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Kinetico–mechanistic studies of C–H bond activation on new Pd complexes containing *N*,*N*′-chelating ligands†

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The hybrid imine/amine palladium(II) coordination complexes $[PdX_2(\kappa^2\text{-}N_{imino},N_{amino})]$ (X = Cl, AcO; $\kappa^2\text{-}N_{imino},N_{amino} = 4ClC_6H_4CHNCH_2(CH_2)_nN(CH_3)_2$, $n = 1, 2$) have been prepared in different isomeric forms which include *E*/*Z* arrangement around the C=N bond of the hybrid ligand and $\{Pd(\kappa^2\text{-}N_{imino},N_{amino})\}$ ring conformation. The crystal structures of four of them, ***E*-1AcO**, ***Z*-1AcO**, ***E*-2AcO** and ***E*-2Cl**, have been determined and the solution behaviour in acetic acid, the common cyclometallating solvent, for all these systems studied. The complexes in acetic acid solution are shown to maintain the structure determined by X-ray crystallography, as they do in deuterated chloroform. Nevertheless, a partial opening equilibrium of the $\{Pd(\kappa^2\text{-}N_{imino},N_{amino})\}$ ring is observed by NMR experiments. When the complexes are held in solution for longer periods the corresponding cyclometallated derivatives, **1AcO**-*CM*, **2AcO**-*CM*, **1Cl**-*CM* and **2Cl**-*CM*, containing the $\{Pd(\kappa^2\text{-}C,N_{imino})\}$ palladacycle are obtained, as characterized by ^1H NMR spectroscopy. In these compounds the total opening of the N_{amino} moiety of the ligand has occurred. The C–H bond activation process has been studied kinetico–mechanistically at different temperatures, pressures and acid concentrations; the results agree with the need of an opening of the chelate ring in $[PdX_2(\kappa^2\text{-}N_{imino},N_{amino})]$ prior to the proper cyclometallation reaction. The values of the enthalpies of activation are higher than those observed for known *N*-monodentated cyclometallating ligands, as should correspond to the contribution of a ligand dechelation pre-equilibrium. The entropies and volumes of activation are also indicative of this predissociation that include an important amount of contractive ordering. The presence of small amounts of triflic acid in the reaction medium accelerates the reaction to the value observed for N_{imino}-monodentate systems, indicating that the full opening of the chelate ring has taken place. For the badly oriented isomeric forms of the ligand in the chelated complex (*Z*), the cyclometallation process is even more slow and corresponds directly to the reorganization of the ligand to its cyclopalladation-active (*E*) conformation.

Introduction

C–H Bond activation *via* oxidative addition or electrophilic substitution reactions to produce cyclometallated complexes are well known. These processes are very common with transition metals of group 10 elements containing *N*-donor ligands.[1–4] As a general rule, the preparative procedure for these cyclometallated species is the reaction of a variety of metal salts (*i.e.* acetate, chloride, *etc.*) in presence of the stoichiometric amounts of the desired ligand which generally contains the heteroatom, **B** (**B** = N, P, S or O).[5–10] The process to obtain the final $\kappa^2\text{-}C,\boldsymbol{B}$ metallacycles involves the precoordination of **B** to the metal centre and further ligand topological arrangement allows for the C–H bond activation.[11,12] The mechanistic study of these reactions has been carried out both in innocent and protic solvents, and a good general picture of the reaction mechanism is available.[1,13]

Not many of these processes are known with ligands containing two donor, **B**,**B**′, atoms that permit the preliminary isolation of the corresponding non-organometallic complexes.[14–20] This is especially true for metals with a d^8 configuration, which favours the formation of four-coordinated planar complexes. In this way the formation of bis(*N*-monodentated) coordination complexes, that do not lead to C–H bond activation, is avoided.[21] In this respect, only few metallation studies have been reported from previously prepared coordination complexes.[22,23] Thorough and comprehensive kinetico–mechanistic studies of the reaction from these $[MX_2(\kappa^2\text{-}\boldsymbol{B,B'})]$ complexes to produce the cyclometallated compounds is even more scarce, and they have been only described for platinum derivatives.[22]

In this paper we present the preparation of the new $[PdX_2(\kappa^2\text{-}N_{imino},N_{amino})]$ coordination complexes, indicated in Chart 1, where $\kappa^2\text{-}N_{imino},N_{amino}$ corresponds to the hybrid imine/amine ligands indicated by **1** and **2**. The crystal structures have been determined for ***E*-1AcO**, ***Z*-1AcO**, ***E*-2AcO** and ***E*-2Cl**.

The solution behaviour of these complexes has also been studied, both structurally and reactivity-wise, by NMR and UV-Vis spectrometries in acetic acid, a common metallating medium for this type of process,[14] and the cyclometallation process established. The flexibility of the $\{Pd(\kappa^2\text{-}N_{imino},N_{amino})\}$ rings of the non-cyclometallated complexes enabled for the existence of two isomeric forms in the starting ***E*-2AcO** and ***E*-2Cl** compounds, while for the complexes derived from ligand ***E*-1** are isomerically unique. The final cyclometallated complexes in acetic acid solution correspond in all cases to species that have the $\kappa^2\text{-}C,N_{imino}$ coordination skeleton. The amino nitrogen acts, in some cases, in bridging form to another metal centre.[14]

The kinetico–mechanistic study of the reactions has been carried out at variable temperature, pressure and acidic conditions, and the corresponding relevant kinetic and activation parameters have been determined. In all cases the processes are one order of magnitude slower than those observed for *N*-monodentate cyclometallating systems,[13] and a dramatic acceleration of the process in the presence of triflic acid is detected. This acceleration has been ascribed to a preliminary dechelating reaction producing *N*-monodentate complexes very

† Electronic supplementary information (ESI) available: Tables S1 and S2: values of k_{obs} for the systems studied. Figs. S1–3: Plots of k_{obs} values. See http://www.rsc.org/suppdata/dt/b4/b415613g/

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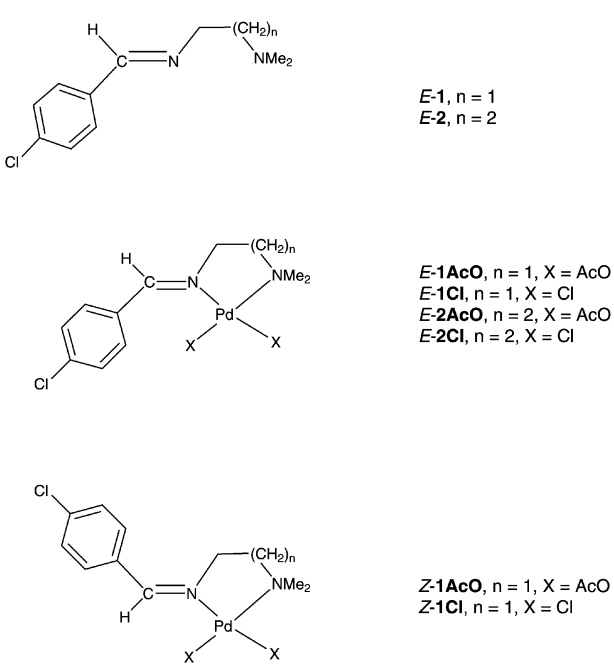


Chart 1 Imino–amine ligands, *E*-**1** and *E*-**2**, and the palladium coordination complexes prepared.

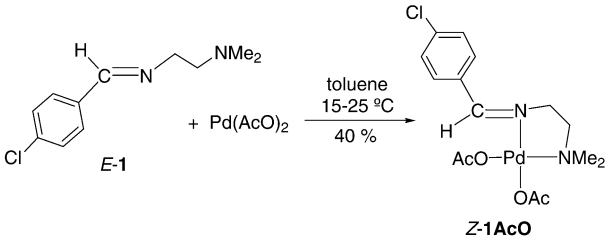
similar to those already studied. The values determined for the activation enthalpies, entropies and volumes agree extremely well with a transition state involving this partial chelate opening due to the protonation of the amino group in the presence of acids.

Results

[$PdX_2(\kappa^2\text{-}N_{imino},N_{amino})$] complexes

Preparation. Ligands *E*-**1** and *E*-**2** were prepared according to procedures previously described by condensation of the aldehyde, 4-ClC_6H_4CHO, and the corresponding diamine, $H_2NCH_2(CH_2)_nNMe_2$ ($n = 1, 2$).[14] Only the isomer having an *E* conformation was observed in solution (as determined by NOE contacts between imine and methylene protons), analogously to other similar ligands.[22] Neutral acetato (**1AcO**, **2AcO**) and chloro (**1Cl**, **2Cl**) palladium complexes containing *E*-**1** and *E*-**2** imine/amines, were obtained in toluene solution from palladium acetate and bis(benzonitrile)dichloropalladium, respectively, as starting materials (Scheme 1). All these complexes show an *E* conformation of the ligand, as observed for the free imine/amine ligands.

However, at temperatures higher than 10 °C, the acetato complex **1AcO** shows important amounts of the species having the ligand in a *Z* conformation; *Z*-**1AcO** can then be obtained as the major component at room temperature (Scheme 2). In



Scheme 2 Synthesis of *Z*-**1AcO**.

contrast, the compounds derived from ligand *E*-**2** always exhibit an *E* arrangement around the C=N bond.

The serendipitous exchange of acetato by chloro ligands in complexes *Z*-**1AcO** and *E*-**2AcO** occurred in heterogeneous medium.[24,25] When an ethyl acetate–methanol (4 : 1) solution of the complexes were stirred with commercial acid alumina (*ca.* 0.2% of chloride), compounds *Z*-**1Cl** and *E*-**2Cl** were obtained in quantitative yields (eqn. (1)).

$$[Pd(AcO)_2(\kappa^2\text{-}N_{imino},N_{amino})] \xrightarrow{Al_2O_3} [PdCl_2(\kappa^2\text{-}N_{imino},N_{amino})] \quad (1)$$

Z-**1AcO** / *E*-**2AcO** → *Z*-**1Cl** / *E*-**2Cl**

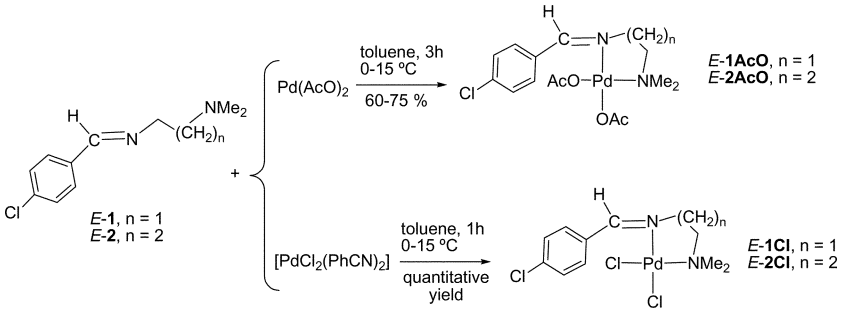
Alternatively these compounds can also be obtained by column chromatography over alumina of the corresponding acetato derivatives (see Experimental section).

Formation of very small amounts of the corresponding cyclometallated complexes was also observed during the process (less than 10% for *E*-**2Cl** and less than 2% for *Z*-**1Cl**). For compound *E*-**1AcO**, the presence of alumina leads to decomposition, and the corresponding chloro complex, the cyclopalladated derivative, and free *p*-chlorobenzaldehyde were observed in the reaction medium. From these results, it seems clear that for ligand **1**, coordination complexes adopting *Z* conformation are more robust than the analogous derivatives of type-*E*.

According to the analytical data, the compounds of stoichiometry corresponding to **1Cl**, **2Cl**, **1AcO** and **2AcO** were obtained as monometallic complexes of general formula [PdX_2(**L**)] (**L** = **1**, **2**; X = AcO, Cl), where **L** acts as a κ^2-N_{imino},N_{amino} bidentated ligand. The complexes were fully characterized by the usual techniques. IR spectra showed signals at 1530–1590 cm^{-1} assigned to stretching of the C=N bond. Structural studies were carried out, both in solid state (by X-ray diffraction) and in solution (by NMR spectrometry).

X-Ray structures. Suitable single crystals for X-ray diffraction measurements were obtained by slow diffusion of diethyl ether into dichloromethane solutions of *E*-**1AcO**, *Z*-**1AcO**, *E*-**2AcO** and *E*-**2Cl**. Figs. 1 and 2 and Table 1 collect the structures and relevant information of these complexes.

In these structures, the palladium atom has a distorted square-planar coordination formed by two *cis*-oriented nitrogen and two oxygen (*E*-**1AcO**, *Z*-**1AcO**, *E*-**2AcO**) or chlorine atoms (*E*-**2Cl**). The ring of the complexes are nearly coplanar (torsion



Scheme 1 Synthesis of type-*E* palladium complexes: *E*-**1AcO**, *E*-**1Cl**, *E*-**2AcO** and *E*-**2Cl**.

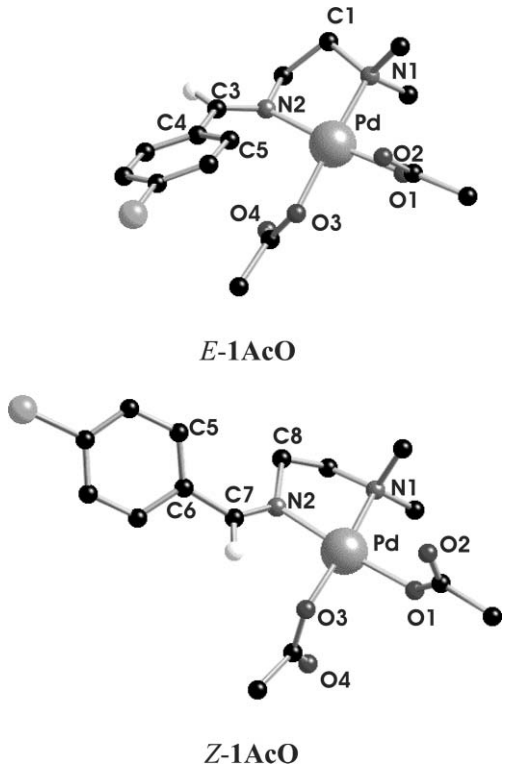


Fig. 1 View of the molecular structures of *E*-**1AcO** and *Z*-**1AcO**. Hydrogen atoms (except iminic hydrogen) have been omitted for clarity.

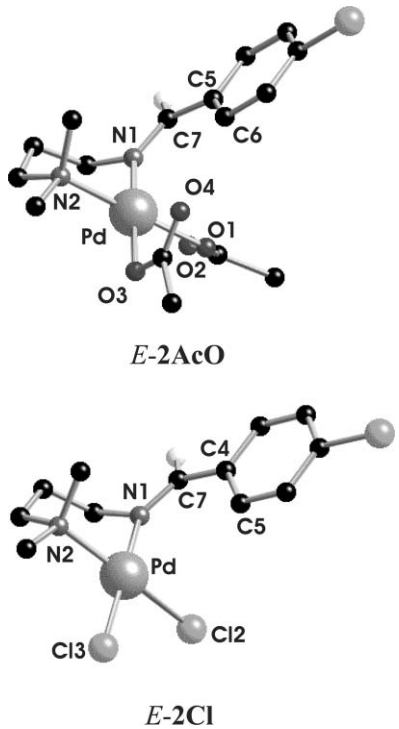


Fig. 2 View of the molecular structures of *E*-**2AcO** and *E*-**2Cl**. Hydrogen atoms (except iminic hydrogen) have been omitted for clarity.

angles O(1)–O(3)–N(2)–N(1) = 2.6, 4.0 and 2.4° for *E*-**1AcO**, *Z*-**1AcO** and *E*-**2AcO**, respectively, and Cl(2)–Cl(3)–N(2)–N(1) = 1.2° for *E*-**2Cl**). The imine ligand exhibits the *E* conformation for the two complexes containing ligand **2** (Fig. 2) and for those with ligand **1**, *E* and *Z* structures were determined (Fig. 1).

For type-**1** complexes, the five-membered metallacycle has a pseudo-chair conformation, with the palladium, the two nitrogen and one of the methylenic carbon atoms being nearly coplanar (torsion angle Pd–N(1)–C(1)–N(2) 1.2° and Pd–N(2)–C(8)–N(1) 2.8°, for *E*-**1AcO** and *Z*-**1AcO**, respectively). The substituent on the iminic nitrogen atom occupies a pseudo-equatorial position relative to the methyl groups of the dimethylamino moiety for both structures. Another relevant feature is the non-coplanarity between the imino (C=N) and the aryl groups (torsion angle N(2)–C(3)–C(4)–C(5) 32.2° and N(2)–C(7)–C(6)–C(5) 32.8° for *E*-**1AcO** and *Z*-**1AcO**, respectively).

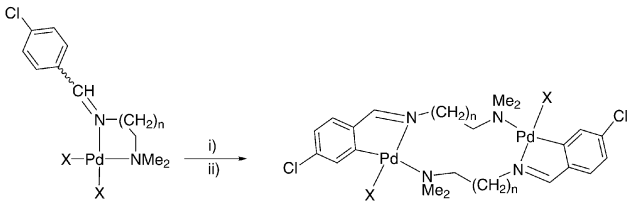
Table 1 Selected bond lengths (Å) and angles (°) for *E*-**1AcO**, *Z*-**1AcO**, *E*-**2AcO** and *E*-**2Cl** (esds in parentheses)

	E-**1AcO**	*Z*-**1AcO**	*E*-**2AcO**	*E*-**2Cl**
Pd–N(1)	2.044(4)	2.050(2)	1.991(2)	2.010(3)
Pd–N(2)	2.006(2)	2.007(2)	2.0683(19)	2.099(4)
Pd–O(1)	2.010(2)	2.0142(19)	2.0224(17)	—
Pd–O(3)	2.006(2)	2.029(2)	2.0235(19)	—
Pd–Cl(2)	—	—	—	2.3021(14)
Pd–Cl(3)	—	—	—	2.2922(16)
N(1)–Pd–N(2)	83.77(13)	84.06(9)	87.53(8)	87.30(15)
O(1)–Pd–O(3)	89.75(11)	91.26(9)	84.21(8)	—
Cl(2)–Pd–Cl(3)	—	—	—	88.66(6)

For complexes containing ligand **2**, *E*-**2AcO** and *E*-**2Cl**, the six-membered metallacycle shows a chair arrangement, with the substituent on the iminic nitrogen atom occupies a pseudo-axial position. In contrast to *E*-**1AcO**, the aryl and iminic groups are nearly coplanar (torsion angles N(1)–C(7)–C(5)–C(6) 6.2° for *E*-**2AcO** and N(1)–C(7)–C(4)–C(5) 5.6° for *E*-**2Cl**).

Solution behaviour. The complexes containing ligand *E*-**1** (*E*-**1AcO**, *Z*-**1AcO**, *E*-**1Cl** and *Z*-**1Cl**) exhibited only one isomer in chloroform solution as observed by ^{1}H NMR spectroscopy. However, compounds with ligand *E*-**2** (*E*-**2AcO** and *E*-**2Cl**) present two isomeric forms in chloroform solution. The two isomers detected for complexes *E*-**2AcO** and *E*-**2Cl** appear in an isomeric ratio of *ca.* (4–6) : 1, constant within the temperature range studied (323–273 K in $CDCl_3$). NOE contacts revealed that all the isomers possess an *E* conformation, consequently they have to be probably based on different metallacycle conformations having an exchange energy high enough to be distinguished in the NMR time scale. The major component of the *E*-**2AcO** and *E*-**2Cl** mixture (from now on *E*-**2AcO(M)** and *E*-**2Cl(M)**) could be obtained as the sole compound when the mixture of isomers (*E*-**2AcO(M)** + *E*-**2AcO(m)** or *E*-**2Cl(M)** + *E*-**2Cl(m)**) was purified by flash column chromatography over acid silica or alumina, for the acetato or chloro complexes, respectively, using ethyl acetate–methanol (4 : 1) as eluent. Under these conditions, the minor isomer is not stable as such, and the corresponding cyclometallated product is formed (see below in the kinetics section).

Metallation reaction. Coordination complexes [PdX_2(κ^2-N_{imino},N_{amino})] containing ligands **1** and **2** gave the corresponding cyclometallated compounds when heated in acetic acid solutions at 50–60 °C for *ca.* 4–6 h (Scheme 3). The results are analogous



E-**1AcO**, X = AcO, n = 1
E-**1Cl**, X = Cl, n = 1
Z-**1AcO**, X = AcO, n = 1
Z-**1Cl**, X = Cl, n = 1
E-**2AcO**, X = AcO, n = 2
E-**2Cl**, X = Cl, n = 2

1AcO-*CM*, X = AcO, n = 1
1Cl-*CM*, X = Cl, n = 1
2AcO-*CM*, X = AcO, n = 2
2Cl-*CM*, X = Cl, n = 2

Scheme 3 Preparation of cyclometallated compounds **1AcO**-*CM*, **1Cl**-*CM*, **2AcO**-*CM* and **2Cl**-*CM*. *Reagents and conditions*: (i) AcOH, 60 °C, 5 h; (ii) solvent evaporation and precipitation with diethyl ether.

from the preparation already described using palladium acetate and free ligand as starting materials.[14] ^{1}H NMR spectra in $CDCl_3$ of these complexes indicate a metallated structure where the ligand acts as a κ^2-*C*,N_{imino} bidentated ligand. From the data available,[14] we suggest that the N_{amino} donor functions can act, in some cases, as a bridge to a second palladium atom. The greater *trans* influence of the phenyl group when compared with the anionic ligands in the starting material,[11] justifies this observation.

When ^{1}H NMR spectra of the acetato derivatives, **1AcO**-*CM* and **2AcO**-*CM*, were recorded in deuterated acetic acid, three different metallated species in solution are evident in relative equilibrium ratios 1 : 1.7 : 4 and 1 : 2 : 5.7, respectively. Phase sensitive 2D NOESY experiments show positive cross-peaks connecting the methinic protons of these species, thereby indicating that these compounds exchange in solution. The methylamine signal of one of these species appears at δ values similar to those of the free ligand indicating so that the amine group is not coordinated to palladium;[15,26] a dinuclear structure with bridging acetato ligand can be proposed for this compound. The same signals of the other two equilibrium species are shifted to higher frequencies than for the free ligand, indicating that the amine nitrogen is probably coordinated to palladium. The lability of Pd–acetate bonds in protic medium can explain the equilibrium here reported.[13,21]

In contrast, the ^{1}H NMR spectrum of **2Cl**-*CM* in deuterated acetic acid shows only one species. The spectral data indicate that it corresponds to the same species than that seen in deuterochloroform, no changes take place in the presence of acid. It is also worth mentioning that there is a definitive absence of palladium-coordinated acetato groups.

Kinetics. The reactions of all the non-metallated complexes of ligands *E*-**1** and *E*-**2**, kinetically monitored by UV-Vis spectroscopy in neat acetic acid solution, proved to be the real cyclometallation reactions as checked by ^{1}H NMR evaluation of the reaction mixture under the same time and concentration conditions. Despite the fact that for similar reactions, carried out on platinum complexes, a preliminary chloride substitution process by acetate is observed, the chloro ligand remains in the coordination sphere of the Pd^{II}, even after the C–H bond activation process has occurred (see above). As already indicated, the final reaction mixture corresponds to an equilibrium mixture of complexes when the acetato compounds are used as starting material, while only one species is detected in the case of the chloro derivatives. In all cases the NMR pattern of the aromatic region is indicative of the formation of a five-membered cyclometallated ring. The reactions are very clean under the conditions used in the study as can be seen in Fig. 3(a), where sharp isosbestic points are envisaged. Although the concentration of the palladium complexes had to be kept very low due to the low solubility of the complexes in neat acetic acid, no dependence of the value of the observed rate constant on the palladium complex concentration was observed. Interestingly, the reactions carried out with complexes *Z*-**1AcO** and *Z*-**1Cl** showed observed rate constants dramatically smaller than those found for their *E* counterparts (Chart 1). Furthermore, for *Z*-**1Cl**, decomposition competes with the C–H bond activation reaction; this fact prevented the determination of the activation volume for the process.

The cyclometallation reactions monitored from the crude mixtures of *E*-**2AcO** and *E*-**2Cl** (see Metallation section), indicated the existence of a fast process with very small spectral amplitude variations. These changes are the typical for a cyclometallation reaction, they occur at much shorter times, and that had to be measured independently. The low solubility of the complexes did not allow the evaluation of the observed rate constants under the same experimental conditions than those used for the main process; in these cases the methodology indicated in the Experimental section, referring to the use of concentrated stock solutions in CH_2Cl_2, had to be used. The procedure used, together with the high pressure range needed (producing the solidification of acetic acid at temperatures below 25 °C) did not allow the determination of the activation volume for the reaction. From the two consecutive processes observed, the second one produces the same values of k_{obs} determined before, and was associated the metallation of the major component, while the first one was associated with the metallation of the minor component of the mixture. The amplitude of the spectral changes agrees very well with the mixture (**M**/**m**) ratio determined by ^{1}H NMR spectrometry. The proton NMR spectra in deuterated (d_4) acetic acid effectively shows that *E*-**2AcO**(**M**)/*E*-**2AcO**(**m**) or *E*-**2Cl**(**M**)/*E*-**2Cl**(**m**) compound ratio increases with time, due to the faster cyclometallation reaction of the minor isomers, *E*-**2AcO**(**m**) and *E*-**2Cl**(**m**). Table S1, ESI† collects all the values of k_{obs} as a function of the cyclometallating complex, temperature and pressure. The concentration of acetic acid proved to be an important factor for the value of the observed rate constant as shown in Fig. S1, ESI†as already shown for similar palladium cyclometallating systems studied.[13,21,27]

In the same context, and given the fact that the presence of triflic acid produced an important acceleration in cyclometallation reactions on $\{Rh^{II}\}_2$ carboxylato complexes,[5,28] the C–H bond activation reactions of some of the complexes have also been monitored in the presence of varying concentrations of triflic acid in acetic acid solutions. For complexes *E*-**1AcO**, *E*-**1Cl** and *E*-**2AcO**(**M**) the spectral changes correspond to those expected for cyclometallation reactions, although the starting spectrum does not correspond to the original palladium complex. This is expected, taking into account that protonation must occur (Fig. 3(b)). In these cases a dramatic acceleration of

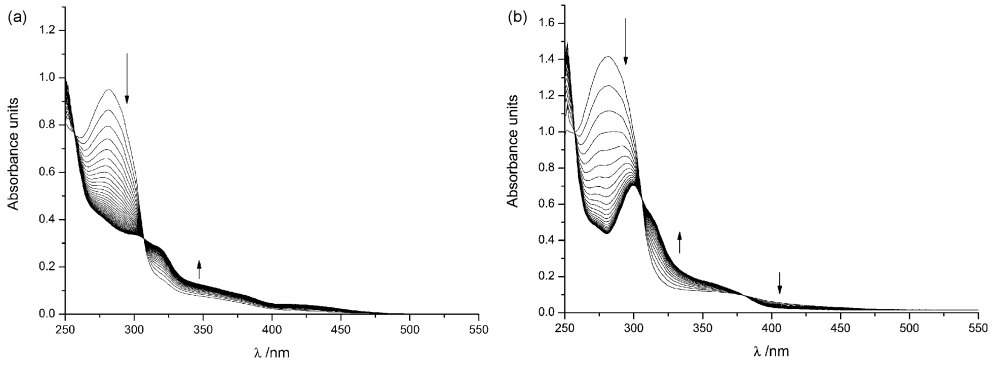


Fig. 3 (a) UV-Vis spectral changes of the cyclometallation reaction of complex *E*-**2AcO**(**M**) in neat acetic acid solution at 40 °C and [Pd] = 1 × 10^{-4} M. (b) UV-Vis spectral changes of the cyclometallation reaction of complex *E*-**2AcO**(**M**) in triflic acid solutions in acetic acid at 40 °C [HTrifl] = 0.012 M and [Pd] = 1 × 10^{-4} M.

Table 2 Values of kinetic (calculated at 25 °C from Eyring plots) and activation parameters for the systems studied, as a function of the starting coordination compound, in neat acetic acid

Complex	$10^4 k_{obs}/s^{-1}$	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}	$\Delta V^{\neq}$/cm^3 mol^{-1}
***E*-1AcO**	0.30	94 ± 5	−16 ± 15	−12 ± 2 (324 K)
***E*-1Cl**	0.18	84 ± 4	−54 ± 13	−10 ± 1(327 K)
***Z*-1AcO**	0.0026	104 ± 3	−22 ± 9	−0 (348 K)
***Z*-1Cl**	0.0021	92 ± 5	−64 ± 14	Not measured[a]
***E*-2AcO(M)**	0.16	109 ± 4	29 ± 12	−21 ± 2 (323 K)
***E*-2Cl(M)**	0.10	91 ± 5	−35 ± 15	−15 ± 2 (329 K)
***E*-2AcO(m)**	9.0	40 ± 9	−169 ± 30	Not measured[b]
***E*-2Cl(m)**	2.7	40 ± 3	−179 ± 11	Not measured[b]

[a] Decomposition is too fast under cyclometallation conditions. [b] The procedure needed, indicated in the text, does not allow for its measurement.

the reaction rate is observed, although further increase of the acid concentration produces an asymptotic decrease (Fig S2, ESI†). The reactions under these conditions showed a final drift due to decomposition of the complexes under the high acidity conditions, as monitored by ^{1}H NMR. When this study is carried out on the chloro complex ***E*-2Cl**, the spectral changes observed are complex and no reliable rate constants could be determined; probably for these complexes a preliminary reaction takes place that enhances the decomposition of the complex. The same type of decomposition process was observed for type-*Z* complexes of ligand **1** (Chart 1) under these conditions. Table S2, ESI,†collects all the values of k_{obs} for the systems studied as a function of palladium complex, acetic and triflic acid concentrations and temperature.

The fitting of the variation of the values of the rate constants obtained at different temperatures and pressures to the standard Eyring and ln*k vs. P* equations, produced the values of the thermal and pressure activation parameters indicated in Table 2; the values of the kinetic parameters calculated at 60 °C are also collected for comparison. A representative sample of the fittings of the determined values of k_{obs} to the variations in temperature and pressure is shown in Fig. S3 (ESI†) and Fig. 4.

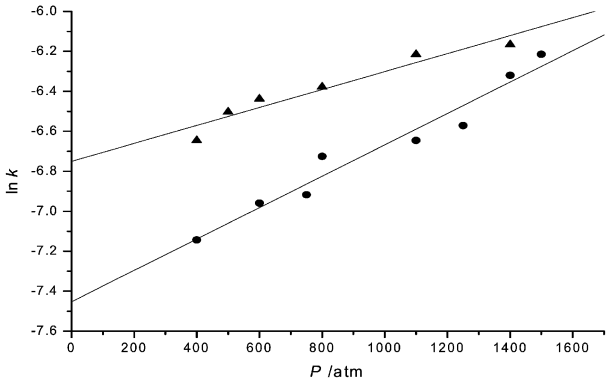


Fig. 4 Plot for the variation with pressure of the rate constants for the cyclometallation reaction of compounds ***E*-1AcO** (▲) and ***E*-2AcO(M)** (●) in acetic acid solution.

Discussion

For the simple cyclometallation process of complexes with the imine ligand in an *E* conformation, ***E*-1AcO**, ***E*-1Cl**, ***E*-2AcO(M)**, ***E*-2AcO(m)**, ***E*-2Cl(M)** and ***E*-2Cl(m)**, the values determined for the thermal and pressure activation parameters (Table 2) are within the margin expected, and similar to those obtained for the cyclometallation reaction of a series of *N*-monodentate imines in protic solvents.[13,27] Nevertheless, the processes are, except for the minor components of the crude ***E*-2AcO** and ***E*-2Cl** mixtures, much slower than for the previously published systems.[13] The isokinetic relationship existing between all the C–H activation reaction processes of the 4-ClC_6H_4CHNR groups (Fig. 5) indicates that the mechanism for the process is the same for all the complexes. The transition state proposed for such reactions is that indicated in Scheme 4, and it should applicable to all the systems studied.

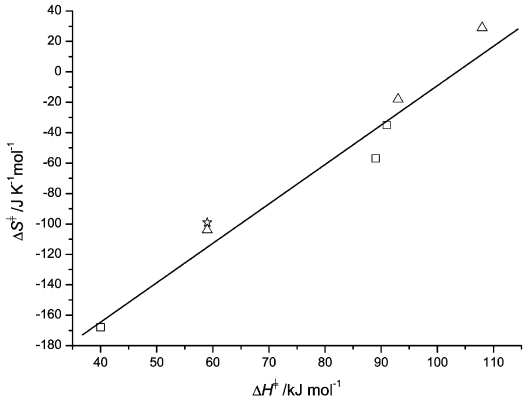
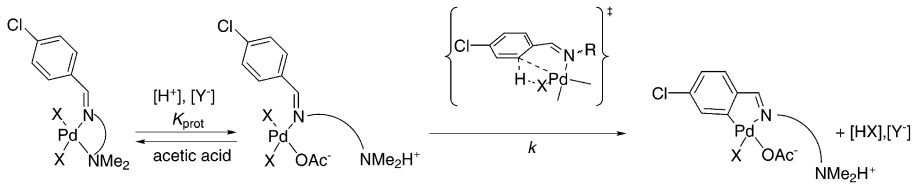


Fig. 5 Isokinetic relationship for the C–H bond activation on Pd^{II} of 4ClC_6H_4CHNR containing **1** and **2** ligands in neat acetic acid solvent: △ corresponds to the acetato derivatives ***E*-1AcO** and ***E*-2AcO**, □ to the chloro derivatives, ***E*-1Cl** and ***E*-2Cl**, and ⋆ to that of palladium acetate with the equivalent monodentate imine ligand, 4ClC_6H_4CHNCH_2Ph, of ref. 13.

The acid concentration dependence found for the systems studied and shown in Figs. S1 and S2 (ESI†) is revealing. A clear indication of the possibility of a proton assistance facilitating the exit of the fully protonated anionic (acetato or chloro) group from the transition state, as observed in many other Pd^{II} and Rh^{II} cyclometallating compounds, is envisaged.[5,13,28] The increase of the reaction rate constant in neat acetic acid is a scarce three-fold difference from the value in dilute solutions in toluene, the system being *de facto* buffered.[5] The dependence observed does not correspond with that observed in other systems (limiting kinetics behaviour) and expected from a neat pre-equilibrium protonation of the bound anionic X-ligand. When triflic acid is added to the reaction system the acceleration is enormous, and the initial UV-Vis spectrum for the C–H bond activation reaction does not coincide with the observed in neat acetic acid solution (Fig. 3). If we speculate that the addition of small concentrations of triflic acid provokes the opening of the chelate ring, *via* protonation of the N_{amino} donor, the metallation process should take place from the monodentate mode of the ligand indicated in Scheme 4.

The rate constants obtained for the reaction at low concentrations of triflic acid for ***E*-2AcO(M)** (Table S2, ESI†) are the same within experimental error than those observed for the ***E*-2AcO(m)** isomer. These observations agree with a very facile complete dechelation of the ligand with acid buffered solutions (neat acetic acid) for ***E*-2AcO(m)**, and a more difficult one for compound ***E*-2AcO(M)**, only taking place in strong



Scheme 4 Proposed general mechanism for the cyclometallation process studied.

acidic solutions (triflic acid solutions). ^{1}H NMR monitoring of the reaction of *E*-**2AcO(M)** effectively indicates that, although decomposition occurs, the initial complex undergoes a much faster cyclometallation reaction in the presence of very small quantities of triflic acid. The further decrease observed in the rate constant with acid concentration, shown in Fig. S2 (ESI†), is more difficult to explain, and probably relates with a decomposition process. In fact, as indicated in the Kinetics section the reactions of *E*-**2Cl(M)** in triflic acid solutions lead to decomposition. In this respect, the effect of added triflic acid on the known cyclometallation reactions of palladium acetate by the $C_6H_5CHNCH_2Ph$ imine was checked;[13] in all cases the spectral changes indicated decomposition of the ligand.

The ^{1}H NMR spectrum in deuterated (d_4) acetic acid of *E*-**2Cl** is even more revealing. Apart from the two inequivalent methyl signals of the palladium coordinated amino moiety, a singlet integrating *ca.* 5–7% of the total aminomethyl groups is observed. This signal is assigned to the methyl groups of protonated free amino group, by comparison of the proton NMR spectrum of the parent non-condensed amine, $H_2N(CH_2)_3N(CH_3)_2$, in the same medium. Being this so, the metallation process clearly must take place *via* the mechanism proposed in Scheme 4. The κ^2-N_{imino},N_{amino} complex is in a very little displaced pre-equilibrium with the N_{imino}-monodentate complex, that further undergoes the proper C–H activation reaction. This equilibrium is driven completely to the non-chelated situation by strong acids, as indicated above. As a result, the observed rate constants correspond *de facto* to a product of equilibrium and kinetic constants, $k_{obs} = K_{prot}k$. Thermal and pressure activation parameters correspond to this product, and include the values of ΔH°, ΔS° and ΔV° for the protonation/dechelation equilibrium constant.

The values of the activation entropy for the reaction of complexes *E*-**1AcO**, *E*-**1Cl**, *E*-**2AcO(M)** and *E*-**2Cl(M)** are less negative than that observed for the N_{imino}-monodentate 4-$ClC_6H_4CHNCH_2Ph$ imine system, indicating that the bidentate systems must undergo a lesser organization on going to the transition state. Taking into account the pre-equilibrium involved in the process the results agree with the operation of an ordered transition state (Scheme 4) with a positive ΔS° contribution from the dissociation of the amino group of the ligand. Despite the creation of charges, neither electrostriction, nor or solvent-assisted hydrogen bonding, seem to cancel the entropy increase due to dechelation. Possibly the interaction of the positive NMe_2H^+ with the negative Pd-bound acetato group avoids any one of these ordering. The effect should clearly involve a larger activation enthalpy, given the energetics involved on a chelate bond dissociation, ΔH°. Effectively, the values collected in Table 2 are 30–40 kJ mol^{-1} larger than the obtained for the N_{imino}-monodentate system.[13]

The differences between the values found for $\Delta S^{\neq}$ between the acetato and chloro complexes of the same imine ligand merit some attention, given the fact the ΔS° contributions should be equivalent for the two species. For complexes derived from both ligands *E*-**1** and *E*-**2**, the acetato compounds have more positive activation entropies. The different nature of the X aniono ligand in the transition state indicated in Scheme 4, easily explains this fact. The organizational increase on going to the transition state has to be larger for the chloro complexes, given the absence of possible charge delocalization in the ligand. This factor further agrees with the non-involvement in the full process of the acetato group occupying the dechelated position (Scheme 4) (see below).

Contrarily to the entropies, the volumes of activation for the systems studied do not show significant differences from the values for the N_{imino}-monodentate system. The most negative values are those for complexes with the less negative activation entropy, indicating that, as indicated above, changes in solvent-assisted hydrogen-bond interactions are not dominant in the system.[29–31] The charge separation produced in the intermediate dechelated species (Scheme 4) must directly electrostrict enough amounts of acetic acid molecules to compensate for the expected dechelating positive contribution that would produce less negative values of $\Delta V^{\neq}$. If these molecules were previously ordered by hydrogen bonding, the electrostrictive contraction would not imply a negative entropic contribution, as indicated above. The effect should be larger for the acetato complex, *E*-**2AcO**, more prone to hydrogen bonding interactions with the solvent, than for the equivalent chloro complex *E*-**2Cl**. Although this is the trend observed, further studies are needed for a more thorough explanation of the facts.

With respect to the cyclometallation reaction occurring on complexes *E*-**2AcO(m)** and *E*-**2Cl(m)**, the values of the parameters indicated in Table 2 are extremely similar to those for the cyclometallation of the related 4-$ClC_6H_4CHNCH_2Ph$ monodentate imine. These values determined in neat acetic acid are: $\Delta H^{\neq} = 59$ kJ mol^{-1}, $\Delta S^{\neq} = -99$ J K^{-1}mol^{-1} and $\Delta V^{\neq} = -17$ cm^{3}mol^{-1},[13] practically the same than those for the cyclometallation reaction of compound *E*-**2AcO(m)** (Fig. 5). It is reasonable to conclude that the minor components of the crude *E*-**2AcO** and *E*-**2Cl** mixtures are completely converted, in acetic acid solution, to complexes with the hybrid ligand in a N_{imino}-monodentate mode. From there on, the cyclometallation process has to show very similar characteristics to those observed for the monodentate imine ligands mentioned; Scheme 4 shows this process. If this assumption is true, the ratio observed for the k_{obs}(**m**)/k_{obs}(**M**) ratio for both complexes is revealing. The value indicates that the rate of C–H bond activation of the complex having the ligand in the κ^2-N_{imino},N_{amino} form represents only a 5–8% of that observed for the monodentated form of the hybrid ligand. These values agree extremely well with the NMR-estimated κ^1-N_{imino}/κ^2-N_{imino},N_{amino} ratio for *E*-**2Cl**, which is a clear indicative of the different equilibrium composition of the complexes in acetic acid medium. The same conclusions could be drawn if the minor isomers of the *E*-**2AcO** and *E*-**2Cl** crude mixtures correspond directly to monodentate systems with a dangling N_{amino} group, or to dinuclear systems with the N_{imino},N_{amino} donor ligand acting as a bridge between two Pd centres. ^{1}H NMR spectrometry does not allow for any further distinction given the nature of the minor component and the rapid cyclometallation reaction observed.

For the complexes where ligand **1** is in a *Z* arrangement (Chart 1) within the non-metallated complex, an isomerization

process to the *E* conformation has to take place before the C–H bond activation occurs. Given the fact that the observed rate constants collected in Table 2 are much smaller than those obtained for the *E* counterparts, it is clear that the process measured *de facto* as cyclometallation, corresponds to the simple *Z* to *E* isomerization reaction, the C–H bond activation to produce the cyclometallated complex not being the rate limiting process. Although the differences in the thermal activation parameters indicated in Table 2 are not very important, they depend on the presence of acetato or chloro ligands in the coordination sphere of Pd^{II}. Furthermore, the value determined for $\Delta V^{\neq}$ definitively differs from the values expected for a cyclometallation reaction. These differences were not expected, but they have already been found for similar platinum cyclometallation processes, where the involvement of the acetato ligand favouring the rotation of the N=CH bond has been established.[22] For the rotation of C=N bond to take place, the loss of the double bond character for the $C^{(+)}$–$N^{(-)}$ tautomeric form has to be stabilized. The existence of a well oriented dangling acetato-oxygen in the transition state, capable of interaction with the positive charge situated on the iminic carbon, should facilitate better than a palladium-bonded chloro ligand the reorganization of the double bond. The mentioned pseudo-equatorial position of the iminic carbon, as determined in the solid state structure, agrees with this easy interaction. This trend is the one observed in Table 2, where the effect is seen to be mainly entropic, given the important difference from −24 to −63 J K^{-1} mol^{-1} on going from the acetato (*Z*-**1AcO**) to the chloro derivatives (*Z*-**1Cl**). Evidently if the above mentioned effect is true it would be more feasible in non-acidic media, and further studies in this field are being carried out.

Conclusions

The cyclometallation processes occurring on the series of compounds having chelate κ^2-N_{imino},N_{amino} ligands, depicted in Chart 1, have been studied from a kinetico–mechanistic perspective in neat acetic acid solutions. The processes are seen to take place with the intervention of a tetracentered transition state as that established in previous studies. Nevertheless, the reaction of this bidentate ligands is one order of magnitude slower than that for their N_{imino}-monodentate counterparts, and the differences are assigned to the chelate κ^2-N_{imino},N_{amino} nature of the ligand. A pre-equilibrium dechelation process has been established as needed for the C–H bond activation to occur. The dramatic acceleration observed when strong acid is present in the medium is related with the total opening of the κ^2-N_{imino},N_{amino} chelate. The resulting species undergoes the C–H bond activation at the same rate than that observed previously for monodentate systems; activation parameters corroborate this fact.

Isolation of the *Z* badly oriented analogues of some of the non-metallated compounds has also been achieved, and their cyclometallation mechanism studied. The reaction is found to be more than one order of magnitude slower, and it is associated with the *Z* to *E* isomerization of the ligand geometry previous to the C–H activation. Both the crystal structure determined and the thermal and baric activation parameters prove the previously suggested implication of the spectator ligand in the transition state for the C=N bond rotation.

Experimental

General

Alumina was purchased from Merck. $[PdCl_2(PhCN)_2]$ was prepared as previously described.[32] Ligands *E*-**1** and *E*-**2** were prepared by the methodology previously described.[14] The solvents were purified by standard procedures and distilled under nitrogen. NMR spectra were recorded on Varian XL-500 (^{1}H), Bruker DRX-500 (^{1}H), Bruker DRX-250 (^{1}H), Varian Mercury-400 (^{1}H, ^{13}C 100.6 MHz) and Varian Gemini (^{13}C, 50 MHz) spectrometers in $CDCl_3$ and with $SiMe_4$ standard, unless otherwise cited. IR spectra were recorded on a Nicolet 520 FT-IR, Nicolet 510 FT-IR and FT-IR Nicolet Impact 400 spectrometers. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. Elemental analyses were carried out by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili with a Carlo Erba EA1108-elemental analyzer.

Complexes

(*E*)-Bis(acetato){[*N*′-(4-chlorobenzylidene)-*N*,*N*′-dimethylethane-1,3-diamine]-*N*,*N*′}palladium(II), *E*-1AcO. 0.543 g (2.4 × 10^{-3} mol) of $Pd(AcO)_2$ were dissolved in 20 cm^3 of toluene, the mixture was stirred during 30 min at −10 °C, and then 0.509 g (2.4 × 10^{-3} mol) of *E*-**1** were added. A yellow precipitate is immediately formed, the mixture was stirred for a further 2 h and then filtered. The solid obtained was washed with diethyl ether and dried under reduced pressure. Purification was carried out by recrystallization in a mixture of CH_2Cl_2–Et_2O. Yield: 0.460 g (35%). Anal. Calc. for $C_{15}H_{21}ClO_4N_2Pd$ (435.2): C, 41.39; H, 4.86; N, 6.44%. Found: C, 41.05; H, 4.10; N, 6.25%. MS (FAB) *m*/*z* 376.9 ([M − AcO]$^+$). IR (KBr): 1630 (CH=N); 1567 and 1412 (AcO) cm^{-1}. ^{1}H NMR (500 MHz) δ 8.28 (d, 8.5 Hz, 2H), 8.03 (s, 1H), 7.47 (d, 8.5 Hz, 2H), 4.17 (m, 2H), 2.78 (2, 6H), 2.53 (m, 2H), 1.96 (s, 3H), 1.21 (s, 3H) ppm. ^{13}C NMR (100.6 MHz) δ 178.7 (C), 178.3 (C), 169.1 (CH), 139.9 (C), 132.5 (CH), 128.8 (CH), 128.0 (C), 65.4 (CH_2), 63.9 (CH_2), 51.3 (CH_3), 48.2 (CH_3), 23.6 (CH_3), 22.1 (CH_3) ppm.

(*E*)-Dichloro{[*N*′-(4-chlorobenzylidene)-*N*,*N*′-dimethylethane-1,3-diamine]-*N*,*N*′}palladium(II), *E*-1Cl. 0.078 g (2 × 10^{-4} mol) of $[PdCl_2(PhCN)_2]$ was dissolved in 5 cm^3 of toluene and 0.043 g (2 × 10^{-4} mol) of *E*-**1** was then added. A yellow precipitate was immediately observed from the brown solution. It was filtered, washed with toluene and dried under vacuum. The product was purified by dissolving it in dichloromethane, filtered over Celite and the solvent removed to dryness under vacuum. Yield 0.048 g (62%). Anal. Calc. for $C_{11}H_{15}Cl_3N_2Pd$ (388.0): C, 34.05; H, 3.90; N, 7.22%. Found: C, 35.51; H, 4.94; N, 7.02%. IR (KBr): 1643 (CH=N); 1098 and 1025 (amine) cm^{-1}. ^{1}H NMR (500 MHz) δ 9.13 (d, 8.5 Hz, 2H), 8.09 (s, 1H), 7.60 (d, 8.5 Hz, 2H), 4.85 (m, 1H), 3.74 (m, 1H), 2.77 (s, 3H), 2.56 (s, 3H), 2.40 (m, 1H), 1.95 (m, 1H) ppm. ^{13}C NMR (100.6 MHz) δ 170.0 (CH), 141.1 (C), 133.2 (CH), 129.8 (CH), 128.4 (C), 62.0 (CH_2), 61.0 (CH_2), 51.8 (CH_3) ppm.

(*Z*)-Bis(acetato){[*N*′-(4-chlorobenzylidene)-*N*,*N*′-dimethylethane-1,3-diamine]-*N*,*N*′}palladium(II), *Z*-1AcO. 0.530 g (2.4 × 10^{-3} mol) of $Pd(AcO)_2$ were dissolved in 20 cm^3 of toluene and 3 cm^3 of a 0.9 M solution of *E*-**1** in toluene (2.7 × 10^{-3} mol) were added at room temperature. The mixture was stirred overnight and then filtered. The pale yellow solid was washed with diethyl ether and dried under reduced pressure. Yield: 0.400 g (39%). Anal. Calc. for $C_{15}H_{21}ClO_4N_2Pd{\cdot}1.7H_2O$ (465.6): C, 38.66; H, 5.24; N, 6.01%. Found: C, 38.65; H, 5.72; N, 6.27%. IR (KBr): 1637 (CH=N); 1604, 1394 (AcO); 1104 and 1019 (amine) cm^{-1}. ^{1}H NMR (500 MHz) δ 8.09 (bs, 1H), 7.46 (d, 8.5 Hz, 2H), 7.37 (d, 8.5 Hz, 2H), 3.84 (dd, 6.0 Hz, 2.0 Hz, 2H), 2.75 (s, 6H), 2.61 (t, 6.0 Hz, 2H), 1.98 (s, 3H), 1.94 (s, 3H) ppm. ^{13}C NMR (100.6 MHz) δ 178.7 (C), 178.4 (C), 169.2 (CH), 139.2 (C), 130.9 (CH), 129.8 (CH), 128.6 (C), 64.7 (CH_2), 54.7 (CH_2), 50.7 (CH_3), 23.6 (CH_3), 23.5 (CH_3) ppm.

(*Z*)-Dichloro{[*N*′-(4-chlorobenzylidene)-*N*,*N*′-dimethylethane-1,3-diamine]-*N*,*N*′}palladium(II), *Z*-1Cl. Complex *Z*-**1Cl** was obtained by column chromatography of *Z*-**1AcO** (0.086 g) using acid alumina (% Cl^- < 0.2) and a mixture of AcOEt–MeOH = 4 : 1 as eluent. Yield: 0.071 g (92%). Anal. Calc. for $C_{11}H_{15}Cl_3N_2Pd$ (388.0): C, 34.05; H, 3.90; N, 7.22%. Found: C, 33.61; H, 4.61; N, 8.06%. IR (KBr): 1637 (CH=N); and 1104, 1019 (amine) cm^{-1}. ^{1}H NMR (500 MHz) δ 9.03 (bs,

1H), 7.40 (m, 4H), 3.97 (m, 2H), 2.96 (s, 6H), 2.63 (t, 6.0 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz) δ 170.5 (CH), 139.0 (C), 131.1 (CH), 129.7 (CH), 129.1 (C), 65.7 (CH_2), 55.5 (CH_2), 51.9 (CH_3) ppm.

(*E*)-Bis(acetato)-{[*N*′-(4-chlorobenzylidene)-*N*,*N*′-dimethylpropane-1,3-diamine]-*N*,*N*′}palladium(II), *E*-2AcO. 0.264 g (1.3×10^{-3} mol) of $Pd(AcO)_2$ were dissolved in 20 cm^3 of toluene and 0.264 g (1.3×10^{-3} mol) of *E*-**2** were then added at room temperature. The mixture was stirred for 3 h and then filtered. The pale yellow solid was washed with diethyl ether and dried under reduced pressure. Yield: 0.326 g (62%). Anal. Calc. for $C_{16}H_{23}ClO_4N_2Pd$ (449.2): C, 42.78; H, 5.16; N, 6.24%. Found: C, 42.13; H, 5.36; N, 6.92%. MS (FAB) *m*/*z* 391.0 ([M–AcO]$^+$). IR (KBr): 1620 (CH=N); 1560 and 1405 (AcO) cm^{-1}. ^{1}H NMR *Major isomer (80%)*: (500 MHz) δ 9.42 (d, 8.5 Hz, 2H), 7.88 (s, 1H), 7.65 (d, 8.5 Hz, 2H), 5.21 (m, 1H), 3.56 (m, 2H), 2.44 (s, 3H), 2.34 (s, 3H), 2.20 (m, 2H), 1.95 (s, 3H), 1.70 (m, 1H), 1.54 (s, 3H) ppm. ^{13}C NMR (100.6 MHz) δ 178.8 (C), 178.2 (C), 168.6 (CH), 140.5 (C), 132.6 (CH), 129.7 (CH), 129.1 (C), 62.9 (CH_2), 62.8 (CH_2), 52.7 (CH_3), 49.7 (CH_3), 27.2 (CH_2), 23.3 (CH_3), 22.5 (CH_3) ppm. *Minor isomer (20%)*: (500 MHz, selected signals) δ 9.32 (d, 8.5 Hz, 2H), 8.12 (s, 1H), 7.63 (d, 8.5 Hz, 2H), 4.85 (m, 1H), 3.76 (m, 1H), 3.56 (m), 2.52 (s, 3H), 2.35 (s, 3H), 1.98 (s, 3H) ppm.

(*E*)-Dichloro{[*N*′-(4-chlorobenzylidene)-*N*,*N*′-dimethylpropane-1,3-diamine]-*N*,*N*′}palladium(II), *E*-2Cl. 0.5 g (1.3×10^{-3} mol) of $[PdCl_2(PhCN)_2]$ was dissolved in 20 cm^3 of toluene and 0.250 g (1.1×10^{-3} mol) of *E*-**2** was added. A yellow precipitate was immediately formed from the brown solution. It was filtered, washed with toluene and the dried under vacuum. The product was purified by dissolving it in dichloromethane, filtering over Celite and drying under vacuum. Yield: 0.468 g (100%). The compound consists in an isomer mixture as that indicated above for *E*-**2AcO**. Selected ^{1}H NMR signals for the minor isomer, *E*-**2Cl(m)**, are: (500 MHz) δ 9.0 (d, 8.5 Hz, 2H), 8.22 (s, 1H), 7.65 (d, 8.5 Hz, 2H) ppm.

The major isomer component for the *E*-**2Cl** isomer mixture was obtained by column chromatography of *E*-**2AcO** (0.150 g) using acid alumina (%Cl^- < 0.2) and a mixture of AcOEt–MeOH = 4 : 1 as eluent. Yield: 0.113 g (93%). Anal. Calc. for $C_{12}H_{17}Cl_3N_2Pd$ (402.03): C, 35.85; H, 4.26; N, 6.97%. Found: C, 35.51; H, 4.66; N, 7.07%. IR (KBr): 1590 (CH=N); 1105, 1045 (amine) cm^{-1}. MS (FAB) *m*/*z* 331 ([M − 2Cl]$^+$). ^{1}H NMR (500 MHz) δ 9.14 (d, 8.5 Hz, 2H), 8.11 (s, 1H), 7.59 (d, 8.5 Hz, 1H), 4.90 (m, 1H), 3.77 (q, 5.8 Hz, 1H), 3.0 (m, 1H), 2.77 (s, 3H), 2.57 (s, 3H), 2.5 (m, 1H), 2.4 (ddd, 13 Hz, 7.5 Hz, 3 Hz, 1H), 1.96 (m, 1H). ^{13}C NMR (100.6 MHz) δ 169.9 (CH), 141.2 (C), 133.2 (CH), 129.8 (CH), 129.3 (C), 62.0 (CH_2), 61.1 (CH_2), 53.6 (CH_3), 51.7 (CH_3), 26.2 (CH_2) ppm.

Cyclometallated complexes, 1AcO-*CM*, 1Cl-*CM*, 2AcO-*CM* and 2Cl-*CM*

These were prepared from the corresponding coordination complexes by the same procedure further described. 5×10^{-5} mol of the appropriate coordination complex (*E*-**1AcO**, 21.5×10^{-3} g; *E*-**1Cl**, 19.4×10^{-3} g; *Z*-**1AcO**, 21.5×10^{-3} g; *Z*-**1Cl**, 19.4×10^{-3} g; *E*-**2AcO**, 22.0×10^{-3} g; *E*-**2Cl**, 20.0×10^{-3} g) were dissolved in 10 cm^3 of acetic acid and the solution heated at 60 °C for 5–6 h. The solvent was then reduced to *ca.* 1 cm^3 under vacuum. The corresponding cyclometallated compound was precipitated by addition of diethyl ether. The products were obtained in quantitative yields. Analytical data described in ref. 14.

Crystallography

Orange crystals of *E*-**1AcO**, *Z*-**1AcO**, *E*-**2AcO** and *E*-**2Cl** were grown by diffusing diethyl ether into a dichloromethane solution. They were mounted on a MAR345 with image plate detector (*E*-**1AcO**, *Z*-**1AcO**, *E*-**2AcO**) and on a Enraf-Nonius CAD4 four-circle (*E*-**2Cl**) diffractometers. Intensities were collected with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å), operating at room temperature. Lorentz-polarization but no absorption corrections were made. The structures were solved by direct methods using SHELXS computer program[33] and refined by full-matrix least-squares method on with SHELX97 computer program.[34] Crystal data are summarized in Table 3.

***E*-1AcO.** The structure was determined using 5901 reflections. The function minimized was $\Sigma w[(|F_o|^2 - |F_c|^2)^2]$ where $w = [\sigma^2(I) + (0.0514P)^2 + 1.7165P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f'' and f'' were taken from International Tables of X ray Crystallography.[35] Five hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. 21 hydrogen atoms were computed and refined using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked.

***Z*-1AcO.** The structure was determined using 6183 reflections. The function minimized was $\Sigma w[(|F_o|^2 - |F_c|^2)^2]$ where $w = [\sigma^2(I) + (0.0944P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f'' and f'' were taken from International Tables of X ray Crystallography.[35] Three hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. 20 hydrogen atoms were computed and refined using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked.

***E*-2AcO.** The structure was determined using 5288 reflections. The function minimized was $\Sigma w[(|F_o|^2 - |F_c|^2)^2]$ where $w = [\sigma^2(I) + (0.0574P)^2 + 0.289P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f'' and f'' were taken from International Tables of X ray Crystallography.[35] Seven hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. 17 hydrogen atoms were computed and refined using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked.

***E*-2Cl.** The structure was determined using 4478 reflections. The function minimized was $\Sigma w[(|F_o|^2 - |F_c|^2)^2]$ where $w = [\sigma^2(I) + (0.304P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f'' and f'' were taken from International Tables of X ray Crystallography.[35] Four hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. 13 hydrogen atoms were computed and refined using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked.

CCDC reference numbers 238987 (*E*-**1AcO**), 238988 (*E*-**2AcO**), 238989 (*E*-**2Cl**) and 238990 (*Z*-**1AcO**).

See http://www.rsc.org/suppdata/dt/b4/b415613g/ for crystallographic data in CIF or other electronic format.

Kinetics

The reactions at atmospheric pressure were followed by UV-Vis spectroscopy in the full 750–300 nm range on a HP8542A or Cary 50 instruments equipped with a multicell transport, thermostated (±0.1 EC) with a circulation bath. Observed rate constants were derived from the absorbance *vs*. time traces at the wavelengths where a maximum increase and/or decrease of absorbance was observed. No dependence of the values on the selected wavelengths was detected, as expected for reactions where a good retention of isosbestic points is observed (Fig. 3). For runs at elevated pressure, a previously described pressurizing system and high-pressure cell were used.[13,22] In these cases the absorbance *vs*. time traces were recorded on a Cary 50

Table 3 Crystal data for complexes ***E*-1AcO**, ***Z*-1AcO**, ***E*-2AcO** and ***E*-2Cl**

	***E*-1AcO**	***Z*-1AcO**	***E*-2AcO**	***E*-2Cl**
Empirical formula	$C_{13}H_{21}ClO_4N_2Pd{\cdot}CH_2Cl_2{\cdot}H_2O$	$C_{13}H_{21}ClO_4N_2Pd{\cdot}CH_2Cl_2$	$C_{16}H_{23}ClO_4N_2Pd{\cdot}H_2O$	$C_{12}H_{17}Cl_3N_2Pd$
M_r	538.13	520.11	467.23	402.02
Crystal size/mm	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.1 × 0.2 × 0.2
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	8.060(10)	27.802(3)	10.1620(10)	7.651(4)
b/Å	14.1970(10)	11.8510(10)	10.5199(17)	10.646(2)
c/Å	20.2390(10)	14.7720(10)	10.5800(10)	10.904(2)
α/°	90	90	93.169(14)	117.14(2)
β/°	104.190(3)	118.737(12)	99.090(10)	100.86(2)
γ/°	90	90	115.404(9)	91.26(3)
V/Å^3	2245.8(3)	4267.6(7)	999.2(2)	770.3(5)
Z, D_c/Mg m^{-3}	4, 1.592	8, 1.619	2, 1.553	2, 1.733
μ/mm^{-1}	1.210	1.267	1.089	1.709
θ Range for data collection/°	2.52–31.61	1.67–31.64	2.16–31.65	2.15–29.98
Reflections collected/unique (R_{int})	7674/5901 (0.0241)	14548/6183 (0.0312)	43084/5288 (0.0282)	4478/4478 (0.0000)
Data/restraints/parameters	5901/0/274	6183/0/248	5288/0/254	4478/0/179
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0360$, $wR2 = 0.0952$	$R1 = 0.0407$, $wR2 = 0.1206$	$R1 = 0.0300$, $wR2 = 0.0964$	$R1 = 0.0362$, $wR2 = 0.0805$
R indices (all data)	$R1 = 0.0531$, $wR2 = 0.1070$	$R1 = 0.0606$, $wR2 = 0.1385$	$R1 = 0.0308$, $wR2 = 0.0973$	$R1 = 0.1060$, $wR2 = 0.0919$
GOF on F^2	1.059	1.013	1.221	1.011
Largest diff. peak and hole/e Å^{-3}	0.817 and −0.557	0.825 and −0.736	0.971 and −0.896	0.597 and −0.782

instrument at a fixed wavelength chosen from the atmospheric pressure experiments; alternatively a J&M TIDAS instrument was also used in the full wavelength range.

The general kinetic technique is that previously described;[5,13,31] solutions for the kinetic runs were prepared by dissolving the calculated amounts of the palladium compounds in acetic acid. In all cases no dependence on the concentration of palladium was detected and it was kept in the (2–5) × 10^{-4} M margin, given the low solubility of the complexes in acetic acid. In some cases concentrated solutions of the palladium complexes in CH_2Cl_2 were prepared, and 1–2% was added to prethermostated acetic acid. Rate constants were derived from exponential least-square fitting by the standard routines. Tables S1 and S2 (ESI†) collect all the obtained k_{obs} values for all the complexes studied as a function of the metallating starting complex, added acid, temperature and pressure. Least-square errors for the rate constants were always in the range of 10–15% of the calculated value. All post-run fittings to rate laws were done by standard fitting programs commercially available.

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