Metal–Hydride Complexes

Oxidative Addition of Imidazolium Salts to Ni0 and Pd0: Synthesis and Structural Characterization of Unusually Stable Metal–Hydride Complexes**

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Ionic liquids (ILs) and especially imidazolium-based ionic liquids have found important applications in catalysis over the last decade or so as non-aqueous solvents for biphasic catalysis.[1] Interestingly, improved catalyst stability and, in some examples, improved overall catalytic performance were observed for reactions conducted in ILs. Although ILs have been considered to be nonparticipative or "innocent" solvents, a number of reports have suggested possible formation of metal–carbene complexes in situ during the course of catalysis.[2] Deprotonation of C2 of imidazolium salts to generate N-heterocyclic carbene ligands (NHC) is well-documented.[3] A weak base is often all that is necessary to deprotonate such salts under the reaction conditions and therefore it seems likely that carbene formation may occur if a basic entity is present during catalytic reactions. This has effectively been demonstrated through isolation of carbene–metal complexes from the ionic liquid solvents used for Heck and Suzuki–Miyaura coupling reactions.[2b,c]

We have also shown, using theoretical and experimental methods, that in the absence of base, imidazolium cations can oxidatively add to a low-valent metal center of Group 10 to form carbene complexes via C2–X (X = halogen) or –H activation.[4] Stone and co-workers,[5a] and more recently Fürstner et al.[5b] utilized the oxidative addition of C2–X species in the synthesis of metal–carbene complexes. Nolan and co-workers[6a] and Crabtree and co-workers[6b] provided evidence for the oxidative addition of imidazolium salts to Pd0, although no Pd–hydride complex was isolated. Experimentally, C2–H activation and M–H formation had only been unambiguously observed with Pt0 complexes.[4b,c] We

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now report the synthesis of stable (carbene)M–hydride complexes of Ni and Pd formed by "insertion" of the metal center into the C2−H bond of imidazolium salts.
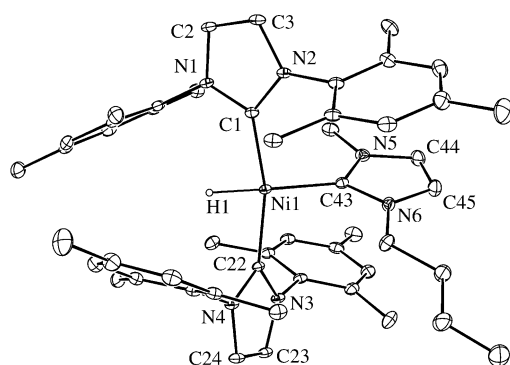
We employed electron-rich, coordinatively unsaturated L_2M^0 complexes (L = 1,3-aryl-NHC) to facilitate low-temperature oxidative addition of imidazolium salts. When equimolar quantities of various imidazolium salts **2a–c** were stirred with the Ni^0 complex **1** generated in situ,[7] the deep purple color of **1** quickly disappeared at room temperature to give a light yellow solution (Scheme 1). Concentration of the
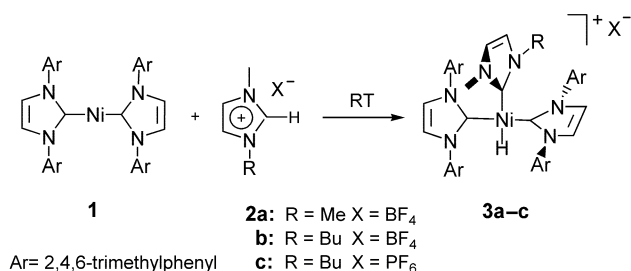
Scheme 1. C−H oxidative addition of imidazolium salts to Ni^0 complex **1**: a) THF, 5 min; b) toluene, 1 h; c) toluene, 5 min.

solution and addition of *n*-hexane led to the isolation of triscarbene–nickel–hydrido complexes **3a–c** as light-yellow crystalline solids in 70–76% yield. The Ni–H signals appear at $\delta = -14.96$, -15.02, and -15.02 ppm, respectively in the ^1H NMR spectra (CD_2Cl_2). These represent the first examples of (carbene)nickel–hydride complexes. All three complexes are surprisingly stable both in solution and in the solid state. They can be heated at reflux in THF for 16 hours without evidence of major decomposition and they can be stored under an inert atmosphere for an extended period of time. They also may be manipulated in air without any sign of degradation.

The full molecular geometry of complex **3b** was elucidated by single-crystal X-ray diffraction, and the ORTEP diagram is given in Figure 1 together with selected bond distances and angles.[8]
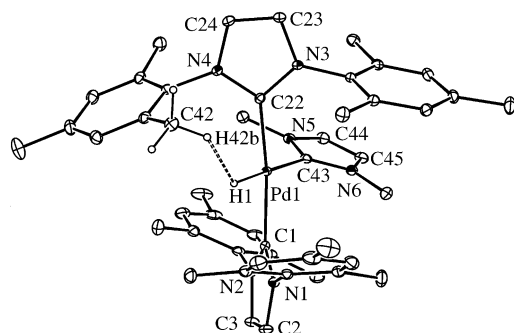

Figure 1. Molecular structure of **3b** (ORTEP diagram drawn at the 25% probability level). Selected bond lengths [Å] and bond angles [°]: Ni1-C22 1.891(3), Ni1-C1 1.895(4), Ni1-C43 1.936(4), Ni1-H1 1.38(5), C22-Ni1-C1 164.22(16), C22-Ni1-C43 98.40(15), C1-Ni1-C43 97.30(15), C22-Ni1-H1 83(2), C1-Ni1-H1 81(2), C43-Ni1-H1 179(2).

Complex **3b** exhibits a distorted square-planar geometry in which the two mesityl-substituted carbenes have a *trans* disposition. Steric crowding between the two mesityl-substituted carbenes and the 1-butyl-3-methyl-substituted carbene causes the bulky mesityl-substituted carbenes to be pushed towards the small hydride group with an angle C22-Ni-C1 of 164.22(16)°. The surprising stability of such complexes could be rationalized in terms of both steric and electronic effects imparted by the three carbene ligands. Steric bulk around the metal center hinders orbital overlap between the hydride and the carbene carbon that would favor reductive elimination of imidazolium salt.[9] As well as protecting the mesityl-substituted carbenes against reductive elimination, the bulk of these two carbenes forces the hydride to be *trans* to the 1-butyl-3-methyl-substituted carbene.

We employed a similar approach to synthesize a stable Pd–H complex from coordinatively unsaturated L_2Pd^0 complexes[10] (L = NHC). For example, when equimolar quantities of imidazolium salt **2a** and complex **4** were stirred together at 55°C in an acetone/THF mixture, the yellow color of **4** quickly disappeared to give a colorless solution (Scheme 2).

Scheme 2. C−H oxidative addition of imidazolium salt to Pd^0 complex **4**: acetone/THF, 15 min.

The triscarbene–palladium–hydrido complex **5**, which was isolated as colorless crystals in 62% yield, gives rise to a Pd–H signal at $\delta = -10.17$ ppm in the ^1H NMR spectrum (C_6D_6). As observed for its nickel counterpart, this complex is surprisingly stable both in solution and in the solid state. The full molecular geometry of **5** was elucidated by single-crystal X-ray crystallography (Figure 2).[8] This complex represents the first fully characterized palladium hydride complex with carbene ligands. During the synthesis of complex **5**, small amounts of several other palladium–hydride complexes were noted in solution in the nonrecrystallized product. A Pd–hydride complex with a ^1H NMR resonance at $\delta = -15.84$ ppm was frequently observed (a Pd–H resonance at $\delta = -14.85$ ppm was reported by Nolan and co-workers for an unidentified complex formed during the reaction of an imidazolium salt with $Pd^{0[6a]}$). We were unable to isolate or identify the complex with the resonance observed at $\delta = -15.84$ ppm.

It is interesting to note in complex **5** a possible $H^{\delta+}\cdots H^{\delta-}$ intramolecular interaction in view of the short H42b–H1 distance of 2.07 Å (significantly less than twice the van der Waals radius for H of 2.4 Å expected in the absence of an attractive interaction) together with angles Pd-H···H and

Figure 2. Molecular structure of **5** (ORTEP diagram drawn at the 25% probability level). Selected bond lengths [Å] and bond angles [°]: Pd1-C1 2.030 (2), Pd1-C22 2.031(2), Pd1-C43 2.111(2), Pd1-H1 1.57(3), C1-Pd1-C22 168.02(8), C1-Pd1-C43 95.78(9), C22-Pd1-C43 96.20(8), C1-Pd1-H1 82.0(10), C22-Pd1-H1 86.0(10), C43-Pd1-H1 177.0(10).

H···H-C of 132.0° and 129.8°, respectively. This is an unusual example of such an H···H interaction; it involves a Group 10 metal hydride (other examples involve Group 8 and 9 metals) with a hydrogen atom coordinated to a carbon atom rather than to an electronegative heteroatom, as is commonly the case.[11] Further characterization of this hydridic-to-protonic interaction will be reported elsewhere. The nickel–hydride complex also shows a similar, but less significant H–H close-approach (shortest H(Me)–H1 distance of 2.41 Å].

These observations have a number of important ramifications for NHC chemistry: a) The results show irrevocably that carbene or carbene–metal–hydride species readily form under mild conditions in the presence of imidazolium salts, especially with Group 10 metals. This is likely to occur in situ when a coordinatively unsaturated, low-valent metal species (particularly when bearing strong σ-donor ligands) are present or are formed during a reaction, for example, under catalytic conditions in an ionic liquid solvent. b) The direct generation of a carbene–M–H species in situ may provide an important atom-efficient route to active catalytic species under mild conditions. Metal–carbene complexes are being applied more and more widely in catalysis, and metal hydrides are implicated in many catalytic processes. c) The almost directional distribution of steric bulk, encapsulating sites on the metal center, and the unusual electronic features of carbene ligands allow the stabilization of normally highly reactive species.[12]

The ease of formation of complexes **3** and **5** together with their remarkable stability is an example of how NHC ligands may allow the isolation of new and normally reactive species. In summary, we have demonstrated that direct C2−H activation of imidazolium salts by coordinatively unsaturated low valent Ni and Pd complexes such as **1** and **4** can be a facile process.

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[8] Crystal data for **3b**·(CH$_2$Cl$_2$)$_2$: C$_{52}$H$_{67}$BCl$_4$F$_4$N$_6$Ni, $M = 1063.44$, monoclinic, space group $P2_1/n$, $a = 14.121(3)$, $b = 15.464(3)$, $c = 25.045(5)$ Å, $\beta = 93.12(3)°$, $V = 5460.9(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.293$ g cm^{-3}, $F(000) = 2232$, $\mu(Mo_{K\alpha}) = 0.604$ mm^{-1}, 150(2) K, 9970 unique reflections ($R_{int} = 0.0669$), R (on F) 0.0679, wR (on F^2) 0.1771 ($I > 2\sigma(I)$). Crystal data for **5**·(C$_6$H$_6$)$_{0.5}$: C$_{50}$H$_{60}$BF$_4$N$_6$Pd, $M = 938.25$, triclinic, space group $P\bar{1}$, $a = 10.697(2)$, $b = 12.118(2)$, $c = 20.101(4)$ Å, $\alpha = 102.78(3)$, $\beta = 90.78(3)$, $\gamma = 108.65(3)°$, $V = 2397.6(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.300$ g cm^{-3}, $F(000) = 978$, $\mu(Mo_{K\alpha}) = 0.442$ mm^{-1}, 150(2) K, 9770 unique reflections ($R_{int} = 0.0684$), R (on F) 0.0352, wR (on F^2) 0.0834 ($I > 2\sigma(I)$). CCDC-223 761 (**3b**) and CCDC-223 762 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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