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Bidentate NHC-alkenyl ruthenium(II) complex via vinyl C-H bond activation.

Renan Cariou,^a Cédric Fischmeister,^a Loïc Toupet^b and Pierre H. Dixneuf^{a}*

^a Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS–Université de Rennes.

^b Groupe Matière Condensée, UMR 6626 CNRS-Université de Rennes,

Campus de Beaulieu, Avenue du général Leclerc, 35042 Rennes, France

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*To whom correspondance should be addressed, Tel: + 33 2 23 23 62 80. Fax: + 33 2 23 23 69 39.

E-mail : pierre.dixneuf@univ-rennes1.fr

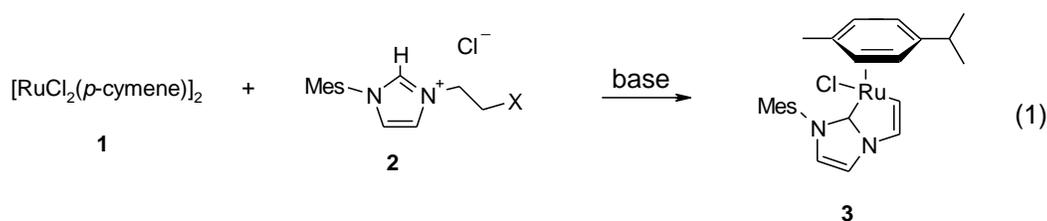
Abstract A bidentate NHC-alkenyl ruthenium(II) complex has been obtained on deprotonation of imidazolium salts with a N-CH₂CH₂X branch (X = OMe, Cl) followed by reaction with [RuCl₂(p-cymene)]₂ and was characterized by spectroscopy and X-ray diffraction. It possesses a planar bicyclic (NHC)-CH=CH-Ru unit. Low temperature NMR studies and intermediate trapping with BH₃ indicate the formation of a CH₂=CH-NHC carbene followed by the intramolecular activation of a vinyl sp² C-H bond on coordination to a ruthenium(II) centre.

Introduction

Nitrogen containing heterocyclic carbene (NHC) metal complexes¹ constitute crucial keys for the development of new catalytic reactions or the creation of more efficient catalysts for the formation of carbon-carbon bonds,² alkene metathesis³ or enantioselective catalysis.⁴ Consequently, a strong motivation is leading to the design of functional NHC carbenes, especially chelating mixed carbenes and bis carbenes for the tuning of catalyst activity.⁵ Of special interest are the functional carbenes containing a weakly coordinating lateral group allowing its reversible coordination to the metal centre, in order to temporarily stabilize a catalyst precursor and at the same time to allow the substrate coordination and activation.

For the design of new alkene metathesis ruthenium catalysts, an objective was to modify the olefin metathesis catalyst precursors $[\text{RuCl}(\text{PCy}_3)(\text{indenylidene})(\text{arene})]\text{X}^6$ by replacing the phosphine PCy_3 with a more electron releasing NHC ligand with a lateral chelating arm. Our attempt to introduce a NHC ligand containing a $\text{N-CH}_2\text{CH}_2\text{OMe}$ chain to $[\text{RuCl}_2(p\text{-cymene})]_2$ **1** led us to discover an unexpected chelating ligand in a ruthenium(II) complex.

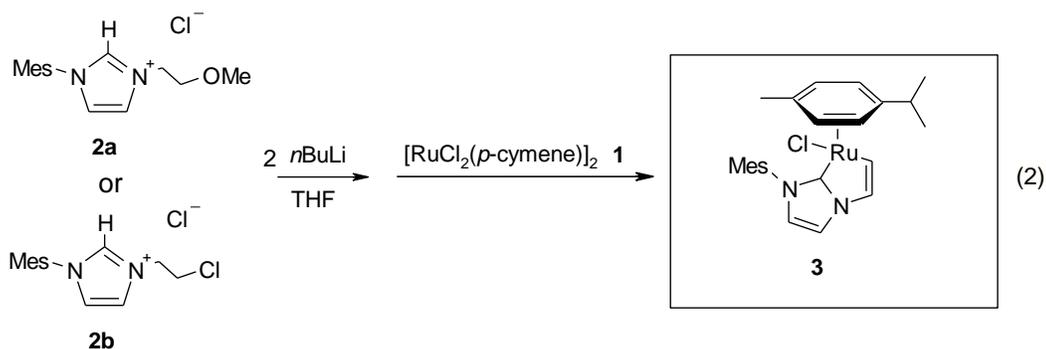
We now wish to report that the deprotonation of the imidazolium salts **2** ($\text{X} = \text{OMe}$ (**a**), Cl (**b**)) and addition of the expected resulting NHC ligand to $[\text{RuCl}_2(p\text{-cymene})]_2$ **1** does not lead to the expected $\text{RuCl}_2(p\text{-cymene})(\text{NHC})$ complex but to the new chelating mixed carbene alkenyl complex **3** (Eq.1). The evidence for an intramolecular vinyl sp^2 CH bond activation is presented.



Results and discussion

We have shown recently that the allenylidene-ruthenium complex **5**, readily obtained from $\text{RuCl}_2(\text{PCy}_3)(p\text{-cymene})$ **4**, is $[\text{Ru}=\text{C}=\text{C}=\text{CPh}_2(\text{Cl})(\text{PCy}_3)(p\text{-cymene})]\text{OTf}$ active in alkene metathesis,⁷ and proceeds *via* a rearrangement leading to the corresponding indenylidene-ruthenium complex **6** either thermally⁸ or more readily and quantitatively on addition of acid⁶.

Whereas the indenylidene complex **6** is very active at room temperature,⁶ its stability in solution at higher temperature is moderate as the catalytic species is highly coordinatively unsaturated by loss of the *p*-cymene ligand. To improve the stability of the system an attempt was made to replace the PCy_3 ligand of precursor **4** by the electron donating, bulky and chelating NHC ligand with a *N*- $\text{CH}_2\text{CH}_2\text{OMe}$ branch arising from the deprotonation of the imidazolium salt **2a** (Eq. 2). Thus, the imidazolium salt **2a** was first prepared by reaction of mesitylimidazole in $\text{ClCH}_2\text{CH}_2\text{OMe}$ and obtained in 75% yield. The imidazolium salt **2a** was dissolved in THF and deprotonated at -20°C by *n*-butyllithium. The reaction mixture was then added to $[\text{RuCl}_2(p\text{-cymene})]_2$ **1** in THF at room temperature. The expected product $[\text{RuCl}_2(\text{NHC})(p\text{-cymene})]$ **7** was not formed. The ^1H NMR analysis of the resulting complex showed the absence of $\text{CH}_2\text{CH}_2\text{OMe}$ branch and the presence of the *p*-cymene ligand, with four different aromatic protons suggesting its coordination to a chiral ruthenium centre. An alkenyl group was observed with deshielded protons [$\delta = 8.65(\text{d}), 7.06(\text{d})$ $^3J_{\text{HH}} = 5.6\text{Hz}$]. The ^{13}C NMR spectrum showed a signal at 188.92 ppm characteristic of the coordinated NHC carbon atom. Another low field signal at 154.71 ppm was attributed to the vinylic carbon atom bonded to the ruthenium. These NMR data were in favour of the complex **3** (Eq. 2). The same complex **3** was also obtained starting from the chlorinated salt **2b** instead of **2a** in a slightly better yield (37% vs 30% from **2a**).



The structure of **3** was confirmed by X-ray diffraction analysis (Fig. 1).

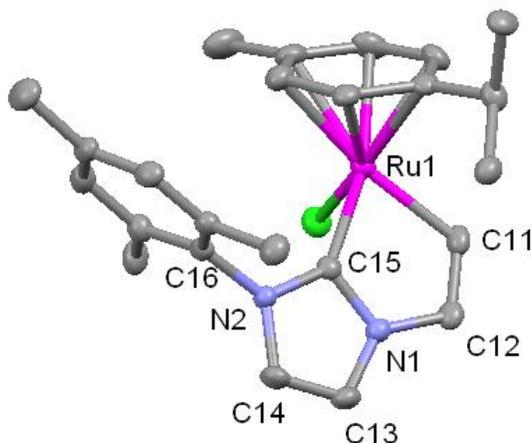


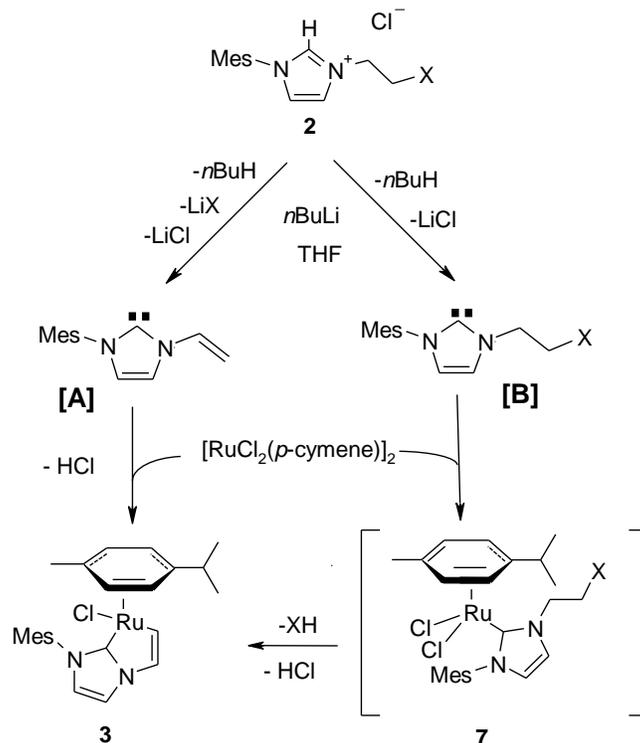
Figure 1: Molecular structure of complex **3** (50% ellipsoid probability). H atoms and the crystallisation CH_2Cl_2 molecule are omitted for clarity. Selected bond lengths (\AA): Ru1-C15 2.028(4), Ru1-C11 2.071(5), C11-C12 1.350(7), N1-C12 1.424(6), N2-C16 1.456(6), C13-C14 1.350(7).

The molecular structure shows the presence of the *p*-cymene ligand and only one chloride ligand. The most surprising feature is the bidentate mixed carbene-vinyl ligand, forming a metallabicyclic unit. The C11-C12 and C13-C14 bond lengths of 1.350 \AA and 1.349 \AA , respectively, are consistent with C=C double bonds. It is noteworthy that the NHC carbene ligand and the 5-membered ruthenacycle Ru1-C11-C12-N1-C15 are coplanar as the sum of the angles (C13N1C15), (C15N1C12), (C12N1C13) reaches 360.0° and the torsion angle (C12N1C15N2) equals 179.45°. The Ru-C15 bond length (2.03 \AA) is slightly shorter than typical ruthenium-carbon bonds of various (arene)ruthenium-monodentate NHC complexes (typically 2.06-2.09).^{5a,9} This feature was previously observed for a ruthenium complex

containing a chelating (NHC) carbene arene ligand $[\text{RuCl}_2\{(\eta^1\text{-CN-}[\text{CH}_2(\eta^6\text{-C}_6\text{H}_2\text{Me}_3\text{-2,4,6})])\text{CHCHN-}(\text{CH}_2(\eta^6\text{-C}_6\text{H}_2\text{Me}_3\text{-2,4,6}))\}]$ with a Ru-C bond length of 2.04 Å.^{5a}

The formation of complex **3** has been investigated by means of NMR experiments. Two reasonable pathways have initially been considered. One route involves the double deprotonation of the imidazolium salt leading to a vinylcarbene **[A]** followed by elimination of HCl on coordination to the ruthenium(II) centre. The second possibility is the formation of the carbene **[B]** leading to complex **7** followed by the elimination of XH and HCl (Scheme 1).

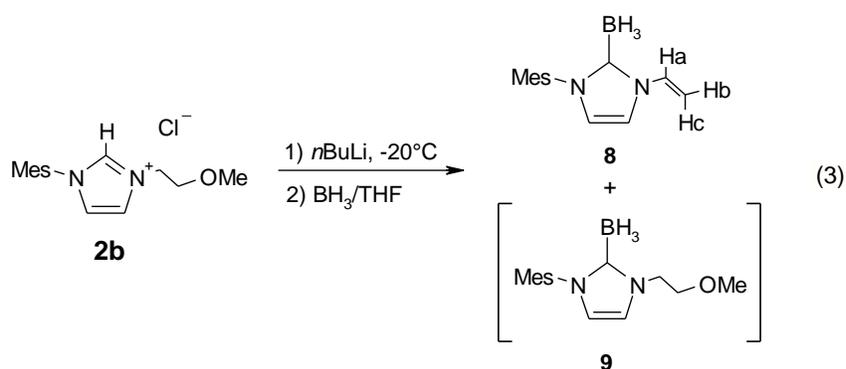
Scheme 1



The deprotonation of **2b** by $n\text{BuLi}$ has been followed by ^1H NMR at low temperature by the observation of the imidazole N-CH=CH-N protons. When the deprotonation was performed at -20°C the total disappearance of the more acidic NCHN proton of the imidazolium salt was observed. The

analysis of the region between 4.7-6.5 ppm showed two important features. First, the presence of four N-CH=CH-N vinylic protons at 5.61 ppm and 6.21 ppm, and 5.71 ppm and 6.13 ppm showing the presence of two carbene species.¹⁰⁻¹² The second information comes from the signals at about 5 ppm and 6.5 ppm characteristic of a CH₂=CH- vinylic system. These observations support the formation of the intermediate vinyl carbene **[A]**. The structure of the second species is likely to be of the **[B]** type, although it was not unambiguously identified by NMR.

A second experiment was carried out to confirm these preliminary observations. It is known that *in situ* generated NHC carbenes can be trapped by BH₃ or BF₃.¹³ Thus **2a** was deprotonated at -20°C and then the formed species were trapped by BH₃. When 1 equiv of *n*BuLi was used at -20°C the ¹H NMR spectrum revealed the absence of the NCHN proton and the presence of two boron adducts, one of these containing a vinyl group. This observation is consistent with the presence of derivative **8** (Eq.4). The second species was not clearly identified but NMR data support derivative **9** (Eq.3). However, when 2 equiv of *n*BuLi were added to **2a**, as in the formation **3**, only species **8** was observed. Its ¹H NMR spectrum shows a vinyl group linked to a heteroatom, as three doublets of doublets were observed [¹H NMR 200MHz : δ = 4.41 (Hb), 4.66 (Hc), 7.82 (Ha) ²J_{HbHc} = 1.6 Hz ; ³J_{HaHb} = 9.0 Hz, ³J_{HaHc} = 16.0 Hz].



These observations support the *in situ* formation of both intermediates **[A]** and **[B]** by deprotonation of salt **2**. In the formation of **3**, 2 equiv. of *n*BuLi are used to deprotonate the salt **2** before addition to complex **1** and under these conditions only the vinyl containing species is observed by NMR. It is thus likely that species **[A]** is predominantly formed from **2** its coordination to the ruthenium atom of **1** favours the intramolecular activation of a vinyl sp² C-H bond with formal elimination of HCl leading to

complex **3**. The released HCl is expected to decompose the carbene [A], thus the yield cannot exceed 50%. However, the addition of NEt₃ to the reaction mixture did not increase the yield of **3**. The addition of HBF₄ to **3** led to its decomposition rather than to the formation of a CH=CH₂ group or the formation of alkylidene ligand as observed by Werner¹⁴ on protonation of a vinyl derivative.

The formation of **3** constitutes a new example of the capability of ruthenium complexes to activate usually inert C-H bonds.¹⁵ Whereas the C-H bond activation by ruthenium(0) is now well established¹⁵ the reaction presented here reveals an unprecedented example of C-H bond activation of a NHC vinyl group by a ruthenium(II) species. Previous C-H bond activation by ruthenium(II) complexes were discovered in orthometallation of phosphites¹⁶ and arylamines.¹⁷ The ethene C-H bond activation with rhodium(I) and iridium(I) complexes is a well known process,¹⁸ whereas vinyl CH bond activation of vinylpyridine is performed with osmium polyhydrides,¹⁹ and mixed pyridine N-heterocyclic carbene on reaction with IrH₅(PPh₃)₂²⁰ is known to ‘abnormally’ bind to iridium via an imidazolium (NCH=CHN)C-H bond activation. These metal polyhydride complexes generate coordinatively unsaturated metal moiety on loss of hydrogen before C-H bond activation¹⁹⁻²⁰. The hypothesis is made here, that for both orthometallation and the present reaction, the coordination of the substrate (arylamine, arylphosphite or vinyl NHC) first takes place followed by C-H bond activation by the 18 electron ruthenium(II) centre.

Conclusion

The above results show the formation of a new chelating mixed carbene vinyl ruthenium complex. The X-ray structure shows the planarity of the NHC ligand with the 5-membered ruthenacycle. Low temperature NMR observations are consistent with the initial formation of a *N*-vinyl-*N*-mesityl imidazolylidene carbene and thus the formation of the complex implies an intramolecular activation of an usually inert vinyl sp² C-H bond

Acknowledgements

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Supporting Information Available. Experimental details and CIF file for complex **3** are available free of charge via the internet at <http://pubs.acs.org>. CCDC reference number 276178 also contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>

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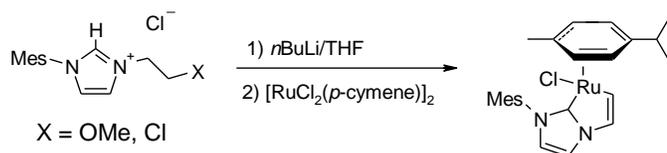
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The deprotonation with *n*BuLi of imidazolium salt with a N-CH₂CH₂X chain (X = OMe, Cl), followed by reaction with [RuCl₂(*p*-cymene)]₂, affords complex **3** with a chelating planar mixed (NHC) carbene-vinyl ligand arising from vinyl (sp²)(C-H) bond activation.

