Pyridine and quinoline-derived imines as *N,N*-bidentate directing groups in palladium *versus* platinum C–H bond activation reactions

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Supporting Information Placeholder

ABSTRACT: The C−H activation by Pd(II) and Pt(II) compounds of a wide range of imines related to 2-pyridinecarboxaldehyde, $ArCH{=}NCH_2(CH_2)_nPh$, Ar = 2-pyridinyl, 2-picolinyl or 2-quinolinyl, n = 0 or 1, that can be useful for bond functionalization assisted by bidentate directing groups, has been studied. Results indicate that the presence of two methyl groups at the α-carbon, relative to the imine nitrogen atom, facilitates the metalation. The heterocyclic fragment of the chelating ligand also shows a relevant influence in the full process, the cyclometalated compounds being more easily formed for the 2-picolinyl than for the 2-quinolinyl derivatives, while for the 2-pyridinyl derivatives the reaction is less favored. These effects have been found determinant for both palladium and platinum compounds. The preparative results can be explained by a steric enhancement of the metalation process: the reaction being strongly favored when bulky substituents are located in the proximity (α-carbon) of the coordinating nitrogen atoms (both with palladium and platinum). Furthermore, surprisingly the formation of six-membered platinacycles is especially favored. The kinetico-mechanistic study of the C−H activation reaction, on some equivalent Pd(II) and Pt(II) coordination complexes of the family, have shown that the nature of the d^8 metal center plays a determinant role in the reactivity observed. In this respect, the Pt(II) square planar center has been found much more involved in the energetics of the reaction than the Pd(II) equivalent. The full process can be seen as a mechanistic-continuum that goes from an electrophilic substitution (Pd(II) centers) to an oxidative addition/reductive elimination sequence (Pt(II) centers). The observation is directly associated to the fact that the Pt(II) center is prone to the existence of oxidatively-added Pt(IV) hydrido complexes.

INTRODUCTION

Cyclometalation processes have received considerable attention because they permit the regioselective activation of strong aromatic or even aliphatic carbon-hydrogen bonds.[1] Furthermore, the metallacycles obtained have potential applications in many areas, such as organic synthesis and homogeneous catalysis[2] or bioorganometallic chemistry. In the latter, the biological activity of these type of complexes has led to the discovery of an important number of cyclometalated compounds having a high potential as anticancer metallodrugs.[3]

In addition, these complexes have also been employed in materials science. Some remarkable examples are its use in photophysical devices,[4] for light harvesting and energy transfer in photovoltaic cells,[5] and as liquid crystals.[6] Moreover, the development of catalytic C−H functionalization processes by ligand-directed reactions has also led to a renewed interest in the study of the cyclometalation reactions and the reactivity of their derivatives.[3]

The direct conversion of carbon–hydrogen bonds into carbon–heteroatom and carbon–carbon bonds remains a critical challenge in organic chemistry. An interesting approach to address this issue involves the use of substrates that contain directing groups that bind to the metal center in a first step.[7] A further rearrangement of the molecules allows the C−H bond activation, being this latter process called cyclometalation. Although ligand-directed catalytic reactions have been historically focused mainly in monodentate directing groups, in the last decade an increasing number of reports on carbon–hydrogen bond functionalization assisted by bidentate directing groups have appeared.[8] The easy metal coordination and tunability of properties of a bidentate directing group, *versus* those of a monodentate ligand, have resulted in an increase in their use as directing groups in catalytic C−H functionalization processes. In addition, the use of bidentate directing groups can also have an important effect in the catalytic process by producing important changes in the reaction mechanism. Finally, when using monodentate directing groups, unexpected secondary reactions may occur due to the relatively weaker coordination capabilities of these functional groups to the metal center when compared with bidentate units.

We have already reported the synthesis of 2,2-disubstituted indolines via Pd-catalyzed C−H activation of imines derived from 2-pyridinecarboxaldehyde using $PhI(OAc)_2$ as an oxidant.[9] The ability of the pyridine moiety to coordinate to the Pd(II) center seems to be essential for this catalytic process involving a new bidentate N_{imine},$N_{pyridine}$ directing group. The absence of hydrogens in α-position of the amine fragment is also a requirement for the formation of indolines.

Here we report the study of a wide range of imines related to 2-pyridinecarboxaldehyde $ArCH{=}NCH_2(CH_2)_nPh$, Ar = 2-pyridinyl, 2-picolinyl or 2-quinolinyl, n = 0 or 1 in order to

evaluate the relative importance of different factors in the C−H activation by Pd(II) and Pt(II) compounds in these imine systems. The group of imines selected presents the additional advantage that it is possible to obtain a great number of ligands with different features by means of standard organic synthesis. A set of kinetico-mechanistic studies on selected representative Pd(II) and Pt(II) complexes of the new bidentate ligands has also been carried out in order to establish possible effects of the metal center, the nature of the substituents on the [N,N'] and organometallic [C−N] fused final [C,N,N'] cycles, and final metalated ring size.

RESULTS AND DISCUSSION

As part of an ongoing research project on the study of stoichiometric[10] and catalytic[9,11] C−H bond activation processes, we have conducted the study of the reaction between palladium(II) acetate or *cis*-bis(dimethylsulfoxide)dichloridoplatinum(II) with imines $ArCH{=}NCH_2(CH_2)_nPh$, Ar = 2-pyridinyl, 2-picolinyl or 2-quinolinyl, n = 0 or 1, in which the $CH_2(CH_2)_n$ fragment presents methyl groups in different positions, see Figure 1. The synthesis of all these imines is straightforward and is easily accomplished by condensation of the corresponding primary amines and the suitable aldehydes under dehydrating conditions.

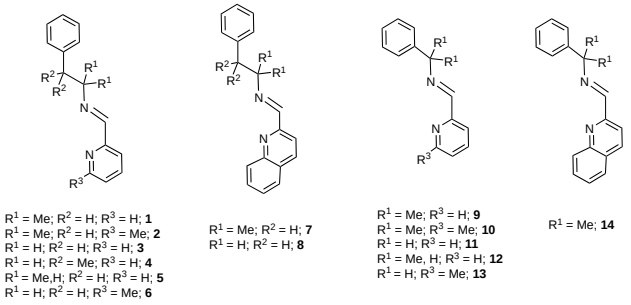


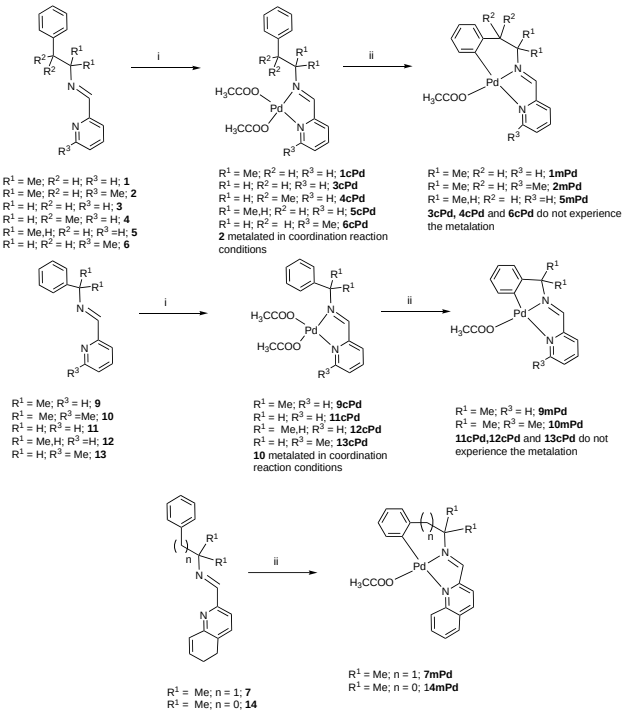
Figure 1. Imines studied.

These imines show the presence of two nitrogen atoms that would facilitate the isolation of the corresponding bidentate coordination compounds. These complexes have been proposed as intermediates for the cyclometalation reaction leading to a [C,N,N'] terdentate final structure. This fact allows the study of the cyclometalation process separately, that is, without being affected by the previous coordination reaction of the directing groups of the ligand. In this respect, it should be noted that palladium acetate, the most useful reagent for catalytic or stoichiometric C−H bond activation reactions, presents a huge variety of structures in solution, depending on the solvent used and the presence of moisture, making very difficult the study of the metalation process.[12] In addition, these imines can be useful systems in the field of C−H bond functionalization assisted by bidentate ligands, a new and attractive area of research.[8] In fact, we have previously shown that this system is useful in the synthesis of 2,2-disubstituted indolines via Pd-catalyzed C−H activation.[9]

Synthesis of palladium compounds

Imines described in Figure 1 were reacted with palladium(II) acetate under mild conditions (toluene, room temperature, 1 hour of reaction) in order to obtain the corresponding coordination derivatives. Imines **1**, **3**, **4**, **5**, **9**, **11** and **12** afforded the expected coordination complexes containing the imines in a chelate *N,N'*-bidentate coordination mode in good yields and the compounds were characterized by elemental analysis, NMR and mass spectrometry (Scheme 1).

Scheme 1. Synthesis of palladium compounds[a]



[a]Reagents and conditions: i) $Pd(AcO)_2$, toluene, room temperature, 1 h; ii) $Pd(AcO)_2$, toluene, 90 °C 1 h.

While the coordination compounds were obtained from all the [N,N'] bidentate imines containing the pyridinyl fragment, imines **2** and **10**, which have a picolinyl fragment and methyl substituents at the α-carbon (relative to the imine nitrogen) behave in a rather distinct manner. In these latter cases, the palladacycles with the imines coordinated in a [C,N,N'] terdentate coordination mode were obtained in good yields. Even the use of the mild conditions indicated in Scheme 1 do not allow the detection of the corresponding [N,N'] coordination compounds. Interestingly, imines **6** and **13**, also containing the picolinyl moiety, but without any methyl substituents at the α-carbon (relative to the imine nitrogen), do allow the synthesis of the corresponding [N,N'] coordination compounds. Finally, when the reaction was performed in mild conditions with imines containing the quinolinyl fragment (**7** and **14**), mixtures of [N,N'] coordination and [C,N,N'] cyclometalated compounds were obtained. All these results suggest that the presence of two methyl groups at the α position relative to the imine nitrogen donor facilitates metalation, and that the heterocyclic fragment also shows an important effect on the outcome of the process. That is, the trend of these imines to experience the cyclometalation follows the sequence picolinyl > quinolinyl > pyridinyl for the same imine metalating moiety.

Cyclopalladated 2-pyridinyl derivatives **1mPd** and **9mPd** were obtained in good yields when their corresponding coor-

dination compounds **1cPd** and **9cPd**, which present two methyl groups at the carbon at the α position relative to the imine nitrogen atom, were treated in toluene at 90 ºC. When the same reaction was performed with 2-pyridinyl coordination compound **5cPd**, which presents only one methyl group at the carbon at the α position relative to the imine nitrogen atom, the cyclometalated derivative **5mPd** was detected but in very low yield (5%). No metalated compounds were obtained from coordination compounds **3cPd**, **6cPd**, **11cPd** and **13cPd**, which do not present any methyl substituent in the $(CH_2)_nCH_2$, fragment. Finally, the 2-pyridyl complex **4cPd**, which presents two methyl groups at the β-position in the CH_2-CH_2 chain, and 2-pycolyl complex **12cPd**, which presents only one methyl at the α position relative to the nitrogen atom in the CH_2-CH_2 fragment do not experience cyclopalladation either.

It seems that the metalation reaction is strongly favored when bulky substituents are in the proximity of coordinating nitrogen atoms, so imines with picolinyl and quinolinyl fragments can easily be metalated. In the same sense, the cyclopalladated derivative of imine **1** is easy to obtain (which presents two methyl groups in α position relative to imine nitrogen), but imine **4** (which presents two methyl groups in β position) does not experience the metalation.

All these results suggest that the bulkiness of the imine plays an important role in the cyclopalladation reaction. The steric promotion in the cyclometalation reactions of some N-donor ligands have been reported,[1] and also the beneficial effect of the bulkiness of the phosphines in their cyclometalation processes due to entropic factors has also been known for quite a long time.[13] Although the use of geminal substitution is an important tool for synthetic chemists to increase the rate of formation and yield of cyclization processes,[14] it does not seem to be the main factor in our case. When cyclometalation of imine **1** and imine **4** are compared, the steric promotion at the nearby of the coordinating nitrogen atoms in the cyclometalation reactions seems to be a more important factor than the *gem*-disubstituent effect.

The new compounds have been characterized by elemental analyses, ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy and Electrospray Mass Spectrometry. The high resolution electrospray mass spectra of all metalated derivatives show the signal corresponding to $[M - AcO]^+$ fragment (being M the molecular mass of the corresponding metalated derivative), in agreement with the results described for related cyclopalladated compounds.[15] It is remarkable that palladium acetato coordination complexes with undergo metalation inside the ionization chamber, with the signal corresponding to the above mentioned $[M - AcO]^+$ fragment being observed. It should be noted that room temperature ^{1}H NMR spectra of all the six-membered cyclopalladated derivatives present the expected signals in the aromatic region, but for the aliphatic chain protons only broad signals are observed. The existence of a fluxional process concerning the six-membered metallacycle has been confirmed by the measure of the same spectra at 240 K, where the signals corresponding to the non-equivalent CH_2 protons and methyl groups are observed (Figure 2). The XRD of the related platinum complex **7mPt** (see below), confirms the lack of planarity of the six-membered metallacycle, which adopts a half-skew-chair conformation, agreeing with the spectrum in Figure 2.

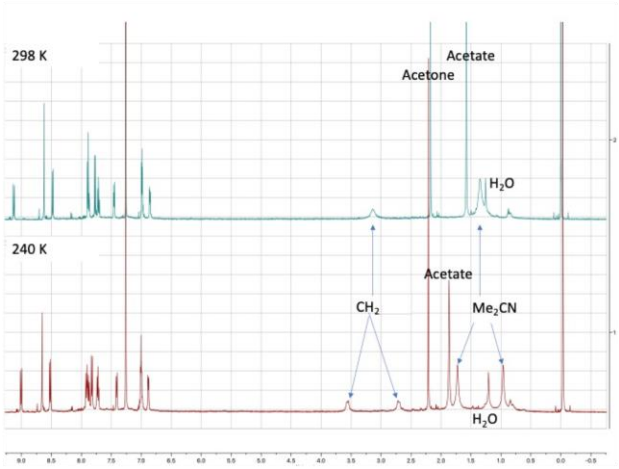


Figure 2. ^{1}H NMR of **7mPd** at 298 and 240 K.

Synthesis of platinum compounds

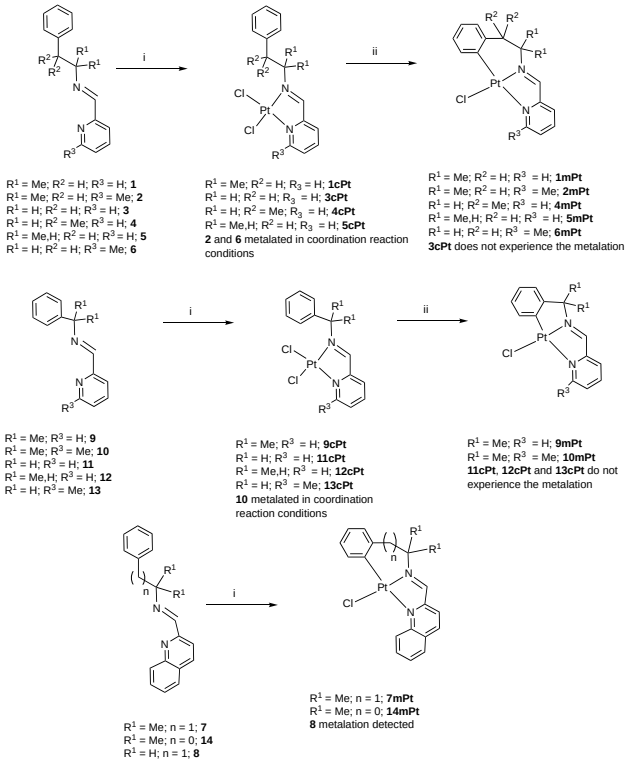
Contrarily to cyclopalladated complexes, one of the best synthetic strategies to obtain cycloplatinated compounds is the use of *cis*-[$PtCl_2(DMSO)_2$] as a starting platinum material. The best reaction conditions involve the use of methanol as solvent and long reaction times, in agreement with the fact that platinum compounds are much more inert than the equivalent palladium derivatives. Furthermore, in these processes sodium acetate was generally added as an external base to promote C−H bond activation by base-assisted deprotonations, and avoid acidolysis decomposition equilibria.[16] Scheme 2 collects a summary of the conditions used for the reaction of the imines indicated in Figure 1 with *cis*-bis(dimethylsulfoxide)dichloridoplatinum(II). Reactions without an external base were conducted in order to favor the obtention of the corresponding coordination compounds intermediates.

Imines **1**, **3**, **5**, **9**, **11**, **12**, and **13** afforded the expected non-metalated coordination complexes in good yields in the absence of sodium acetate. It is noticeable that all these imines contain an unsubstituted pyridine moiety with the exception of **13**, which is a picolinyl derivative with a non-substituted imine nitrogen α-carbon. When the same reaction was carried out with α-substituted imines but with substituted pyridine fragments (picolinyl or quinolinyl fragments **2**, **7**, **10**, and **14**), the cycloplatinated derivatives were obtained with good yield and the corresponding coordination compounds were not detected. All these results are in good agreement with the described above for cyclopalladation of the same imines, indicating that both the presence of two methyl groups on the imine nitrogen α-carbon and that the pyridine moiety bulkiness have considerable beneficial influences on the process.

Interestingly, the ring size of the resulting cyclometalated compound is also a variable that has a dramatic influence on the cycloplatination reaction. While imine **1** affords the corresponding six-membered platinacycle by refluxing in methanol for 4 h, even in absence of an external base, the reaction of the closely related imine **9** requires the presence of sodium acetate to achieve the formation of the corresponding five-membered platinacycle. It is even possible to cycloplatinate imines **5** and **6** (having a single or no methyl groups on the aliphatic chain, respectively), in the presence of sodium acetate with the formation of the six-membered platinacycles. Contrarily, when

the same reaction was performed with the analogous imines **12** and **13** the formation of the corresponding five-membered platinacycles was not observed and only coordination compounds were obtained. In conclusion, results indicate that, surprisingly, the formation of six-membered platinacycles is especially favored.

Scheme 2. Synthesis of platinum compounds[a]



[a]Reagents and conditions: i) *cis*-[$PtCl_2(DMSO)_2$], MeOH; ii) *cis*-[$PtCl_2(DMSO)_2$], MeOH, NaAcO (temperature and reaction time depend on the imine).

All the new [N,N] and [C,N,N'] platinum compounds were characterized by elemental analyses, ^1H and ^{13}C-{^1H} NMR spectroscopy, and Electrospray Mass Spectrometry. The coupling of the imine proton to platinum is in the 88-95 Hz range for [N,N'] coordination compounds and in the 100-110 Hz range for cycloplatinated [C,N,N'] derivatives, as for other cycloplatinated imines. An effect that has been associated with the higher electron density at the metal center in the cyclometalated complex.[17]

As indicated above for the cyclopalladated compounds, the ^1H NMR spectra of all six-membered derivatives present broad signals in the CH_2N and methyl proton regions, suggesting the existence of a fluxional process for the six-membered cycle; again the ^1H spectra at 240 K confirms this fact.

Suitable crystals for X-ray diffraction of complexes **7mPt** and **10mPt** were obtained from solutions in mixtures of dichloromethane-diethyl ether. The crystal structures correspond to discrete molecules separated by Van der Waals distances. Structures and selected bond lengths and angles are collected in Figures 3 and 4 for **7mPt** and **10mPt**, respectively. Although four different molecules (A, B, C and D) were found per unit cell for compound **10mPt**, only slight differences in bond lengths and angles are found between them and the average values are reported in Figure 4. Crystal and structure refinement data are collected in Tables S1 and S2.

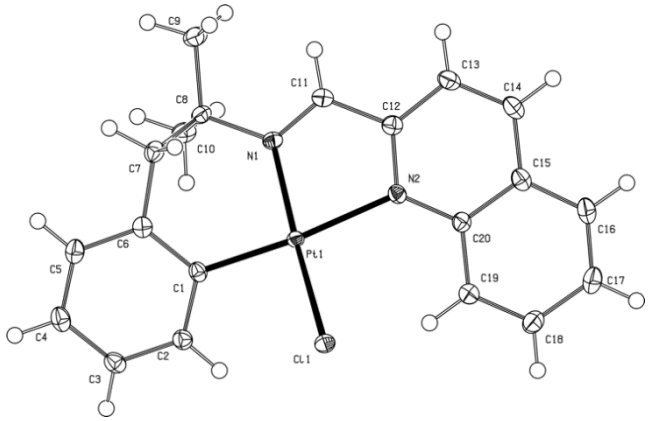


Figure 3. Molecular crystal structure of **7mPt**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pt(1)-N(1) = 2.0022(18), Pt(1)-C(1) = 2.0047(19), Pt(1)-N(2) = 2.1688(17), Pt(1)-Cl(1) = 2.3124(5), N(1)-C(11) = 1.289(3), N(1)-C(8) = 1.494(3), N(2)-C(12) = 1.340(3), N(2)-C(20) = 1.375(3), N(1)-Pt(1)-C(1) = 94.62(8), N(1)-Pt(1)-N(2) = 78.69(7), C(1)-Pt(1)-Cl(1) = 88.86(6), N(2)-Pt(1)-Cl(1) = 99.11(5).

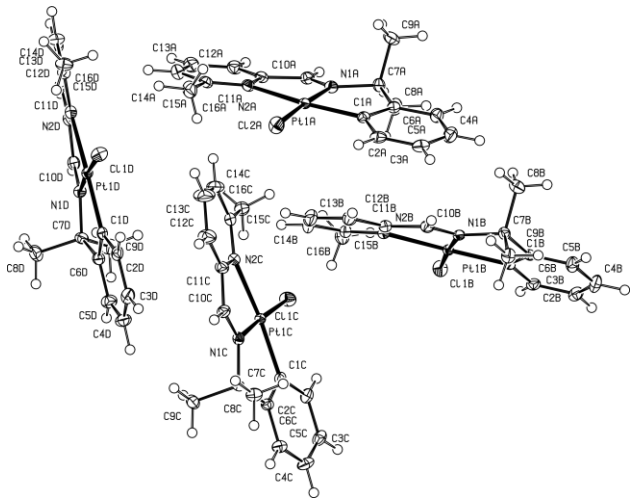


Figure 4. Molecular crystal structure of **10mPt**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pt(1)-N(1) = 1.948 (3), Pt(1)-C(1) = 1.975(3), Pt(1)-N(2) = 2.209 (3), Pt(1)-Cl(1) = 2.3115(11); N(1)-C(10) = 1.285 (5), N(1)-C(7) = 1.506 (4), N(3)-C(15) = 1.348 (4), N(3)-C(11) = 1.373(5), N(1)-Pt(1)-C(1) = 82.92 (15), N(1)-Pt(1)-N(3) = 79.11(13), C(1)-Pt(1)-Cl(1) = 93.78(11), N(3)-Pt(1)-Cl(1) = 104.14(8).

In the two structures, the platinum atoms have the expected square planar coordination with the tridentate [C,N,N'] ligand. All bond distances are in the expected range for both complexes.[18] The 2.1688(17) Å distance for Pt-N(2) is significantly longer than that for Pt-N(1) (2.0022(18) Å) for **7mPt**, while for **10mPt** the same trend is true (2.209(3) *versus*

1.948(3)Å), consistent with the strong *trans* influence of the carbon donor ligands.

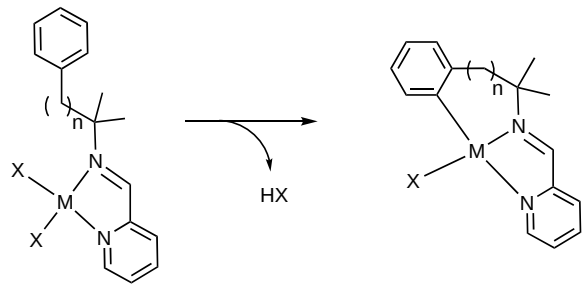
The structure of **7mPt** confirms the lack of planarity of the six-membered metallacycle, which adopts a screw-boat conformation with a deviation from the mean plane of -0.199(1), 0.240(2), 0.054(2), -0.436(2), 0.348(2 and -0.007(2) Å for Pt(1), C(1), C(6), C(7), C(8), and N(1), respectively. Contrarily, the structure of **10mPt** shows a planar five-membered platinacycle, the deviation from the mean plane being -0,0005(1), 0,0298(4), 0,0143(4), 0,0183(4) and -0,0078(3) Å for Pt(1), C(1), C(6), C(7), and N(1), respectively. These facts explain the observed fluxionality for all the six-membered metallacycles of palladium, while the corresponding five-membered metallacycles show non-dynamic NMR spectra.

Kinetico-mechanistic studies on the C-H activation processes

In view of the very interesting results on the preparation of the cyclometalated compounds of Pd(II) and Pt(II) and their relevance in some catalytic processes,[1,2] we decided to take advantage of the above mentioned uncommon preparative isolation of the complexes with the directing groups already coordinated.[19]

Given our previous knowledge of the mechanisms participating in these C−H and other C−X bond activation reactions,[19a,f,20] we have carried out an study from a kinetico-mechanistic perspective of the proper C−H activation reaction on these d^8 metal-center complexes. For this purpose, we have selected equivalent Pd(II) and Pt(II) complexes, for which the coordination compounds have been isolated in good yield. Furthermore, those having two methyl groups at the imine nitrogen α-carbon and none at the β-position, and an aliphatic chain length that allowed the formation of 5- and 6-membered metalated species represent the best choice (Scheme 3). All the processes have been monitored at variable temperature and pressure in order to obtain the relevant thermal and pressure activation parameters, which have to be indicative on the mechanism actuating in the reaction.

Scheme 3. Metalation process studied



X = AcO, M = Pd, n = 0, **9cPd**
X = AcO, M = Pd, n = 1, **1cPd**
X = Cl, M = Pt, n = 0, **9cPt**
X = Cl, M = Pt, n = 1, **1cPt**

For M = Pd(II) the C–H bond activation process of the acetate derivatives (**1cPd** and **9cPd**) was conducted in toluene solution, as for the preparative procedures. Given the fact that these complexes have a very low solubility at room temperature in this solvent, some experiments were also carried out in acetone or chloroform solution. The results obtained indicated that no significant differences could be associated with the solvent used, and thus the addition of a 5 % chloroform concentrated solution of the complexes to pre-heated toluene has been used as the standard technique for the monitoring of the reactions. The data collected for these reactions occurring on the Pd(II) complexes indicated in Scheme 3 produced the set of Eyring and lnk *versus* P plots shown in Figure 5. In this Figure it is clear that the above-mentioned solvent independence of the process applies. The Figure also indicates the different activation parameter features of the reactions occurring for the n=0 and n=1 coordination compounds, producing the 5- and 6-membered (**1mPd** and **9mPd**) final metallacycles (first two entries of Table 1).

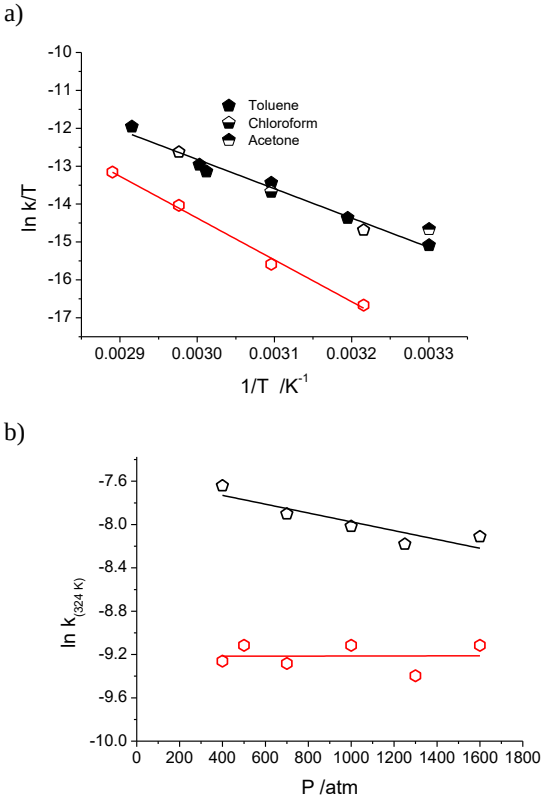


Figure 5. Eyring, a), and lnk *versus* P, b), plots for the C−H bond activation reaction on Pd(II) compounds **9cPd** (leading to a 5-membered ring) and **1cPd** (leading to a 6-membered ring). Toluene solution unless specified, empty points indicate solution made by the addition of a concentrated solution in chloroform to preheated toluene.

Table 1. Thermal and pressure activation parameters for the C−H bond activation reactions indicated in Scheme 3.

Metal X	Metalated ring (n) cyclometalated compound	Ligand	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1}mol^{-1}	$\Delta V^{\ddagger}$ /cm^{3}mol^{-1}
Pd AcO	5-membered (n=0) **9mPd**	**9**	65±5	-112±15	11±3
Pd AcO	6-membered (n=1) **1mPd**	**1**	92±5	-43±14	≈ 0
Pt Cl	5-membered (n=0) **9mPt**	**9**	102±9	-12±30	-3.7±0.2
Pt Cl	6-membered (n=1 **1mPt**	**1**	92±6	-42±20	-7.0±0.4

Clearly, from the data collected in the first two entries of Table 1, the electrophilic substitution reaction occurring on the metalating phenyl ring[19f,21] needs a large degree of ordering and expansion for the formation of the 5-membered **9mPd** cyclopalladated compound. For the formation of the equivalent **1mPd** (six-membered metallacycle) the values of entropy are less negative, and the activation volume falls to zero within error. As described in similar systems,[19d,22] the transition state for electrophilic C−H bond activations on Pd(II) is rather advanced in the reaction coordinate. This is, the reactions are occurring with a fairly dissociated acetate ligand on acceptance of the proton from the C−H bond; thus an ordered but otherwise expanded transition state situation is expected.[19b,23] This effect is much more pronounced on the more rigid and sterically demanding n=1 system, as effectively observed. The recently appeared eCMD mechanistic classification can also be applied for the processes monitored,[24] as it also applies to our previously studied systems.

The same kinetico/mechanistic study on the C–H bond activation was conducted with the equivalent **1cPt** and **9cPt** Pt(II) chloride complexes in methanol solution (again the solvent used in the preparative procedures). In this case the intimate mechanism of the reaction can be viewed as an electrophilic substitution (or electrophilic concerted metalation–deprotonation mechanism) liberating protons or an alternative oxidative addition to produce a Pt(IV) hydrido complex, followed by a reductive elimination of HCl.[19f,25] In this respect, we have been involved for some time in the study of such processes and the results indicated that, for non-organometallic starting materials, the process can be more adequately viewed as an electrophilic substitution with liberation of H^+. Nevertheless, the intimate mechanics of the reaction is far from unambiguous, and some important literature exists on the matter.[24,26]

In view of these premises, and from our previous studies on similar {Pt^{II}[N,N']Cl} cyclometalating units, stoichiometric sodium acetate, as an external base, was also added to the methanol solution (as done in the preparative procedures indicated above) in some experiments. UV-Vis time-resolved monitoring indicated that a neat reaction occurs even in the absence of added sodium acetate; furthermore, the process monitored is equivalent to that observed when 10-60 fold excesses of acetate has been added to the reaction medium (Table S3). It is important to note that, at the 10^{-4} M concentration level used in the kinetic studies even in the absence of sodium acetate, the NMR characterization of the final product of the reaction shows that the C−H bond activation has effectively taken place. Furthermore, the compound isolated under the same conditions but in the presence of sodium acetate has undergone the chloride by acetate exchange, as for other {Pt^{II}[N,N']Cl} units.[25] It is thus clear that concentration factors are extremely relevant in the processes studied; probably the formation of a high concentration of acid under the standard preparative conditions has to be prevented to avoid Pt(II)-C bond acidolysis,[21,27] while at the concentration level used for kinetic runs this is not necessary.

Once these preliminary features were clarified, we have carried out the kinetico-mechanistic study of the cycloplatination reaction of compounds **1cPt** and **9cPt** in methanol solution at variable temperatures and pressures. The data collected for these reactions occurring on the Pt(II) complexes (indicated in Scheme 3) produced the set of Eyring and lnk *versus* P plots shown in Figure 6. In the Figure the aforementioned acetate concentration independence of the process is indicated. Furthermore, although the activation volumes are diverse, extremely similar thermal activation parameters are obtained for the two reactions producing the 5- and 6-membered (**1mPt** and **9mPt**) final metallacycles. These data are collected in the last two entries of Table 1.

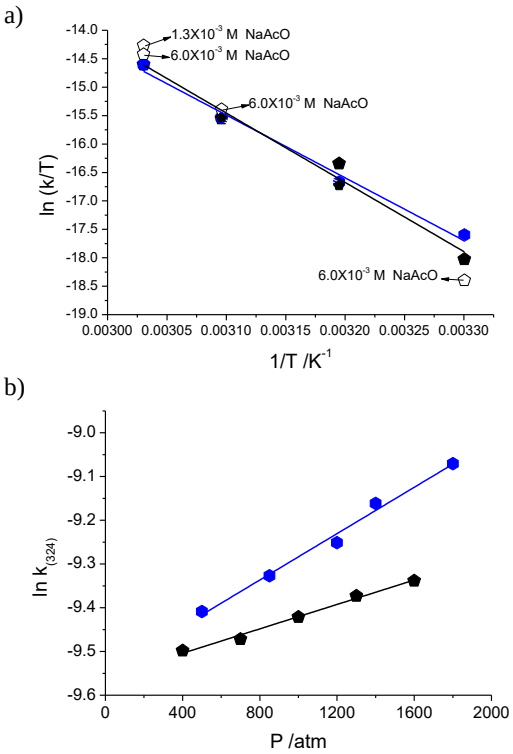


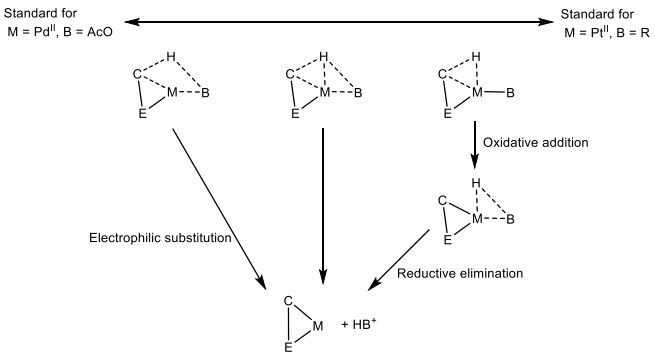
Figure 6. Eyring (a), and lnk *versus* P (b) plots for the C−H bond activation reaction on Pt(II) compounds **9cPt** (leading to a 5-membered ring) and **1cPt** (leading to a 6-membered ring). Methanol solution, empty points indicate values for solutions containing excess of sodium acetate at the concentrations indicated.

From the data shown in Table 1 we can state that the reaction of C−H bond activation on complexes **9cPt** and **1cPt** takes place with extremely similar thermal activation parameters (see Figure 6), a rather high enthalpy of activation and close to zero activation entropies, especially for the formation of the 5-membered compound. In contrast, the values of the activation volumes indicate that the contraction observed for the transition state in both systems doubles on going from the 5-membered to the 6-membered metallacycles (-3.7 *versus* -7.0 cm^3/mol). As expected, the size of the ring formed produces a larger compression for compound **1cPt** due to the flexibility of the longer metalating chain of the **1** ligand. Furthermore, this higher compression (or lower expansion) has been also observed for the Pd(II) systems studied in this work. Clearly, if the process relates to an electrophilic substitution mechanism, the systems show a much earlier transition state with respect to the Pd(II) counterparts in the reaction coordinate. The chloride anion seems to be still rather close to the

metal center on accepting the proton from the cyclometalating ligand, thus being contracted by the approaching C–H bond to be activated.

Surprisingly, the noticeable differences observed in the thermal activation parameters for the formation of the 5- and 6-membered acetato palladacycles, do not transfer to the equivalent Pt(II) systems. Clearly, the nature of the d^8 metal centers is playing a determinant role in the reactivity observed, with the Pt(II) square planar center much more involved in the energetics of the reaction. That is, the length of the metalating arm on the **1** and **9** ligand does not seem to be too important for the values of the enthalpies of activation, only the value of $\Delta S^{\ddagger}$ is slightly more negative for the formation of the 6-membered ring, in line with the higher flexibility and contraction of the system. As a whole, this effect can be related to the continuum mechanism tuning of this type of reactions that go from an electrophilic substitution (Scheme 4, left) to an oxidative addition/reductive elimination sequence (Scheme 4, right).[26] The Pt(II) center is known to be more prone to the existence of oxidatively-added Pt(IV) hydrido complexes, which should play its role in the abstraction by chloride of the proton from the C–H bonds, with low discrimination in the thermal activation parameters for the **1** and **9** ligands (Scheme 4, middle).[26b]

Scheme 4. Mechanisms proposed for C-H activation.



CONCLUSIONS

It has been shown that for the cyclometalation of α- and β-substituted imines of the $ArCH{=}NCH_2(CH_2)_nPh$ (Ar = 2-pyridinyl, 2-picolinyl or 2-quinolinyl, n = 0, 1) family, the presence of two methyl groups in the imine nitrogen α-carbon facilities the process. The heterocyclic Ar fragment also has been found to have a relevant influence in the process, the trend following the picolinyl > quinolinyl > pyridinyl sequence. The combination of these two effects have been found determinant for both palladium and platinum chemistry. All these results can be explained by the steric promotion of the metalation process: the reaction is strongly favored when bulky substituents are located in the proximity of coordinating nitrogen atoms (both with palladium and platinum). Unexpectedly, it has also been shown that the formation of six-membered platinacycles (n=1) is especially favored.

The kinetico-mechanistic study of the C–H activation reaction, on some equivalent Pd(II) and Pt(II) coordination complexes have shown that the nature of the d^8 metal center plays a determinant role in the reactivity observed. In this respect, the full process can be seen as a mechanistic-continuum that goes from an electrophilic substitution (Pd(II) centers) to an oxidative addition/reductive elimination sequence (Pt(II) centers).

The findings here described provide new and relevant information about the metalation process by palladium or platinum reagents, which can be useful in the design of new efficient catalytic or stoichiometric C–H activation processes.

EXPERIMENTAL SECTION

Materials and Methods. All the operations were carried out in air. All chemicals were obtained from commercial sources and used as received otherwise specified. Solvents were distilled and dried before use.

Proton NMR spectra were recorded at 298 K with Varian Mercury 400 and at 240K with Bruker Avance I 500 spectrometers. ^{13}C NMR spectra were recorded with a Varian Mercury 400 or a Bruker 400 spectrometers. The deuterated solvent is specified for each compound, and chemical shifts are given in δ values (ppm) relative to $SiMe_4$. Coupling constants are given in Hz and multiplicity is expressed as: s (singlet), d (doublet), t (triplet), and m (multiplet). High resolution mass spectrometry (HRMS) and low resolution mass spectrometry (LRMS) analyses were performed with electrospray ionization. ESI spectra were acquired either on an LC/MSD-TOF instrument or on a ZQ mass spectrometer, utilizing a mixture of H_2O:CH_3CN (1:1, v/v) as the eluent. Elemental analyses were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona).

X-ray Diffraction. In both cases, a prismatic crystal was selected and used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS) and the structure was solved and refined using the Bruker SHELXTL Software Package.

CCDC nos. 2038592 (**7mPt**) and 2038593 (**10mPt**) contain the supplementary crystallographic data for this paper. These data are also available free of charge via www.ccdc.cam.ac.uk/cgi-bin/catreqcgi or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk).

Kinetics. The kinetic profiles for the reactions were followed by UV-Vis spectroscopy in the full 700-300 nm range on HP8452A or Cary50 instruments equipped with thermostated multicell transports. Observed rate constants were derived from absorbance *versus* time traces at the wavelengths where a maximum increase and/or decrease of absorbance were observed; alternatively, the full spectral time-resolved changes were used. For the reactions carried out at varying pressure, the previously described pillbox cell and pressurizing system[28] were used and final treatment of data was the same described before. The calculation of the observed rate constants from the absorbance *versus* time monitoring of reactions, studied under first order concentration conditions, were carried out using the SPECFIT or RecatLab softwares.[29] The general kinetic technique is that previously described.[19g,30] Table S3 collects all the obtained k_{obs} values for all the systems studied as a function of the reaction studied, solvent, temperature and pressure. All post-run fittings were carried out by the standard available commercial programs. All experiments were carried out on solutions being $(1\text{-}4)\times10^{-4}$ M in metal complex; the low solubility of the palladium compounds was sorted out by preparing 50-fold more concentrated chloroform solutions and adding a small amount of these to pre-heated toluene. Sodium acetate solution in

methanol were prepared by weight in the spectrophotometric cells used for the kinetic runs.

Synthesis of imines

All imines were synthesized following the general procedure already known:[9] the corresponding primary amine and 2-formylpyridine, 2-formyl-6-picoline or 2-formylquinoline (1:1 molar ratio) were dissolved in toluene (10 mL/mmol). The mixture was heated to reflux overnight under nitrogen with a Dean–Stark apparatus. After cooling down to room temperature, the solvent was eliminated to afford the pure imine.

Phenethylamine, cumylamine, benzylamine and (*R*)-1-phenylethan-1-amine were purchased from commercial sources. 2-Methyl-1-phenylpropan-2-amine was synthesized as in previous works.[9,11c] 2-Methyl-2-phenylpropan-1-amine was prepared from 2-methyl-2-phenylpropanenitrile by reduction.[31] 1-Phenylpropan-2-amine was obtained by the oxidation of 1-phenylpropan-2-ol[32] followed by aminative reduction of the ketone.[33] Imine **1** has been previously reported.[9]

(*E*)-*N*-(2-Methyl-1-phenylpropan-2-yl)-1-(pyridin-2-yl)methanimine (1).

Brown oil, 798 mg (3.35 mmol, 100% yield) from 2-methyl-1-phenylpropan-2-amine and 2-formylpyridine. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.13 (s, 1H), 8.07 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.30 (ddt, *J* = 6.9, 4.9, 1.0 Hz, 1H), 7.22 – 7.12 (m, 5H), 2.92 (s, 2H), 1.28 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.2, 155.5, 149.4, 138.4, 136.7, 130.9, 127.8, 126.2, 124.6, 121.0, 61.1, 49.8, 27.0. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3062, 3031, 2964, 2917, 1465. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 239.1543, found 239.1549.

(*E*)-*N*-(2-Methyl-1-phenylpropan-2-yl)-1-(6-methylpyridin-2-yl)methanimine (2).

Brown-reddish oil, 254 mg (1.01 mmol, 100% yield) from 2-methyl-1-phenylpropan-2-amine and 2-formyl-6-picoline. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.12 (m, 6H), 2.91 (s, 2H), 2.57 (s, 3H), 1.27 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 157.5, 155.1, 138.5, 136.9, 130.8, 127.7, 126.2, 124.2, 117.8, 61.0, 49.8, 27.0, 24.4. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3062, 3024, 2964, 2917, 1454. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 253.1699, found 253.1702.

(*E*)-*N*-Phenethyl-1-(pyridin-2-yl)methanimine (3).

Brown oil, 420 mg (2.00 mmol, 100% yield) from phenethylamine and 2-formylpyridine. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.9, 1.8, 1.1 Hz, 1H), 8.30 (td, *J* = 1.4, 0.7 Hz, 1H), 7.98 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.74 (tdd, *J* = 7.9, 1.8, 0.7 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.30 – 7.28 (m, 1H), 7.28 – 7.24 (m, 1H), 7.26 – 7.17 (m, 3H), 3.93 (td, *J* = 7.6, 1.4 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 154.6, 149.6, 139.8, 136.7, 129.1, 128.5, 126.3, 124.8, 121.4, 63.1, 37.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3060, 3029, 2880, 2836, 1650, 1434. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 211.1230, found 211.1229.

(*E*)-*N*-(2-Methyl-2-phenylpropyl)-1-(pyridin-2-yl)methanimine (4).

Brown oil, 300 mg (1.26 mmol, 100% yield) from 2-methyl-2-phenylpropan-1-amine and 2-formylpyridine. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.9, 0.8 Hz, 1H), 8.26 (s, 1H), 7.98 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.71 (td, *J* = 7.9, 1.7 Hz, 1H), 7.43 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.36 – 7.24 (m, 3H), 7.21 – 7.16 (m, 1H), 3.79 (d, *J* = 1.4 Hz, 2H), 1.43 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 154.8, 149.4, 148.3, 136.6, 128.2, 126.2, 126.0, 124.7, 121.2, 73.6, 39.7, 27.1. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3056, 3024, 2965, 2917, 1644, 1585, 1465. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 239.1550, found 239.1543.

(*E*)-*N*-(1-Phenylpropan-2-yl)-1-(pyridin-2-yl)methanimine (5).

Brown oil, 367 mg (1.64 mmol, 92% yield) from 1-phenylpropan-2-amine and 2-formylpyridine. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.16 (s, 1H), 7.97 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.73 (dddd, *J* = 8.0, 7.6, 1.8, 0.6 Hz, 1H), 7.29 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.18 – 7.13 (m, 3H), 3.72 – 3.62 (m, 1H), 2.93 (qd, *J* = 13.4, 6.7 Hz, 2H), 1.32 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 154.6, 149.4, 139.2, 136.5, 129.6, 128.2, 126.1, 124.6, 121.4, 67.9, 44.4, 22.0. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3056, 3018, 2967, 2923, 2853, 1644, 1586, 1467. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 225.1386, found 225.1396.

(*E*)-1-(6-Methylpyridin-2-yl)-*N*-phenethylmethanimine (6).

Yellow oil, 224 mg (1.00 mmol, 100% yield) from phenethylamine and 2-formyl-6-picoline. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (t, *J* = 0.7 Hz, 1H), 7.78 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.15 (m, 6H), 3.91 (ddd, *J* = 8.0, 7.3, 1.4 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 158.3, 154.0, 139.9, 136.9, 129.0, 128.5, 126.3, 124.5, 118.5, 63.1, 37.5, 24.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3062, 3024, 2926, 2860, 2831, 1454. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 225.1386, found 225.1393.

(*E*)-*N*-(2-Methyl-1-phenylpropan-2-yl)-1-(quinolin-2-yl)methanimine (7).

Brown oil, 288 mg (1.00 mmol, 100% yield) from 2-methyl-1-phenylpropan-2-amine and 2-formylquinoline. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 – 8.29 (m, 1H), 8.28 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.10 (ddt, *J* = 8.5, 1.4, 0.8 Hz, 1H), 7.85 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.73 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.57 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.23 – 7.15 (m, 5H), 2.96 (s, 2H), 1.33 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6, 155.8, 147.9, 138.4, 136.6, 130.9, 129.8, 129.6, 128.9, 127.9, 127.8, 127.3, 126.2, 118.4, 61.4, 49.9, 27.1. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3056, 3024, 2964, 2913, 1642, 1595, 1502. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 289.1699, found 289.1700.

(*E*)-*N*-Phenethyl-1-(quinolin-2-yl)methanimine (8).

Yellow solid, 286 mg (1.10 mmol, 100% yield) from phenethylamine and 2-formylquinoline. **Mp** (°C) = 51-52. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.23 – 8.08 (m, 3H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.23 – 7.17 (m, 1H), 4.00 (td, *J* = 7.5, 1.4 Hz, 2H), 3.08 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 154.9, 147.9, 139.8, 136.7, 129.9, 129.8, 129.1, 128.9, 128.6, 127.8, 127.5, 126.4, 118.5, 63.2, 37.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3062, 302, 2955, 2917, 2863, 2825, 1498. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 261.1386, found 261.1389.

(*E*)-*N*-(2-Phenylpropan-2-yl)-1-(pyridin-2-yl)methanimine (9).

Brown oil, 830 mg (3.70 mmol, 100% yield) from cumylamine and 2-formylpyridine. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.9, 1.7, 0.8 Hz, 1H), 8.34 (d, *J* = 0.8 Hz, 1H), 8.13 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.74 (tdd, *J* = 8.1, 1.7, 0.7 Hz, 1H), 7.44 (dt, *J* = 7.9, 1.2 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.27 – 7.19 (m, 1H), 1.68 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 155.5, 149.4, 147.7, 136.7, 128.4, 126.6, 126.2, 124.7, 121.2, 63.3, 29.7. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3056, 2970, 2923, 1465. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 225.1386, found 225.1389.

(*E*)-1-(6-Methylpyridin-2-yl)-*N*-(2-phenylpropan-2-yl)methanimine (10).

Colorless oil, 238 mg (1.00 mmol, 100% yield) from cumylamine and 2-formyl-6-picoline. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 – 7.28 (m, 2H), 7.27 – 7.17 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 2.59 (s, 3H), 1.66 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 158.0, 155.1, 148.0, 136.9, 128.3, 126.5, 126.1, 124.3, 118.1, 63.2,

29.7, 24.4. **IR** (FTIR-ATR, ν, cm^{-1}): 3056, 3015, 2974, 2920, 1454. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 239.1543, found 239.1547.

(*E*)-*N*-Benzyl-1-(pyridin-2-yl)methanimine (11).

Brown oil, 385 mg (1.96 mmol, 98%) from benzylamine and 2-formylpyridine. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.8, 1.8, 1.1 Hz, 1H), 8.49 (q, *J* = 1.1 Hz, 1H), 8.07 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.74 (td, *J* = 7.8, 1.8 Hz, 1H), 7.36 (s, 2H), 7.35 (s, 2H), 7.34 – 7.27 (m, 2H), 4.88 (d, *J* = 1.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 154.7, 149.5, 138.8, 136.7, 128.7, 128.3, 127.3, 125.0, 121.5, 65.1. **IR** (FTIR-ATR, ν, cm^{-1}): 3056, 3024, 2882, 2834, 1644, 1585, 1566, 1434. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 197.1073, found 197.1074.

(*R,E*)-*N*-(1-Phenylethyl)-1-(pyridin-2-yl)methanimine (12).

Yellowish oil, 421 mg (2.00 mmol, 100% yield) from (*R*)-1-phenylethan-1-amine and 2-formylpyridine. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.9, 1.7, 1.1 Hz, 1H), 8.47 (s, 1H), 8.09 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.46 – 7.41 (m, 2H), 7.37 – 7.21 (m, 4H), 4.64 (q, *J* = 6.6 Hz, 1H), 1.61 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 154.9, 149.4, 144.7, 136.6, 128.6, 127.1, 126.8, 124.8, 121.6, 69.7, 24.7. **IR** (FTIR-ATR, ν, cm^{-1}): 3059, 2955, 2912, 2848, 1467. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 211.1230, found 211.1228.

(*E*)-*N*-Benzyl-1-(6-methylpyridin-2-yl)methanimine (13).

Yellow oil, 294 mg (1.40 mmol, 100% yield) from benzylamine and 2-formyl-6-picoline. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (p, *J* = 0.8 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.24 (m, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 4.87 (d, *J* = 1.5 Hz, 2H), 2.60 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.3, 158.3, 154.1, 138.9, 136.9, 128.7, 128.3, 127.3, 124.6, 118.6, 65.1, 24.5. **IR** (FTIR-ATR, ν, cm^{-1}): 3062, 3027, 2913, 2869, 2828, 1589, 1452. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 211.1230, found 211.1232.

(*E*)-*N*-(2-Phenylpropan-2-yl)-1-(quinolin-2-yl)methanimine (14).

Yellow oil, 274 mg (1.00 mmol, 100% yield) from cumylamine and 2-formylquinoline. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 0.9 Hz, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.11 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.73 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.57 (ddt, *J* = 8.1, 6.9, 0.7 Hz, 1H), 7.48 (dt, *J* = 7.8, 1.1 Hz, 2H), 7.35 (ddd, *J* = 7.8, 7.0, 0.7 Hz, 2H), 7.27 – 7.22 (m, 1H), 1.72 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 155.8, 147.9, 147.8, 136.6, 129.9, 129.6, 129.0, 128.4, 127.9, 127.4, 126.7, 126.2, 118.6, 63.5, 29.7. **IR** (FTIR-ATR, ν, cm^{-1}): 3059, 2970, 2926, 1637, 1595, 1493. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 275.1543, found 275.1538.

(*E*)-*N*-Benzyl-1-(quinolin-2-yl)methanimine (15).

Red oil, 483 mg (1.96 mmol, 98% yield) from benzylamine and 2-formylquinoline. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.24 – 8.16 (m, 2H), 8.13 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.84 (ddd, *J* = 8.1, 1.5, 0.8 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.58 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.42 – 7.26 (m, 5H), 4.95 (d, *J* = 1.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.3, 154.8, 147.8, 138.6, 136.5, 129.8, 129.6, 128.8, 128.6, 128.2, 127.7, 127.4, 127.2, 118.5, 65.0. **IR** (FTIR-ATR, ν, cm^{-1}): 3059, 3027, 2869, 2828, 1642, 1595, 1501. **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 247.1230, found 247.1230.

Palladium compounds

1cPd and **1mPd** have been previously reported.[9]

2mPd. A mixture of imine **2** (110 mg, 0.44 mmol) and palladium acetate (99 mg, 0.44 mmol) in an 1/1 molar ratio was stirred at room temperature in 15 mL of toluene for 2 h. The brown precipitate was filtered in vacuo to obtain **2mPd** (154 mg, 85%).

A second fraction of **2mPd** can be obtained from the toluene solution. The solvent was removed in a rotary evaporator and the residue was recrystallized in cold dichloromethane-diethyl ether, yielding a solid which was filtered *in vacuo*.

Brown solid. **R_f** (DCM/MeOH 90:10) = 0.28. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 8.37 (s, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.52 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.38 – 7.35 (m, 1H), 6.97 – 6.94 (m, 2H), 6.82 (dd, *J* = 5.9, 3.0 Hz, 1H), 3.07 (br, 2H), 2.82 (s, 3H), 2.07 (s, 3H), 1.27 (br, 6H); **^{1}H NMR** (500 MHz, $CDCl_3$, 240 K) δ 8.42 (s, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.87 (dd, *J* = 6.6, 2.3 Hz, 1H), 3.52 (d, *J* = 13.7 Hz, 1H), 2.81 (s, 3H), 2.70 – 2.63 (m, 1H), 2.14 (s, 3H), 1.68 (s, 3H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 164.0, 152.7, 139.7, 138.4, 136.6, 130.0, 128.0, 124.7, 124.6, 124.5, 60.7, 54.4, 27.8, 26.2. **IR** (FTIR-ATR, ν, cm^{-1}): 3043, 2970, 2926, 1592, 1556, 1416, 1385. **EA** (calc. for $C_{19}H_{22}N_2O_2Pd$; %): C: 53.9 (54.75); H: 5.3 (5.32); N: 6.9 (6.72). **LRMS** (ESI+, m/z): calc. for $[M-OAc]^+$ 357.06, found 357.06.

3cPd. A mixture of imine **3** (142 mg, 0.68 mmol) and palladium acetate (152 mg, 0.68 mmol) in an 1/1 molar ratio was stirred at room temperature in 15 mL of toluene for 1 h. The beige precipitate was filtered in vacuo to obtain **3cPd** (20 mg, 68%).

Beige solid. **R_f** (hexane/EtOAc 1:1) = 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (ddd, *J* = 5.5, 1.5, 0.7 Hz, 1H), 8.02 (td, *J* = 7.8, 1.5 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.49 (ddd, *J* = 7.8, 5.5, 1.4 Hz, 1H), 7.28 – 7.15 (m, 5H), 3.72 (td, *J* = 7.1, 1.2 Hz, 2H), 3.15 (t, *J* = 7.1 Hz, 2H), 2.11 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ , ν, cm^{-1}): 3031, 2974, 2920, 1621, 1590, 1361, 1307. **EA** (calc. for $C_{19}H_{22}N_2O_4Pd$; %): C: 48.8 (50.85); H: 4.9 (4.94); N: 6.0 (6.24). **LRMS** (ESI+, m/z): calc. for $[M-OAc]^+$ 329.03, found 329.03.[34]

5mPd. Coordination compound **5cPd** (60 mg, 0.13 mmol) was allowed to react in dry toluene (6 mL) at 90 178.7, 178.6, 167.5, 154.8, 150.8, 140.4, 137.2, 129.4, 128.9, 127.8, 127.5, 127.1, 61.7, 35.9, 23.5, 23.3. **IR** (FTIR-ATR, ν, cm^{-1}): 3059, 3002, 2983, 1622, 1593, 1302. **HRMS** (ESI+, m/z): calc. for $[M-AcO]^+$ 315.0114, found 315.0119.[34]

4cPd. A mixture of imine **4** (103 mg, 0.43 mmol) and palladium acetate (96 mg, 0.43 mmol) in an 1/1 molar ratio was stirred at room temperature in 10 mL of toluene for 1 h. The brown precipitate was filtered in vacuo to obtain **4cPd** (198 mg, 99%).

Brown solid. **R_f** (DCM/MeOH 95:5) = 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 5.5, 1.4 Hz, 1H), 7.96 (td, *J* = 7.8, 1.5 Hz, 1H), 7.61 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.45 (ddd, *J* = 7.8, 5.5, 1.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.22 (m, 1H), 7.21 (s, 1H), 3.53 (s, 2H), 2.08 (s, 3H), 2.08 (s, 3H), 1.60 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.5, 178.1, 168.7, 154.6, 150.8, 145.1, 140.3, 128.8, 127.7, 127.1, 126.9, 126.7, 69.2, 41.6, 26.5, 23.5, 23.4. **IR** (FTIR-ATR, ν, cm^{-1}): 3069, 3034, 2961, 2929, 1710, 1590, 1368, 1315. **EA** (calc. for $C_{20}H_{24}N_2O_4Pd$; %): C: 49.7 (51.90); H: 5.0 (5.23); N: 6.1 (6.05). **LRMS** (ESI+, m/z): calc. for $[M-OAc]^+$ 343.04, found 343.04.[34]

5cPd. A mixture of imine **5** (81 mg, 0.36 mmol) and palladium acetate (80 mg, 0.36 mmol) in an 1/1 molar ratio was stirred at room temperature in 10 mL of toluene for 1 h. The brown precipitate was filtered in vacuo to obtain **5cPd** (148 mg, 91%).

Brown solid. **R_f** (DCM/MeOH 95:5) = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.06 (tt, *J* = 7.7, 1.6 Hz, 1H), 7.98 – 7.85 (m, 2H), 7.53 (ddd, *J* = 7.7, 5.6, 1.5 Hz, 1H), 7.19 (dd, *J* = 14.3, 7.0 Hz, 5H), 4.06 (q, *J* = 7.0 Hz, 1H), 3.36 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.83 (ddd, *J* = 13.4, 7.4, 1.8 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.34 (dd, *J* = 6.6, 1.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.4, 178.3, 165.0, 155.1, 150.6, 140.4, 136.7, 129.8, 128.6, 127.8, 127.3, 126.9, 65.0, 41.8, 23.5, 18.3. **IR** (FTIR-ATR ºC for 2.5 h and then filtered. The solvent was removed in a rotary evaporator and the residue was

eluted in a flash chromatography column (DCM/MeOH 97:3 to 95:5), yielding a solid which was filtered *in vacuo* to obtain **5mPd** in 5% yield.

Brown solid. $\mathbf{R_f}$ (DCM/MeOH 95:5) = 0.65. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (dd, *J* = 5.1, 0.8 Hz, 1H), 8.61 (d, *J* = 1.1 Hz, 1H), 8.00 (td, *J* = 7.7, 1.7 Hz, 1H), 7.96 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.67 (ddd, *J* = 7.7, 5.1, 1.3 Hz, 1H), 7.03 – 6.90 (m, 2H), 6.87 (dd, *J* = 6.9, 2.1 Hz, 1H), 3.96 (dt, *J* = 6.7, 3.5 Hz, 1H), 3.32 (dd, *J* = 14.3, 2.9 Hz, 1H), 2.86 (dd, *J* = 14.3, 3.9 Hz, 1H), 1.56 (s, 3H), 1.02 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 152.1, 150.7, 140.3, 139.1, 138.9, 128.7, 128.0, 125.7, 125.0, 124.7, 61.0, 46.6, 29.8, 20.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3056, 3027, 2951, 2920, 2847, 1732, 1587, 1438. **HRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 329.0264, found 329.0266.

6cPd. A mixture of imine **6** (100 mg, 0.45 mmol) and palladium acetate (100 mg, 0.45 mmol) in an 1/1 molar ratio was stirred at room temperature in 10 mL of toluene for 1.5 h. The yellow precipitate was filtered in vacuo to obtain **6cPd** (185 mg, 93%).

Yellow solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.28. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 7.8 Hz, 1H), 7.66 (s, 1H), 7.51 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.21 (dt, *J* = 8.5, 4.1 Hz, 1H), 3.64 (t, *J* = 6.9 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.70 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.8, 178.5, 169.0, 165.7, 155.2, 139.6, 137.3, 130.3, 129.3, 128.8, 127.0, 125.8, 77.4, 61.0, 36.0, 23.6, 23.2. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3072, 3002, 2974, 2923, 1591, 1366, 1311. **EA** (calc. for $C_{19}H_{22}N_2O_4Pd$; %): C: 50.2 (50.85); H: 5.1 (4.94); N: 6.1 (6.24). **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 329.03, found 329.03.[34]

7mPd. A mixture of imine **7** (87 mg, 0.30 mmol) and palladium acetate (67 mg, 0.30 mmol) in dry toluene (10 mL) was heated with stirring in a bath at 90 ºC for 1 h and then filtered. The solvent was removed in a rotary evaporator and the residue was washed with diethyl ether, yielding a brown solid which was filtered *in vacuo* to obtain **7mPd** as a brown solid (109 mg, 80%).

Brown solid. $\mathbf{R_f}$ (DCM/MeOH 95:5) = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 9.13 (d, *J* = 9.2 Hz, 1H), 8.62 (s, 1H), 8.48 (d, *J* = 8.2 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.71 (td, *J* = 7.3, 6.8, 1.1 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.02 – 6.96 (m, 2H), 6.87 – 6.84 (m, 1H), 3.12 (s, 2H), 2.17 (s, 3H), 1.35 (s, 6H); **^{1}H NMR** (500 MHz, $CDCl_3$, 240 K) δ 9.04 (d, *J* = 8.8 Hz, 1H), 8.69 (s, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.91 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.91 (dd, *J* = 6.4, 2.2 Hz, 1H), 3.59 (d, *J* = 14.3 Hz, 1H), 2.74 (d, *J* = 14.3 Hz, 1H), 2.24 (s, 3H), 1.76 (s, 3H), 1.00 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 152.5, 148.3, 140.6, 140.0, 136.9, 133.8, 132.3, 130.2, 129.5, 128.8, 127.8, 124.7, 124.6, 122.2, 61.8, 53.9, 27.8. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3043, 2964, 2926, 1588, 1556, 1366. **EA** (calc. for $C_{22}H_{22}N_2O_2Pd$; %): C: 57.6 (58.35); H: 4.9 (4.90); N: 6.3 (6.19). **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 393.06, found 393.06.

9cPd. A mixture of imine **9** (215 mg, 0.96 mmol) and palladium acetate (215 mg, 0.96 mmol) in an 1/1 molar ratio was stirred at room temperature in 20 mL of toluene for 1 h. The yellow precipitate was filtered in vacuo to obtain **9cPd** (381 mg, 88%).

Yellow solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 5.6, 1.5 Hz, 1H), 8.04 (td, *J* = 7.8, 1.5 Hz, 1H), 7.68 (s, 1H), 7.65 (ddd, *J* = 7.8, 1.4, 0.7 Hz, 1H), 7.56 (ddd, *J* = 7.8, 5.5, 1.4 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.33 (m, 3H), 2.06 (s, 3H), 1.91 (s, 6H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.2, 163.7, 155.2, 151.1, 142.1, 140.0, 129.3, 128.4, 127.8, 127.0, 126.4, 70.7, 28.2, 23.3. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3053, 3027, 2915, 2848, 1723, 1598, 1376. **EA** (calc. for $C_{19}H_{22}N_2O_4Pd$; %): C: 49.8 (50.85); H: 5.0 (4.94); N: 6.3 (6.24). **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc+MeCN]^+$ 430.07, found 430.09.

9mPd. Coordination compound **9cPd** (200 mg, 0.45 mmol) was allowed to react in dry toluene (6 mL) at 90 ºC for 1 h and then filtered. The solvent was removed in a rotary evaporator and the residue was recrystallized in cold dichloromethane-diethyl ether, yielding a brown solid which was filtered *in vacuo* to obtain **9mPd 38** (169 mg, 99%)

Brown solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.38. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 5.1 Hz, 1H), 8.48 (s, 1H), 7.96 (td, *J* = 7.8, 1.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 7.8, 5.1 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.08 (td, *J* = 7.2, 1.2 Hz, 1H), 7.02 (td, *J* = 7.2, 1.1 Hz, 1H), 6.69 (dd, *J* = 7.6, 1.5 Hz, 1H), 2.24 (s, 3H), 1.73 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.2, 160.7, 158.2, 155.0, 151.9, 144.1, 139.1, 132.6, 128.7, 126.0, 125.9, 125.6, 121.6, 76.7, 30.9, 24.4. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3069, 3034, 2977, 2932, 1591, 1375. **EA** (calc. for $C_{17}H_{18}N_2O_2Pd$; %): C: 52.4 (52.52); H: 5.1 (4.67); N: 7.2 (7.21). **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc+MeCN]^+$ 370.05, found 370.05.

10mPd. A mixture of imine **10** (116 mg, 0.49 mmol)) and palladium acetate (110 mg, 0.49 mmol) in an 1/1 molar ratio was stirred at room temperature in 15 mL of toluene for 2 h. The yellow precipitate was filtered in vacuo to obtain **10mPd** (154 mg, 85%).

A second fraction of **10mPd** can be obtained from the toluene solution. The solvent was removed in a rotary evaporator and the residue was recrystallized in cold dichloromethane-diethyl ether, yielding a solid which was filtered *in vacuo*. The overall yield of the process was 87%, (170 mg).

Yellow solid. $\mathbf{R_f}$ (DCM/MeOH 95:5) = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.11 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.06 (td, *J* = 7.5, 1.5 Hz, 1H), 6.99 (td, *J* = 7.4, 1.6 Hz, 1H), 6.66 (dd, *J* = 7.5, 1.6 Hz, 1H), 2.74 (s, 3H), 2.19 (s, 3H), 1.68 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 163.2, 161.2, 157.9, 154.7, 142.6, 138.8, 132.6, 129.6, 126.1, 125.5, 124.0, 121.5, 76.4, 30.9, 24.8, 23.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3031, 2964, 2923, 1612, 1593, 1315. **EA** (calc. for $C_{18}H_{20}N_2O_2Pd$; %): C: 51.9 (53.68); H: 5.0 (5.01); N: 6.7 (6.95). **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 343.04, found 343.04.

11cPd. A mixture of imine **11** (100 mg, 0.51 mmol) and palladium acetate (114 mg, 0.51 mmol) in an 1/1 molar ratio was stirred at room temperature in 15 mL of toluene for 1 h. The yellow precipitate was filtered in vacuo to obtain **11cPd** (160 mg, 75%).

Yellow solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.63. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 5.5 Hz, 1H), 8.03 (t, *J* = 7.7 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.54 (t, *J* = 6.7 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.40 – 7.30 (m, 2H), 4.93 (d, *J* = 2.0 Hz, 2H), 2.12 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.7, 178.5, 166.6, 155.1, 151.0, 140.3, 132.8, 130.3, 129.7, 129.4, 127.9, 127.3, 62.0, 23.5, 23.3. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3029, 2917, 2844, 1701, 1361. **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 301.0, found 301.00.[34]

12cPd. A mixture of imine **12** (110 mg, 0.52 mmol) and palladium acetate (116 mg, 0.52 mmol) in an 1/1 molar ratio was stirred at room temperature in 10 mL of toluene for 1 h. The brown precipitate was filtered in vacuo to obtain **12cPd** (147 mg, 65%).

Brown solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.13. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 4.8, 2.9 Hz, 1H), 8.07 (td, *J* = 7.8, 1.6 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.67 (s, 1H), 7.54 (dd, *J* = 7.6, 5.8 Hz, 1H), 7.47 – 7.36 (m, 5H), 5.22 (q, *J* = 7.0 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.80 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.7, 178.5, 165.0, 155.1, 151.1, 140.4, 137.2, 129.5, 129.3, 128.5, 127.95, 127.1, 65.5, 23.5, 23.4, 20.3. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3032, 2992, 2917, 1494, 1403. **EA** (calc. for $C_{18}H_{20}N_2O_4Pd$; %): C: 49.4 (49.72); H: 4.6 (4.64); N: 6.6 (6.44). **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 315.01, found 315.01.[34]

13cPd. A mixture of imine **13** (105 mg, 0.5 mmol) and palladium acetate (100 mg, 0.45 mmol) in an 1/1 molar ratio was stirred at room

temperature in 10 mL of toluene for 1 h. The yellow precipitate was filtered in vacuo to obtain **13cPd** (147 mg, 68%).

Yellow solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 1.9 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.36 – 7.30 (m, 3H), 4.83 (d, *J* = 1.9 Hz, 2H), 2.70 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.7, 167.0, 166.1, 155.4, 139.4, 132.5, 130.5, 130.5, 129.7, 129.4, 125.1, 61.4, 23.7, 23.3, 23.1. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3062, 3034, 2996, 2967, 2920, 1637, 1613, 1595, 1293. **HRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 315.0114, found 315.0124.[34]

14mPd. A mixture of imine **14** (100 mg, 0.37 mmol) and palladium acetate (83 mg, 0.37 mmol) in dry toluene (10 mL) was heated with stirring in a bath at 90 ºC for 1 h and then filtered. The red precipitate was filtered in vacuo to obtain **14mPd** (114 mg, 71%).

Red solid. $\mathbf{R_f}$ (DCM/MeOH 95:5) = 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.72 (dt, *J* = 8.7, 0.9 Hz, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.65 (m, 1H), 7.17 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.09 (td, *J* = 7.4, 1.4 Hz, 1H), 7.04 (td, *J* = 7.4, 1.6 Hz, 1H), 6.66 (dd, *J* = 7.5, 1.6 Hz, 1H), 2.34 (s, 3H), 1.69 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 161.6, 157.9, 154.7, 148.1, 143.1, 139.7, 132.8, 132.7, 130.6, 129.6, 129.3, 127.6, 126.3, 125.7, 121.9, 121.7, 76.6, 30.9, 25.1. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3065, 3034, 2967, 2955, 2920, 1610, 1591, 1371, 1323. **EA** (calc. for $C_{21}H_{20}N_2O_2Pd$; %): C: 56.4 (57.48); H: 4.6 (4.59); N: 6.3 (6.38). **LRMS** (ESI+, m/z): calc. for $[M\text{-}OAc]^+$ 379.04, found 379.04.

Platinum compounds

cis-$[PtCl_2(DMSO)_2]$ was prepared as reported elsewhere.[35]

1mPt. A mixture of imine **1** (100 mg, 0.42 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (177 mg, 0.42 mmol) was allowed to react in refluxing methanol (20 mL) for 4 h. The orange precipitate was filtered in vacuo to obtain **1mPt** (81 mg, 41%).

Orange solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.65. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K) δ 9.71 (d, *J* = 5.4 Hz, 1H), 9.20 (s, $J_{Pt\text{-}H}$ = 107.4 Hz, 1H), 8.10 (t, *J* = 7.7 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.81 (t, *J* = 6.6 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H); **^{1}H NMR** (600 MHz, $CDCl_3$, 233 K) δ 9.67 (d, *J* = 5.4 Hz, 1H), 9.25 (s, $J_{Pt\text{-}H}$ = 99.7 Hz, 1H), 8.18 (t, *J* = 7.7 Hz, 1H), 7.95 (t, *J* = 8.4 Hz, 2H), 7.86 (t, *J* = 6.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 3.45 (d, *J* = 14.5 Hz, 1H), 2.74 (d, *J* = 14.5 Hz, 1H), 1.86 (s, 3H), 1.11 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.5, 155.5, 147.9, 140.0, 139.8, 137.7, 131.3, 128.5, 127.7, 127.1, 123.5, 123.2, 62.4, 53.7, 27.0. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3053, 3037, 2964, 2926, 2891, 1425. **EA** (calc. for $C_{16}H_{17}ClN_2Pt$; %): C: 40.2 (41.08); H: 3.7 (3.66); N: 5.8 (5.99). **LRMS** (ESI+, m/z): calc. for $[M+H]^+$ 468.08, found 468.08.

1cPt. A mixture of imine **1** (100 mg, 0.42 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (177 mg, 0.42 mmol) was stirred at room temperature in 10 mL of methanol for 4 h. The solvent was removed in a rotary evaporator and the residue was washed with diethyl ether, yielding a brown solid which was filtered *in vacuo* to obtain **1cPt** (175 mg, 83%).

Brown solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.57. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.84 (dd, *J* = 5.9, 1.3 Hz, 1H), 8.35 (s, $J_{Pt\text{-}H}$ = 92.8 Hz, 1H), 8.14 (td, *J* = 7.8, 1.4 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.65 (ddd, *J* = 7.6, 5.9, 1.5 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.24 – 7.15 (m, 3H), 3.71 (s, 2H), 1.71 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 157.7, 150.1, 139.6, 137.0, 131.0, 128.3, 128.2, 128.1, 126.8, 72.1, 46.0, 28.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3059, 3027, 2967, 2920, 2866, 1444. **EA** (calc. for $C_{16}H_{18}Cl_2N_2Pt$; %): C: 36.4 (38.11); H: 3.4 (3.60); N: 5.3 (5.55). **LRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 521.08, found 521.08.

2mPt. A mixture of imine **2** (144 mg, 0.57 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (240 mg, 0.42 mmol) was allowed to react in refluxing methanol (20 mL) for 24 h.

The solvent was removed a rotary evaporator and the residue was eluted in a flash chromatography column (DCM/MeOH 98:2) yielding a solid which was filtered *in vacuo* to obtain **2mPt** (155 mg, 56%).

Orange solid. $\mathbf{R_f}$ (DCM/MeOH 98:2) = 0.82. **^{1}H NMR** (500 MHz, acetone-d_6, 298 K) δ 9.75 (s, $J_{Pt\text{-}H}$ = 100.4 Hz, 1H), 8.16 (t, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.71 – 7.69 (m, 1H), 6.85 – 6.78 (m, 3H), 3.18 (s, 3H); **^{1}H NMR** (500 MHz, acetone-d_6, 240 K) δ 9.79 (s, $J_{Pt\text{-}H}$ = 100.3 Hz, 1H), 8.21 (t, *J* = 7.7 Hz, 1H), 8.07 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.69 – 7.63 (m, 1H), 6.86 – 6.77 (m, 3H), 3.31 – 3.26 (m, 1H), 3.12 (s, 3H), 2.68 (d, *J* = 14.0 Hz, 1H), 1.80 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.0, 164.0, 155.3, 139.4, 139.0, 137.6, 130.9, 126.6, 126.4, 125.7, 123.4, 123.0, 61.7, 53.4, 27.2, 25.8. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3059, 3037, 2967, 2923, 1454. **EA** (calc. for $C_{17}H_{19}ClN_2Pt$; %): C: 42.7 (42.37); H: 3.9 (3.97); N: 5.5 (5.81). **LRMS** (ESI+, m/z): calc. for $[M\text{-}Cl+MeCN]^+$ 487.15, found 487.14.

3cPt. A mixture of imine **3** (100 mg, 0.48 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (202 mg, 0.48 mmol) and sodium acetate (40 mg, 0.48 mmol), was allowed to react in refluxing methanol (15 mL) for 24 h. The yellow precipitate was filtered in vacuo to obtain **3cPt** (142 mg, 62%).

Yellow solid. $\mathbf{R_f}$ (hexane/EtOAc 1:1) = 0.31. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.35 (ddd, *J* = 5.7, 1.4, 0.6 Hz, 1H), 8.94 (s, $J_{Pt\text{-}H}$ = 92.5 Hz, 1H), 8.32 (td, *J* = 7.7, 1.4 Hz, 1H), 8.02 (ddd, *J* = 7.8, 1.6, 0.7 Hz, 1H), 7.87 (ddd, *J* = 7.8, 5.8, 1.6 Hz, 1H), 7.32 – 7.22 (m, 4H), 7.23 – 7.14 (m, 1H), 4.18 (td, *J* = 7.7, 1.0 Hz, 2H), 3.12 (dd, *J* = 8.2, 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.0, 156.7, 149.07, 140.8, 137.7, 129.1, 128.9, 128.6, 128.3, 126.6, 60.5, 36.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3065, 3024, 1690, 1494, 1475. **EA** (calc. for $C_{14}H_{14}Cl_2N_2Pt$; %): C: 35.7 (35.31); H: 3.0 (2.96); N: 5.7 (5.88). **LRMS** (ESI+, m/z): calc. for $[M\text{-}Cl]^+$ 440.05, found 440.05.

4cPt and **4mPt.** A mixture of imine **4** (100 mg, 0.42 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (177 mg, 0.42 mmol) and sodium acetate (34 mg, 0.42 mmol), was allowed to react in refluxing methanol (15 mL) for 24 h. The precipitate was filtered in vacuo to obtain a mixture of **4cPt** (99 mg, 47%) and **4mPt** (74 mg, 37%). The elution of this mixture in a flash chromatography column (DCM/MeOH 98:2) permits to obtain a small quantity of pure **4cPt** and **4mPt**.

4mPt. A mixture of imine **4** (100 mg, 0.42 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (177 mg, 0.42 mmol) and sodium acetate (34 mg, 0.42 mmol), was allowed to react in refluxing ethanol (15 mL) for 72 h. The precipitate was filtered in vacuo to obtain pure **4mPt** (185 mg, 97%).

4cPt. Orange solid. $\mathbf{R_f}$ (DCM) = 0.10. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (dt, *J* = 5.8, 0.8 Hz, 1H), 8.01 (tdd, *J* = 7.7, 1.4, 0.5 Hz, 1H), 7.55 (ddd, *J* = 7.7, 5.8, 1.5 Hz, 1H), 7.34 – 7.25 (m, 6H), 7.20 (s, 1H), 4.32 (s, 2H), 1.61 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 156.9, 149.9, 145.5, 139.4, 128.9, 128.1, 127.2, 126.9, 126.7, 68.2, 42.3, 26.5. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3046, 2964, 2913, 1470. **HRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 521.0833, found 521.0837.

4mPt. Red solid. $\mathbf{R_f}$ (DCM) = 0.25. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.69 (t, *J* = 1.5 Hz, $J_{Pt\text{-}H}$ = 111.3 Hz, 1H), 9.34 (ddd, *J* = 5.3, 1.6, 0.8 Hz, 1H), 8.35 (td, *J* = 7.7, 1.6 Hz, 1H), 8.20 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 8.05 (ddd, *J* = 7.7, 5.4, 1.4 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.18 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.93 (ddd, *J* = 7.8, 7.1, 1.5 Hz, 1H), 6.80 (ddd, *J* = 7.7, 7.0, 1.5 Hz, 1H), 3.79 (br, 2H), 1.49 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.3, 153.8, 148.8, 148.6, 140.2, 139.4, 130.4, 128.7, 127.0, 123.4, 123.1, 121.4, 67.5, 43.6. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3103, 3072, 3034, 2951, 2920, 2860, 1441, 1296. **EA** (calc. for $C_{16}H_{17}ClN_2Pt$; %): C: 41.3 (41.08); H: 3.6 (3.66); N: 6.0 (5.99). **HRMS** (ESI+, m/z): calc. for $[M+H]^+$ 468.0800, found 468.0795.

5cPt. A mixture of imine **5** (80 mg, 0.36 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (152 mg, 0.36 mmol) and sodium acetate (30 mg, 0.36 mmol), was allowed to react in refluxing methanol (15 mL) for 24 h. The precipitate was filtered in vacuo to obtain **5cPt** (101 mg, 62%).

Yellow solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.55. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.41 (ddd, J = 5.8, 1.4, 0.6 Hz, 1H), 9.12 (d, J = 1.0 Hz, J_{Pt-H} = 93.9 Hz, 1H), 8.38 (td, J = 7.7, 1.5 Hz, 1H), 8.11 (ddd, J = 7.7, 1.6, 0.7 Hz, 1H), 7.91 (ddd, J = 7.6, 5.8, 1.6 Hz, 1H), 7.36 – 7.25 (m, 4H), 7.28 – 7.18 (m, 1H), 5.09 – 4.99 (m, 1H), 3.44 (dd, J = 13.2, 5.0 Hz, 1H), 2.88 (dd, J = 13.3, 8.5 Hz, 1H), 1.35 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.8, 157.6, 148.8, 140.8, 137.4, 129.4, 129.0, 128.5, 128.4, 126.6, 41.5, 18.6. **IR** (FTIR-ATR, ν, cm^{-1}): 3043, 2970, 2920, 2863, 1448, 1365. **HRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 507.0676, found 507.0684.

5mPt. A mixture of imine **5** (100 mg, 0.42 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (177 mg, 0.42 mmol) and sodium acetate (34 mg, 0.42 mmol), was allowed to react in refluxing ethanol (15 mL) for 72 h. The precipitate was filtered in vacuo to obtain a solid. The elution of this solid in a flash chromatography column (DCM) permits to obtain pure **5mPt** (13 mg, 25%).

Red solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.68. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (d, J = 5.3 Hz, 1H), 9.25 (s, J_{Pt-H} = 107.6 Hz, 1H), 8.04 (td, J = 7.7, 1.6 Hz, 1H), 7.98 (dd, J = 7.6, 1.5 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.05 (td, J = 7.4, 1.7 Hz, 1H), 6.99 (td, J = 7.2, 1.5 Hz, 1H), 6.90 (dd, J = 7.3, 1.7 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.28 (d, J = 14.5 Hz, 1H), 2.75 (dd, J = 14.5, 3.8 Hz, 1H), 1.10 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 154.4, 149.8, 139.1, 138.4, 128.1, 125.7, 125.0, 124.4, 62.6, 46.9, 21.2. **IR** (FTIR-ATR, ν, cm^{-1}): 3034, 2961, 2917, 2856, 1454. **HRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 471.0909, found 471.0900.

6mPt. A mixture of imine **6** (73 mg, 0.33 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (140 mg, 0.33 mmol) and sodium acetate (27 mg, 0.33 mmol), was allowed to react in refluxing ethanol (10 mL) for 72 h. The precipitate was eluted in a flash chromatography column (DCM/MeOH 97:3) to obtain **6mPt** (27 mg, 18%).

Orange solid. $\mathbf{R_f}$ (DCM/MeOH 95:5) = 0.78. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.71 (t, J = 1.5 Hz, J_{Pt-H} = 101.7 Hz, 1H), 8.17 (t, J = 7.7 Hz, 1H), 7.99 (dd, J = 7.8, 1.3 Hz, 1H), 7.81 (dd, J = 7.9, 1.4 Hz, 1H), 7.56 (dd, J = 7.0, 2.0 Hz, 1H), 6.91 – 6.77 (m, 3H), 3.77 – 3.73 (m, 2H), 3.09 (s, 3H), 2.88 (dd, J = 6.5, 3.8 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.1, 164.4, 154.0, 141.1, 139.6, 138.5, 131.1, 125.4, 125.1, 125.0, 123.4, 123.1, 57.9, 25.7. **IR** (FTIR-ATR, ν, cm^{-1}): 3056, 3037, 2999, 2913, 1593, 1463. **HRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 471.0909, found 471.0904.

7mPt. A mixture of imine **7** (170 mg, 0.56 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (236 mg, 0.56 mmol) was allowed to react in refluxing methanol (25 mL) for 24 h. The precipitate was filtered in vacuo to obtain **7mPt** (131 mg, 46%).

Brown solid. $\mathbf{R_f}$ (DCM/MeOH 98:2) = 0.87. **^{1}H NMR** (500 MHz, acetone-d_6, 298 K) δ 10.37 (dd, J = 9.0, 0.9 Hz, 1H), 10.09 (s, J_{Pt-H} = 103.8 Hz, 1H), 8.91 (dd, J = 8.3, 0.7 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), 8.15 (dd, J = 8.2, 1.5 Hz, 1H), 7.97 (ddd, J = 8.8, 6.8, 1.6 Hz, 1H), 7.86 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 7.76 – 7.73 (m, 1H), 6.90 – 6.84 (m, 3H); **^{1}H NMR** (500 MHz, acetone-d_6, 240 K) δ 10.30 (dd, J = 8.9, 0.9 Hz, 1H), 10.12 (s, J_{Pt-H} = 104.5 Hz, 1H), 8.97 (d, J = 8.2 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.20 (dd, J = 8.3, 1.5 Hz, 1H), 8.00 (ddd, J = 8.7, 6.8, 1.5 Hz, 1H), 7.89 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.74 – 7.68 (m, 1H), 6.90 – 6.84 (m, 3H), 3.37 (d, J = 15.0 Hz, 1H), 2.77 (d, J = 14.0 Hz, 1H), 1.88 (s, 3H), 0.97 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.7, 156.77, 148.1, 140.9, 139.2, 137.5, 131.6, 130.8, 129.0, 128.9, 128.5, 126.8, 126.5, 123.5, 123.3, 123.0, 62.5, 53.5, 27.3. **IR** (FTIR-ATR, ν, cm^{-1}): 3069, 3034, 2970, 2923, 1590, 1432. **EA** (calc. for $C_{20}H_{19}ClN_2Pt$; %): C: 43.7 (46.38); H: 3.4 (3.70); N: 5.2 (5.41). **LRMS** (ESI+, m/z): calc. for $[M-Cl]^+$ 482.12, found 482.12.

9cPt. A mixture of imine **9** (108 mg, 0.44 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (186 mg, 0.44 mmol) in an 1/1 molar ratio was stirred at room temperature in 10 mL of methanol for 4 h. The yellow precipitate was filtered in vacuo to obtain **9cPt 60** (168 mg, 77%).

Yellow solid. $\mathbf{R_f}$ (DCM/MeOH 98:2) = 0.34. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.50 (dd, J = 5.9, 1.4 Hz, 1H), 9.26 (s, J_{Pt-H} = 88.1 Hz, 1H), 8.43 (td, J = 7.7, 1.4 Hz, 1H), 8.28 (dd, J = 7.8, 1.5 Hz, 1H), 7.89 (ddd, J = 7.6, 5.8, 1.7 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.21 (ddd, J = 7.5, 5.4, 3.5 Hz, 1H), 1.94 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.4, 158.1, 148.5, 145.2, 140.3, 129.4, 128.8, 127.7, 126.2, 125.4, 72.0, 30.4. **IR** (FTIR-ATR, ν, cm^{-1}): 3034, 2983, 2920, 1242. **EA** (calc. for $C_{15}H_{16}Cl_2N_2Pt$; %): C: 36.8 (36.75); H: 3.3 (3.29); N: 5.8 (5.71). **LRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 507.07, found 507.07.

9mPt. A mixture of imine **9** (100 mg, 0.45 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (177 mg, 0.42 mmol) and sodium acetate (38 mg, 0.45 mmol), was allowed to react in refluxing methanol (15 mL) for 72 h. The orange precipitate was filtered in vacuo to obtain **9cPt** (170 mg, 84%).

Orange solid. $\mathbf{R_f}$ (DCM/MeOH 98:2) = 0.65. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.96 (s, J_{Pt-H} = 110.0 Hz, 1H), 8.92 (d, J = 5.2 Hz, 1H), 8.33 (t, J = 7.7 Hz, 1H), 8.15 – 8.05 (m, 2H), 7.41 (d, J = 6.7 Hz, J_{Pt-H} = 42.7 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.3 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 1.75 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 162.5, 160.2, 158.8, 148.2, 140.5, 134.0, 133.6, 129.5, 127.4, 124.6, 124.4, 121.7, 76.5, 30.3. **IR** (FTIR-ATR, ν, cm^{-1}): 3018, 2974, 2961, 2920, 1432, 1362. **EA** (calc. for $C_{15}H_{15}ClN_2Pt$; %): C: 39.1 (39.70); H: 3.2 (3.33); N: 6.2 (5.89). **LRMS** (ESI+, m/z): calc. for $[M-Cl]^+$ 418.09, found 418.08.

10mPt. A mixture of imine **10** (76 mg, 0.32 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (177 mg, 0.42 mmol) was allowed to react in refluxing methanol (15 mL) for 24 h. The red precipitate was filtered in vacuo to obtain **10mPt** (55 mg, 37%).

Red solid. $\mathbf{R_f}$ (DCM/MeOH 98:2) = 0.69. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.04 (s, J_{Pt-H} = 105.6 Hz, 1H), 8.17 (t, J = 7.7 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.57 (dd, J = 7.7, 1.4 Hz, 1H), 6.99 (td, J = 7.4, 1.5 Hz, 1H), 6.91 (td, J = 7.5, 1.4 Hz, 1H), 6.82 (dd, J = 7.6, 1.2 Hz, 1H), 3.01 (s, 3H), 1.72 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.9, 163.4, 159.3, 158.1, 140.0, 132.6, 131.1, 128.1, 125.2, 124.4, 124.4, 121.6, 75.6, 30.4, 25.5. **IR** (FTIR-ATR, ν, cm^{-1}): 3037, 2977, 2923, 1454, 1429. **EA** (calc. for $C_{16}H_{17}ClN_2Pt$; %): C: 40.9 (41.08); H: 3.5 (3.66); N 6.0 (5.99). **LRMS** (ESI+, m/z): calculada para $[M-Cl]^+$ 432.10, encontrada 432.10.

11cPt. A mixture of imine **11** (80 mg, 0.41 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (173 mg, 0.41 mmol) and sodium acetate (34 mg, 0.41 mmol), was allowed to react in refluxing methanol (15 mL) for 24 h. The greenish precipitate was filtered in vacuo to obtain **11cPt** (118 mg, 63%).

Greenish solid. $\mathbf{R_f}$ (DCM/MeOH 97:3) = 0.60. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.91 (dd, J = 5.8, 0.8 Hz, 1H), 8.86 (s, 1H), 7.92 (td, J = 7.8, 1.5 Hz, 1H), 7.71 (ddd, J = 7.8, 1.6, 0.7 Hz, 1H), 7.46 (ddd, J = 7.6, 5.8, 1.6 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.99 – 6.85 (m, 3H), 4.87 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 172.1, 156.9, 149.0, 140.7, 136.2, 129.2, 128.9, 128.8, 128.6, 128.0, 60.7. **IR** (FTIR-ATR, ν, cm^{-1}): 3157, 3024, 1555, 1406. **EA** (calc. for $C_{13}H_{12}Cl_2N_2Pt$; %): C: 32.5 (33.78); H: 2.3 (2.62); N: 6.1 (6.06). **LRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 479.04, found 479.04.

12cPt. A mixture of imine **12** (147 mg, 0.70 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (295 mg, 0.70 mmol) and sodium acetate (57 mg, 0.70 mmol), was allowed to react in refluxing methanol (15 mL) for 24 h. The greenish precipitate was filtered in vacuo to obtain **12cPt** (64 mg, 20%).

Brown solid. $\mathbf{R_f}$ (DCM/MeOH 98:2) = 0.50. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, J = 4.9 Hz, 1H), 8.42 (d, J = 3.7 Hz, J_{Pt-H} = 95.1 Hz,

1H), 8.09 (td, *J* = 7.8, 1.4 Hz, 1H), 7.71 (dd, *J* = 8.0, 3.9 Hz, 1H), 7.66 (ddd, *J* = 7.6, 5.6, 1.4 Hz, 1H), 7.50 – 7.37 (m, 5H), 6.41 (q, *J* = 6.2 Hz, 1H), 1.92 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 157.4, 150.4, 139.5, 138.2, 129.5, 129.3, 128.7, 128.6, 127.3, 65.1, 21.4. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3043, 2977, 2932, 1600, 1441, 1302. **HRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 493.0520, found 493.0522.

13cPt. A mixture of imine **13** (80 mg, 0.38 mmol), *cis*-$[PtCl_2(DMSO)_2]$ (160 mg, 0.38 mmol) and sodium acetate (32 mg, 0.38 mmol), was allowed to react in refluxing ethanol (10 mL) for 72 h. The precipitate was eluted in a flash chromatography column (DCM/MeOH 97:3), to obtain **13cPt** (12 mg, 6%).

Brown solid. **R_f** (DCM/MeOH 97:3) = 0.68. **1H NMR** (400 MHz, $CDCl_3$) δ 8.61 (t, *J* = 1.2 Hz, 1H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.38 – 7.34 (m, 4H), 5.36 (d, *J* = 1.1 Hz, 2H), 3.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 134.7, 131.4, 130.0, 129.4, 129.0, 125.6, 62.2, 28.1. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3046, 2951, 2920, 2850, 1463, 1261. **HRMS** (ESI+, m/z): calc. for $[M+NH_4]^+$ 493.0520, found 493.0516.

14mPt. A mixture of imine **14** (104 mg, 0.38 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (160 mg, 0.38 mmol) was allowed to react in refluxing methanol (15 mL) for 24 h. The brown precipitate was filtered in vacuo to obtain **14mPt** (118 mg, 62%).

Brown solid. **R_f** (DCM/MeOH 98:2) = 0.85. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.32 (s, J_{Pt-H} = 107.6 Hz, 1H), 10.03 (dd, *J* = 8.8, 1.0 Hz, 1H), 8.96 (d, *J* = 8.3 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.99 (ddd, *J* = 8.7, 6.8, 1.6 Hz, 1H), 7.87 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.05 (td, *J* = 7.3, 1.4 Hz, 1H), 6.97 (td, *J* = 7.4, 1.6 Hz, 1H), 6.87 (dd, *J* = 7.6, 1.6 Hz, 1H), 1.80 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.1, 159.7, 159.2, 148.6, 141.4, 132.5, 132.5, 131.3, 129.1, 128.8, 128.7, 128.2, 124.8, 124.6, 122.9, 121.8, 76.2, 30.4. **IR** (FTIR-ATR, *ν*, cm^{-1}): 3050, 3015, 2993, 2961, 2923, 1425. **EA** (calc. for $C_{19}H_{17}ClN_2Pt$; %): C: 44.7 (45.29); H: 3.2 (3.40); N: 5.3 (5.56). **LRMS** (ESI+, m/z): calc. for $[M-Cl]^+$ 468.10, found 468.10.

ASSOCIATED CONTENT

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H-NMR and ^{13}C spectra.

Table S1. Crystal data and structure refinement for **7mPt** (pdf).

Table S2. Crystal data and structure refinement for **10mPt** (pdf).

Table S3 Values of k_{obs} for all the systems studied as a function of temperature and pressure.

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The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the Ministerio de Economía y Competitividad: grant numbers CTQ2015- 65040-P, 2017SGR474, SAF2017-83813-C3-1-R, PCI2018-092997 and PID2019-107006GB-C21.

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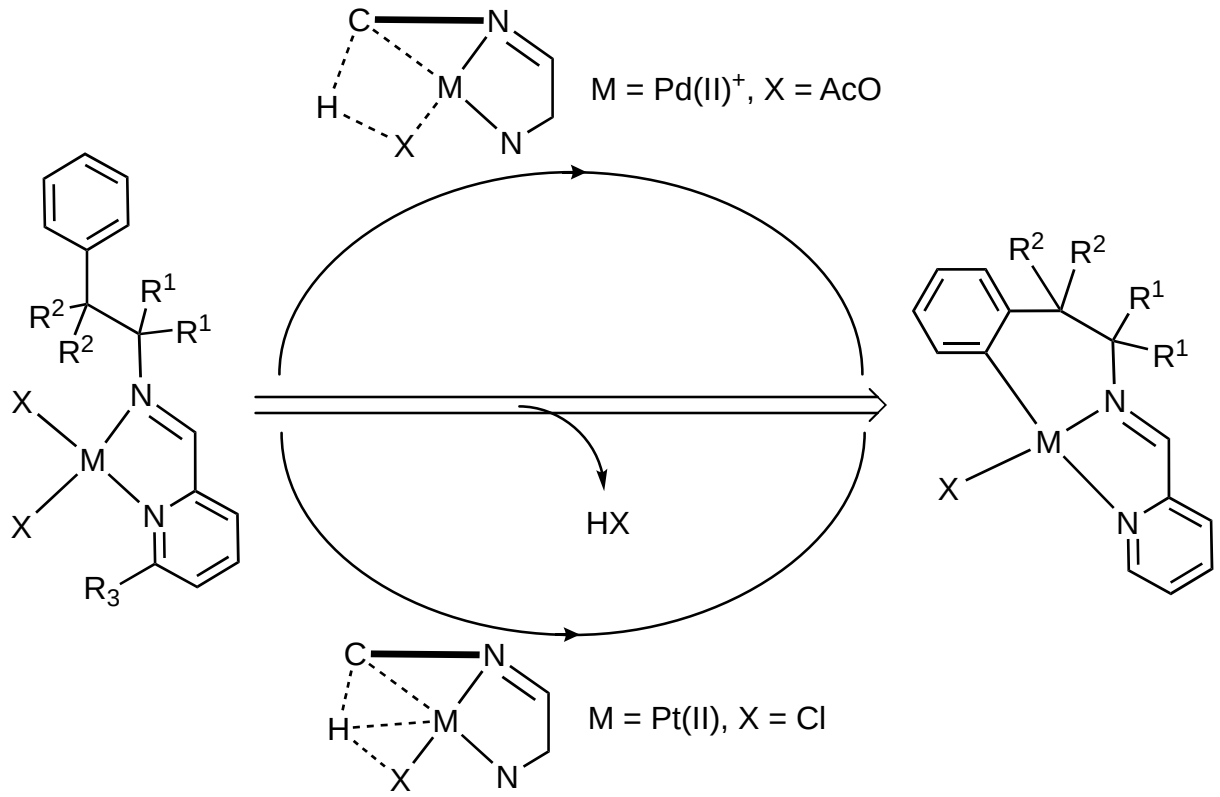
(35) (a) Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. Palladium(II) and platinum(II) alkyl sulfoxide complexes. Examples of sulfur-bonded, mixed sulfur- and oxygen-bonded, and totally oxygen-bonded complexes. *Inorg. Chem.* **1972**, *11*, 1280–1284. (b) Kukushkin, V. Y.; Pombeiro, A. J. L.; Ferreira, C. M. P.; Elding, L. I. Dimethylsulfoxide Complexes of Platinum(II): $K[PtCl_3(Me_2SO)]$, *cis*-$[PtCl_2L(Me_2SO)]$ (L = Me_2SO, MeCN),

[PtCl(μ-Cl)(Me_2SO)]$_2$, and [Pt(Me_2SO)$_4$](CF_3SO_3)$_2$ *Inorg. Synth.* **2002**, *33*, 189–196.

Insert Table of Contents artwork here


C
N
M
H
X
N
M = Pd(II)+, X = AcO
R2
R1
R2
R1
X
N
M
X
N
R3
HX
R2
R2
R1
R1
N
M
X
N
C
N
M
H
X
N
M = Pt(II), X = Cl