

# Unprecedented C–H bond oxidative addition of the imidazolium cation to Pt<sup>0</sup>: a combined density functional analysis and experimental study

David S. McGuinness,<sup>a</sup> Kingsley J. Cavell<sup>\*b</sup> and Brian F. Yates<sup>\*a</sup>

<sup>a</sup> School of Chemistry, University of Tasmania, GPO Box 252-75 Hobart, Tasmania 7001, Australia

<sup>b</sup> Department of Chemistry, Cardiff University, PO Box 912, Cardiff, UK CF1 3TB. E-mail: cavellkj@cf.ac.uk

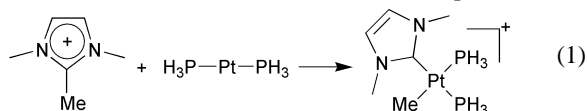
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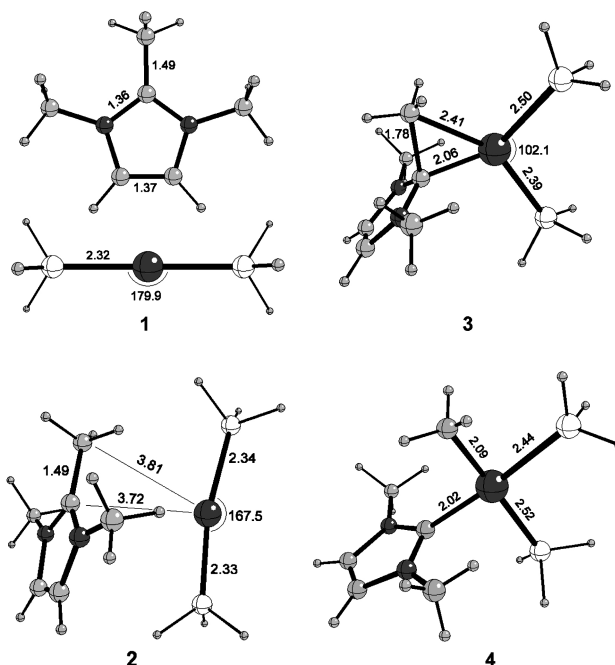
Density functional studies predict that oxidative addition of an imidazolium salt to a Pt<sup>0</sup> complex is an exothermic process, and consistent with this proposal, the reaction of the 1,3-dimethylimidazolium cation with Pt(PPh<sub>3</sub>)<sub>4</sub> yields a hydrido–Pt<sup>II</sup> carbene complex.

Heterocyclic carbene complexes of transition metals have been reported to act as precatalysts for a variety of reactions,<sup>1</sup> in particular complexes of the group 10 metals have been found to catalyse a number of C–C couplings.<sup>2–5</sup> In recent reports we have shown that heterocyclic carbene complexes of Pd<sup>II</sup> and Ni<sup>II</sup> which contain alkyl, aryl or acyl groups may decompose *via* elimination of 2-organyl imidazolium salts,<sup>4,6,7</sup> and that this reaction occurs *via* concerted reductive elimination of the hydrocarbyl and carbene moieties.<sup>8</sup> Inasmuch as hydrocarbyl–metal species are considered to be intermediates in many catalytic reactions, this reaction represents a significant pathway for catalyst deactivation. As a method of catalyst stabilisation, it seems possible that the energetics of this reaction may be shifted such that the oxidative addition of imidazolium to M<sup>0</sup> is favoured over reductive elimination. Related to this, the use of group 10 metals for catalysis in imidazolium based ionic liquids (ILs) is common, and in several cases heterocyclic carbene complexes have been implicated as the active species.<sup>9,10</sup> A recent report on the use of Pd<sup>0</sup> complexes in imidazolium based ionic liquids<sup>11</sup> prompted us to report our results of a density functional theoretical study, which shows oxidative addition of imidazolium to Pt<sup>0</sup> to be energetically feasible, and experimental results which confirm this.

As oxidative addition to Pt<sup>0</sup> is expected to be more favourable than to Pd<sup>0</sup>,<sup>12</sup> the oxidative addition of the 1,2,3-trimethylimidazolium cation to Pt(PH<sub>3</sub>)<sub>2</sub> was modelled† [eqn. (1)]. The



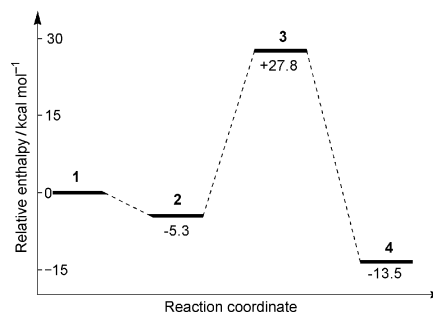
2-methylimidazolium cation was studied instead of 2*H*-imidazolium to allow comparison with the same reaction with Pd.<sup>8</sup> Furthermore, this reaction is the reverse of the ubiquitous reductive elimination reaction we have observed for hydrocarbyl–Pd carbene complexes.<sup>4,6–8</sup> Optimised geometries of the reactants **1**, precursor complex **2**, transition structure **3** and product **4** are shown in Scheme 1 while a potential energy profile for the reaction is shown in Fig. 1. The first step in the reaction yields the precursor complex **2** with a stabilisation energy of 5.3 kcal mol<sup>-1</sup>. The initially linear PH<sub>3</sub> groups are slightly distorted such that the angle between them is 167.5°, however the imidazolium cation remains unchanged indicating a weak interaction with Pt. The transition structure **3** lies 33.1 kcal mol<sup>-1</sup> above **2**, giving an apparent activation enthalpy ( $\Delta H^\ddagger$ ) of 27.8 kcal mol<sup>-1</sup> relative to the separated reactants. The Me–C<sub>carbenoid</sub> distance increases to 1.78 Å in the transition structure and the Pt–C<sub>carbenoid</sub> distance is short at 2.06 Å. Importantly, the product of oxidative addition lies 13.5 kcal mol<sup>-1</sup> below the reactants, showing that oxidative addition is



**Scheme 1** Optimised geometries (Å and °) of the reactants **1**, precursor complex **2**, transition structure **3** and product **4**.

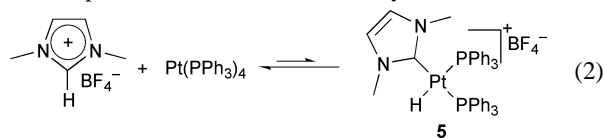
predicted to be exothermic. In contrast, oxidative addition to the analogous Pd system is found to be slightly endothermic.<sup>8</sup> The Gibbs free energy change of the gas phase reaction ( $\Delta G_{\text{react}}$ ) is predicted to be 0.1 kcal mol<sup>-1</sup>, indicating that oxidative addition should proceed to some extent.

To date we have not been able to observe oxidative addition of the 1,2,3-trimethylimidazolium cation to Pt<sup>0</sup> (or Pd<sup>0</sup>). However, oxidative addition of a C–H bond is known to proceed with a lower barrier than oxidative addition of a C–C bond. Furthermore, imidazolium salts used as ILs are usually unsubstituted and have a proton in the 2-position. We therefore studied the reaction of 1,3-dimethylimidazolium tetrafluoroborate with Pt(PPh<sub>3</sub>)<sub>4</sub>. Heating equimolar quantities of the imidazolium salt and Pt(PPh<sub>3</sub>)<sub>4</sub> in refluxing THF resulted in the formation of *ca.* 15% (by NMR) of the oxidative addition



**Fig. 1** Potential energy profile for oxidative addition.

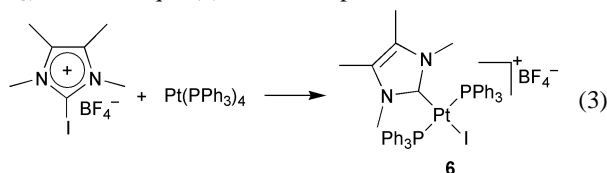
product *cis*-[PtH(1,3-dimethylimidazolin-2-ylidene)(PPh<sub>3</sub>)<sub>2</sub>]-BF<sub>4</sub> **5** relative to unreacted imidazolium and Pt(PPh<sub>3</sub>)<sub>4</sub> [eqn. (2)]. Complex **5** was identified by <sup>1</sup>H, <sup>31</sup>P NMR



and HRMS. The <sup>1</sup>H NMR spectrum of **5** features a doublet of doublets centred at  $\delta -5.23$  ( $J_{\text{PH}} 19, 176$  Hz) with Pt satellites ( $J_{\text{PtH}} 511$  Hz) corresponding to PtH. The <sup>31</sup>P NMR spectrum of **5** gives rise to two doublets ( $J_{\text{PP}} 18$  Hz) at  $\delta 24.0$  and  $20.1$  with Pt satellites ( $J_{\text{PtP}} 654, 663$  Hz). To the best of our knowledge, this is the first example of oxidative addition of a C–H bond to a Pt<sup>0</sup> complex that does not contain a chelating ligand,<sup>13</sup> which was thought to be requisite for this reaction.<sup>12</sup>

Attempts to drive the reaction to completion by heating the reactants to 150 °C in DMSO resulted in approximately the same amount of oxidative addition product relative to the reactants, however, in this case the *trans* isomer of **5** was formed. This result suggests that the oxidative addition product is in equilibrium with the reactants, and the low amount of **5** results not from a high barrier to oxidative addition but rather the equilibrium concentration of the reactants and product. The  $\Delta G_{\text{react}}$  value is therefore close to zero, which is consistent with the value predicted by the calculations on the theoretical system. The formation of *trans*-**5** can be explained by a *cis*–*trans* isomerisation of *cis*-**5**, which is probably the kinetically favoured product obtained from oxidative addition. Thermally induced or polar solvent induced isomerisations of Pt carbene complexes are well known,<sup>14</sup> it is therefore not surprising that hot DMSO can promote the isomerisation. The PtH resonance for *trans*-**5** appears as a triplet ( $J_{\text{PH}} 13$  Hz) with Pt satellites ( $J_{\text{PtH}} 336$  Hz) at  $\delta -6.03$  in the <sup>1</sup>H NMR spectrum. The related complex [PtH(1,3-dimethylimidazolin-2-ylidene)(PEt<sub>3</sub>)<sub>2</sub>]-BF<sub>4</sub> has a very similar hydride resonance.<sup>14</sup>

The oxidative addition of 2-iodo-1,3,4,5-tetramethylimidazolium tetrafluoroborate has also been successfully carried out to give *trans*-[Pt(1,3,4,5-tetramethylimidazolin-2-ylidene)-(PPh<sub>3</sub>)<sub>2</sub>]-BF<sub>4</sub> **6** [eqn. (3)]. The complex has been isolated as



colourless crystals and an X-ray structure analysis carried out. Details will be reported in a full paper on this topic.

The above results indicate a potentially important method of limiting decomposition of M–carbene catalysts, by operating in a large excess of the imidazolium ion, any M<sup>0</sup> that forms as a consequence of alkyl–carbene reductive elimination may reform the M<sup>II</sup>–carbene complex through oxidative addition of the imidazolium ion. For this reason, catalysts based on heterocyclic carbene complexes should be particularly suited to reactions in imidazolium based ILs. Furthermore, these results show unambiguously for the first time that the imidazolium cation, which is usually considered an unreactive solvent when used as an ionic liquid, can react with low valent metals to give a carbene complex. While interaction of the imidazolium cation with Pd(OAc)<sub>2</sub> has been shown to yield carbene complexes,<sup>10</sup> this work shows that a basic metal salt is not necessarily required to deprotonate the imidazolium. Thus, when group 10 metal complexes, particularly M<sup>0</sup> complexes, are used in imidazolium based ILs the possibility of carbene complexes as the active species must be considered. The large excess of imidazolium present under these conditions can be expected to drive the oxidative addition reaction. It is important to note that not only does oxidative addition of an imidazolium ion produce

a carbene complex, but it also generates a metal hydride that could effectively initiate numerous catalytic processes.

In summary, density functional studies show that oxidative addition of an imidazolium cation to Pt<sup>0</sup> is possible both in terms of the activation barrier and relative energies of the reactants and product. We have experimentally demonstrated this by the reaction between Pt(PPh<sub>3</sub>)<sub>4</sub> and the 1,3-dimethylimidazolium cation, which yields the hydrido–Pt carbene complex **5**. Further theoretical and experimental studies are in progress dealing with the effect of different metals, ligands and imidazolium salts on this remarkable oxidative addition reaction. A full account of these results will be reported shortly.

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## Notes and references

† Full geometry optimisations were carried out with the use of the B3LYP<sup>15,16</sup> density functional level of theory combined with the LANL2DZ basis set which incorporates the Hay and Wadt<sup>17</sup> small-core relativistic effective core potential and double-zeta valence basis set on Pt and P together with the Dunning/Huzinaga<sup>18</sup> double-zeta basis set on other atoms. Sets of five d-functions were used in the basis sets throughout these calculations. For the optimised geometries, harmonic vibrational frequencies were calculated at the B3LYP level and zero-point vibrational energy corrections obtained using unscaled frequencies. The vibrational frequencies were also used to obtain thermodynamic corrections and entropies. All transition structures possessed one and only one imaginary frequency, and they were further characterised by following the corresponding normal mode towards each product and reactant. All structures were treated as singlets and electronic wavefunction stability optimisations reveal no singlet–triplet instability. Finally, single-point energies on B3LYP/LANL2DZ optimised geometries were calculated at the B3LYP level with the LANL2augmented:6-311 + G(2d,p) basis set, which incorporates the LANL2TZ + (3f) basis set on platinum<sup>19</sup> and 6-311 + G(2d,p) on all other atoms.<sup>20–22</sup> The energy values in the text refer to this final level of theory. All calculations were carried out with the Gaussian 98 program.<sup>23</sup>

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