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Unusual rearrangement of an N-heterocyclic carbene via a ring-opening and ring-closing process

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The reaction of the a pentadentate NHC ligand precursor with Ni(OAc)₂ or Pd(OAc)₂ in the presence of a weak base yields four-coordinate square-planar Ni(II) and Pd(II) complexes with the an in-situ generating unusual ligand generated in-situ. Based on a series of experimental studies, point to a ring-opening and ring-closing process via novel C-N bond cleavage and formation has been discussed.

N-Heterocyclic carbenes (NHC) have been widely used in organometallic chemistry¹ and organic methodology² since the first isolation of a free NHC in 1991.³ NHCs can coordinate with nearly all metal elements in the periodic table. They normally act as spectator ligands due to the inert metal-NHC bonds, affording an enhanced stability for numerous robust metal-NHC catalysts. However, many there have been reports experimental evidences have shown that NHC ligands are quite reactive and can undergo several types of unexpected reactions in under some certain circumstances,⁴ which could potentially leading to the irreversible decomposition of the in-situ formed and preformed metal-NHC catalysts. These reactivities include C-H and C-C bond activations occurring at the N-substituent⁵ and NHC backbone.⁶ Besides, the carbenic carbon atom in the NHC ring are may also be involved in the reactions. These reactive pathways include the migratory insertion,⁷ reductive elimination,⁸ heterocyclic C-N bond cleavage^{9,12}, and other unusual rearrangement.¹³ An increasing number of examples involving C-N bond activation in NHCs have been reported, which could lead to the heterocyclic C-N bond cleavage and possibly further transformations. Ring-opening triggered by the presence of moisture or strong base has been found, when using imidazolium precursor salts to prepare NHC complexes.⁹ The which reaction leads to the complexes bearing the in-situ formed, unusual ligand containing a ring-opening structure.⁹ Ring expansion formed by C-N bond activation and subsequent insertion into element-H and element-C bonds have been found.¹⁰ The complete removal of carbenic carbon from the NHC unit have has been revealed in Hf

and Ir complexes.¹¹ Recently Hevia et al. have reported a novel ring-opening process and subsequent formation of 1-indolyl ring in the reaction between a saturated carbene and alkali metal reagents.¹² Although these examples are still considered as exceptions, identifying studies of the reactions involving these NHC ligands would enhance further our understanding of the activation or deactivation of metal-NHC catalysts.

Multidentate NHC ligands have attracted much interest, among which the non-cyclic ligands with more than four donors¹⁴ have been rarely studied in contrast to those with 2-4 donors.^{14,16} We are interested in coordination behaviour of pentadentate bis-(pyridine-NHC) amino ligand L. Herein we report unexpected Ni(II) and Pd(II) complexes via ring-opening, and ring-closing and in-situ generation of a pentadentate NHC ligand from the NHC precursor (H₂L)(PF₆)₂ (Scheme 1). A strong base or the presence of moisture is usually required in the reported ring-opening reactions.^{9,12} In contrast, in our cases, a weak base such as NaOAc is used adequate to promote the ring-opening in the reactions of Ni(II) and Pd(II) nickel or palladium sources with the NHC ligand precursor (H₂L)(PF₆)₂ (Scheme 1).

The pentadentate NHC precursor salt (H₂L)(PF₆)₂ was synthesized via a three-step procedure (Scheme 1). The first step starting from 1-(pyridin-2-yl)-1H-benzimidazole (a)¹⁵ and ethane-1,2-ditosylate (b)¹⁶ affords a white benzimidazolium salt c, in which the secondary amine is protected by the tosyl group. The resulting white solid was treated by 48% aqueous HBr aqueous solution in the presence of PhOH to give the detosylated salt d, which was converted to the target product (H₂L)(PF₆)₂ by anion exchange. ¹H NMR and ¹³C NMR in CD₃CN show the resonances at 9.33 ppm and 150.23 ppm for the carbene protons and carbon atoms, respectively.

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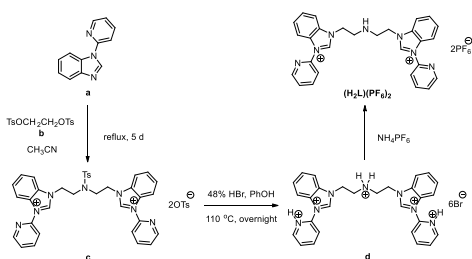
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Electronic Supplementary Information (ESI) available: Synthetic procedures and characterizations, crystallographic data. CCDC: ?????????? For ESI and crystallographic data in CIF or other electronic format see ??????????//

Scheme 1 Three-step synthesis of $(H_2L)(PF_6)_2$

It is well known that metal complexes can be prepared by the transmetalation reaction via Ag-NHC complex as the precursor.¹⁷ This procedure was used as the first route to prepare Ni(II) and Pd(II) complexes with $(H_2L)(PF_6)_2$. As shown in Scheme 2, the expected four-coordinate mononuclear nickel and palladium complexes **1a** and **1b** were prepared in 30- and 22- % yields by transmetalation of the *in-situ* generated silver-Ag(I) complex with $M(PPh_3)_2Cl_2$ ($M = Ni, Pd$) in acetonitrile. NMR spectra of **1a** in CD_3CN show the resonances at 4.59–4.43 ppm for the secondary amino hydrogen and 151.89 ppm and 150.58 ppm for the two carbenic carbon atoms. Similar signals for **1b** are 4.84–4.56 ppm in 1H NMR in CD_3CN and 151.58 ppm, 151.04 ppm in ^{13}C NMR in d^6 -DMSO.

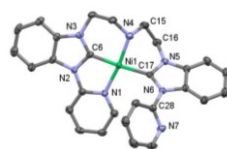
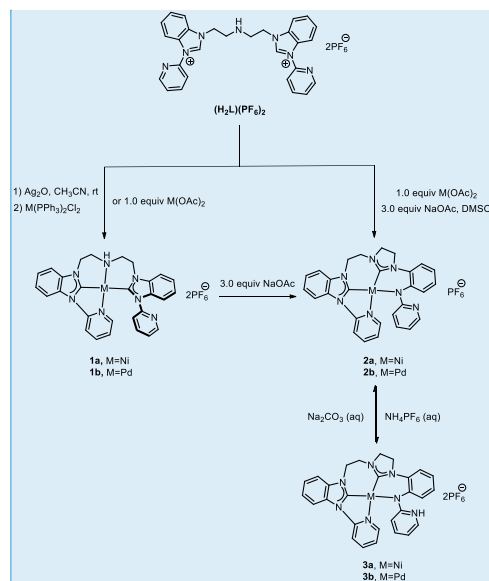


Figure 1 Structure of the cationic portion of **1a** with ellipsoids set at 50-%. All hydrogen atoms, solvent molecules and PF_6^- anions are removed for clarity. Relevant bond lengths [Å] and angles [°]: Ni1-C6 1.844(3), Ni1-N1 1.931(2), Ni1-C17 1.933(3), Ni1-N4 1.939(3), C6-Ni1-N1 81.64(12), N1-Ni1-C17 101.55(12), C6-Ni1-N4 91.15(13), C17-Ni1-N4 85.63(13).

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Scheme 2 Synthesis and transformation of three types of complexes.

The crystal structure of **1a**· CH_3CN was established with single-crystal X-ray crystallography. **1a**· CH_3CN crystallizes in orthorhombic space group $P2_12_12_1$. The structure of the cationic

The second procedure we used is subjecting the NHC precursor $(H_2L)(PF_6)_2$ to $M(OAc)_2$, which is an effective method to prepare group 10 metal-NHC complexes.¹⁸ The reaction of $(H_2L)(PF_6)_2$ with 1.0 equiv of $M(OAc)_2$ also gave **1a** and **1b** in 55- and 25- % yield, respectively. Interestingly, the same reaction of $(H_2L)(PF_6)_2$ with 1.0 equiv of $M(OAc)_2$ ($M = Ni, Pd$) in the presence of 3.0 equiv of NaOAc unexpectedly resulted in the formation of complexes **2a** and **2b** (Scheme 2). The amount of NaOAc should be at least 1.0 equiv relative to that of $M(OAc)_2$. Only a mixture of **1a/2a** or **1b/2b** was formed when 0.5 equiv of NaOAc was employed.

The unsymmetrical structures of **2a** and **2b** can be deduced from their more complicated 1H NMR spectra, where 16 aryl hydrogens and 8 alkyl hydrogens signals are observed. The ^{13}C NMR signals at 183.69 and 178.73 ppm in **2a** and 181.61 and 176.45 ppm in **2b** correspond to the two different carbenic carbons. The molecular structure of **2a** has been determined by single-crystal X-ray diffraction crystallography, which is shown in Figure 2. **2a** crystallizes in the monoclinic space group $P2_1/n$. A distorted square-planar geometry around the central nickel atom is constructed by one pyridine nitrogen, two carbene units and one amide nitrogen atom, leaving a pyridine ring uncoordinated. Obviously, an unexpected ligand rearrangement occurs in the formation of **2a**. Compared with the structure of **1a**, NHC ring containing C17, N5, N6 in **1a** has broken via the cleavage of the C17-N6 bond. At the same time, a new saturated NHC ring is generated via the formation of the C17-N4 bond accompanying with a breakage of the Ni-N4 bond and a formation of the Ni-N6 bond. Nitrogen atom N6

coordinates to the central metal atom as an amide with a Ni–N length of 1.890(3) Å, comparable with those reported values for the terminal Ni(II)–amide bonds.¹⁹

It was found that adding excess NaOAc to the DMSO solution of **1a** or **1b** resulted in **2a** or **2b** at room temperature, with the yellow solution turning into dark red visibly. This means that the four-coordinate complexes **1a** and **1b** can be transformed into **2a** and **2b** accompanying with the ligand rearrangement.

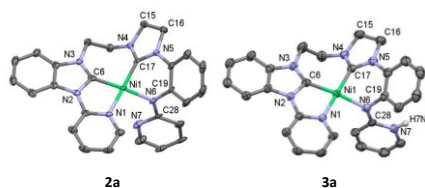


Figure 2 The structure of **2a** and **3a** with ellipsoids set at 50%. All hydrogen atoms and PF₆ anions are removed for clarity. Only the pyridinium hydrogen atom is shown. Relevant bond lengths [Å] and angles [°] of **2a**: Ni1–N1 1.965(3), Ni1–C6 1.884(4), Ni1–C17 1.866(3), Ni1–N6 1.890(3), N6–C19 1.405(5), N6–C28 1.376(4), N1–Ni1–C6 81.86(14), C6–Ni1–C17 98.21(15), C17–Ni1–N6 85.56(14), N6–Ni1–N1 95.00(13). Relevant bond lengths [Å] and angles [°] of **3a**: Ni1–N1 1.949(4), Ni1–C6 1.878(4), Ni1–C17 1.873(4), Ni1–N6 1.900(4), N6–C19 1.423(6), N6–C28 1.342(6), N1–Ni1–C6 82.38(17), C6–Ni1–C17 98.76(19), C17–Ni1–N6 85.38(17), N6–Ni1–N1 94.15(15).

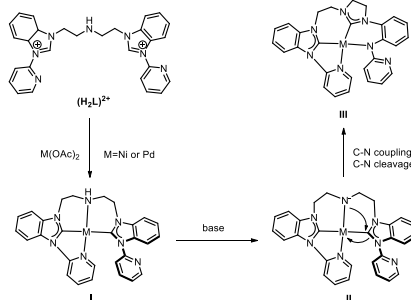
The fact that **1a/1b** can be converted into **2a/2b** has stimulated us to test if the reverse conversion could occur by the treatment of **2a/2b** with acid. The latter reaction gives only the protonated adducts of **2a** and **2b**, respectively. By reacting **2a/2b** with aqueous NH₄PF₆ aqueous solution, high-quality single crystals of protonated adducts **3a** and **3b** were obtained. In CD₃CN, ¹H NMR resonances for pyridinium N–H of **3a** and **3b** are observed as broad signals at 10.43–10.16 and 10.90–10.0 ppm, respectively. Besides, the signals of 16 aryl hydrogens and 8 alkyl hydrogens similar to those of **2a** and **2b** were also observed. In d₆-DMSO, the ¹³C NMR spectrum show signals at 180.37 and 170.70 ppm for the two carbenic carbons of **3a**. Similar resonances at 181.17 and 172.23 ppm in CD₃CN for the two carbenic carbons were found for **3b**. Unlike the transformation from **1a/1b** to **2a/2b**, the protonation is reversible. Treatment of **3a/3b** with base such as Na₂CO₃ aqueous solution can turn **3a/3b** back to the deprotonated products **2a/2b**.

The molecular structures of **3a** and **3b** have been studied by single-crystal X-ray diffraction. Both of **3a**·CH₃CN and **3b**·2CH₃CN crystallize in the monoclinic space group P2₁/c. The X-ray diffraction data illustrate the distorted square-planar geometry around the central metal in **3a** (Figure 2) and **3b** (Figure S2). Similar to **2a** and **2b**, the central metal ion in **3a** or **3b** is coordinated by one pyridine nitrogen, two carbene units and one amide nitrogen atom (N6). The uncoordinated pyridine nitrogen is protonated to render a zwitterionic ligand. Similar feature has been reported in some other metal complexes.²⁰ The N6–C28 bond length is 1.342(6) Å in **3a** and

1.332(5) Å in **3b**, appreciably shorter than that in **2a** (1.376(4) Å). Notably, they fall in between the range between a typical C–N bond (1.48 Å) and a normal C=N bond (1.26 Å). The bond length for C19–N6 is 1.423(6) Å in **3a** and 1.421(5) Å in **3b**. Both are longer than that in **2a** (1.405(5) Å). These suggest electronic distribution after the conversion of **2a/2b** to **3a/3b** and a considerable degree of delocalization between N6 and the pyridine in **3a** and **3b**.

To get gain a further insight into the reaction leading to the novel ligand rearrangement, we reacted (H₂L)(PF₆)₂ with 1.0 equiv Ni(OAc)₂·4H₂O in the presence of several frequently used bases like NEt₃, Na₂CO₃, Na₂HPO₄, K₃PO₄ and NaOH (Table S3). It was found that these bases can also promote the reaction to give **2a** in 25–52% yields. Furthermore, an acetate-free reaction between NiCl₂·6H₂O and (H₂L)(PF₆)₂ in the presence of 5.0 equivalent equiv. of NaOH in DMSO at room temperature gave **2a** in 37% yield, indicating the acetate anion was not indispensable in the ring-opening transformation.

Based on the experimental data outlined above observations, we suggest the following mechanism. It can be proposed that a C–N bond cleavage and a new C–N bond forming formation, which corresponds to a ring-opening and ring-closing process, occurs in the reaction. Initially, the product I (**1a/1b**) with a clearly characterized structure is probably formed. In the absence of a base, the reaction stops at that stage and **1a/1b** can be isolated. When a base is present in the reaction system, the amino N–H group in **1a/1b** can be deprotonated by the base to form an intermediate II. Intermediate II can be rapidly transformed into the ring-opening product III by C–N bond coupling of the carbonic carbon and the anionic amine accompanied by cleavage of the C–N bond.^{12, 21}



Scheme 3 Probable mechanism of the ring-opening and generating process

In conclusion, an unusual ligand rearrangement via unusual ring-opening and ring-closing process have been found in the reactions of a new type NHC ligand precursor with metal sources in the presence of base. Unlike previously reported examples, the presence of moisture or some harsh conditions such as a the use of strong base are not indispensable in this the ring-opening reactions here. This novel reaction involves the opening of an NHC ring and forming formation of a new saturated NHC ring in which is an

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unprecedented [process](#). This unusual rearrangement of NHC, [demonstrating new carbene reactivity](#), may broaden the horizons [of NHC chemistry and present new evidence of carbene's reactivity](#).

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Conflicts of interest

There are no conflicts to declare.

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