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# Lutidine-Derived Ru-CNC Hydrogenation Pincer Catalysts with Versatile Coordination Properties

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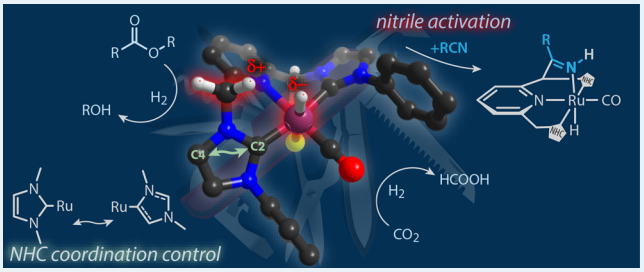
Supporting Information

**ABSTRACT:** Lutidine-derived bis-N-heterocyclic carbene (NHC) ruthenium CNC−pincer complexes (Ru-CNC's) were prepared. Depending on the synthetic procedure, normal (**1**, **2**) or mixed normal/abnormal NHC-complexes (**3**) are formed. In the presence of phosphazene base, Ru-CNC complexes activate nitriles to give ketimino compounds **4**−**6**. Nitrile adduct **4** shows reactivity toward strong bases to yield dearomatized complex **7**, which heterolytically activates $H_2$ to form the bis-hydrido complex **8**. Finally, these Ru-CNC's are active in catalytic hydrogenation of $CO_2$ to formate salts, and unlike the phosphine-containing Ru-PNP counterpart, they also catalyze the selective hydrogenation of esters to alcohols.

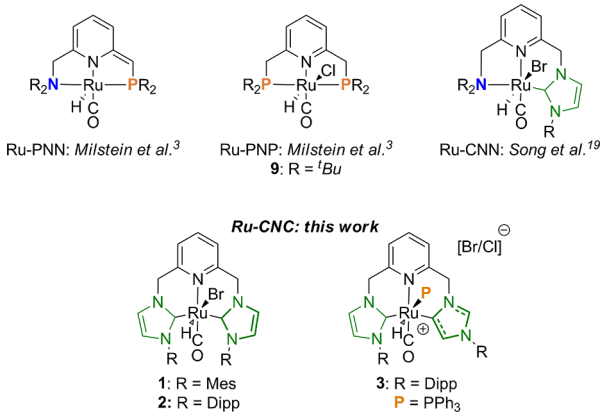



**KEYWORDS:** *ruthenium, hydrogenation, metal−ligand cooperation, N-heterocyclic carbene, nitrile activation*

Ruthenium lutidine-derived pincer complexes containing PNX-type ligands are efficient catalysts for a wide range of important chemical transformations. They show catalytic activity in acceptorless dehydrogenation,[1] hydrogenation of carboxylic acid derivatives,[2,3] synthesis of amides from esters,[4] and hydrogenation of $CO_2$.[5,6] Reversible ligand dearomatization is often invoked to explain the catalytic properties of Ru-PNX catalysts. Reacting Ru-PNX complexes with a strong base triggers ligand-assisted cooperative activation of $H_2$, carbonyl compounds, and $CO_2$.[7−12] N-Heterocyclic carbene (NHC) complexes have attracted considerable attention in catalysis because they offer several advantages over phosphines.[13−18] In the context of pincer complexes, replacement of phosphines in Ru-PNN with NHC ligands yields Ru-CNN catalysts that match or outperform their phosphine-based counterparts.[19−22] In addition, Ru-CNN pincers reported by Song and co-workers show similar chemical reactivity toward ligand dearomatization and heterolytic $H_2$ activation. Although many examples of pyridine-based ruthenium bis-NHC pincers have been reported,[23−26] ruthenium complexes based on potentially cooperative CNC ligands are rare.[22,27,28] Consequently, no comparison to existing PNP analogues has been offered.

Here, we report the synthesis of Ru-CNC complexes and explore their reactivity and catalytic properties. We demonstrate that the coordination mode of the NHC fragments (Scheme 1) can be controlled by the sterics of the ligand or the addition of LiBr during complexation. The reactivity toward strong bases and $H_2$ draws a parallel between Ru-CNC's and the thoroughly studied Ru-PNX pincers developed by the Milstein group (Scheme 1). Deprotonation of Ru-CNC's yields dearomatized species that promote heterolytic cleavage of $H_2$.

**Scheme 1. Selected Lutidine-Derived Ru Pincer Complexes**

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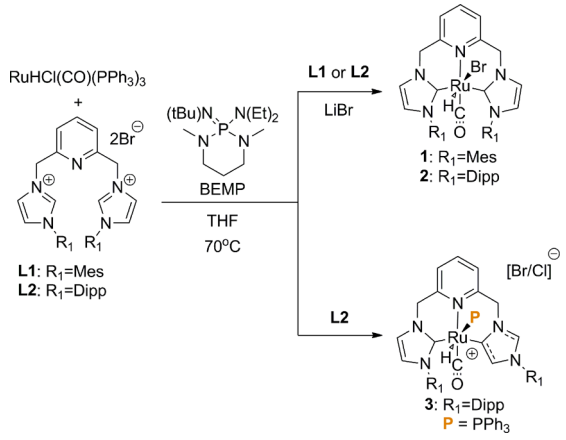
Ru-CNC catalysts are active in $CO_2$ hydrogenation to formates, and unlike structurally analogous pyridine-based Ru-PNP pincers, they also catalyze ester hydrogenation, also referred to as ester hydrogenolysis.

The Ru-CNC pincer complex **1** was synthesized by reacting bis-imidazolium ligand **L1** containing mesityl (Mes) substituents, the base 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), and $RuHCl(CO)(PPh_3)_3$ in THF (Scheme 2). Alternative approaches involving

**Scheme 2. Complexation of Ru with bis-NHC Ligands in THF**




transmetalation or using strong anionic bases were unsuccessful. Initially, **1** was obtained as a bromide/chloride mixture. The molecular structure in the crystal is shown in Figure 1. The

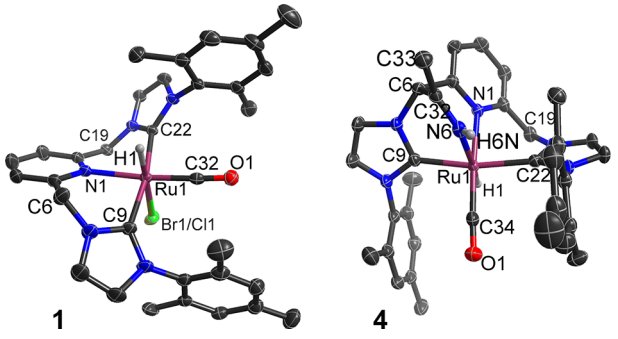



**Figure 1.** X-ray crystal structures of **1** and **4** (50% probability ellipsoids, solvent molecules, hydrogen atoms on the ligand, and the bromide anion in **4** are omitted for clarity). Selected bond lengths (Å): (**1**) Ru1−C9, 2.0886(12); Ru1−C22, 2.0751(12); Ru1−C32, 1.8080(13). (**4**) Ru1−N6, 2.1614(16); Ru1−C9, 2.0470(18); Ru1−C22, 2.0737(18); Ru1−C34, 1.833(2); Ru1−N1, 2.1667(15).

pure bromide **1** was isolated when the reaction was conducted in the presence of LiBr.[19] The product is stable to ambient atmosphere in the solid state. In $CD_2Cl_2$, the NHC backbone protons appear as two doublets at 7.17 and 6.66 ppm ($^3J_{HH}$ = 2 Hz), and the pyridine protons appear as a triplet and doublet (7.82 and 7.46 ppm, $^3J_{HH}$ = 8 Hz). Upon ligand coordination, the ortho-$CH_3$ groups and aromatic protons of the mesityl substituents are no longer equivalent and appear as separate singlets. The Ru−H signal is shifted significantly upfield to −15.6 ppm, similar to that observed in related Ru pincers.[19] Methylene protons in **1** appear as a broad peak at 5.1 ppm.[29]

The reaction of **L2** containing 2,6-diisopropylphenyl (dipp) substituents with $RuHCl(CO)(PPh_3)_3$ in the presence of LiBr resulted in complex **2**, containing normally bound NHC groups (Scheme 2). Exchange of the bromide for a triflate by treatment of **2** with silver triflate yielded the more soluble **2*OTf**, allowing the detection of the Ru−C resonances at 191.3 ppm in the $^{13}C$ NMR spectrum. In contrast, complexation of **L2** with $RuHCl(CO)(PPh_3)_3$ in the absence of LiBr led to **3** (Scheme 2), in which one of the NHC arms was coordinated abnormally to Ru through the C4 carbon.[30−32] The hydride ligand in **3** is trans to the $PPh_3$ as evident from the large $J_{PH}$ (100 Hz). The signature C2 imidazolium proton of the abnormally bound NHC moiety appears at 9.66 ppm, while the remaining C5 imidazolium proton is significantly shifted upfield to 4.46 ppm. The solid-state structure of **3** is shown in Figure 2. Complex **3**

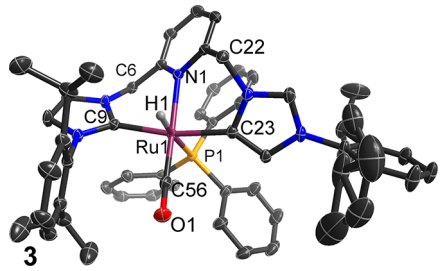
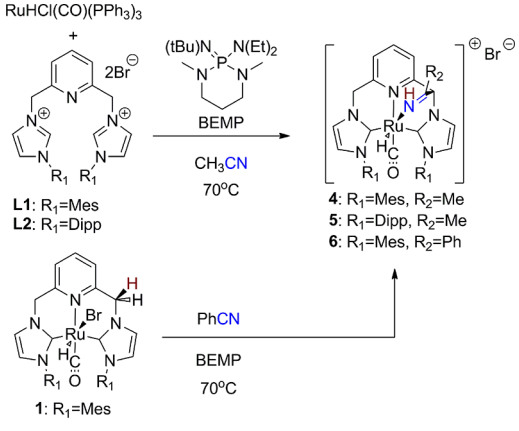



**Figure 2.** X-ray crystal structure of 3 (50% probability ellipsoids, solvent molecules, hydrogens, and the halide anion are omitted for clarity). Selected bond lengths (Å): Ru1−P1, 2.4353(5); Ru1−C9, 2.0672(16); Ru1−C23, 2.1124(17); Ru1−C56, 1.8283(18); Ru1−N1, 2.2034(14).

is a rare example of bis-NHC pincers with mixed normal/abnormal composition.[33,34] Our findings are consistent with previous reports on Os and Ir NHC's, for which counterion and steric effects were shown to control the NHC coordination mode.[35−38] In particular, it has been shown that in the presence of $Br^-$ anions, the C−H heterolysis at C2 position is accelerated, resulting in the preferential normal NHC coordination.[38] The possibility of selecting the NHC binding mode of the CNC pincer ligand reported here provides yet another useful tool for tuning properties of Ru-CNC's.

When $CH_3CN$ was used as a solvent, the complexation of the Ru precursor with **L1** and **L2** led to the formation of $CH_3CN$ adducts **4** and **5**, respectively (Scheme 3). The $^1H$ NMR of **4**

**Scheme 3. Complexation of Ru with bis-NHC Ligands in the Presence of Nitriles**





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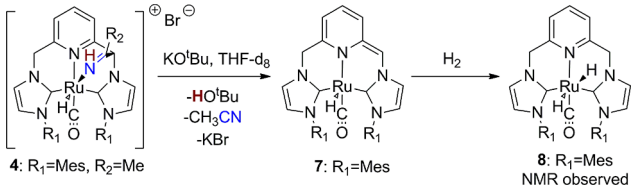
contains a high frequency imino proton signal at 9.89 ppm. Three methylene bridge protons appear as two sharp doublets at 5.40 and 5.30 ppm ($^2J_{HH}$ = 14 and 8 Hz) and a sharp singlet at 8.53 ppm, indicating nitrile insertion into the C−H bond of the methylene group. The Ru-NHC resonances of **4** appear at 191.9 and 191.2 ppm in the $^{13}$C NMR spectrum. Complex **5** with dipp groups on the NHC's has an NMR spectrum similar to that of **4**. The crystal structure analysis of **4** and **5** (Figure 1 and Supporting Information) confirms the nitrile addition across the metal center and the methylene bridge of the ligand. The coordination of the CNC ligand in **4** and **5** is similar to that in **1**.

Organonitrile activation resulting in the formation of a new C−C bond was reported for Rh[34] and Ir[35] complexes. The nitrile binding mode in **4** and **5** resembles that in Re-PNP ketimido and enamido adducts, with the difference that the addition to Re-PNP occurs only after the deprotonation of the ligand with a strong base.[39] Similar nitrile addition with subsequent coordination of an imine group to the metal center was previously described for macrocyclic complexes of Fe, Co, W, and Mo.[40−42] In addition, iron complexes with tetradentate nitrogen ligands were shown to attack nitriles and form similar adducts in the presence of base ($NEt_3$).[43] Interestingly, **1** can also undergo a direct transformation to nitrile adducts in the presence of BEMP. In $CH_3CN$, ∼47% of **1** was transformed to **4** overnight. In the presence of benzonitrile, **1** is converted to **6** in 91% yield (see the Supporting Information). Note that the related phosphine-based pincer (Ru-PNP, **9**, Scheme 1) did not react with nitriles under these conditions.

Catalysis with lutidine-derived pincer complexes is often triggered by activation with a base. The strong base deprotonates the ligand side arm and generates five-coordinate active species. The reactivity of Ru-CNC's with strong bases was probed with NMR spectroscopy. The reaction of **1** with KHMDS or KO$^t$Bu at room temperature led to incomplete conversion, providing impure mixtures containing dearomatized complex **7** within hours.

Alternatively, **7** can be prepared quantitatively from **4** by a reaction with KO$^t$Bu (Scheme 4). Relatively unstable **7** was

**Scheme 4. Generation and Reactivity of Complex 7**




characterized in situ by NMR spectroscopy. Dearomatization of the pyridine ring is evidenced by a significant upfield shift of the corresponding $^1$H NMR signals to ∼6.20 and 4.81 ppm. The methylene group resonances appear at 4.90 and 4.74 ppm as doublets, and the signal from the deprotonated bridge appears at 5.83 ppm. These results point to a more facile transformation of the nitrile adducts **4**−**6** to catalytically active dearomatized Ru-pincer complexes in the presence of a strong base compared with the parent Ru-CNC's **1** and **2**. Similar to Ru-PNP analogues,[7] **7** reacts with $H_2$ to form the dihydrido complex **8** (Figure S36 in the Supporting Information). The $^1$H resonance of the Ru−H in **8** is shifted downfield to −5.94 ppm, the typical position for Ru-dihydrido complexes.[44] Upon addition of $H_2$, the pyridine ring is rearomatized, and all four methylene protons are observed as doublets at 5.59 and 5.33 ppm.

Similar to the structurally analogous Ru-PNP catalysts, Ru-CNC's were active in $CO_2$ hydrogenation to formate salts (see Table S1 in the Supporting Information).[6] The conversion of an equimolar $H_2/CO_2$ mixture (40 bar) at 70 °C in the presence of DBU resulted in near full base consumption within 1 h, giving a TON up to 2600. Nevertheless, under these conditions, Ru-PNP complex **9** (RuHCl(CO)($^t$BuPNP)) outperforms bis-NHC pincers (see Table S1, Supporting Information). This may be due to the stronger donor properties of the PNP ligand, resulting in a more electron-rich Ru center in **9** compared with that in Ru-CNC's **1**−**6**, evident from the slight difference in the position of the CO stretching band in these complexes ($\nu$(CO) = 1906 cm$^{-1}$ for **9** vs 1916−1927 cm$^{-1}$ for **1**−**6**).

Hydrogenation of esters to alcohols, which can also be referred to as ester hydrogenolysis, is usually more challenging compared with hydrogenation of $CO_2$.[3,45−48] The Ru-PNP complex **9** is inactive in ester hydrogenation. In sharp contrast, Ru-CNC complexes **1**−**6** hydrogenate a wide range of esters to the corresponding alcohols (Table 1). Ru-CNC catalysts effectively hydrogenate aromatic esters, including chloro- and methoxy-functionalized derivatives (Table 1, entries 23−26), aliphatic esters, and lactones. The hydrogenation of methyl 10-undecenoate (Table 1, entries 21, 22) resulted in the predominant formation of the fully saturated undecanol product. Good to quantitative yields were obtained in 4−16 h at 70−100 °C and 50 bar $H_2$ in the presence of KOMe or KO$^t$Bu base promoters. This activity was achieved at a relatively low catalyst loading (0.1−0.5 mol % Ru, Table 1 and Supporting Information). Mercury poisoning[49−52] (315 equiv per Ru, 850 rpm stirring) does not affect the hydrogenation of methyl benzoate catalyzed by **1** or **3** (entries 2 and 5, Table 1), thus showing that the active catalyst is molecular and not associated with heterogeneous Ru species. Postcatalytic ESI-MS measurements (Figure S40, Supporting Information) indicate the preservation of the Ru-CNC moiety in complex **3** under the ester hydrogenation conditions. Molecular ions corresponding to mononuclear [RuCl(CNC)]$^+$, [Ru(BnO)(CNC)]$^+$, [RuH(CO)(PPh$_3$)(CNC)]$^+$, and [RuCl(PPh$_3$)(CNC)]$^+$ species were observed in the mass spectrum of the reaction mixture corresponding to entry 5, Table 1.

At elevated substrate/catalyst ratios (S/C = 1000, 0.1% Ru), **1** converts methyl benzoate quantitatively to methanol and benzyl alcohol at 70 °C and 50 bar $H_2$ within 16 h (see section S4 of Supporting Information). The kinetics of hydrogenation was unaffected by the base concentration. For base loadings of 2−10%$_{mol}$, the reactions showed very similar time−conversion profiles, characterized by initial turnover frequencies (TOF) of 150−160 h$^{-1}$ (see Figure S41 in the Supporting Information). Decreasing the reaction temperature to 40 °C or $H_2$ pressure to 5 bar strongly reduced the catalytic performance of **1** (Supporting Information Figure S41). The obtained rates of ester hydrogenation are comparable to those reported for other NHC-based catalysts and superior to the rates attainable with the lutidine-derived Ru-PNN and Ru-CNN systems.[2,3,19,53] The catalytic reactions can be carried out under conditions significantly milder than in the case of the TriPhos and TriSulph Ru catalysts.[54−56] However, Ru-CNC catalysts display lower activity than the state-of-the-art aliphatic Ru pincer complexes;[46,57] the Noyori-type catalysts;[58,59] and, in particular, the most active catalytic system based on aliphatic Ru-SNS


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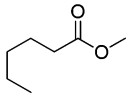
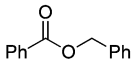
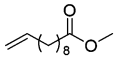
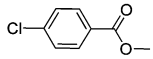
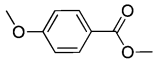
**Table 1. Catalytic Ester Hydrogenation to Alcohols with RuCNC's.[a]**

| Entry | Substrate | Catalyst | Yield,[c] % |
|---|---|---|---|
| *1* |  | **1** | 97 |
| *2*[b] | | **1**+xsHg[g] | 100 |
| *3* | | **2**[b] | 95 |
| *4* | | **3** | 96 |
| *5*[b] | | **3**+xsHg[g] | 100 |
| *6* | | **4** | 98 |
| *7* | | **5** | 55 |
| *8* | | **6** | 98 |
| *9* | | **9** | NR[f] |
| *10* |  | **1** | 98 |
| *11* | | **2**[b] | 99 |
| *12* | | **3** | 99 |
| *13* | | **4** | 100 |
| *14* | | **5** | 92 |
| *15* | | **6** | 100 |
| *16* | | **9** | NR |
| *17*[d] |  | **1** | 98 |
| *18*[d] | | **6** | 96 |
| *19*[d] |  | **1** | 100 |
| *20*[d] | | **6** | 100 |
| *21* |  | **1** | 86[e] |
| *22* | | **6** | 79[e] |
| *23* |  | **1** | 89 |
| *24* | | **6** | 100 |
| *25* |  | **1** | 60 |
| *26* | | **6** | 90 |

[a]2 mL of THF, 10%$_{mol}$ KOMe, 6.4 $\mu$mol of catalyst, S/C =200, 70 °C, 50 bar $H_2$, 4 h. [b]KO$^t$Bu used. [c]Yield of corresponding alcohols. [d]16 h time, 100 °C. [e]Undecanol yield. [f]NR = not active. [g]315 equiv of Hg per Ru was added after catalyst activation.

pincer,[60] which is capable of hydrogenating a wide range of organic esters at 40 °C with TOFs above 4000 $h^{-1}$.

In summary, we have developed a new family of ruthenium pincer catalysts with NHC donor groups. CNC ligands enable typical metal−ligand cooperative behavior in reactions with strong bases (**7**) and hydrogen (**8**). In addition, we present the examples of nitrile activation (**4**−**6**) and normal/abnormal NHC binding (**2**, **3**) control that are new for ruthenium pincer chemistry. Similar to structurally analogous Ru-PNP catalyst **9**, our Ru-CNC complexes show pronounced activity in $CO_2$ hydrogenation. Moreover, Ru-CNC's can hydrogenate esters under mild conditions, whereas the phosphine analogue Ru-PNP (**9**) is inactive in this reaction. These results establish that bis-NHC pincer ligands are promising and versatile platforms for catalytic applications.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, hydrogenation procedures, X-ray data for **1**, **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## NOTE ADDED AFTER ASAP PUBLICATION

The version of this paper that was published ASAP on July 11, 2014, was missing some text corrections. The corrected version was reposted July 11, 2014.