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Isolation and Interconversion of Protic N-Heterocyclic Carbene and Imidazolyl Complexes: Application to Catalytic Dehydrative Condensation of *N*-(2-Pyridyl)benzimidazole and Allyl Alcohol

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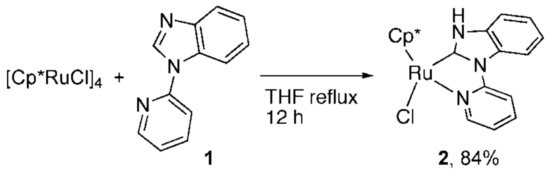
*Summary: Treatment of the protic N-heterocyclic carbene (NHC) complex [Cp*RuCl(LH)] (**2**; LH = N-(2-pyridyl)benzimidazolin-2-ylidene-κ^2N,C) with $AgNO_2$ gives the nitrosyl–imidazolyl complex [Cp*Ru(NO)(L)][OTf] (OTf = OSO_2CF_3), which undergoes reversible protonation to afford the NHC complex [Cp*Ru(NO)(LH)]$[OTf]_2$. The bifunctional complex **2** also catalyzes the dehydrative condensation of N-(2-pyridyl-)benzimidazole and allyl alcohol, leading to the formation of trans- and cis-2-(1-propenyl)-N-(2-pyridyl)benzimidazole.*

The N-heterocyclic carbenes containing an NH group (NH-NHCs)[1–6] remain significantly less common in contrast to the ubiquitous NR-stabilized derivatives.[7] The NH-NHC and related NH-stabilized carbene complexes have been synthesized by metal-templated cyclization of isocyanides and amines[1] as well as tautomerization of N-heterocycles.[2,3] Transmetalation of C-metalated imidazoles followed by N-protonation provides an alternative route to NH-NHC complexes, although the intermediary C-imidazolyl complexes are often elusive.[4] In our extensive studies on the M/NH bifunctional catalysts featuring the amine−amido interconversion,[8] we postulated that the reversible deprotonation of NH-NHC ligands coupled with metal-centered reactions would lead to the development of novel bifunctional catalysts. We report here the synthesis of chelate-stabilized NH-NHC complexes and their (NH-NHC)−imidazolyl interconversion. The NH-NHC complex also catalyzes the dehydrative condensation of an N-heterocycle with allyl alcohol, in which the NH-NHC plays a role beyond a spectator ligand.[9]

The treatment of [Cp*Ru(μ_3-Cl)]$_4$ (Cp* = η^5-$C_5(CH_3)_5$) with *N*-(2-pyridyl)benzimidazole (**1**) in an Ru:**1** ratio of 1:1 led to tautomerization of the imidazole, giving the C,N-chelating NH-NHC complex **2**, as shown in eq 1. The $^{13}C\{^1H\}$ and ^1H NMR spectra of **2** show Ru−C and NH resonances at δ_C 211.2 and δ_H 12.90, respectively, being consistent with the NH-NHC formation. The X-ray analysis has revealed a dimeric solid-state structure for **2** involving intermolecular hydrogen bonds between the NH group and the chloro ligand (Figure 1 and Table 1).[10]



(1)

The Brønsted acidity of the NH proton in the NH-NHC ligand is further suggested by the dehydrative conversion of a nitrite ion to a nitrosyl ligand involving intramolecular proton migration. In fact, treatment of **2** with an equimolar amount of silver nitrite in acetonitrile cleanly afforded a nitrosyl−imidazolyl

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[10] For analogous intramolecular NH···Cl hydrogen bonds, see refs 3 and 5.

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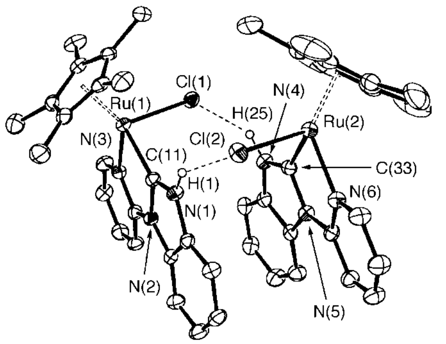
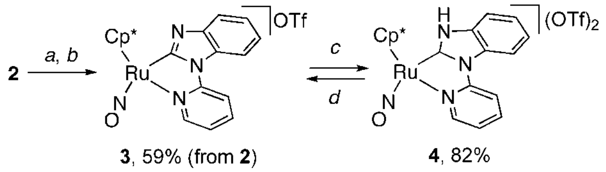


Figure 1. Structure of **2** with thermal ellipsoids at the 30% probability level. A pair of two crystallographically independent molecules is shown.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 2·1.5THF

	molecule A	molecule B
Ru(1)−Cl(1)	2.4759(12)	2.4753(12)
Ru(1)−N(3)	2.107(3)	2.108(3)
Ru(1)−C(11)	1.991(4)	1.986(4)
C(11)−N(1)	1.360(5)	1.350(5)
C(11)−N(2)	1.403(5)	1.419(5)
Cl(1)···H(25)	2.378	2.413
N(1)−C(11)−N(2)	104.1(3)	104.5(3)

Scheme 1. Synthesis and Reversible Protonation of 3[a]



[a] Conditions: (a) $AgNO_2$ (1 equiv), CH_3CN, rt, 12 h; (b) KOTf (5 equiv), CH_3CN, rt, 2 h; (c) TfOH (1 equiv), CH_2Cl_2, −78 °C → rt, 12 h; (d) K_2CO_3 (1 equiv), CH_2Cl_2, rt, 12 h (OTf = OSO_2CF_3).

complex under neutral conditions;[11] after anion exchange, the triflate salt **3** was isolated (Scheme 1). The $^{13}C\{^1H\}$ and ^1H NMR spectra of **3** no longer exhibit carbene and NH resonances. Furthermore, proton-coupled interconversion between imidazolyl and NH-NHC ligands has been demonstrated clearly by using the nitrosyl−imidazolyl complex **3**. First, protonation of the imidazolyl complex **3** exclusively gave the dicationic NH-NHC complex **4**. The $^{13}C\{^1H\}$ and ^1H NMR spectra (δ_C 182.2, δ_H 14.82) are again diagnostic for the formation of the NH-NHC. As expected, deprotonation of **4** regenerated **3** in 81% yield. Figure 2 depicts the molecular structures of the imidazolyl complex **3** and the NH-NHC complex **4**; the important bond distances in **3** and **4** with exactly the same ancillary ligand sets are also summarized. In line with the NHC formulation of **4**, the double bonds in the five-membered ring in the chelate ligand are obviously more delocalized upon protonation, and the N−C(11)−N angle in **4** is more acute than that in **3** (106.5(4)° vs 111.4(3)°).[5,7]

We also found that the NH-NHC complex **2** reacts with allyl alcohol at room temperature to afford the 2-allylbenzimidazole complex **5** (Scheme 2). The crystal structure of **5** is shown in Figure 3. The 2-allylbenzimidazole ligand, derived from dehydrative coupling of the NH-NHC ligand in **2** and allyl alcohol, is coordinated only through the imidazole nitrogen and the olefinic part, and the pyridyl group is dangling. The facile dehydration may be ascribed to the dual binding of the allyl alcohol to the NH-NHC complex through the olefin coordination and the hydrogen bond between the NH group and the allylic O atom (**A**). Subsequent oxidative addition of the allyl group would afford a (*π*-allyl)(imidazolyl)ruthenium(IV) intermediate **B** with a loss of water. Such donor−acceptor bifunctionality has been proposed in dehydrative allylation of alcohols catalyzed by a (2-quinolinecarboxylato)ruthenium complex.[12] The imi-

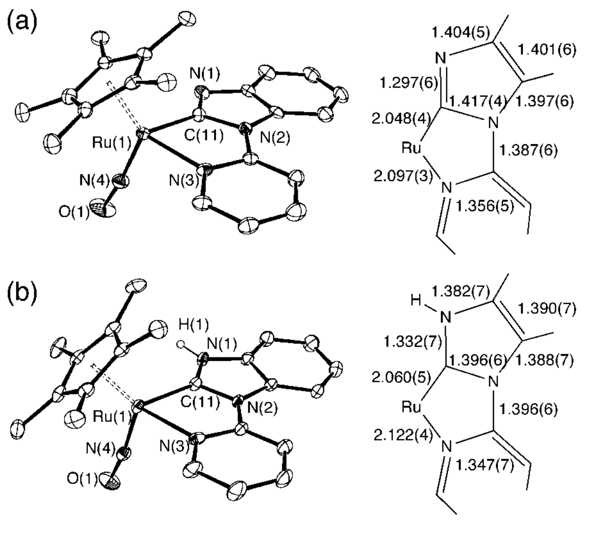
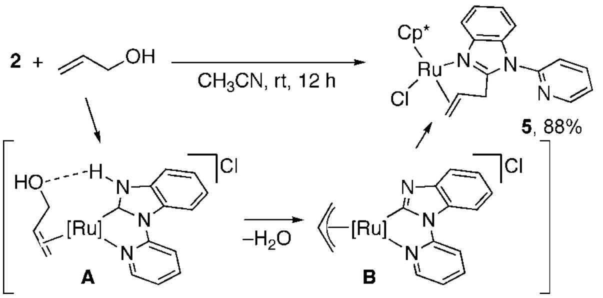


Figure 2. Structures of the cationic part of **3** (a) and **4** (b) with thermal ellipsoids at the 30% probability level.

Scheme 2. Reaction of 2 with Allyl Alcohol[a]



[a] [Ru] = Cp*Ru.

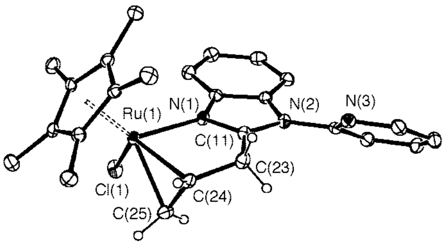


Figure 3. Structure of **5** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angle (deg): Ru(1)−Cl(1), 2.4473(7); Ru(1)−N(1), 2.113(2); Ru(1)−C(24), 2.177(2); Ru(1)−C(25), 2.171(3); N(1)−C(11), 1.322(3); N(2)−C(11), 1.372(3); C(24)−C(25), 1.391(4); N(1)−C(11)−N(2), 111.8(2).

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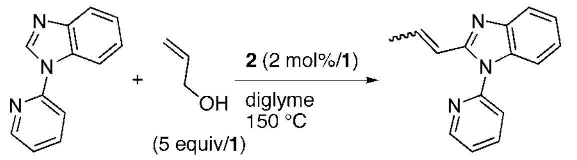
[11] In contrast, similar treatment of the bipyridyl (bipy) analogue [Cp*RuCl(bipy)] merely affords the nitro complex [Cp*Ru(NO_2-*κN*)(bipy)]: Araki, K.; Kuwata, S.; Ikariya, T., unpublished results.

[12] Saburi, H.; Tanaka, S.; Kitamura, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1730–1732.

dazolyl ligand generated by the deprotonation of the NH-NHC would undergo reductive elimination with the π-allyl ligand, leading to the formation of **5**.[13]

On the basis of these findings, we next examined catalytic dehydrative condensation of the pyridylbenzimidazole **1** and allyl alcohol.[14] Treatment of **1** with 5 equiv of allyl alcohol in the presence of a catalytic amount of the NH-NHC complex **2** (2 mol %) in diglyme at 150 °C resulted in the complete conversion of **1**. The products were, however, (*E*)- and (*Z*)-2-(1-propenyl)-*N*-(2-pyridyl)benzimidazoles (*trans*- and *cis*-**6**) instead of the expected 2-allyl isomer (eq 2). As preliminary experiments to clarify the reaction mechanism, we tested the reactions of the 2-allylimidazole complex **5** with **1**, which proved to afford *trans*- and *cis*-**6** at reaction temperatures above 100 °C. We thus consider the 2-allylimidazole complex **5** to be a key intermediate in this catalytic reaction.



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6, >99% (*E*/*Z* = 77/23)

(2)

In summary, we have demonstrated that C−H bond cleavage of the pyridylbenzimidazole **1** on a ruthenium center takes place to afford the NH-NHC complex **2**. The Brønsted acidity of the NH-NHC ligand is evidenced by the interconversion between the NH-NHC and imidazolyl ligands in the nitrosyl complexes **3** and **4**. We have also revealed that the latent Brønsted acidity of benzimidazole elicited by the tautomerization promotes the C−O bond cleavage of allyl alcohol, leading to the catalytic dehydrative condensation of **1** and allyl alcohol. Further studies on the scope and limitation of this coupling reaction along with the mechanism are now under way.

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Supporting Information Available: Experimental procedures and X-ray crystallographic data for **2**−**5** and *trans*-**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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