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VIP **NHC Ligands**

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# Reversible Insertion of 1,3-Di-*tert*-butylimidazol-2-ylidene into a Ru–H Bond and Bimetallic Activation of a N–C Bond of Imidazoline**

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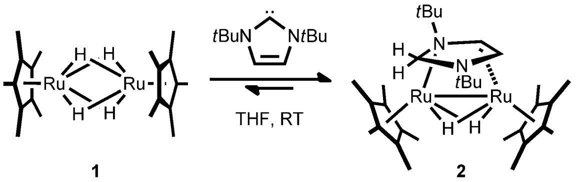
N-Heterocyclic carbenes (NHCs) are strong 2-electron donors and hardly exhibit π-accepting character.[1] NHCs stabilize unsaturated metal centres and have been recently applied as stable spectator ligands in various catalytic transformations of organic molecules in combination with mononuclear transition-metal complexes.[2] However, NHCs can undergo degradation pathways,[3] because they are multifunctional compounds, namely, a lone pair of electrons at C2, which acts as a donor; π-electron lone pairs at N1 and N3; and a C=C double bond between C4 and C5. Because of this multifunctionality, NHCs sometimes undergo a chemical transformation that is possibly related to a deactivation process for catalytically active species.

So far, there have been fewer reports on reactions of NHCs with polynuclear complexes than with mononuclear ones,[4] though a variety of patterns are expected to be obtained in the reaction involving a multimetallic system owing to the multifunctional character of NHC molecules. We previously reported the reactions of dinuclear homo- and heterometallic tetrahydrido complexes, [Cp*Ru(μ-H)$_4$RuCp*] and [Cp*Ru(μ-H)$_4$OsCp*], with *tert*-phosphorus ligand that do not contain aryl substituents.[5,6]

We examined the reaction of [Cp*Ru(μ-H)$_4$RuCp*] (**1**) with 1,3-di-*tert*-butylimidazol-2-ylidene (I*t*Bu), which is a multifunctional, strong 2-electron donor. We report herein an unprecedented reversible insertion of 1,3-di-*tert*-butylimidazol-2-ylidene into the ruthenium–hydride bond of **1** and the dynamic process of the resulting dinuclear imidazoline complex. Furthermore, a bimetallic-system-assisted ring-opening reaction, that is, the cleavage of the N–C bond of the imidazoline ligand to generate pseudo-diazaruthenacycle is also reported.

The treatment of **1** with 2.3 equivalents of I*t*Bu in tetrahydrofuran at room temperature resulted in the formation of a dinuclear ruthenium μ-η$^1$:η$^2$-4-imidazoline complex **2** as a result of migration of the hydrides from the ruthenium atom to the carbenic carbon (C2) [Eq. (1)]. The yield of the conversion from **1** to **2** reached 56% under these conditions. The yield inevitably reached a plateau because of the presence of the reverse process, that is, the de-insertion of I*t*Bu. Therefore, a large excess amount of I*t*Bu must be added to carry out the conversion. Time-conversion curves of the reaction of **1** with I*t*Bu are given in the Supporting Information. Complex **2** was efficiently isolated by crystallization from cold pentane (−30 °C).



**1** **2**

(1)

In complex **2**, the 4-imidazoline molecule is coordinated as a bridging ligand through a C=C bond and one of the nitrogen atoms. Single crystals of **2** suitable for X-ray diffraction studies were obtained from cold (−30 °C) pentane. The X-ray diffraction data clearly showed the dinuclear structure bridged by 4-imidazoline that was formed by hydride migration to the C2 of the I*t*Bu molecule. The molecular structure of **2** is illustrated in Figure 1 with the relevant bond lengths and angles.[7] The imidazoline molecule is coordinated as 4-electron donor, and there must be two bridging hydrogen atoms between Ru1 and Ru2 although the ruthenium-bound hydrogen atoms are not located in the differential Fourier maps.

The interatomic distances Ru2–C4 and Ru2–C5 are 2.078(9) and 2.194(8) Å, respectively, and these values are in the range of those for the π-bonded metal–carbon bonds.

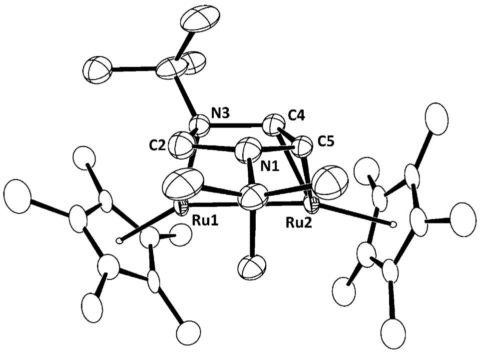


***Figure 1.*** Molecular structure of **2** with thermal ellipsoids set at 30%. Relevant bond lengths [Å] and angles [°]: Ru1–Ru2 2.7435(9), Ru2–C4 2.078(9), Ru2–C5 2.194(8), Ru1–N3 2.262(7), C2–N1 1.434(12), C2–N3 1.511(12); C2-N1-C5 107.2(7), C2-N1-C(CH$_3$)$_3$ 117.3(7), C5-N1-C(CH$_3$)$_3$ 122.0(8).

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The distance between Ru1 and N3 is 2.262(7) Å and this value indicates the occurrence of bonding interaction between Ru1 and N3. The *tert*-butyl group bound to N3 is sharply tilted out of the plane of the imidazoline ring, while the *tert*-butyl group at N1 slightly tilts to the opposite side. As mentioned above, the imidazoline is a 4-electron donor ligand; therefore, a double bond is required between the two ruthenium atoms according to the effective atomic number (EAN) rule. The distance between the Ru1 and Ru2 center is 2.7435(9) Å, which is similar to that of an isoelectronic dinuclear $\mu$-$\eta^2$:$\eta^2$-cyclohexadiene complex of ruthenium (2.7391(15) Å).[8]

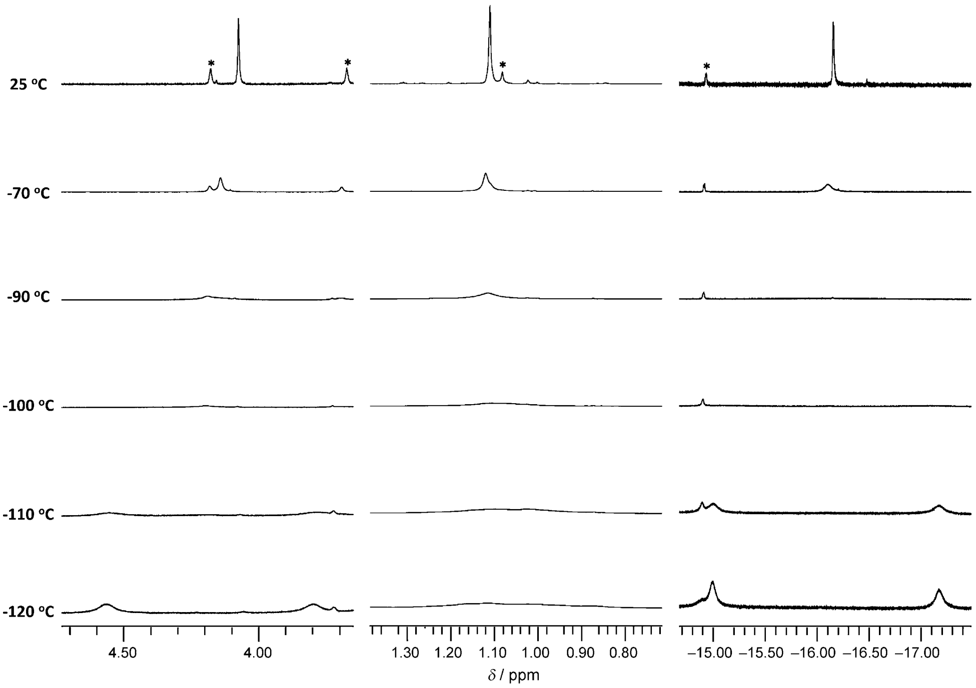
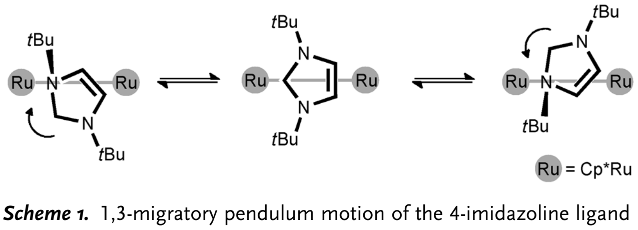


***Figure 2.*** Variable-temperature $^1$H NMR spectra of **2** (left; olefinic protons, center; *t*Bu groups, right; hydrido ligands). The peak labeled with the asterisk is an impurity.

The $^1$H NMR spectrum of **2** recorded in [D$_8$]THF at 23 °C exhibited two sharp singlet resonances for the Cp* groups and the bridging hydride at $\delta = 1.70$ (15 H), 1.83 (15 H) and −16.14 ppm (2 H), respectively. Notably, at 23 °C, four signals for the imidazoline moiety appeared at $\delta = 1.14$ (18 H, *t*Bu), 3.14 (1 H, C2–H$_{endo}$), 3.44 (1 H, C2–H$_{exo}$), and 4.10 ppm (2 H, olefinic). This result clearly indicates that **2** has a time-averaged symmetry plane along the Ru–Ru axis. Therefore, we concluded that **2** underwent a dynamic process in solution as shown in Scheme 1. In this process, the bridging imidazoline ligand swings from side to side like a pendulum on the Ru1 that coordinates the carbon–carbon double bond (C4=C5).

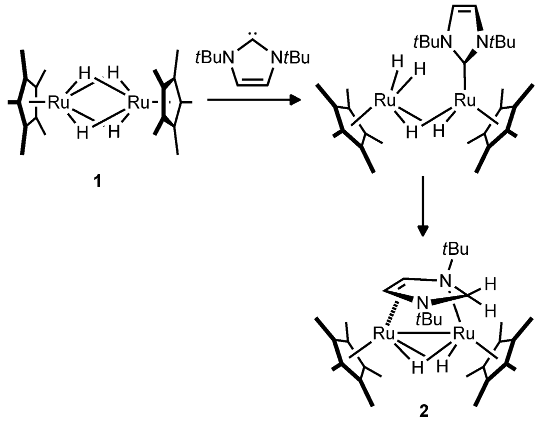


***Scheme 1.*** 1,3-migratory pendulum motion of the 4-imidazoline ligand on dinuclear complex **2**.

The dynamic process of **2** in solution was supported by variable temperature $^1$H NMR experiment performed in the temperature range from 20 to −120 °C (Figure 2). The singlet signals for the olefinic protons, *tert*-butyl groups at the nitrogen atoms, and the hydrido ligands broadened with a drop in temperature. The signals for the olefinic protons and the hydride eventually decoalesced and split into two peaks at low temperature. The proposed unique molecular motion, which is referred to as the 1,3-migratory pendulum motion, adequately accounts for the appreciable changes in the spectra.

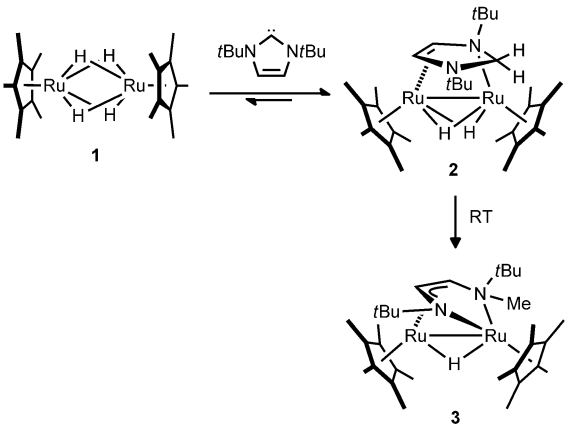
Monitoring the reaction by $^1$H NMR spectroscopy indicated the formation of an intermediate in the initial stage of the reaction; the $^1$H NMR spectrum revealed singlet signals for Cp* groups and hydrides at $\delta = 1.78$ (30 H) and −16.47 ppm (4 H), respectively. The signal for the *tert*-butyl groups of the coordinated I*t*Bu ligand was most likely obscured by the large signal of free I*t*Bu. Based on the singlet patterns of the signals for the Cp* groups and the hydride ligands, it was inferred that the intermediary species have a time-averaged symmetry plane that bisects the Ru–Ru vector. We previously reported reversible migration of tertiary phosphorus ligands between the two metal atoms in dinuclear polyhydrido complexes of group 8 metals.[5] The electronic similarity of the I*t*Bu to the phosphines or phosphites implies that the coordinated I*t*Bu would rapidly migrate between the two ruthenium centres, as observed in the reaction of **1** with the phosphorus compounds. Subsequent intramolecular hydride migration to the carbenic carbon generates $\mu$-imidazoline complex **2** (Scheme 2).

It is noteworthy that double insertion of carbenic carbon atoms into the Ru–H bonds is reversible in solution. Complex **2** was found to gradually revert to **1** upon dissolution in benzene or tetrahydrofurane at room temperature through double C–H bond activation.[9,10] Therefore, the addition of large excess of I*t*Bu to **2** is required to impede the reversion. Complex **1** was gradually converted into a pseudo-diazar-



*Scheme 2.* Proposed reaction mechanism.

uthenacycle **3** in tetrahydrofurane at room temperature through N–C bond cleavage [Eq. (2)].



(2)

Definitive proof of the structure of pseudo-diazaruthenacyclic **3** was provided by X-ray crystallography. The structure shown in Figure 3 clearly depicts the formation of a five-membered pseudo-diazaruthenacycle. Ru2, N1, C4, C5, and N3 comprise the pseudo-metallacycle, while Ru1 is bound to the azaallyl moiety, N3-C4-C5, in a π fashion. The interatomic distances, Ru2–N3 (2.1483(11) Å) and Ru2–N1 (2.2781(11) Å), reveal that they correspond to a σ bond and a coordination bond, respectively.

An important feature of the $^1$H NMR spectrum of **3** is the appearance of a signal for the methyl group bound to N1 at $\delta = 2.38$ ppm. In addition, the signals for the *tert*-butyl groups were observed to be inequivalent, as indicated by the presence of two signals at $\delta = 1.04$ and 1.40, respectively; this observation implies that complex **3** is not fluxional.

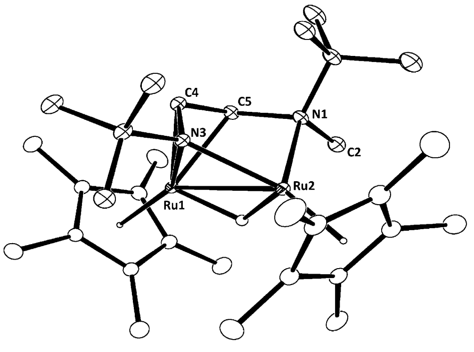
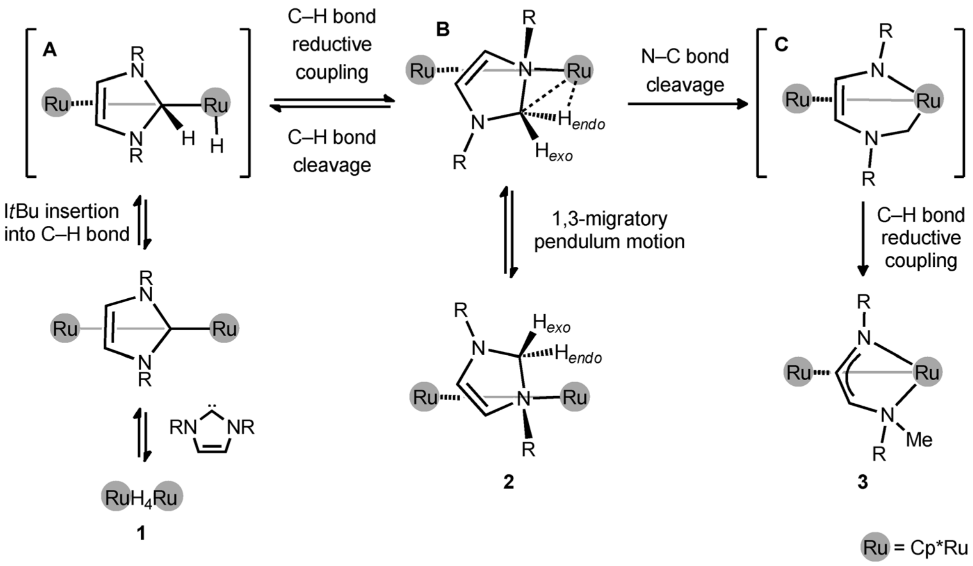


*Figure 3.* Molecular structure of **3** with thermal ellipsoids set at 30% probability. Relevant bond lengths [Å] and angles [°]: Ru1–Ru2 2.86602(15), Ru2–N3 2.1483(11), Ru2–N1 2.2781(11), Ru1–N3 2.1712(11), Ru1–C4 2.0798(14), Ru1–C5 2.1361(13), N3–C4 1.3826(17), C4–C5 1.417(2), N1–C5 1.4718(18); C4-N3-Ru2 112.67(9), $C(CH_3)_3$-N3-Ru2 129.54(8), $C(CH_3)_3$-N3-C4 116.39(11).

The conversion of **2** into **3** is a typical example of bimetallic N–C bond activation that involves assistance of an adjacent metal atom, for example Ru1, as a binding site. The coordination of the C4–C5 moiety to Ru1 closely clasps the imidazoline molecule, which facilitates the bond activation at Ru2. Because the imidazoline ring swings side by side on the Ru1–Ru2 axis, Ru2 could competitively interact with N–C2 and C2–H(endo) bonds. C2–H bond cleavage at Ru2 leads to the formation of **1** through B and NHC complex A. In contrast, N–C2 bond cleavage at Ru2 would produce a diazaruthenacyclohexene, C, which would undergo C–H reductive coupling to generate **3** (Scheme 3).

In summary, I*t*Bu was smoothly inserted into the Ru–H bonds of **1** to form **2**, which is fluxional in solution. The



*Scheme 3.* Mechanism of N–C bond cleavage and reversible insertion into the C–H bond.

dynamic behavior of **2**, that is, a pendulum motion of the imidazoline ligand, was shown by variable temperature $^1$H NMR spectroscopy. The 4-imidazoline ligand in **2** can interact with both of the two ruthenium atoms, because the 4-imidazoline contains two types of reactive sites: a lone pair of electrons and a C4=C5 π bond. Cooperative action of the two ruthenium atoms facilitated N–C bond cleavage of the imidazoline ring to generate a pseudo-azaruthenacycle **3**. Thus, we demonstrated a new degradation pathway of the NHC ligand by a reaction with a bimetallic system.

## Experimental Section

General considerations regarding the experimental procedures, X-ray diffraction, and time-conversion curves of the reaction are provided in the Supporting Information.

Synthesis of **2**: To a solution of **1** (70.5 mg, 0.15 mmol) in tetrahydrofurane (20 mL) I*t*Bu (61.5 mg, 0.35 mmol) was added and the mixture was stirred at room temperature. The color of the solution changed from red to dark purple. After 11 h, 88% of complex **1** were consumed and the yield of complex **2** reached 56%. Complex **3** was formed in 15% yield as well. A dark purple solid was obtained after removal of the solvent under reduced pressure. The imidazoline complex **2** was extracted with pentane and recrystallized from cold (−30°C) pentane as purple blocks.

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**Keywords:** insertion · N–C activation · N-heterocyclic carbenes · polyhydride clusters · ruthenium

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[7] Figure 1 shows the structure of one of two independent molecules of **2** included in a unit cell.

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[10] The time conversion of complex **2** in THF is provided in the Supporting Information.