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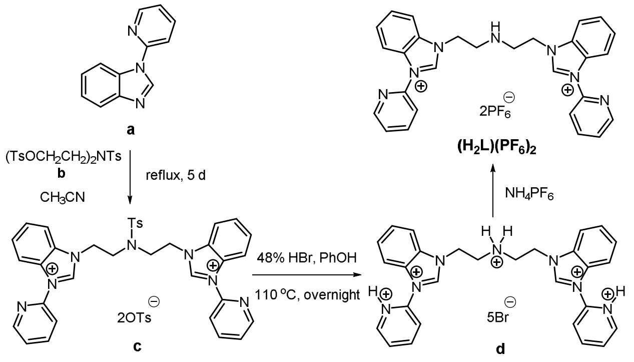
Reaction of a pentadentate NHC ligand precursor with $Ni(OAc)_2{\cdot}4H_2O$ or $Pd(OAc)_2$ in the presence of a base yields four-coordinate square-planar Ni(II) and Pd(II) complexes with an unusual ligand generated *in-situ*. A series of experimental studies point to a ring-opening and ring-closing process via novel C-N bond cleavage and formation.

N-Heterocyclic carbenes (NHC) have been widely used in organometallic chemistry[1] and organic methodology[2] since the first isolation of free NHC in 1991.[3] NHCs can coordinate with nearly all metals in the periodic table. They normally act as spectator ligands due to the inert metal-NHC bonds, affording enhanced stability for numerous robust metal-NHC catalysts. However, many experimental evidences have shown that NHC ligands are quite reactive and can undergo several types of unexpected reactions under certain circumstances,[4] potentially leading to the irreversible decomposition of *in-situ* formed or preformed metal-NHC catalysts. These reactivities include C-H and C-C bond activations occurring at the N-substitutent[5] and NHC backbone.[6] Besides, the carbenic carbon atom in the NHC ring could also be involved in the reactions, which 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 moisture or base has been found for free NHC,[9] or imidazolium precursor salts used to prepare NHC complexes.[10] The reaction leads to the complexes bearing the *in-situ* formed, unusual ligand containing a ring-opening structure.[10] Ring expansion by C-N bond activation and subsequent insertion into element-H or element-C bonds have been found.[11] The complete removal of carbenic carbon from the NHC unit has been revealed in Hf and Ir complexes.[12] Recently Hernán-Gómez 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.[9c] Although these examples are still considered as the exceptions, studies of reactions involving the NHC ligands would enhance our understanding of the activation or de-activation of metal-NHC catalysts.

Multidentate NHC ligands have attracted much interest, among which the non-cyclic ligands with more than four donors[14] have been rarely studied in contrast to those with 2-4 donors.[1d,1e] 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, ring-closing and *in-situ* generation of an unusual NHC ligand from the NHC precursor $(H_2L)(PF_6)_2$ (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 adequate to promote the ring-opening in the reactions of Ni(II) and Pd(II) sources with the NHC ligand precursor $(H_2L)(PF_6)_2$ (Scheme 1).

The pentadentate NHC precursor salt $(H_2L)(PF_6)_2$ was synthesized via a three-step procedure (Scheme 1). The first step starting from 1-(pyridin-2-yl)-1H-benzimidazole (**a**)[15] and tosylbis(2-(tosyloxy)ethyl)amine (**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 solution in the presence of PhOH to give the detosylated salt **d**, which was converted to the target product $(H_2L)(PF_6)_2$ by anion exchange. ^1H and ^{13}C NMR in CD_3CN show the resonances at 9.38 and 150.44 ppm for the carbene proton and carbon atoms, respectively.



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

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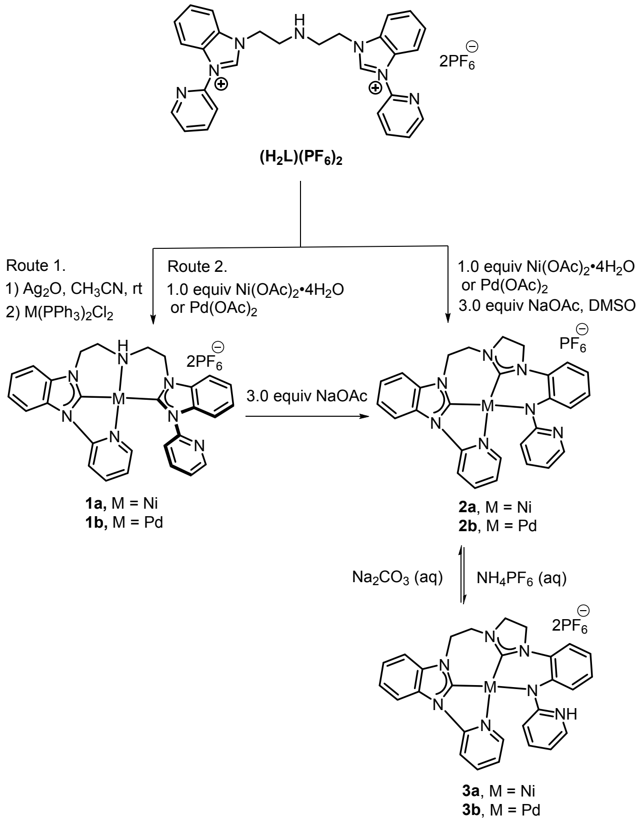
Electronic Supplementary Information (ESI) available: Syntheic procedures and characterizations, crystallographic data and NMR spectra. CCDC: 1839764, 1839765, 1839747, 1839752. For ESI and crystallographic data in CIF or other electronic format see ?????????//

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 Ni(II) and Pd(II) complexes **1a** and **1b** were prepared in 42% and 49% yields by transmetalation of the *in-situ* generated 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.



Scheme 2 Synthesis and transformation of three types of complexes.

The structure of **1a**$\cdot CH_3CN$ was established by single-crystal X-ray diffraction, which is shown in Figure 1 with the selected structural data listed in the caption. A distorted square-planar coordination geometry is found for **1a**, with four *cis*- bond angles in the range of 81.61(12) to 101.55(12)°. The central nickel atom is coordinated by two NHCs, one secondary amine and one pyridine nitrogen. The other pyridine unit remains uncoordinated. The Ni1-C6 bond length is 1.844(3) Å, significantly shorter than the other Ni-carbene bond (Ni1-C17, 1.933(3) Å), probably due to the fusion of the five- and six-membered chelating rings in the former compared with the occurrence of only one six-membered chelating ring associated with the latter. The two pyridine rings are not co-planar with a dihedral angle of about 54° and two benzimidazole rings form a dihedral angle of about 50°. Attempts to obtain high-quality single crystals of **1b** were unsuccessful, but the X-ray crystallography shows the atom connectivity, revealing a structure similar to **1a** (Figure S1).

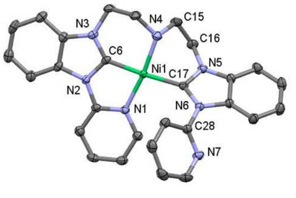
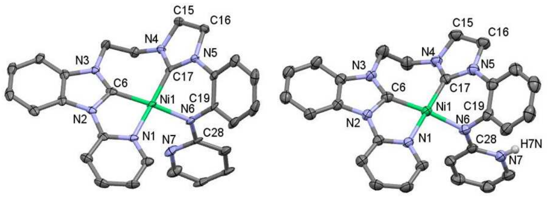


Figure 1 Structure of the cationic portion of **1a** with ellipsoids set at 50%. All hydrogen atoms, solvent molecules and PF_6^- anions are removed for clarity. Relevant bond lengths [Å] and angles [°]: Ni1-C6 1.844(3), Ni1-N1 1.931(2), Ni1-C17 1.933(3), Ni1-N4 1.939(3), C6-Ni1-N1 81.64(12), N1-Ni1-C17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

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] Reaction of $(H_2L)(PF_6)_2$ with 1.0 equiv of $Ni(OAc)_2{\cdot}4H_2O$ or $Pd(OAc)_2$ also gave **1a** and **1b** in 82% and 77% yield, respectively. Interestingly, the same reaction of $(H_2L)(PF_6)_2$ with 1.0 equiv of $Ni(OAc)_2{\cdot}4H_2O$ or $Pd(OAc)_2$ in the presence of 3.0 equiv of NaOAc unexpectedly resulted in the formation of complexes **2a** and **2b** (Scheme 2) in 50% and 54% yield, respectively. The amount of NaOAc should be at least 1.0 equiv relative to that of $Ni(OAc)_2{\cdot}4H_2O$ or $Pd(OAc)_2$. 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 176.44 ppm in **2b** correspond to the two different carbenic carbons. The molecular structure of **2a** has been determined by single-crystal X-ray diffraction, which is shown in Figure 2. 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 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 the reported terminal Ni(II)-amide bonds.[19]

1a and **1b** remain stable under synthetic conditions, while addition of 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. NMR monitoring of the reaction shows that the conversion is clean and complete after 12 hours (Figure S19). This means that the four-coordinate complexes **1a** and **1b** can be transformed into **2a** and **2b** accompanying with the ligand rearrangement.



2a **3a**

Figure 2 The structures of **2a** and **3a** with ellipsoids set at 50%. All hydrogen atoms and PF_6^- 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).

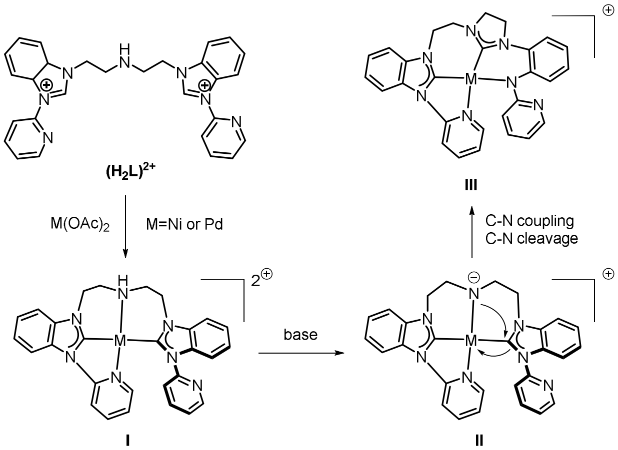
We were unsuccessful in obtaining high-quality single crystals of **2b**. By reacting **2a**/**2b** with NH_4PF_6 aqueous solution, we isolated high-quality single crystals of their protonated adducts **3a**/**3b**, with the similar structures. In CD_3CN, ^1H NMR resonances for pyridinium N-*H* of **3a** 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 d^6-DMSO, the ^{13}C 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 CD_3CN 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 Na_2CO_3 aqueous solution turns **3a**/**3b** back to the deprotonated products **2a**/**2b**.

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**, 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 other metal complexes.[20] The N6-C28 bond length is 1.342(6) Å in **3a** and 1.332(5) Å in **3b**, considerably shorter than in **2a** (1.376(4) Å). Notably, they fall in 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 gain a further insight into the reaction leading to the novel ligand rearrangement, we reacted $(H_2L)(PF_6)_2$ with 1.0 equiv $Ni(OAc)_2{\cdot}4H_2O$ in the presence of several frequently used bases like NEt_3, Na_2CO_3, Na_2HPO_4, K_3PO_4 and NaOH (Table S3). It was found that these bases can also promote the reaction to give **2a** in 44-61% yields. Furthermore, an acetate-free reaction between $NiCl_2{\cdot}6H_2O$ and $(H_2L)(PF_6)_2$ in the presence of 3.0 equiv of NaOH in DMSO at room temperature gave **2a** in 55% yield, indicating the acetate anion was not indispensable in the ring-opening transformation.

Since our reactions with the weak bases are not rigorously anhydrous, the residual water molecules could be involved in the ring-opening and ring-closing reaction. However, the control reactions under the strictly drying condition gave the same products. And no ^1H NMR signals for the formamide molecules, which are expected from the hydrolytic ring-opening of NHC unit,[9-10] were observed by NMR monitoring experiments. Furthermore strong base such as NaH could also promote the formation of **2a** starting from $(H_2L)(PF_6)_2$ (entry 7, Table S3) and the conversion from **1a**/**1b** to **2a**/**2b** (ESI). These experiments show that H_2O could not be essential in the presence of base.

Based on the experimental observations, we suggest the following mechanism. A C-N bond cleavage and a new C-N bond formation, which correspond to a ring-opening and ring-closing process, occurs in the reaction. Initially, the product **I** (**1a**/**1b**) is probably formed. In the absence of a base, the reaction stops at this 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**. **II** can rapidly transform into the ring-opening product **III** (**2a**/**2b**) by C-N bond coupling of the carbonic carbon and the anionic amine accompanied by cleavage of the C-N bond. This C-N bond coupling resembles the intramolecular attack of so generated carbene onto a neighbour NCHN moiety proposed by Huertos et al.[21] and the C-C coupling of the benzylic CH_2 group of the mesityl substituent and the carbenic carbon suggested by Hernán-Gómez et al.[9c] It is noted that similar arrangement has not been observed in metal complexes with secondary amine functionalized NHC ligands without the pyridine substituent.[22] The driving force of this C-N bond cleavage and a new C-N bond formation could be the replacement of a less basic amide on the carbene carbon with a more basic one considering the electron withdrawing nature of pyridine group.



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

In conclusion, an unusual ligand rearrangement has 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 harsh conditions such as a strong base are not indispensable in the ring-opening reactions here. This novel reaction involves the opening of an NHC ring and formation of a new saturated NHC ring in an unprecedented process. This unusual rearrangement of NHC, demonstrating new carbene reactivity, may broaden the horizons of NHC chemistry.

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Conflicts of interest

There are no conflicts to declare.

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