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C–H Activation of imidazolium salts by Pt(0) at ambient temperature: synthesis of hydrido platinum bis(carbene) compounds

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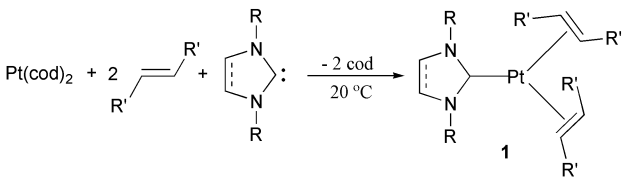
A zerovalent platinum(carbene) complex with two monoalkene ligands, which is able to activate C–H bonds of imidazolium salts at room temperature to yield isolable hydrido platinum(II) bis(carbene) compounds, has been synthesised for the first time.

Heterocyclic carbenes are being applied more and more frequently as ligands in homogeneous catalysis.[1] While initially considered as chemically inert, heterocyclic carbene complexes of palladium(II) and nickel(II) may decompose *via* elimination of 2-organyl imidazolium salts.[2] A combined kinetic and density functional study of the reaction on Pd complexes show that this process can occur with a low activation barrier.[3] The low activation barrier also indicates that this process may be reversible, so actual C–H or C–C activation could be possible. The different behaviour of carbene and non-carbene based catalysts in imidazolium based ionic liquids, compared to that in normal organic and aqueous solvents, demonstrates the importance and interest in studying the reaction behaviour of imidazolium salts.[4]

Another reason for studying these imidazolium salts is to find a better route to prepare metal carbene complexes. The most common route for preparing these complexes involves abstraction of the acidic imidazolium salts by strong bases and isolation of the free carbene.[5] Use of ligand precursors,[6] transmetallation[7] or *in situ*[8] generation of the free carbene are also methods for preparing carbene complexes. Recently, C–H activation of imidazolium salts has been reported for several late transition metals.[3,9] This direct synthesis is promising, because no extra step is required, nor are any undesired side-products obtained. The way in which these reactions proceed remains unclear. Although double C–H activation in the palladium systems has been reported, no metal hydride compounds were isolated. In the case of platinum, platinum carbene hydride complexes were obtained in low to moderate yields.[3]

In view of the lack of isolated C–H activation products of this kind for the late-transition metals and the known *trans*-stabilising propensities of carbene ligands,[10] we decided to study a new class of platinum(0) complexes containing one carbene ligand and two labile alkenes as substrates for investigating the oxidative addition of C–H bonds of imidazolium cations to platinum(0).

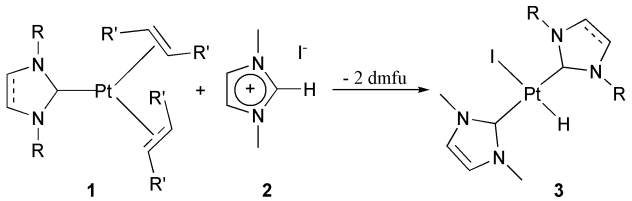
Accordingly, we synthesised the Pt(carbene)(η^2-alkene)$_2$ complexes (**1**)[11] by reaction of 1 equivalent of the free carbene, 1 equivalent of Pt(cod)$_2$ and 2 equivalents of alkene in THF at room temperature (Scheme 1). The white, solid products were obtained in good yield (55–73%). These complexes can be handled safely in air and are also stable for extended periods in solution, even in refluxing acetone. Their stability is surprising, taking into account that the complex may easily loose an alkene.



R = Mes, R' = COOMe, **a** = unsat. carbene, **b** = saturated carbene

Scheme 1 Synthesis of platinum(carbene)(η^2-alkene)$_2$ complexes.

Indeed, compounds **1a** and **1b** are reactive towards C–H bonds of certain imidazolium salts. When we add one or more equivalents of imidazolium salt like IMeHI (**2**) (IMe = 1,3-dimethylimidazol-2-ylidene) to a solution of **1** in THF or acetone, C–H activation selectively takes place at the C-2 position of the imidazolium cation to form the first example of a thermally stable hydridoplatinum(II) biscarbene (**3**).[12] (Scheme 2)



R = Mes, R' = COOMe, **a** = unsat. carbene, **b** = saturated carbene

Scheme 2 C–H activation of imidazolium salts.

A particularly novel aspect of this reaction is the use of a strong donor carbene ligand to increase electron density on the metal centre, making the platinum more reactive towards C–H activation, and subsequently generating a mixed carbene complex. The carbene/imidazolium salt couple is acting as both ligand and substrate.

The product has been characterised by means of ^{1}H, ^{13}C and ^{195}Pt NMR spectroscopy and appears to consist of a square planar platinum complex with two different carbene units in mutual *trans* positions confirmed by ^{1}H-NOE experiments. The hydride was observed at −14.67 ppm for **3a** and at −14.50 ppm for **3b** and exhibited one bond scalar coupling to platinum of 1727 Hz (**3a**) and 1738 Hz (**3b**). This is in agreement with a weak *trans*-ligand such as iodide, but such high values for the $^1J(^{195}\text{Pt},^1\text{H})$-couplings have not been reported before. This is probably due to the presence of two carbenes, which are known toexhibit mainly σ-donating properties.[13] The iodide is co-ordinated—the addition of a weak or strong ligand (*e.g.* acetonitrile, pyridine) does not displace the iodide, as observed by ^{1}H and ^{195}Pt NMR spectroscopy. Successive addition of pyridine and silver tetrafluoroborate to **3b** gives a cationic platinum complex (**3c**). In the ^{1}H NMR spectrum, this complex shows a hydride signal at −16.64 ppm with platinum satellites, $^1J(^{195}\text{Pt},^1\text{H})$ = 989 Hz, indicating the substitution of the iodide. The smaller coupling can be attributed to the coordination of the pyridine, stabilising the cationic platinum centre.

We first performed the C–H activation in refluxing THF or acetone (full conversion in 1 h), but we later found that this reaction even occurs at room temperature. Full conversion to the product **3** has been obtained within 4–7 days at 20 °C. As far as we know this is the first reported C–H activation by Pt(0) under

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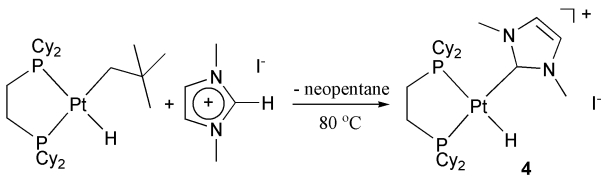
these very mild conditions. Another exciting feature of this reaction is that it proceeds without an assisting 'handle' such as coordination to a heteroatom.[9] This reaction is clearly an intermolecular process because pre-coordination of the imidazolium salt seems impossible. After the reaction the dimethylfumarate is found as the free molecule.

The explanation as to why this reaction can take place at room temperature can be found in the relatively labile coordination of the dimethylfumarate (DMFU) and in the high electron density on the platinum centre. An indication of the high electron density may be obtained from the ^{195}Pt NMR. The chemical shifts of the ^{195}Pt nucleus are indicative of oxidation states and electron density. ^{195}Pt chemical shifts of −5184 and −5200 ppm are found for the complexes (IMes)Pt(DMFU)$_2$ (**1a**) (IMes = 1,3-dimesitylimidazol-2-ylidene) and (SIMes)Pt(DMFU)$_2$ (**1b**) (SIMes = 1,3-dimesityldihydroimidazol-2-ylidene), respectively. Recently, another Pt(0) monocarbene complex with alkenes has been published with a chemical shift for the platinum of −5343 ppm,[14] Comparing our complexes with this complex and with the platinum(0) biscarbene (−5697 ppm) described by Arduengo *et al.*,[15] indicates that the oxidation state of **1a** and **1b** is zero, and that the electron density on the platinum centre for all complexes is quite similar.[16]

For comparison, we also evaluated the familiar Whitesides complex, which is a well established compound for activating C–H bonds.[17] Whitesides method (Scheme 3) was employed to generate *in situ* the very reactive unsaturated [Bis(dicyclohexylphosphino)ethane]platinum(0) species.



Scheme 3 C–H activation of imidazolium salts using Whitesides method.

When the imidazolium salt **2** was added to a solution of *cis*-bis(dicyclohexylphosphino)ethane]hydridoneopentylplatinum(II) in 1,4-dioxane–acetone, and the mixture was heated overnight at 80 °C, we obtained **4** as the main product in good to excellent yield(70–90%).[18]

Clearly, in this case the C–H activated product is also obtained, as apparent from ^{1}H and ^{31}P NMR spectroscopy. The hydride of **4** is found at −2.68 ppm as a doublet of doublets with platinum satellites. ^{31}P{^{1}H}-spectroscopy showed the expected pattern with platinum satellites. As described for the cationic complex **3c**, the ^1J{Pt,H}-couplings for **4** are also slightly larger than those reported in the literature.[19] A drawback of this method is that more bulky imidazolium salts cannot be activated, because the bulky cyclohexylgroups on the phosphorus are needed to prevent cycloplatination of the ligand. Use of different and smaller N-heterocyclic carbenes as ligands in the Pt(carbene)(η^2-alkene)$_2$ systems are now under investigation to demonstrate the principle of C–H activation of imidazolium salts in a broader sense.

In conclusion, the first examples of zerovalent platinum mono-carbene bis(alkene) complexes have been obtained as stable solids that react selectively with C–H bonds in the 2-position of imidazolium salts. As far as we know this is the first C–H activation at room temperature using Pt(0) complexes. The product of this C–H activation is a platinum(II) biscarbene hydride, in which the two different carbenes are orientated in a *trans* fashion. This method of C–H activation has been compared to the well known Whitesides system and found to be more effective.

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11 A full paper concerning the synthesis and reactivity of the complexes **1** will be published elsewhere. **1a**: ^{1}H NMR (500 MHz, acetone-d$_6$, δ(ppm)): 7.61 (2H, s, ^4J{^{195}Pt,^{1}H} 10.5 Hz), 7.08 (2H, s), 6.96 (2H, s), 3.92 (2H, d, ^3J{^{1}H,^{1}H} 9.0 Hz, ^2J{^{195}Pt,^{1}H} 46.0 Hz), 3.40 (6H, s), 3.30 (6H, s), 3.13 (2H, d, ^3J{^{1}H,^{1}H} 9.0 Hz, ^2J{^{195}Pt,^{1}H} 63.0 Hz), 2.39 (6H, s), 2.35 (6H, s), 1.80 (6H, s). ^{13}C NMR (125.7 MHz, acetone-d$_6$, δ(ppm)): 172.27, 170.69 (^2J{^{195}Pt,^{13}C} 38.0 Hz), 169.14 (^2J{^{195}Pt,^{13}C} 36.0 Hz), 138.38, 136.21 (^3J{^{195}Pt,^{13}C} 9.0 Hz), 135.40, 135.34, 129.42, 129.13, 124.90 (^3J{^{195}Pt,^{13}C} 42.2 Hz), 50.22 (^1J{^{195}Pt,^{13}C} 146.6 Hz), 50.16, 50.13, 48.98 (^1J{^{195}Pt,^{13}C} 191.1 Hz), 20.41, 18.75, 17.51. ^{195}Pt NMR (acetone-d$_6$, δ(ppm)): −5184. MS (*m*/*z*): Obs: 788.2512, Calc: 788.2514. **1b**: ^{1}H NMR (500 MHz, acetone-d$_6$, δ(ppm)): 7.03 (2H, s), 6.87 (2H, s), 4.20 (2H, m), 4.05 (2H, m), 3.89 (2H, d, ^3J{^{1}H,^{1}H} 9.0 Hz, ^2J{^{195}Pt,^{1}H} 43.2 Hz), 3.49 (6H, s), 3.21 (6H, s), 3.17 (2H, d, ^3J{^{1}H,^{1}H} 9.0 Hz, ^2J{^{195}Pt,^{1}H} 52.8 Hz), 2.65 (6H, s), 2.29 (6H, s), 1.91 (6H, s). ^{13}C NMR (125.7 MHz, acetone-d$_6$, δ(ppm)): 171.51 (^2J{^{195}Pt,^{13}C} 40.0 Hz), 169.68 (^2J{^{195}Pt,^{13}C} 36.0 Hz), 138.14, 137.33, 136.90, 136.86, 130.26, 129.98, 52.93 (^3J{^{195}Pt,^{13}C} 136.5 Hz), 51.02, 50.89, 49.89 (^3J{^{195}Pt,^{13}C} 136.5 Hz), 21.13, 19.13, 18.17. ^{195}Pt NMR (acetone-d$_6$, δ(ppm)): −5200. EA: Found: 50.26 (C), 5.31 (H), 3.48 (N). Calc.: 50.19, 5.36, 3.55.
12 **3a**: ^{1}H NMR (300 MHz, acetone-d$_6$, δ(ppm)): 7.30 (2H, s, ^4J{^{195}Pt,^{1}H} 6.0 Hz), 6.97 (4H, s), 6.84 (2H, s, ^4J{^{195}Pt,^{1}H} 8.0 Hz), 3.23 (6H, br s), 2.30 (6H, s), 2.26 (12H, s), −14.67 (1H, s, ^1J{^{195}Pt,^{1}H} 1727 Hz). ^{195}Pt NMR (85.6 MHz, acetone-d$_6$, δ(ppm)): −4631. **3b**: ^{1}H NMR (300 MHz, acetone-d$_6$, δ(ppm)): 6.93 (4H, s), 6.85 (2H, br s), 4.06 (4H, s), 3.17 (6H, s), 2.53 (12H, s), 2.28 (6H, s), −14.50 (s, ^1J{^{195}Pt,^{1}H} 1738 Hz). ^{13}C NMR (125.7 MHz, acetone-d$_6$, δ(ppm)): 137.44, 136.99, 136.89, 136.17, 128.92, 120.83, 50.60 (^3J{^{195}Pt,^{13}C} 65.2 Hz), 36.27, 20.47, 19.13. ^{195}Pt NMR (85.6 MHz, acetone-d$_6$, δ(ppm)): −4634.
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18 Using this methology yields also a small amount of activation of the solvent, depending of the amount of imidazolium salt used. **4**: ^{1}H NMR (300 MHz, acetone-d$_6$, δ(ppm)): 7.45 (2H, s ^4J{^{195}Pt,^{1}H} 8.8 Hz), 3.78 (6H, s), 2.2 (4H, m) 1.1–2.0 (20H, m), −2.68 (1H, dd, ^2J{^{31}P$_{cis}$,^{1}H} 13.2 Hz, ^2J{^{31}P$_{cis}$,^{1}H} 170 Hz, ^1J{^{195}Pt,^{1}H} 1019 Hz). ^{31}P{^{1}H} NMR (121.66 MHz, acetone-d$_6$, δ(ppm)): 73.65 (^2J{^{195}Pt,^{31}P} 2394 Hz), 67.71 (^2J{^{195}Pt,^{31}P} 1754 Hz).
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