

Unprecedented intermolecular C–H bond activation of a solvent toluene molecule leading to a seven-membered platinacycle†

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A novel platinum-mediated process involving intermolecular activation of a C_{aryl}–H bond of toluene, intramolecular activation of an imine C_{aryl}–Cl bond and formation of a C–C bond is reported.

The reactions of hydrocarbon C–H bonds with organotransition metal complexes have been a major focus of research over the last two decades.¹ In particular, intermolecular aromatic C–H bond activation at platinum(II) compounds containing N-donor ligands is now well established^{2,3} and three mechanisms have been proposed: oxidative addition, σ -bond metathesis and electrophilic substitution. Progress in understanding the factors that influence the selectivity and reactivity of activation of benzene, toluene or xylenes⁴ and detection of η^2 -arene intermediates are among the most recent achievements in the field. However, there are relatively few examples of intermolecular C–H activation reactions leading to C–C coupling;⁵ one recent example leads to a biaryl ligand bridging two platinum centres in an unusual coordination mode.⁶

On the other hand, insertion of unsaturated compounds into a M–C bond is a fundamental step in many catalytic and stoichiometric reactions. In this extensive field, the insertion of unsaturated molecules into a metal–carbon bond of a metallacycle is a well-known reaction that can be useful in organic synthesis.⁷ This process has been described for unsaturated molecules such as alkynes, alkenes or isonitriles and, recently, the first example of insertion of nitriles into a late-transition-metal–carbon bond has been reported.⁸

Here we present the first example of a formal toluene insertion into a metal–carbon bond, by means of an unprecedented process involving intramolecular activation of a C_{aryl}–Cl bond of an imine, an intermolecular activation of a C_{aryl}–H bond of toluene and the formation of a new carbon–carbon bond, between a toluene molecule and the benzal ring of the imine.

The synthesis of platinum metallacycles has been extensively studied and it should be noted that, in all the reported reactions using *cis*-[PtCl₂(dmsO)₂] as the metallation substrate, the obtained platinacycles derived from imines contain the C=N functionality (*endo*-metallacycles).⁹ In order to explore the synthetic ability of

the platinum(II) sulfoxide complex in the preparation of *exo*-platinacycles, the reactions of *cis*-[PtCl₂(dmsO)₂] with 2,6-Cl₂C₆H₃CH=NCH₂(4-XC₆H₄) (**1a**, X = H; **1b**, X = Cl) were planned, with the aim that the chloro substituents in the *ortho* positions of the benzal ring, would favour the formation of the less common *exo*-platinacycles.

Following the procedures indicated in the literature,⁹ the reactions were carried out using *cis*-[PtCl₂(dmsO)₂], the imine **1a** or **1b** and NaOAc in a 1 : 1 : 1 ratio and heating the obtained mixture in refluxing methanol for 48 h. The reactions produced the expected cyclometallated platinum(II) compounds [PtCl{(2,6-Cl₂C₆H₃)CHNCH₂(4-XC₆H₃)}{SOMe₂}] (**2a**, X = H; **2b**, X = Cl) in extremely low yields along with the formation of large amounts of metallic platinum. In order to improve the obtained yields, the reactions of equimolar amounts of *cis*-[PtCl₂(dmsO)₂], the corresponding imine and sodium acetate (dissolved in a small amount of methanol) were carried out in dry toluene under nitrogen heating the reaction mixture at 90 °C for 48 h. These reactions lead to white (**3a**) or light yellow (**3b**) crystals in addition to *exo*-platinacycles **2a** and **2b**. Compound [PtCl{(MeC₆H₃)ClC₆H₃CHNCH₂(4-ClC₆H₄)}{SOMe₂}] (**3b**) was crystallised in dichloromethane–methanol from the crude product while [PtCl{(MeC₆H₃)ClC₆H₃CHNCH₂C₆H₅)}{SOMe₂}] (**3a**) was crystallised after purifying the crude product by column chromatography (silica, ethyl acetate : hexane = 100 : 20). The new compounds depicted in Scheme 1 arise from a novel process leading to seven-membered platinacycles *via* a formal insertion of a solvent toluene molecule.

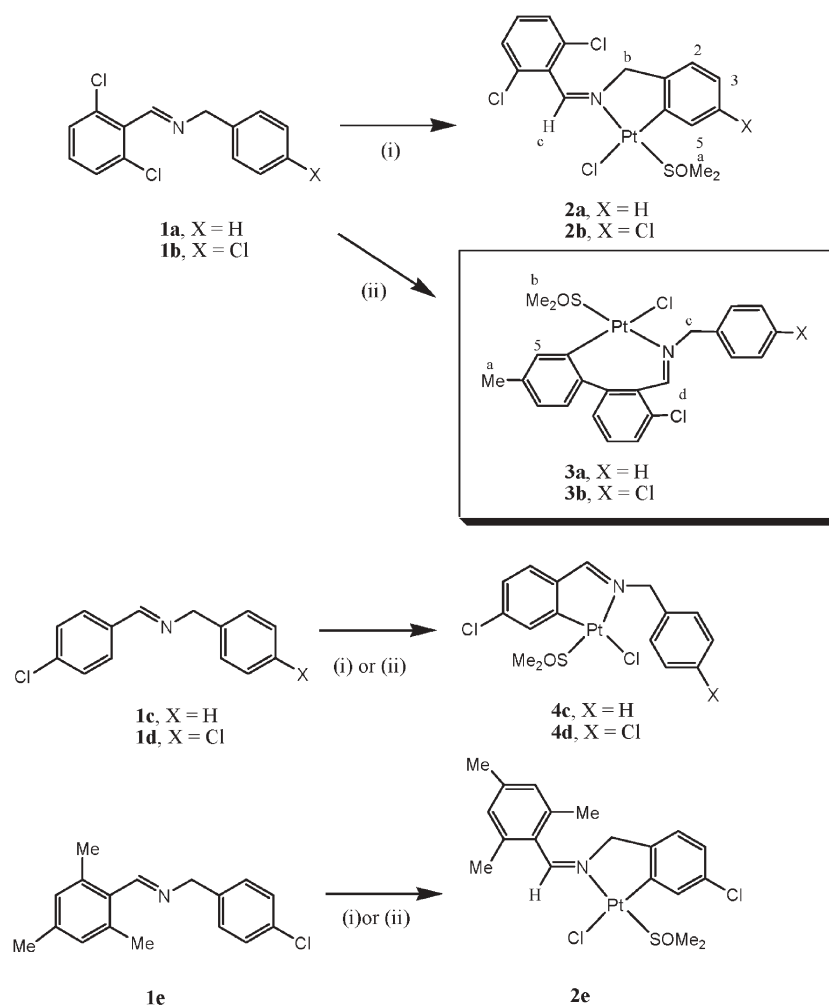
When the same reaction was performed with the imines 4-ClC₆H₃CHNCH₂(4-XC₆H₄) (**1c**, X = H; **1d**, X = Cl) and Me₃C₆H₂CHNCH₂(4-ClC₆H₃) (**1e**) the insertion of toluene was not detected and the expected complexes were obtained: the *endo*-metallacycles [PtCl{(4-ClC₆H₃)CHNCH₂(4-XC₆H₄)}{SOMe₂}] (**4c**, X = H; **4d**, X = Cl), in the case of imines **1c** and **1d** and the corresponding *exo*-derivative [PtCl{(MeC₆H₃)ClC₆H₃CHNCH₂(4-ClC₆H₃)}{SOMe₂}], **2e**, in the case of imine **1e**.

These results show that the presence of C–Cl bonds in the *ortho*-position of the imine plays a crucial role in this process. Furthermore, compounds **3a** and **3b** could also be obtained using [Pt(OAc)₂(dmsO)₂] as platinum substrate, which suggest that the chloro bound to platinum in the final product arises from *ortho* C–Cl bond activation.

In order to rule out the possibility that *exo*-metallacycles could be precursors of compounds **3**, an equimolar mixture of **2b** and NaOAc (in a small amount of methanol) was heated at 90 °C for 48 h, after which time the *exo*-metallacycle was recovered

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for all new compounds. See DOI: 10.1039/b608666g



(i): + *cis*-[PtCl₂(dmsO)₂] + Na(CH₃CO₂) (1:1:1) in MeOH, 65°C, 48h;

(ii): + *cis*-[PtCl₂(dmsO)₂] + Na(CH₃CO₂)/ MeOH (1:1:1) in toluene, 90°C, 48h.

Scheme 1

unchanged. In addition, when the reaction of compound [Pt(OAc)₂(dmsO)₂] and imine **1b** was carried out in d⁸-toluene (90 °C, 48 h), no changes were observed in the ¹H NMR spectrum for the signals corresponding to the imine protons, which indicates that H–D exchange does not occur.

Seven-membered metallacycles analogous to those obtained for **3a** and **3b** have been obtained in the reactions of *cis*-[PtPh₂(SMe)₂] with imines 2-BrC₆H₄CH=NCH₂Ph¹⁰ or RCH=NCH₂CH₂NMe₂ (R = 2,6-C₆Cl₂H₃; 2-ClC₆H₄)¹¹ (structures **I**, **IIa**, and **IIb** in Chart 1) as a result of formal insertion of a phenyl ligand in the cyclometallated Pt–C bond, previously formed *via* C–Br or C–Cl bond activation, and elimination of a C₆H₆ molecule.

The process here reported is more complex since it requires both intramolecular C_{aryl}–Cl activation of the coordinated imine to produce a [C,N]-metallacycle and intermolecular C_{aryl}–H bond activation of the toluene molecule presumably to form a σ-bond Pt–C_{aryl} with elimination of HCl, as previous steps to undergo the formal insertion of toluene in the metallacycle with elimination of

another HCl molecule. It seems that the presence of sodium acetate which facilitates HCl elimination and the lability of SOMe₂¹² in the plausible platinum(IV) intermediates, arising from intramolecular activation of *ortho*-C–Cl bonds, enable this unprecedented process at platinum.

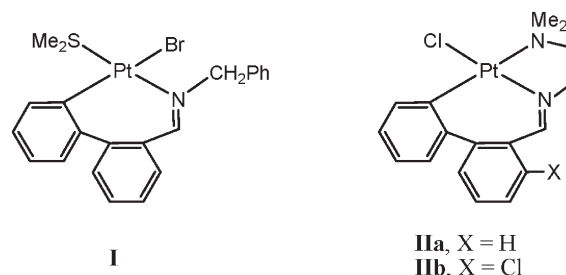


Chart 1 Reported seven-membered metallacycles.

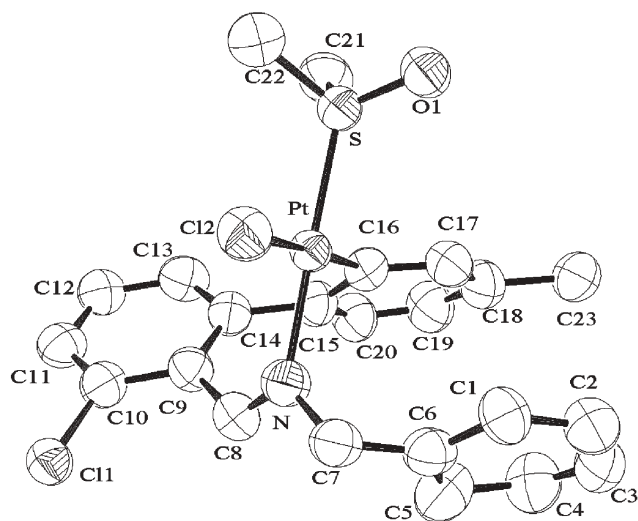


Fig. 1 Molecular structure of compound **3a** showing 50% probability ellipsoids.

All compounds were characterised by elemental analyses, mass spectra, and NMR spectroscopy,¹³ and compound **3a** was also characterised crystallographically (see Fig. 1).¹⁴ In both the ¹H NMR spectra of compounds **3a** and **3b**, in addition to the main set of signals, resonances due to minor isomer (abundance ca. 20% (**3a**) and 30% (**3b**)) with the same spectral pattern were observed. Studies concerning activation of aromatic C–H bonds of toluene⁴ indicate a selectivity order C–H (*meta*) > C–H (*para*) > C–H (*ortho*); therefore, the major isomer could be assigned to that with a *meta* arrangement between the Pt–C bond and the methyl substituent (as in the crystal structure of **3a**) and the minor isomer could correspond to the *para* isomer. A singlet resonance coupled to platinum at 6.63 (**3a**) or 6.56 ppm (**3b**) corresponding to the major isomer is assigned to the aromatic proton adjacent to the Pt–C bond.

In conclusion, the formal insertion of toluene, a typical “innocent” solvent, into platinum–carbon bonds affords seven-membered metallacycles in the reaction of *cis*-[PtCl₂(dms)₂] with imines **1a** and **1b**. This process is an example of intermolecular C–H activation leading to C–C coupling to produce a metallated biphenyl. This result can be related to the Shilov mechanism for platinum(II) mediated C–H bond activation which requires oxidation of platinum(II) to platinum(IV) and indeed a recent review² pointed out that cyclometallated compounds could be promising candidates for developing C–H activation chemistry of platinum.

Further work aimed at clarifying the toluene insertion described here, and expanding the process to other aromatic hydrocarbons is currently in progress.

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- Experimental procedures and characterization data for all the new compounds reported here are given in the Supporting Information.† In the ¹H NMR spectra of **2a**, **2b**, **2e**, **3a**, **3b**, **4c** and **4d**, the coupling to platinum observed for the imine and the methylene protons as well as for the aromatic hydrogen adjacent to the metallation site are diagnostic of formation of a bidentate [C,N] chelate system. The *J*(H–Pt) values for the imine in the range 112.8–116.8 Hz for **3a**, **3b**, **4c** and **4d** or in the range 50.0–52.7 for **2a**, **2b** and **2e** indicate, respectively, a conformation E or Z around the C=N bond. For **3a** and **3b**, the methyl groups of the dimethylsulfide ligand and the methylene protons appear as non-equivalent, consistent with the lack of planarity of the metallacycle. The presence of the methyl substituent in the tolyl group is confirmed by the corresponding signal in the ¹H NMR spectra.
- CCDC-299686 contain the supplementary crystallographic data for compound **3a**: C₂₃H₂₃Cl₂NOPtS, *M*_w = 627.47, monoclinic, space group *P*2₁/*a*, *a* = 10.301 (5) Å, *b* = 22.018(9) Å, *c* = 10.850 (4) Å, β = 109.34°, *V* = 2322.0 (17) Å³, *Z* = 4, μ = 6.337 mm^{−1}, number of reflections collected/unique = 18892/5735 [*R*(int) = 0.0605], final *R* indices [*I* > 2σ(*I*)] *R*₁ = 0.0281, *wR*₂ = 0.0724, *R* indices (all data) *R*₁ = 0.0410, *wR*₂ = 0.0921, GOF = 1.191. The methyl H atoms at C23 were generated using the SHELXL HFIX 33 command and their orientation may not be totally reliable.