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VIP N-Heterocyclic Carbenes

A Labile and Catalytically Active Imidazol-2-yl Fragment System**

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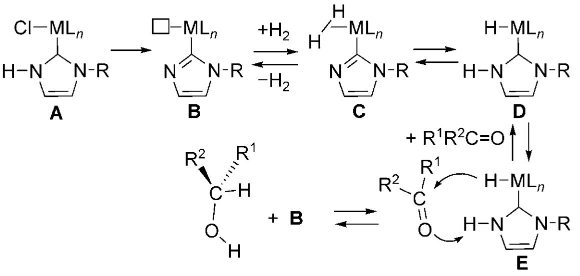
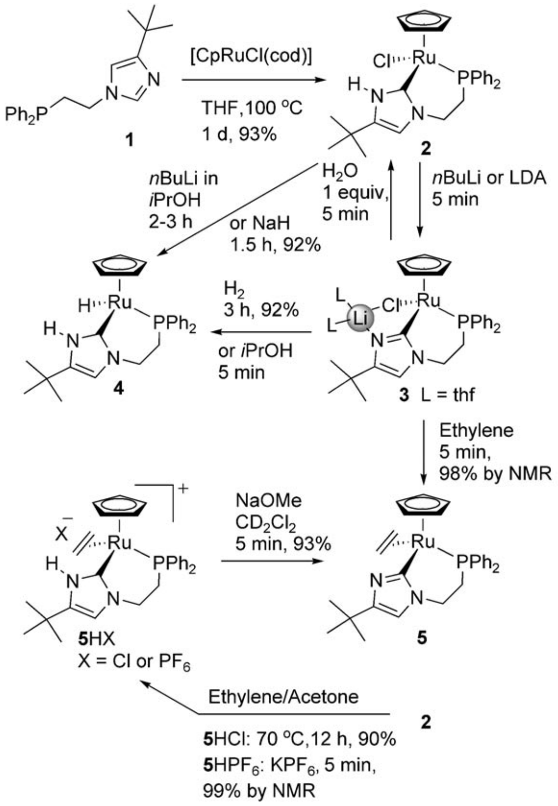
N-heterocyclic carbenes (NHCs)[1] and their complexes[2] are excellent catalysts for a broad array of organic transformations, where the NHC ligands impart useful electronic and steric properties to metal centers.[3] In these systems, with commonly used ancilliary NHC ligands that are substituted at nitrogen atom(s) by alkyl, aryl, or other groups,[2,3] all catalytic transformations take place at the metal center, which is stabilized and/or activated by the NHC ligand. However, transformations that may possibly involve both the metal center and at one ring nitrogen of the NHC ligand are much less common,[4,5c,e–g] and are limited to protic NHC complexes[4–6] or their conjugated bases. Thus, the N−H function of a protic NHC complex (**A** or **D**; Scheme 1) could behave as Brønsted acid, whereas the basic nitrogen atom in the imidazol-2-yl complex (**B** or **C**) may behave as a Brønsted base. Moreover, reactivity of **A** with a base could lead to **B**, a transient species with both a vacant metal coordination site and a basic nitrogen atom, which could bind (**C**) and activate a substrate (**C** to **D**). These reactivity patterns might also be compatible with protic NHC complexes derived from other NHC ligands.



Scheme 1. Imidazol-2-yl and imidazol-2-ylidene fragment systems. The square indicates a vacant site.

Herein, we report a versatile organometallic system in which the combined reactivity of the imidazol-2-ylidene or imidazol-2-yl fragments and the metal center lead to ligand exchange processes that involve **A** and **B**, hydrogen activation (**B**→**C**→**D**), and ultimately, catalytic behavior (**D** + ketone→**E**→**B** + alcohol). Key differences between results herein from previous work[4] include: 1) greatly enhanced rates of reaction (for example, ligand exchange within minutes instead of days); 2) the ability to tune ligand exchange rates over several orders of magnitude; and perhaps most importantly 3) catalytic behavior, which was not at all apparent before. Moreover, we show that ^{15}N chemical shift information on natural-abundance samples gives valuable information on the environment of the imidazol-2-yl or imidazolylidene ligand.

Reaction of **1**[4] with [CpRuCl(cod)] (Cp = cyclopentadienyl, cod = 1,5-cyclooctadiene) in THF at 100 °C led to phosphorus coordination and complete tautomerization of the imidazole to carbene **2**, which shows a low-field ^{1}H NMR signal ($\delta = 10.28$ ppm, NH) and a doublet in the ^{13}C{^{1}H} NMR ($\delta = 184.1$ ppm, $^2J_{CP} = 22.5$ Hz, C2) that are consistent with structure **2** (Scheme 2).



Scheme 2. Synthesis and reactivity of imidazol-2-yl and imidazol-2-ylidene complexes (in [D$_8$]THF at room temperature unless otherwise specified). Yields are of isolated products unless otherwise specified. LDA = lithium diisopropylamide.

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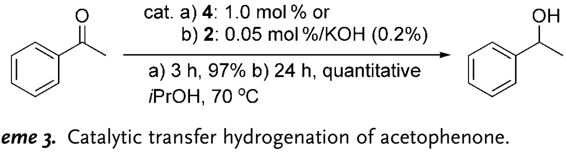
To illustrate reactivity of the protic NHC moiety toward bases, treatment of an orange-yellow solution of **2** in [D$_8$]THF with 1 equivalent of *n*BuLi (or lithium diisopropylamide, LDA) at room temperature gives a reddish-orange solution. The single organometallic product was at first tentatively formulated as **3** because its ^{1}H NMR spectrum showed absence of an NH signal and the presence of a resonance at $\delta = 2.48$ ppm in the ^{7}Li spectrum; the ^{13}C NMR spectrum contained a doublet for the imidazolyl carbon ($\delta = 175.0$ ppm, $^2J_{CP} = 31.4$ Hz).[7] Ultimately, a single crystal of this highly reactive complex was analyzed by X-ray diffraction (see below). In contrast, when *i*PrOH is used as solvent instead THF, the reaction of **2** with *n*BuLi gave hydride **4** rather than **3**; this result, along with conversion of preformed **3** into **4** by *i*PrOH, is taken as evidence of conversions of type **B**→**E**. Moreover, hydride **4** can also be synthesized by either heterolysis of hydrogen gas by **3** (**B**→**C**→**D**) or in a one-pot synthesis from **2** and NaH. The ^{1}H NMR spectrum of **4** showed the presence of an NH ($\delta = 9.13$ ppm) and a hydride ligand ($\delta = -13.06$ ppm, d, $^2J_{HP} = 36.5$ Hz). Conversion of **2** into **4** involves deprotonation of the NH group by using strong bases. When lithium-containing base *n*BuLi was used, the lithiated ruthenium complex **3** was observed spectroscopically. In contrast, when NaH reacts with **2**, the sodium analogue (**3**Na) of **3** is not seen. Reaction of **2** deuterated at the NH group (**2**ND) with NaH afforded **4** with at least 90% H at the hydride position, suggesting NaCl release with rapid transfer of the hydride to ruthenium.[8]

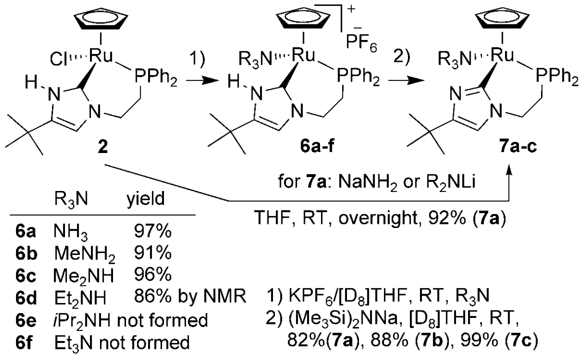
Further reactivity studies on **3** with ethylene afforded neutral complex **5**, whereas its reaction with 1 equivalent of H_2O regenerates **2** with precipitation of solid LiOH. Ethylene complex **5** can also be synthesized in two steps, first by facile ionization of **2** by saturating a solution in acetone or THF as solvent[7] with ethylene, a process requiring 12 h at 70°C, but which is carried out in 5 min at ambient temperature with the aid of KPF$_6$. Subsequent deprotonation of **5**·HCl by NaOMe readily forms **5**.

On the basis of these findings, we tested **4** as catalyst for transfer hydrogenation of acetophenone using *i*PrOH. This reaction is significant because most but not all catalysts require added base.[9] Thus, under the conditions of Scheme 3, complex **4** catalyzes the reduction of acetophenone to afford 1-phenylethanol in 97% yield, a process that may proceed as shown in **E** in Scheme 1. The conversion of acetophenone (2 M in *i*PrOH) into 1-phenylethanol using low catalyst loadings (0.05%) can also be achieved by catalyst precursor **2** and base (to generate **4** in situ) with quantitative yields.



Scheme 3. Catalytic transfer hydrogenation of acetophenone.

Reactivity studies on **2** also showed that the chloride ligand can be easily removed using KPF$_6$ in presence of suitable amines and ammonia. Treatment of a solution of **2** in [D$_8$]THF with KPF$_6$ deepens the initial orange color to slightly red, and when an amine is added, the reaction color turns to yellow instantaneously and reactions go to completion within minutes to give protic NHC complexes **6a–d** (Scheme 4). In particular, the ^{1}H spectrum of **6a** showed the presence of an NH and the appearance of singlet for the coordinated NH$_3$ ($\delta = 11.51$ and 2.07 ppm, respectively), whereas the bonded methylamine in complex **6b** showed diasterotopic NH$_2$ protons with different chemical shifts.[7] Interestingly, under the same conditions, diethylamine incompletely formed the analogue **6d**, whereas the larger amines diisopropylamine and triethylamine did not form **6e**,**f**, probably because of steric factors. Deprotonation of protic NHC complexes **6a–c** with (Me$_3$Si)$_2$NNa gave imidazol-2-yl complexes **7a–c**, wherein **7a** can also be obtained from **2** using NaNH$_2$. However, a surprising result, already shown in Scheme 2, was that LDA reacted with **2** to form **3** instead an analogue of **7** (with R$_3$N = diisopropylamine) as NaNH$_2$ did forming **7a**.



	R$_3$N	yield
6a	NH$_3$	97%
6b	MeNH$_2$	91%
6c	Me$_2$NH	96%
6d	Et$_2$NH	86% by NMR
6e	*i*Pr$_2$NH not formed	
6f	Et$_3$N not formed	

Scheme 4. Synthesis of protic NHC complexes and their deprotonation with strong bases.

X-ray structures[10] of **2**, **5**, **5**·HCl, and **7a** show different hydrogen-bonding networks involving the imidazole ring and confirm the presence of an NH group in **2** and **5**·HCl and its absence in **5** and **7a**.[7] The intramolecular NH···Cl distance in **2** is large (4.47(2) Å), whereas a closer mutual intermolecular contact between two molecules with NH···Cl 2.56(3) Å exists. In contrast, **5**·HCl showed intramolecular hydrogen bonding between the chloride anion and the NH group (NH···Cl 2.44(5) Å; Figure 1). The structure of **5** had a C$_{imidazolyl}$–Ru bond of 2.071(2) Å, whereas the C$_{carbene}$–Ru bond in **5**·HCl is shorter (2.061(4) Å). Finally, the crystalline structure of **7a** showed intermolecular hydrogen bonding between protons of the coordinated NH$_3$ and the basic nitrogen atom of the imidazol-2-yl fragment, with NH$_3$···N 2.17(3) Å. In contrast, **3**[10] (Figure 2) shows clearly the attachment of a {(thf)$_2$LiCl} fragment to proposed species **B**.

Single-crystal X-ray structures (Table 1) show that imidazol-2-yl ligands are characterized by small differences (0.029–0.041 Å) in N–C bond lengths to the metal-bound carbon atom, whereas protic NHC complexes show experimentally indistinguishable distances. Despite this trend, a more general technique applicable to solution-phase studies was sought. Observation of ^{15}N chemical shifts is an extremely useful tool

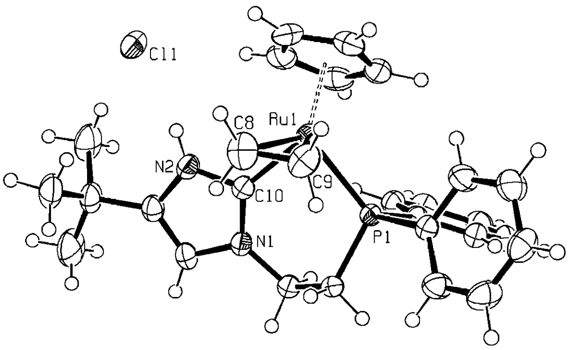


Figure 1. Molecular structure of protic N-heterocyclic carbene complex **5**·HCl, in which a hydrogen bond is formed between the N–H group and the chloride anion. Thermal ellipsoids are set at 50% probability.

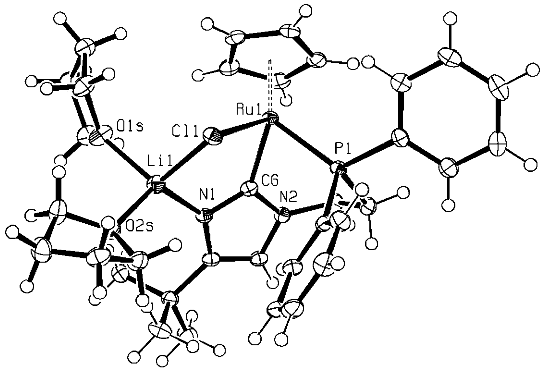
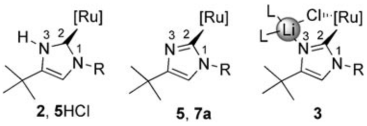


Figure 2. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Ru1–C6 2.0659(17), Ru1–Cl1 2.4629(5), Li1–Cl1 2.317(3), Li1–N1 1.997(3), N1–C6 1.351(2); Ru1-C6-N1 130.41(13), Ru1-Cl1-Li1 89.468, Cl1-Ru1-C6 91.05(5), Cl1-Li1-N1 104.95(15), Li1-N1-C6 108.96(14). Thermal ellipsoids are set at 50% probability.

Table 1: Differences in bond lengths [Å] and ^{15}N chemical shifts [ppm] show the nature of the bonding in the heterocycle for **2**, **3**, **5**, **5**·HCl, and **7a**.

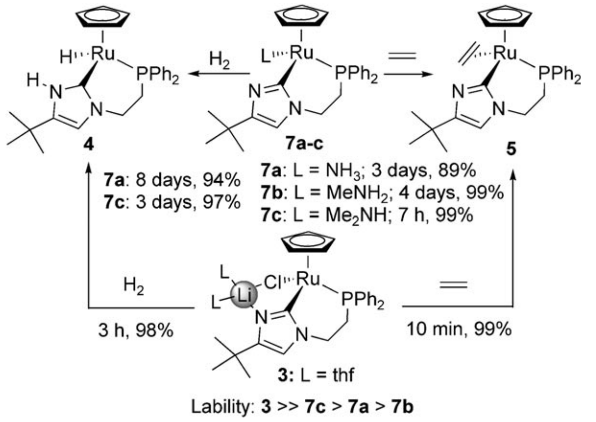


	Ru–C2	N1–C2	N3–C2	Δ[a]	δ_{N1}	δ_{N3}	δ_{N3}–δ_{N1}
2	2.047(2)	1.361(3)	1.360(3)	0.001(6)	−198.6	−197.1	1.5
3	2.0659(17)	1.3761(2)	1.351(2)	0.025(2)	−196.8	−122.1	74.7
5	2.0715(17)	1.383(2)	1.342(2)	0.041(4)	−200.8	–[b]	nd
5·HCl	2.060(4)	1.351(5)	1.361(4)	−0.010(09)	−197.6	−183.1	14.5
7a	2.045(2)	1.374(3)	1.345(3)	0.029(6)	−199.9	−110.4	89.5

[a] Δ = (N1-C2) − (N3-C2). [b] Not observed.

to determine metal or hydrogen bonding or protonation of imidazole nitrogen atoms.[11] Therefore, we obtained ^{15}N chemical shifts on natural abundance samples by 2D ^{1}H–^{15}N correlations as a diagnostic method for either the basic nitrogen atom or the NH function at the imidazole fragment (both at N3). For example, the protic NHC complexes **2** and **4** showed two ^{15}N peaks very close in chemical shift (**2**: $\delta_{N3\text{-}N1}$ = 1.5 ppm), with the NH peak assigned using gHSQC (similar trends were seen in **5**·HCl and **6a–c**). In contrast, a dramatic change in ^{15}N chemical shift of N3 is seen when the NH of a protic NHC is deprotonated and converted into basic nitrogen of an imidazol-2-yl system, for example **7a** ($\delta_{N3\text{-}N1}$ = 89.5 ppm). In general, we observe that the ^{15}N chemical shift of the N3 in protic NHC complexes is shifted to low field when they are converted into imidazol-2-yl complexes, whereas the difference between N3-H and N1-R (R = methylene) in a protic NHC complex is quite small.[7]

Turning toward ligand exchange and reactivity studies on complexes **7a–c** and **3**, we found that all of the complexes react with ethylene and hydrogen, but with dramatically different rates (Scheme 5): in reactions with ethylene, substitution on **3** was 40 to more than 500 times faster than ligand substitution on **7a–c**; in reactions with hydrogen, substitution on **3** was approximately 20 to 60 times faster.



Scheme 5. Reactivity of **3** and **7a–c** with hydrogen gas and ethylene. Conditions: [D$_8$]THF, room temperature.

Among amine complexes, reactions of NH$_3$ analogue **7a** were the slowest of all, which in the NH$_3$ case would be consistent with less relief of steric strain in rate-determining dissociation.[12] Consistent with this observation, **6e**,**f** could not be synthesized, whereas **6a–d** could. To examine the feasibility of reaction of **7** and **3** with hydrogen by bond activation on **C** prompted by the basic heterocyclic nitrogen of the imidazol-2-yl fragment, we are currently performing calculations, which so far predict that **4** (compare with **D**) is 11.5 kcal mol^{-1} lower in energy than its tautomer **C** in this system. Experimentally, exposure of **4** to D$_2$[13] (1 atm, [D$_8$]THF, room temperature) led to appearance of deuterium at the NH and RuH positions. No HD was seen by ^{1}H NMR (estimated detection limit 5%), which is consistent with pairwise loss of both reactive hydrogen atoms from **4** and intermediacy of **C** and **B** in hydrogen activation.

In summary, we have synthesized a versatile protic NHC complex **2** that can be easily transformed at room temperature into different organometallic species by using bases (NaH, *n*BuLi, alkoxides, LDA, $NaNH_2$) or ionizing agents (such as KPF_6) in presence of ethylene or amines. Ionization of the chloride ligand in **2** in the presence of ethylene or amines allowed formation of cationic complexes **5**·HX and **6**. In particular, complex **2** undergoes slow but spontaneous ligand exchange of the chloride by ethylene to give **5**·HCl, which was dramatically accelerated to be complete within 5 min by addition of KPF_6 forming **5**·HX ($X = PF_6$); similar fast reaction rates at room temperature were observed in formation of **6a–c** aided by KPF_6. Our previously reported {Cp*Ir} system required more than 16 h at 70 °C for ionization and alkene binding.[4] All of these protic NHC complexes (**5**·HX and **6a–c**) were deprotonated with strong bases to give their conjugated bases **5** and **7a–c**. However, direct deprotonation of the NH function in **2** with $NaNH_2$ or *n*BuLi in dry THF allowed formation of **7a**, and surprisingly **3**, respectively, whereas the use of *n*BuLi in *i*PrOH gave **4** instead **3**. Ligand exchange studies on **3** and **7a–c** with ethylene and hydrogen gas leads to formation of complex **5** and hydride **4**, respectively. The observed lability in these studies showed that the rate formation of **5** and **4** increases in the order $\mathbf{3} \gg \mathbf{7c} > \mathbf{7a} > \mathbf{7b}$, showing a striking ability to tune reactivity. Notably, **4** alone or **2** with added base were excellent catalysts for the transfer hydrogenation of acetophenone with low catalyst loading (1 % and 0.05 %) and good yield, in complete contrast to the previously reported {Cp*Ir} system, which was disappointingly inactive as a catalyst.[4] Furthermore, our structural studies on protic NHC complexes and imidazol-2-yl systems using 2D ^1H–^{15}N correlations, showed the profound differences in the N3 nitrogen environment between the proton-substituted N3 and the basic N3 in imidazol-2-yl complexes, results which are expected to be a useful basis for further studies of protic NHC complexes.

Taken together, the fundamental reactivity of protic NHC carbene complex **2** in presence of ionizing agents or bases allows its facile transformation, consistent with structures **B**–**E**. Secondary interactions at N3 that involve either hydrogen acceptance or hydrogen-bond donation together with ligand exchange processes are highlighted by catalytic behavior of hydride **4** and the useful reactivity of complexes **3**–**7a–c**. Our results add protic NHC complexes to a variety of other diverse compound classes[14] capable of bifunctional activation of hydrogen or alcohols, but additional work will be needed to adequately compare the promising chemistry of protic NHC derivatives with previous work. Thus, further synthetic, reactivity and catalysis studies on **2** and related protic NHC complexes are a topic of active investigation.

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[7] See the Supporting Information for full details.

[8] We thank a reviewer for suggesting this possible mechanism and the means to test it. Whereas the Ru–H position of **4** was occupied by protium, the N–H position of the product **4** was only approximately 50 % deuterated, which is most likely a result of H/D exchange with traces of water.

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[13] We thank a reviewer for suggesting this experiment. After 1 day, the N–H position was occupied by only 26 % protium, whereas the Ru–H position was occupied by 69 %. This difference may reflect the fact that after longer times, evidence for HD exchange into the Cp ring was seen, a finding which will require further investigation.

[14] Leading references to other bifunctional systems, and particularly those of Ru: a) C. P. Casey, J. B. Johnson, S. W. Singer, Q. Cui, *J. Am. Chem. Soc.* **2005**, *127*, 3100 – 3109; b) J. Wettergren, E. Buitrago, P. Ryberg, H. Adolfsson, *Chem. Eur. J.* **2009**, *15*, 5709 – 5718; c) M. Ito, A. Osaku, A. Shiibashi, T. Ikariya, *Org. Lett.* **2007**, *9*, 1821 – 1824; d) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300 – 1308; e) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201 – 2237.