285
Independent reflections	2114 [R_{int} = 0.0185]
Completeness to θ = 25.00° [%]	97.2
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.740 and 0.514
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2114/0/182
Goodness-of-fit on F^2	S = 1.185
R indices [for 2008 reflections with $I > 2\sigma(I)$]	R_1 = 0.0281, wR_2 = 0.0843
R indices (for all 2114 data points)	R_1 = 0.0295, wR_2 = 0.0853
Weighting scheme	$w^{-1} = \sigma^2(F_o2) + (aP)^2 + (bP)$ $P = [\max(F_o^2, 0) + 2F_c^2]/3$ a = 0.0508, b = 0.0000
Largest diff. peak and hole [e/Å^3]	0.516 and –0.682

bridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Study: DFT calculations were performed with the hybrid method known as B3LYP, in which the Becke three-parameter exchange functional[45] and the Lee–Yang–Parr correlation functional were used,[46] implemented in the Gaussian 03 (Revision B.04) program suite.[47] The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (Lanl2DZ)[48] adding polarization functions ($\zeta_f = 1.472$)[49] were used in describing Pd. The basis set for the main group elements was split-valence and included polarization functions in all atoms [C, N, O, and H, abbreviated as 6-31G(d,p)].[50] The structures were optimized at the level B3LYP/Lanl2DZ and transition states were confirmed by a vibrational analysis (one imaginary frequency) and IRC calculations.[39] Energies of the structures were calculated with the specific basis sets.

Supporting Information (see also the footnote on the first page of this article): Tables of atomic coordinates of optimized structures (Tables S1–S8).

Acknowledgments

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