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Nucleophilic Attack on Coordinated Imines: The Synthesis of C-Bonded Acetylacetonates of Palladium(II) and Mechanistic Insights

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The reactivity of complexes $[PdCl_2(\kappa^2\text{-}\widehat{NN}')]$ [$\widehat{NN}'$ = 2-C_5H_4N-CH=N-Ar; Ar = 2-MeC_6H_4, **a**; 4-MeC_6H_4, **b**; 2-$MeOC_6H_4$, **c**; 4-$MeOC_6H_4$, **d**; 4-$CF_3C_6H_4$, **e**; 2,6-$Me_2C_6H_3$, **f**; 2-*i*PrC_6H_4, **g**] and $[Pd(\kappa^2\text{-acac})(\kappa^2\text{-}\widehat{NN}')][BF_4]$ toward the nucleophilic reagent acetylacetonate (acac) has been explored. This reaction starts with nucleophilic attack on the cabonylic atom of the coordinated imine generating a new C–C bond and an amido complex. The next step in the reaction is proton migration leading to the protonation of the amido nitrogen, and finally replacement of this coordinated nitrogen atom with an anionic carbon atom. The final consequence of the nucleophilic attack on the coordinated imines is the formation of new complexes and the generation of new C–C and C–Pd bonds.

Introduction

Among metal-based catalysts, complexes with Schiff base ligands belong indisputably to a very important group because of their multifunctionality and versatility.[1] One of the fields in which palladium(II) complexes containing imine ligands have displayed interesting activity is the allylic alkylation with soft carbon nucleophiles to form C–C bonds.[2] In these reactions, the metal activates a substrate to enhance its reactivity towards carbanionic nucleophilic reagents. At the same time, the coordinated imine can be attacked by nucleophilic reagents yielding amido complexes that can evolve to give different products.[3] Understanding this reactivity can be very helpful in avoiding the degradation of the ligands within complexes and extending the lifespan of the catalyst.

Our group has reported the nucleophilic attack of carbanionic nitronate on a coordinated imine.[3b] The nitronate formed by deprotonation of the nitromethane attacks the carbonylic carbon of the coordinated imine. In this context, we have been studying the reactivity, in basic media, of imine complexes with 2,4-pentanedione. This diketone is a weak acid[4] and its nucleophilic reactivity has been studied recently.[5] Herein, we report the reactivity of imine complexes of palladium(II) towards acetylacetonate. After the nucleophilic attack on the imine carbon, a new carbon–carbon bond was formed, and then the complex evolves to give a palladium carbon bonded diketonate. Previous works have focused on the nucleophilic attack by acetylacetonate on imines bound to Co^{III},[3a,3k] but to the best of our knowledge, this is the first reported study of nucleophilic attack on an imine coordinated to Pd leading to the formation of a *C*-bonded acetylacacetonato (carbon-bonded γ-acac) complex. Carbon-bonded acetylacetonato complexes (γ-acac) of Pd^{II}[6] and Pt^{II}[7] have been known for a half century. The synthetic procedure for preparing these complexes almost exclusively relies on the reaction between $[M(O,O\text{-acac})_2]$ (M = Pd or Pt) and ligands (L) that are nitrogen based (py and Et_2NH), tertiary phosphanes (PPh_3, PCy_3 and PEt_3) or arsanes, leading to the formation of complexes with the general formula [M(*O,O*-acac)(γ-acac)-L].[8] More recently, the same procedure has been used to prepare [M(*O,O*-acac)(γ-acac)L] where M = Pd,[9] L = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene and M = Pt,[10] L = dimethyl sulfoxide. At least in one reported case the donor atom of the ligand (pyridine) and the γ-carbon of the γ-acac are connected, forming a five-membered palladacycle [Pd(*O,O*-acac)(γ-acac-S-py)].[11] A revival of research into this kind of complex containing acac displaying both coordination modes (*O*,*O*-acac and γ-acac) has recently been observed, and is a consequence of their reported cytotoxic activity on several cancer lines.[12]

Results and Discussion

The pyridine-imine ligands **a**–**g**, which are shown in Scheme 1, were prepared in a similar way to a previously reported method by the simple condensation of the relevant piridine-2-carboxaldehyde with the corresponding aniline.[13] Reactions of equimolar amounts of the ligands **a**–**g** with [$PdCl_2$(1,5-COD)] afforded the complexes $[PdCl_2(\widehat{NN}')]$, **1a**–**g**, in high yields.[14]

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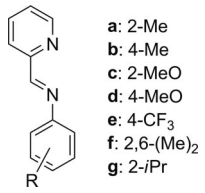
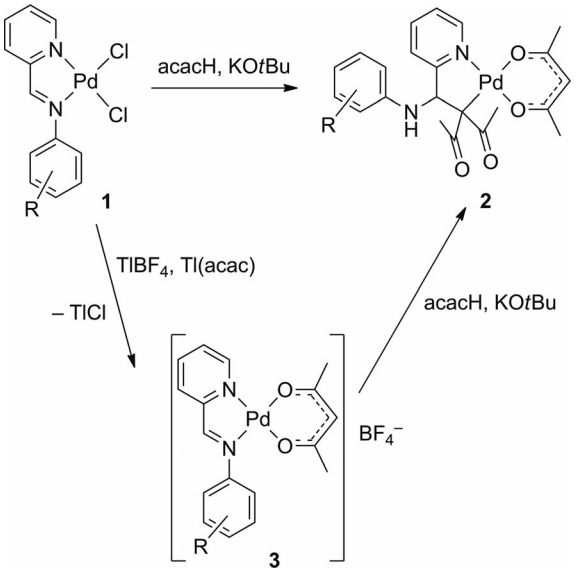


Scheme 1. General structure of the ligands **a**–**g**.

When complexes **1a**–**e** reacted with a fivefold excess of a mixture of 2,4-pentanedione and potassium *tert*-butoxide a new family of compounds was obtained, **2a**–**e** (see Scheme 2). These compounds were characterized by NMR and IR spectroscopy. The ^{1}H NMR spectra of these compounds displayed four singlets that when integrated were shown to correspond to three protons each.



Scheme 2. Reactions for the preparation of complexes **2** and **3**
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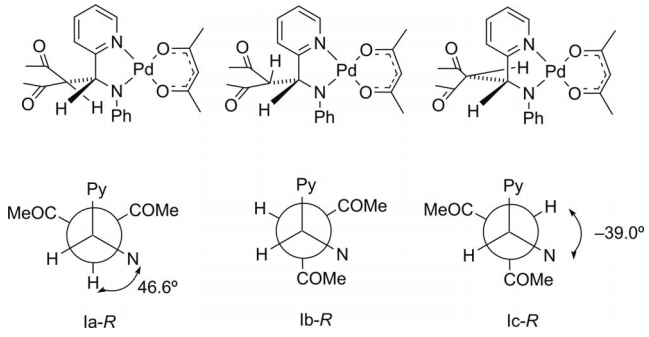
Two of these singlets (appearing at about 2.5 ppm) were assigned to the inequivalent methyl groups of the *O*,*O*-coordinated β-diketonate, and the other two singlets (appearing at about 2.1 and 2.0 ppm) were assigned to the methyl groups of the *C*-metallated diketone (note that the adjacent asymmetric carbon makes the acetyl groups diastereotopic). The H–C(sp^2) iminic hydrogen atoms of compounds **1** displayed singlets in the ^{1}H NMR spectra at about 8.5 ppm. In compounds **2** this hydrogen atom is now bonded to sp^3 aminic carbon atoms and thus appears as doublets in the spectra of **2**, by coupling with the NH hydrogen atoms, and its chemical shift is upfield from the corresponding signals observed in the spectra of **1**. These two hydrogen atoms displayed an AB spin system with coupling constants in the 10.2–9.9 Hz range. As expected, the H–C(sp^2) of the *O*,*O*-coordinated β-diketonato groups displayed a singlet at about 5.4 ppm in the spectra of **2**. NOESY experiments with **2** demonstrated the expected proximity between the two methyl groups of the β-diketonato groups, and the proximity between the two methyl groups of the metallated diketone groups, but the analysis of the exchange spectroscopy (EXSY) phase showed no exchange between the methyl groups, which is consistent with the absence of dynamic behaviour.

The ligands present in complexes **2** can be considered as *C*-deprotonated 2-C_5H_4N–CH(NHAr)-CH($COCH_3$)$_2$ species. Attempts to synthesize the molecule 2-C_5H_4N–CH(NHPh)-CH($COCH_3$)$_2$ following published procedures were unsuccessful.[15] For this reason it was not possible to synthesize complexes **2** following a direct procedure.

Interestingly, complexes **1f** and **1g** that bear bulky aryl substituents did not show this reactivity. In order to shed light on this reaction, the chlorido ligands in complexes **1** were substituted with *O*,*O*-acetylacetonato ligands leading to the ionic compounds **3** (prepared with ligands **a**, **c**, **f**, **g**). The compounds selected for these syntheses displayed different degrees of steric hindrance, and the substituents on the aryl groups had different electronic properties. As shown in Scheme 2, the reaction of complexes **1** with equimolar amounts of thallium acetylacetonate and thallium tetrafluoroborate afforded compounds **3** in good yields. These compounds were characterized by NMR and IR spectroscopy, and complex **3a** was also subjected to X-ray diffraction analysis (see below). The ^{1}H NMR spectra of the compounds displayed three singlet signals corresponding to the *O*,*O*-β-diketonato ligands and were assigned to the two methyl groups and the C–H hydrogen atoms of the central carbon atoms of the acetylacetonato ligands. The nonequivalent character of the methyl groups of the β-acetylacetonato compounds was consistent with the nature of the ancillary chelating pyridine-imine ligand, and also indicated the nondynamic behaviour of these compounds in solution. The signals from the pyridine-imine ligands were in the same range observed for the related compounds **1**. The reactions of compounds **3** (including **3f** and **3g**) with a fivefold excess of a mixture of 2,4-pentanedione and potassium *tert*-butoxide yielded the corresponding complexes **2**.

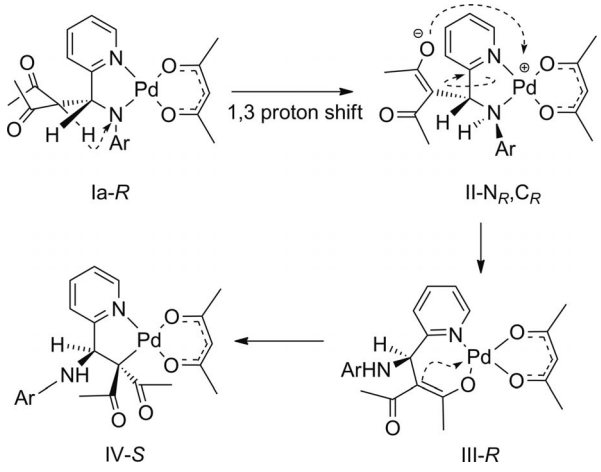
These results can give us some information about the initial stages of the mechanism of the observed process. In the first place, substitution of the two chlorido ligands of **1** with chelating *O*,*O*-acetylacetonato ligands leading to the cationic complex **3** seems to be necessary.[16] For complexes **1f** and **1g** that bear bulky aryl substituents on their ligands there is no reaction, but for compounds **3f** and **3g** the reaction occurs readily. This fact can be understood by considering the electrostatic attraction between the cations of compounds **3** and the anionic nucleophile acetylacetonate. In addition, the cationic charge increases the back-donation from the imines to the palladium atoms, thus favouring nucleophilic attack. Once the substitution of the chlorido ligands with chelating acetylacetonato has occurred, attack of the carbanionic acetylacetonate anions on the carbonylic carbon atoms of the coordinated imines affords nonisolated amido complexes (see Scheme 3). In spite of the sometimes claimed mismatch between soft Pd^{II} and hard N(amido), palladium complexes containing terminal Pd–N amido bonds have been well characterized in more than few

cases.[17] The formation of this type of amido complex involved transformation of the sp^2 iminic carbon atom into an sp^3 carbon atom leading to chirality (*R* enantiomer shown in Scheme 3) and the generation of three possible rotamers (**Ia**, **Ib** and **Ic**). The difference in energy between the rotamers is small (around 3 kcal/mol according to DFT calculations, see Supporting Information) and the main structural difference between them is the torsional angle (H–C–C–N) between the hydrogen atoms of the diketone fragments and the amido nitrogen atoms (46.6° in structure **Ia**, 171.3° in structure **Ib** and –39.0° in structure **Ic**, see Supporting Information). As the spatial arrangements of the N_{amido}–C–C–H atoms are similar in **Ia** and **Ic**, only the two most stable rotamers, which are those with the greatest difference in torsion angles, namely **Ia** and **Ib**, have been considered.



Scheme 3. Rotamers arising from rotation around the C–C bond in the nonisolated amido complexes. The values of the angles displayed in the Newman projections were determined by DFT calculations (see Supporting Information).

Following the formation of Pd–N(amido) bonds, migration of a proton to the nitrogen atoms takes place. Although intermolecular mechanisms cannot be ruled out, the spatial arrangement of the atoms in **Ia-*R*** suggests a 1,3-C→N prototropic shift of the proton bonded to the central carbon atoms of the diketones, as depicted in Scheme 4.



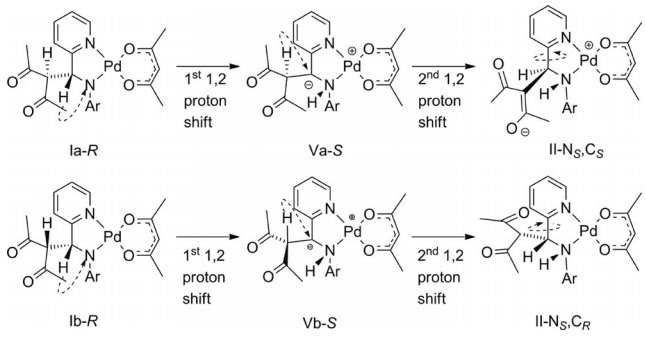
Scheme 4. Proposed mechanism for the conversion of the nonisolated amido complex **Ia** to the final product **IV-*S***.

The 1,3-C→N prototropic shift in **Ia-*R*** (Scheme 4) involves a hydrogen atom that belongs to a central carbon of the 1,3-diketone, and leads to the formation of a zwitterionic structure **II-N$_R$,C$_R$** (Scheme 4) where the negative charge resides on the oxygen or on the central carbon atom of the β-diketonate. Zwitterionic species of platinum group metal complexes have been described.[18] At this point, note that chiral diastereomers N_R,C_R and N_S,C_R can be depicted for **II** (the enantiomer N_R,C_R is shown in Scheme 4).

Finally, the conversion of **II** to **IV** involves substitution of a coordinated amine by a *C*-bonded β-diketonate. Two putative pathways can be considered. Pathway 1 involves oxygen as the donor atom, whereas pathway 2 has the carbon as the donor atom. Pathway 1 leads to the final product **IV** through the intermediate *O*-bonded 7-membered chelating ring **III**. Pathway 2 involves the direct displacement of the coordinated nitrogen atom by the carbanionic atom. Nevertheless, careful analysis of the structure of **II** (DFT-optimized, see Supporting Information) shows that in the process of rotation around the carbon–carbon bond, as indicated in Scheme 4, the oxygen atom initially binds to the palladium atom, indicating the formation of **III**. For structure **III** it is possible to propose two enantiomers (considering that inversion at the uncoordinated nitrogen atom is very fast, there is only one chiral centre).

Note that by following the Cahn–Ingold–Prelog rules, **IV-*S*** has an *S* configuration but the chiral carbon atom has its subsituents in the same order as those in **Ia-*R***, **II-C$_R$** and **III-*R*** (i.e. no inversion of the configuration takes place in this mechanism).

The 1,3-migration described above is not possible in **Ib** because of the transoidal orientation of the hydrogen and nitrogen atoms (as can be seen in Scheme 3). However, both structures **Ia** and **Ib** can undergo double 1,2-C→N and 1,2-C→C proton migration. This second option can be ruled out because it involves the participation of a hydrogen atom that is less acidic in the first 1,2-proton shift (see Scheme 5) when compared with the hydrogen atom in the 1,3-C→N prototropic shift. DFT calculations showed higher barriers for the steps in the 1,2-C→N and 1,2-C→C proton migrations than the barrier calculated for the 1,3-C→N prototropic shift (see Supporting Information).



Scheme 5. Proposed mechanisms for the double 1,2-C→N and 1,2-C→C proton migrations in the model structures **Ia** and **Ib**.

Structural Characterization of the Complexes

Single crystals suitable for X-ray diffraction studies were obtained by layering hexane or ether over dichloromethane solutions of the compounds.

The structures of complexes **2a**, **2d**, and **2f** are shown in Figures 1, 2 and 3, respectively. For complex **2d**, the crystal structure contains only the *S* isomer *S*/*R* enantiomeric pair, while for complexes **2a** and **2f** a racemic mixture of *S*/*R* enantiomers is found in the crystals (enantiomer *S* of **2a** is shown in Figure 1 and enantiomer *R* of **2f** is shown in Figure 3). Selected bond lengths, bond angles, and torsion angles for complexes **2a**, **2d** and **2f** are given in Table 1. For complex **2d**, the chelating ligand binds to the metal through a pyridyl donor atom, N1, and a quaternary carbon atom, C14. The N1–Pd1–C14 bond angle is 81.84(14)°. The palladium atom has a nearly square planar coordination geometry, nevertheless, the atom C14 is slightly out of the plane as the torsion angle O5–O4–N1–C14 is 3.01°. The Pd–O bond distances are in good agreement with the values found for other palladium *O*,*O*-coordinated β-diketonates. Also, the Pd1–C14 bond distance is in good agreement with other *C*-bonded β-diketonates. The nonequivalence of the four methyl groups in the β-diketonates, *O*,*O*-coordinated and *C*-coordinated complexes in solution (see comments regarding the ^{1}H NMR analysis that are given above) is in good agreement with the structure found in the solid state in which the four methyl groups are found in different chemical environments. All the comments made above concerning the solid state structure of complex **2d** also apply to complexes **2a** and **2f**. However, the coordination environments around the palladium atoms in these two complexes are planar.

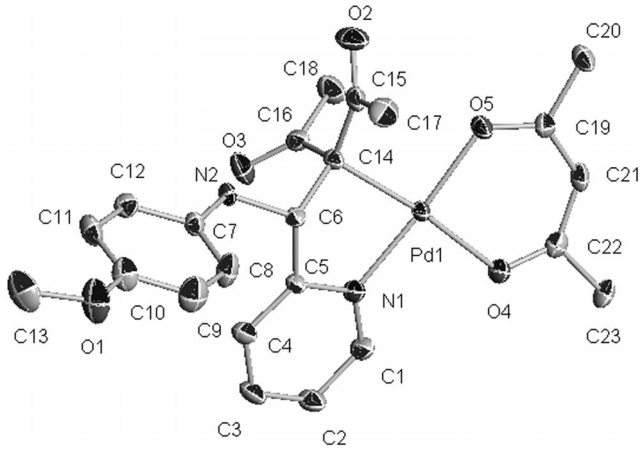


Figure 2. Molecular structure of complex of **2d**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

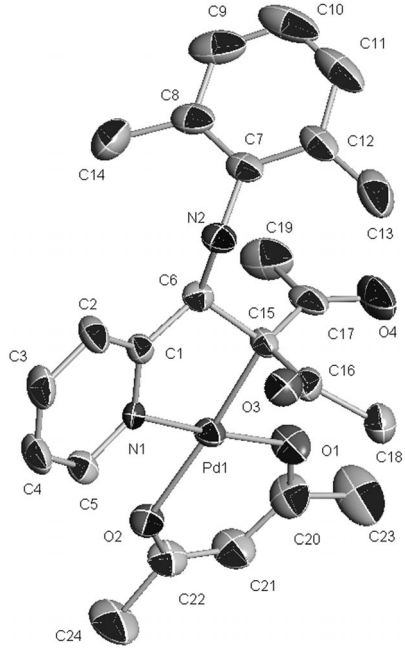


Figure 3. Molecular structure of complex of **2f**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

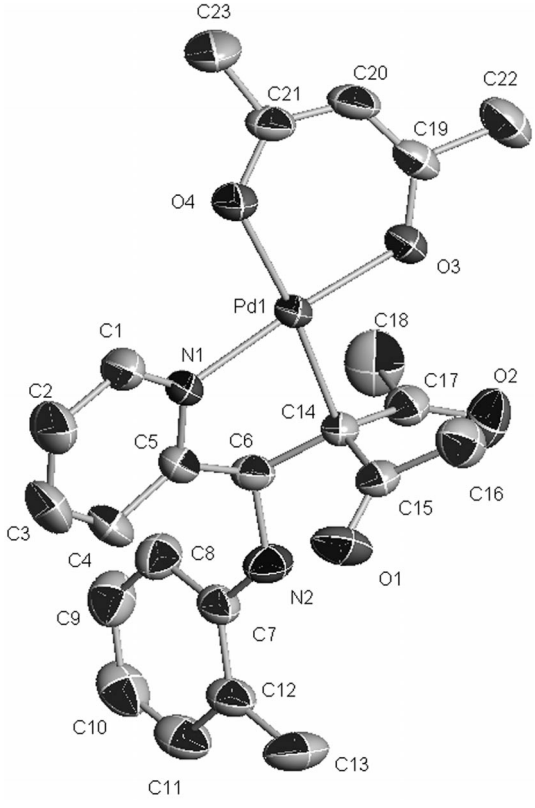


Figure 1. Molecular structure of complex of **2a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

X-ray diffraction quality crystals were also grown for **3a**. The molecular structure of this complex is shown in Figure 4, and selected bond lengths, bond angles, and torsion angles are given in Table 2. In this complex, the bond angles subtended by the chelating ligand bound to the metal are 94.0(1)° for the angle O1–Pd1–O2, and 80.8(1)° for the angle N1–Pd1–N2. The *o*-tolyl group bonded to the iminic nitrogen atom is twisted out of the coordination plane of

Table 1. Selected bond lengths [Å], bond angles [°] and torsion angles [°] for complexex **2a**, **2d** and **2f**.

2a		**2d**		**2f**	
Pd1–C14	2.070(2)	Pd1–C14	2.077(4)	Pd1–C15	2.078(8)
Pd1–O4	2.045(2)	Pd1–O4	2.053(3)	Pd1–O2	2.072(6)
Pd1–N1	2.002(3)	Pd1–N1	2.002(3)	Pd1–N1	2.001(6)
Pd1–O3	1.989(2)	Pd1–O5	2.002(3)	Pd1–O1	1.996(6)
N1–C5	1.337(3)	N1–C5	1.351(5)	N1–C1	1.35(1)
C5–C6	1.517(4)	C6–C5	1.515(5)	C6–C1	1.50(1)
C14–C6	1.542(4)	C14–C6	1.545(5)	C6–C15	1.55(1)
O4–Pd1–O3	93.33(9)	O5–Pd1–O4	93.3(1)	O2–Pd1–O1	92.6(2)
C14–Pd1–N1	82.1(1)	N1–Pd1–C14	81.8(1)	C15–Pd1–N1	82.6(3)
N1–C5–C6–C14	34.5(3)	C14–C6–C5–N1	33.0(4)	C15–C6–C1–N1	–32.2(9)

the metal. The angle between the plane of the *o*-tolyl group ring and the coordination plane of the palladium atom is 66.14°.

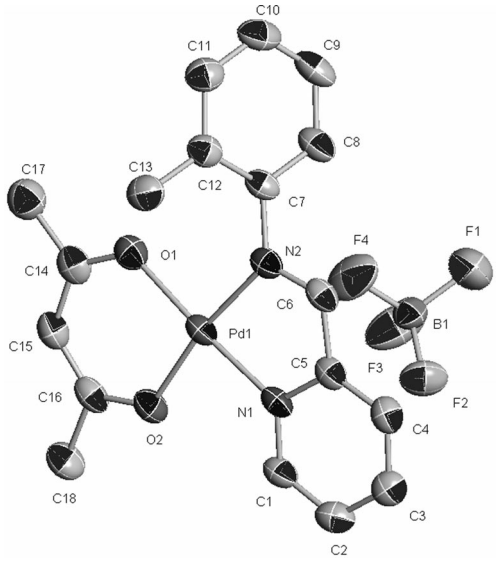


Figure 4. Molecular structure of compound **3a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Table 2. Selected bond lengths [Å], bond angles [°] and torsion angles [°] for complex **3a**.

Pd1–O2	1.971(3)
Pd1–N1	1.996(4)
Pd1–O1	1.980(4)
Pd1–N2	2.022(4)
N1–C5	1.365(7)
C5–C6	1.457(7)
N2–C6	1.273(7)
O2–Pd1–O1	94.0(1)
N1–Pd1–N2	80.8(2)
N1–C5–C6–N2	2.5(7)

Conclusions

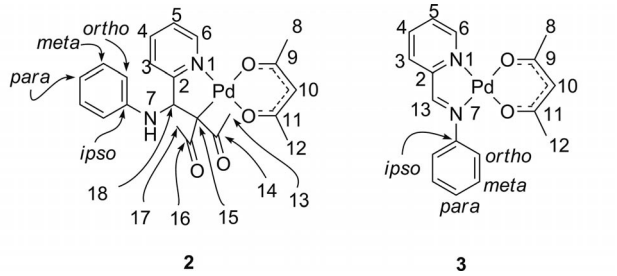
In complexes of palladium with pyridine-imine ligands nucleophilic attack by acetylacetonate on the carbonylic atom of the imine is observed. This attack depends on the steric nature of the ligand and on the ionic charge of the complex, occurring more easily for cationic complexes than for neutral complexes. This reaction should be taken into account when attempting to understand the degradation of catalysts in processes in which nucleophiles are involved. In this reaction a new C–C bond is formed and complexes with acac displaying both *O,O*-acac and γ-acac coordination modes are synthesized. The mechanism for the formation of these complexes starts with the substitution of the chlorido ligands with a chelating acetylacetonato ligand, then a second acetylacetonate anion attacks the coordinated imine to generate a nonisolated amido complex. This amido complex undergoes a 1,3-C→N proton migration process in which protonation of the amido nitrogen occurs (although other mechanisms can be proposed, these involve less acidic protons and proceed via pathways of higher energy). Finally, the displacement of this nitrogen atom by a carbanionic atom yields the final product.

Experimental Section

General Procedures: All manipulations were carried out in an ambient atmosphere. All solvents were purified by standard procedures and distilled. Infrared spectra were obtained on a Nicolet Impact 410 over a frequency range of 4000 cm^{-1} to 400 cm^{-1}, data collections were controlled with the Software OMNIC version 3.1. The spectra were collected with samples prepared as KBr pellets. Deuterated solvents for NMR experiments were stored in a fridge. ^{1}H, ^{13}C NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer and VARIAN MERCURY 300 MHz spectrometer owned by the technological support team of the University of Burgos. NMR experiments were carried out with the samples in deuterated trichloromethane ($CDCl_3$) and deuterated dimethyl sulfoxide ([D_6]DMSO) with tetramethylsilane (TMS) as an internal standard. X-ray data were obtained with a Monocrystal BRUKER instrument equipped with the following parts: SMART APEX CCD area detector, D8 goniometer, graphite monochromator and a Kristalloflex K760–80 X-ray generator; this X-ray instrumentation is owned by the technological support team of the University of Burgos. Elemental analyses (C, H, N) were performed with a Thermo EuroGlas TN/TS 3000. All reagents were purchased from Sigma–Aldrich and were used without further purification. The ligands and compounds **1** were prepared according to published procedures.[14]

Representative Procedure for Synthesis of Complexes 2: With a reference the amount of complex **1**, a fivefold excess of potassium *tert*-butoxide was stirred for 1 h with a fivefold excess of acetylacetone in dichloromethane. The complex **1** in dichloromethane was added

to the solution. The mixture was stirred for 24 h and then filtered through kieselgur. The resultant solution was concentrated by evaporation, and the product was precipitated from solution by the addition of a mixture of ether/hexane (1:1). The thus obtained product was washed with diethyl ether and dried under high vacuum (18 mbar). The atom numbering schemes for the complexes is as shown below.



2

3

[Pd(acac){$C_5H_4NCH(NHPh\text{-}2\text{-}CH_3)C(COCH_3)_2$}] (2a): Starting materials: {$Pd(Cl)_2[C_5H_4N(2\text{-}CH{=}N\text{-}Ph\text{-}4\text{-}CH_3)]$} (100.0 mg, 0.268 mmol), acetylacetone (134.0 mg, 1.340 mmol), potassium *tert*-butoxide (163.8 mg, 1.340 mmol); yield 131.7 mg (0.261 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, $^3J_{HH}$ = 4.8 Hz, 1 H, 6-H), 7.74 (dd, $^3J_{HH}$ = 7.8, $^3J_{HH}$ = 7.6 Hz, 1 H, 4-H), 7.30 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 3-H), 7.20 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 4.8 Hz, 1 H, 5-H), 7.06 (m, 2 H, H^{ar}), 6.73–6.66 (m, 2 H, H^{ar}), 5.58 (d, $^3J_{HH}$ = 10.0 Hz, 1 H, 18-H), 5.41 (s, 1 H, 10-H), 5.26 (d, $^3J_{HH}$ = 10.1 Hz, 1 H, 7-H), 2.48 (s, 3 H, 13-H), 2.47 (s, 3 H, 17-H), 2.13 [s, 3 H, R (*ortho*-CH_3)], 2.07 (s, 3 H, 8-H), 2.00 (s, 3 H, 12-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.84 (s, 1 C, C-16), 206.62 (s, 1 C, C-14), 187.57 (s, 1 C, C-11), 186.75 (s, 1 C, C-9), 169.62 (s, 1 C, C-2), 146.73 (s, 1 C, C-6), 145.27 (s, 1 C, C^{ipso}), 139.25 (s, 1 C, C-4), 130.93 (s, 1 C, C^{ar}), 127.52 (s, 1 C, C^{ar}), 122.97 (s, 1 C, C-3), 122.61 (s, 1 C, C-5), 122.15 (s, 1 C, C^{ortho}), 117.90 (s, 1 C, C^{ar}), 109.58 (s, 1 C, C^{ar}), 100.88 (s, 1 C, C-10), 73.26 (s, 1 C, C-15), 62.57 (s, 1 C, C-18), 31.81 (s, 1 C, C-13), 30.71 (s, 1 C, C-17), 27.73 (s, 1 C, C-8), 27.56 (s, 1 C, C-12), 17.83 [s, 1 C, R (*ortho*-CH_3)] ppm. Selected IR bands: 667, 750, 808, 1025, 1076, 1145, 1238, 1444, 1519, 1567, 1668, 2923, 2971, 3068, 3320 cm^{-1}. $C_{23}H_{29}N_2O_4Pd$ (503.89): calcd. C 54.82, H 5.80, N 5.56; found C 54.82, H 5.63, N 5.75.

[Pd(acac){$C_5H_4NCH(NHPh\text{-}4\text{-}CH_3)C(COCH_3)_2$}] (2b): Starting materials: [$Pd(Cl)_2${$C_5H_4N(2\text{-}CH{=}N\text{-}Ph\text{-}4\text{-}CH_3$)}] (73.8 mg, 0.197 mmol), acetylacetone (98.9 mg, 0.987 mmol), potassium *tert*-butoxide (120.7 mg, 0.987 mmol); yield 92.4 mg (0.184 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, $^3J_{HH}$ = 5.5 Hz, 1 H, 6-H), 7.73 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 7.7 Hz, 1 H, 4-H), 7.37 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 3-H), 7.19 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 5.5 Hz, 1 H, 5-H), 7.00 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, H^{meta}), 6.60 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, H^{ortho}), 5.48 (d, $^3J_{HH}$ = 9.9 Hz, 1 H, 18-H), 5.41 (s, 1 H, 10-H), 5.14 (d, $^3J_{HH}$ = 10.0 Hz, 1 H, 7-H), 2.48 (s, 3 H, 13-H), 2.46 (s, 3 H, 17-H), 2.24 [s, 3 H, R (*para*-CH_3)], 2.06 (s, 3 H, 8-H), 2.00 (s, 3 H, 12-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.73 (s, 1 C, 13-C), 206.06 (s, 1 C, C-16), 187.55 (s, 1 C, C-11), 186.74 (s, 1 C, C-9), 169.81 (s, 1 C, C-2), 146.70 (s, 1 C, C-6), 144.92 (s, 1 C, C^{ipso}), 139.12 (s, 1 C, C-4), 130.32 (s, 2 C, C^{meta}), 127.34 (s, 1 C, C^{para}), 123.01 (s, 1 C, C-3), 122.60 (s, 1 C, C-5), 112.70 (s, 2 C, C^{ortho}), 100.84 (s, 1 C, C-10), 73.10 (s, 1 C, C-15), 62.79 (s, 1 C, C-18), 31.80 (s, 1 C, C-17), 30.78 (s, 1 C, C-13), 27.74 (s, 1 C, C-8), 27.56 (s, 1 C, C-12), 20.59 [s, 1 C, R (*para*-CH_3)] ppm. Selected IR bands: 779, 1020, 1085, 1159, 1199, 1228, 1444, 1479, 1519, 1575, 1668, 2863, 2917, 3077, 3390 cm^{-1}. $C_{23}H_{29}N_2O_4Pd$ (503.89): calcd. C 54.82, H 5.80, N 5.56; found C 54.50, H 6.12, N 5.89.

[Pd(acac){$C_5H_4NCH(NHPh\text{-}2\text{-}OCH_3)C(COCH_3)_2$}] (2c): Starting materials: [Pd(acac){$C_5H_4N(2\text{-}CH{=}N\text{-}Ph\text{-}2\text{-}OCH_3$)}]$^+$[$BF_4^-$] (30 mg, 0.060 mmol), acetylacetone (29.7 mg, 0.297 mmol), potassium *tert*-butoxide (36.4 mg, 0.297 mmol); yield 19.1 mg (0.037 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, $^3J_{HH}$ = 5.5 Hz, 1 H, 6-H), 7.70 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 7.7 Hz, 1 H, 4-H), 7.29 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 3-H), 7.18 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 5.5 Hz, 1 H, 5-H), 6.85–6.78 (m, 2 H, H^{ar}), 6.73–6.67 (m, 2 H, H^{ar}), 5.74 (d, $^3J_{HH}$ = 9.9 Hz, 1 H, 18-H), 5.55 (d, $^3J_{HH}$ = 10.0 Hz, 1 H, 7-H), 5.41 (s, 1 H, 10-H), 3.82 [s, 3 H, R (*ortho*-OCH_3)], 2.49 (s, 3 H, 13-H), 2.48 (s, 3 H, 17-H), 2.06 (s, 3 H, 8-H), 2.00 (s, 3 H, 12-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.44 (s, 1 C, C-16), 205.49 (s, 1 C, C-14), 187.51 (s, 1 C, C-9), 186.76 (s, 1 C, C-11), 169.82 (s, 1 C, C-2), 146.79 (s, 1 C, C-6 or C^{ipso}), 146.63 (s, 1 C, C-6 or C^{ispo}), 139.13 (s, 1 C, C-4), 137.22 (s, 1 C, C^{ar}), 122.92 (s, 1 C, C-3 or C-5), 122.50 (s, 1 C, C-3 or C-5), 121.43 (s, 1 C, C^{ortho}), 117.29 (s, 1 C, C^{ar}), 110.31 (s, 1 C, H^{ar}), 109.15 (s, 1 C, C^{ar}), 100.83 (s, 1 C, C-10), 73.06 (s, 1 C, C-15), 62.13 (s, 1 C, C-18), 55.64 [s, 1 C, R (*ortho*-OCH_3)], 31.81 (s, 1 C, C-17), 30.83 (s, 1 C, C-13), 27.76 (s, 1 C, C-8), 27.56 (s, 1 C, C-12) ppm. Selected IR bands: 738, 1025, 1095, 1234, 1455, 1515, 1573, 1666, 2830, 2921, 3064, 3423 cm^{-1}. $C_{23}H_{29}N_2O_5Pd$ (519.89): calcd. C 53.13, H 5.62, N 5.39; found C 52.61, H 5.19, N 5.43.

[Pd(acac)(C_5H_4NCH{$NHPh\text{-}4\text{-}OCH_3$}$C(COCH_3)_2$)] (2d): Starting materials: [$Pd(Cl)_2${$C_5H_4N(2\text{-}CH{=}N\text{-}Ph\text{-}4\text{-}OCH_3$)}] (150 mg, 0.385 mmol), acetylacetone (193 mg, 1.925 mmol), potassium *tert*-butoxide (215 mg, 1.925 mmol); yield 76.6 mg (0.147 mmol, 38%). ^{1}H NMR (400 MHz, $CDCl_3$; TMS): δ = 8.41 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, 6-H), 7.74 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7.7 Hz, 1 H, 4-H), 7.42 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, 3-H), 7.19 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 5.0 Hz, 1 H, 5-H), 6.77 (d, $^3J_{HH}$ = 8.9 Hz, 2 H, H^{meta}), 6.65 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, H^{ortho}), 5.41 (d, $^3J_{HH}$ = 10.5 Hz, 1 H, 18-H), 5.40 (s, 1 H, 10-H), 5.01 (d, $^3J_{HH}$ = 10.2 Hz, 1 H, 7-H), 3.75 [s, 3 H, R (*para*-CH_3)], 2.46 (s, 3 H, 13-H), 2.45 (s, 3 H, 17 H), 2.06 (s, 3 H, 8-H), 2.00 (s, 3 H, 12-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.02 (s, 2 C, C-14, C-16), 186 (s, 2 C, C-9, C-11), 163.16 (s, 1 C, C-2), 152.63 (s, 1 C, C^{ipso}), 146.68 (s, 1 C, C-6), 141.41 (s, 1 C, C^{para}), 139.11 (s, 1 C, C-4), 123.07 (s, 1 C, C-3), 122.60 (s, 1 C, C-5), 115.37 (s, 2 C, C^{meta}), 114.28 (s, 2 C; C^{ortho}), 100.83 (s, 1 C, C-10), 73.26 (s, 1 C, C-15), 63.84 (s, 1 C, C-18), 55.96 [s, 1 C, R (*para*-CH_3)], 31.78 (s, 1 C, C-17), 30.79 (s, 1 C, C-13), 27.41 (s, 1 C, C-8), 24.39 (s, 1 C. C-12) ppm. Selected IR bands: 684, 781, 827, 1035, 1180, 1249, 1380, 1513, 1567, 1662, 2832, 3075, 3353 cm^{-1}. $C_{23}H_{29}N_2O_5Pd$ (519.89): calcd. C 53.13, H 5.62, N 5.39; found C 52.73, H 5.52, N 5.72.

[Pd(acac){$C_5H_4NCH(NHPh\text{-}4\text{-}CF_3)C(COCH_3)_2$}] (2e): Starting materials: [$Pd(Cl)_2${$C_5H_4N(2\text{-}CH{=}N\text{-}Ph\text{-}4\text{-}CF_3$)}] (188 mg, 0.485 mmol), acetylacetone (242.8 mg, 2.425 mmol), potassium *tert*-butoxide (272.1 mg, 2.425 mmol); yield 207.6 mg (0.372 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, $^3J_{HH}$ = 5.6 Hz, 1 H, 6-H), 7.76 (dd, $^3J_{HH}$ = 7.8, $^3J_{HH}$ = 7.7 Hz, 1 H, 4-H), 7.42 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, H^{meta}), 7.29 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 3-H), 7.22 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 5.5 Hz, 1 H, 5-H), 6.70 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, H^{ortho}), 5.61 (s, 1 H, 18-H), 5.61 (s, 1 H, 7-H), 5.42 (s, 1 H, 10-H), 2.49 (s, 6 H, 13-H, 17-H), 2.07 (s, 3 H, 8-H), 2.01 (s, 3 H, 12-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.30 (s, 1 C, C-16), 206.10 (s, 1 C, C-14), 187.64 (s, 1 C, C-9), 186.68 (s, 1 C, C-11), 168.73 (s, 1 C, C-2), 149.67 (s, 1 C, C^{ipso}), 144.99 (s, 1 C, C-6), 139.38 (s, 1 C, C-4), 127.32 (s, 2 C, C^{meta}), 126.34 (s, 1 C, C^{para}), 122.90 (s, 1 C, C-5), 122.68 (s, 1 C, C-3), 119.90 [s, 1 C, R (*para*-CF_3)], 111.64 (s, 2 C, C^{ortho}), 100.94 (s, 1 C, C-10), 72.96 (s, 1 C, C-15), 61.87 (s, 1 C, C-18), 31.81 (s, 1 C, C-13), 30.90 (s, 1 C, C-17), 27.68 (s, 1 C, C-12), 27.52 (s, 1 C, C-8) ppm. Selected IR bands:

688, 713, 771, 829, 1025, 1062, 1101, 1164, 1191, 1249, 1386, 1479, 1519, 1581, 1668, 2925, 2975, 3073, 3411 cm^{-1}. $C_{23}H_{26}F_3N_2O_4Pd$ (557.86): calcd. C 49.52, H 4.70, N 5.02; found C 48.92, H 4.57, N 5.25.

[Pd(acac){C_5H_4NCH(NHPh-2,6-CH_3)C($COCH_3$)$_2$}] (2f): Starting materials: [Pd(acac){C_5H_4N(2-CH=N-Ph-2,6-CH_3)}]$^+$[BF_4^-] (98.2 mg, 0.262 mmol), acetylacetone (131.6 mg, 1.314 mmol), potassium *tert*-butoxide (147.45 mg, 1.314 mmol); yield 95.2 mg (0.183 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, $^3J_{HH}$ = 5.8 Hz, 1 H, 6-H), 7.74 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7.7 Hz, 1 H, 4-H), 7.32 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 3-H), 7.19 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 5.8 Hz, 1 H, 5-H), 6.86–6.69 (m, 3 H, H^{meta}, H^{para}), 5.77 (d, $^3J_{HH}$ = 10.2 Hz, 1 H, 18-H), 5.58 (d, $^3J_{HH}$ = 10.3 Hz, 1 H, 7-H), 5.42 (s, 1 H, 10-H), 2.51 (s, 6 H, 12-H, 17-H), 2.31 [s, 6 H, R (di-*ortho*-CH_3)], 2.08 (s, 3 H, 8-H), 2.02 (s, 3 H, 12-H) ppm. Selected IR bands: 3396, 3025, 2919, 2852, 1671, 1573, 1519, 1228, 1415, 1120, 1199, 1025 cm^{-1}. $C_{24}H_{28}N_2O_4Pd{\cdot}0.5CH_2Cl_2$ (557.38): calcd. C 52.79, H 5.24, N 5.03; found C 52.07, H 5.25, N 4.80.

[Pd(acac){C_5H_4NCH(NHPh-2-*i*Pr)C($COCH_3$)$_2$}] (2g): Starting materials: [Pd(acac){C_5H_4N(2-CH=N-Ph-2-*i*Pr)}]$^+$[BF_4^-] (200 mg, 0.387 mmol), acetylacetone (193.0 mg, 1.935 mmol), potassium *tert*-butoxide (236.0 mg, 1.935 mmol); yield 170.1 mg (0.319 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, $^3J_{HH}$ = 4.9 Hz, 1 H, 6-H), 7.72 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 7.7 Hz, 1 H, 4-H), 7.32 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 3-H), 7.19 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 4.9 Hz, 1 H, 5-H), 7.17 (m, 1 H, H^{ar}), 7.05 (m, 1 H, H^{ar}), 6.72 (m, 2 H, H^{ar}), 5.60 (d, $^3J_{HH}$ = 10.0 Hz, 1 H, 18-H), 5.51 (d, $^3J_{HH}$ = 10.0 Hz, 1 H, 7-H), 5.42 (s, 1 H, 10-H), 2.85 [sept, $^3J_{HH}$ = 6.7 Hz, 1 H, R (*ortho*-*i*Pr-H)], 2.49 (s, 3 H, 13-H), 2.46 (s, 3 H, 17-H), 2.06 (s, 3 H, 8-H), 2.00 (s, 3 H, 12-H), 1.19 [d, $^3J_{HH}$ = 6.8 Hz, 6 H, R (*ortho*-*i*Pr-CH_3)] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.81 (s, 1 C, C-14), 206.57 (s, 1 C, C-16), 187.57 (s, 1 C, C-9), 186.77 (s, 1 C, C-11), 169.67 (s, 1 C, C-2), 149.9 (s, 1 C, C^{ipso}), 146.77 (s, 1 C, C-6), 139.18 (s, 1 C, C-4), 132.71 (s, 1 C, C^{ortho}), 127. (s, 1 C, C^{ar}), 125.71 (s, 1 C, C-5), 122.91 (s, 1 C, C^{ar}), 122.71 (s, 1 C, C-3), 118.0 (s, 1 C, C^{ar}), 109.96 (s, 1 C, C^{ar}), 100.84 (s, 1 C, C-10), 73.08 (s, 1 C, C-15), 62.79 (s, 1 C, C-18), 31.88 (s, 1 C, C-13), 30.72 (s, 1 C, C-17), 29.58 [s, 1 C, R (*ortho*-*i*Pr-CH_3)], 27.58 (s, 1 C, C-12), 27.48 [s, 1 C, R (*i*Pr-C)], 25.67 (s, 1 C, C-8), 22.23 [s, 1 C, R (*ortho*-*i*Pr-CH_3)] ppm. Selected IR bands: 622, 748, 800, 842, 1024, 1097, 1263, 1446, 1515, 1575, 1673, 2854, 2923, 2960, 3073, 3434 cm^{-1}. $C_{25}H_{30}N_2O_4Pd$ (528.92): calcd. C 56.77, H 5.72, N 5.30; found C 56.61, H 5.59, N 5.43.

Representative Procedure for the Synthesis of Complexes 3: To a solution of complex **1** in acetone was added the equivalent amount of Tl(acac) and $TlBF_4$, both in acetone. The mixture was stirred for 24 h. Then the precipitated TlCl was removed by filtration through kieselgur, and the filtrate was evaporated. The substance obtained after evaporation was dissolved in dichloromethane. This solution was again filtered through kieselgur, and the solvent partially evaporated in vacuo. The final product was precipitated from solution by the addition of hexane. The thus obtained product was dried under high vacuum (18 mbar).

[Pd(acac){C_5H_4N(2-CH=N-Ph-2-CH_3)}]$^+$[BF_4^-] (3a): Starting materials: **1a** (100.0 mg, 0. 268 mmol), Tl(acac) (78.0 mg, 0.268 mmol), $TlBF_4$ (78.5 mg, 0.268 mmol); yield 66.6 mg (0.136 mmol, 51%). ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 8.81 (s, 1 H, 13-H), 8.63 [d, ^3J(H,H) = 5.5 Hz, 1 H, 6-H], 8.50 [dd, ^3J(H,H) = 7.8, ^3J(H,H) = 7.7 Hz, 1 H, 4-H], 8.28 [d, ^3J(H,H) = 7.7 Hz, 1 H, 3-H], 8.04 [dd, ^3J(H,H) = 7.7, ^3J(H,H) = 5.5 Hz, 1 H, 5-H], 7.40–7.33 (m, 4 H, H^{ar}), 5.74 (s, 1 H, 10-H), 2.42 [s, 3 H, R (*para*-CH_3)], 2.21 (s, 3 H, 8-H), 1.81 (s, 3 H, 12-H) ppm. Selected IR bands: 669, 717, 782, 1033, 1058, 1236, 1427, 1488, 1519, 1556, 2923, 3037, 3075 cm^{-1}. $C_{18}H_{19}BF_4N_2O_2Pd$ (488.58): calcd. C 44.25, H 3.92, N 5.73; found C 43.05, H 4.13, N 6.21.

[Pd(acac){C_5H_4N(2-CH=N-Ph-2-OCH_3)}]$^+$[BF_4^-] (3c): Starting materials: **1c** (100 mg, 0.256 mmol), Tl(acac) (74.6 mg, 0.256 mmol), $TlBF_4$ (75.0 mg, 0.256 mmol); yield 76.2 mg (0.151 mmol, 59%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71 (s, 1 H, 13-H), 8.58 [d, ^3J(H,H) = 5.5 Hz, 1 H, 6-H], 8.52 [dd, ^3J(H,H) = 7.7, ^3J(H,H) = 7.7 Hz, 1 H, 3-H], 8.28 [d, ^3J(H,H) = 7.7 Hz, 1 H, 4-H], 7.83 [dd, ^3J(H,H) = 7.7, ^3J(H,H) = 5.5 Hz, 1 H, 5-H], 7.41–7.34 (m, 2 H, H^{ar}), 7.10–6.95 (m, 2 H, H^{ar}), 5.51 (s, 1 H, 10-H), 3.88 [s, 3 H, R (*ortho*-OCH_3)], 2.19 (s, 3 H, 8-H), 1.87 (s, 3 H, 12-H) ppm. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 8.86 (s, 1 H, 13-H), 8.62 (s, 1 H, 6-H), 8.49 (s, 1 H, 4-H), 8.29 (s, 1 H, 3-H), 8.03 (s, 1 H, 5-H), 7.46 (m, 2 H, H^{ar}), 7.17 (m, 2 H, H^{ar}), 5.73 (s, 1 H, 10-H), 3.85 [s, 1 H, R (*ortho*-OCH_3)], 2.21 (s, 1 H, 8-H), 1.86 (s, 1 H, 12-H) ppm. Selected IR bands: 771, 1060, 1257, 1434, 1519, 1556, 2921, 3008, 3029, 3073 cm^{-1}. $C_{18}H_{19}BF_4N_2O_3Pd$ (504.58): calcd. C 42.85, H 3.80, N 5.55; found C 44.92, H 4.43, N 5.36.

[Pd(acac){C_5H_4N(2-CH=N-Ph-2,6-CH_3)}]$^+$[BF_4^-] (3f): Starting materials: **1f** (100 mg, 0.258 mmol), Tl(acac) (75.2 mg, 0.258 mmol), $TlBF_4$ (75.3 mg, 0.258 mmol); yield 104.8 mg (0.209 mmol, 81%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 8.82 (s, 1 H, 13-H), 8.66 [d, ^3J(H,H) = 5.5 Hz, 1 H, 6-H], 8.51 [dd, ^3J(H,H) = 7.8, ^3J(H,H) = 7.7 Hz, 1 H, 4-H], 8.25 [d, ^3J(H,H) = 7.7 Hz, 1 H, 3-H], 8.07 [dd, ^3J(H,H) = 7.7, ^3J(H,H) = 5.5 Hz, 1 H, 5-H], 7.24–7.16 (m, 3 H, H^{ar}), 5.72 (s, 1 H, 10-H), 2.32 [s, 3 H, R (di-*ortho*-CH_3)], 2.21 (s, 3 H, 8-H), 1.73 (s, 3 H, 12-H) ppm. Selected IR bands: 777, 1062, 1186, 1230, 1434, 1475, 1519, 1556, 2921, 2969, 3039 cm^{-1}. $C_{19}H_{21}BF_4N_2O_2Pd$ (502.61): calcd. C 45.40, H 4.21, N 5.57; found C 42.69, H 3.69, N 5.59.

[Pd(acac){C_5H_4N(2-CH=N-Ph-2-*i*Pr)}]$^+$[BF_4^-] (3g): Starting materials: **1g** (100 mg, 0.249 mmol), Tl(acac) (72.3 mg, 0.249 mmol), $TlBF_4$ (72.7 mg, 0.249 mmol); yield 79.5 mg (0.153 mmol, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (s, 1 H, 13-H), 8.61 [d, ^3J(H,H) = 5.4 Hz, 1 H, 6-H], 8.58 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-H], 8.32 [dd, ^3J(H,H) = 7.9, ^3J(H,H) = 7.9 Hz, 1 H, 4-H], 7.88 [dd, ^3J(H,H) = 7.8, ^3J(H,H) = 5.5 Hz, 1 H, 5-H], 7.42 [ddd, ^3J(H,H) = 8.1, ^3J(H,H) = 7.4, ^3J(H,H) = 1.5 Hz, 1 H, H^{ar}], 7.36 [dd, ^3J(H,H) = 7.8, ^3J(H,H) = 1.2 Hz, 1 H, H^{ar}], 7.24 [ddd, ^3J(H,H) = 7.8, ^3J(H,H) = 7.8, ^3J(H,H) = 1.2 Hz, 2 H, H^{ar}], 5.50 (s, 1 H, 10-H), 3.60 [s, 3 H, R (*i*Pr-H)], 2.19 (s, 3 H, 8-H), 1.79 (s, 3 H, 12-H), 1.30 [s, 3 H, R (*i*Pr-CH_3)], 1.12 [s, 3 H, R (*i*Pr-CH_3)] ppm. Selected IR bands: 779, 1060, 1236, 1278, 1434, 1446, 1519, 1556, 2964, 3033 cm^{-1}. $C_{20}H_{23}BF_4N_2O_2Pd$ (516.63): calcd. C 46.50, H 4.49, N 5.42; found C 45.78, H 4.39, N 5.74.

X-ray Structure Determination: Crystallographic data for compounds **2a**, **2d**, **2f** and **3a** were collected at 173 K on a Bruker SMART CCD diffractometer, equipped with an area detector, and with Mo-K_α radiation (λ = 0.71073 Å).[19] Integrated intensities[20] were obtained from several series of exposures, each exposure covering 0.3° in ω, and the total datasets comprised complete spheres of reciprocal space. Absorption corrections were applied based on multiple and symmetry equivalent measurements.[21] The structures were solved by direct methods and refined by least-squares methods on weighted F^2 values for all reflections.[22] 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. Refinements proceeded smoothly to give the residual values shown in Table S1 (See Sup-

porting Information). Complex neutral-atom scattering factors were used.[23]

CCDC-859570 (for **2a**), -859571 (for **2d**), -859572 (for **2f**) and -859573 (for **3a**) 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.

Supporting Information (see footnote on the first page of this article): Table summarizing the X-ray crystallography data collection and structure refinement data for compounds **2a**, **2d**, **2f** and **3a** (Table S1). DFT optimization information for model structures of **Ia**, **Ib** and **Ic**, and DFT estimations of the energetic barriers for proton migrations.

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