Organometallics **2006,** *25,* 2126−2128

Communications

A Bidentate NHC−Alkenyl Ruthenium(II) Complex via Vinyl C−H Bond Activation

Renan Cariou,[†] Cédric Fischmeister,[†] Loïc Toupet,[‡] and Pierre H. Dixneuf*,[†]

Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes, and Groupe Matière Condensée, UMR 6626 CNRS- Université de Rennes, Campus de Beaulieu, Avenue du général Leclerc, 35042 Rennes, France

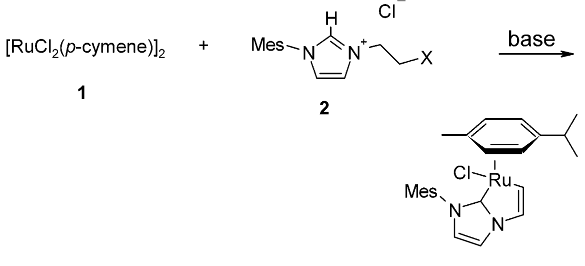
Received January 27, 2006

Summary: A bidentate NHC−alkenyl ruthenium(II) complex has been obtained on deprotonation of imidazolium salts with a N−CH_2CH_2X branch (X = OMe, Cl) followed by reaction with [$RuCl_2$(p-cymene)]$_2$. Low-temperature NMR studies and intermediate trapping with BH_3 indicate the formation of a CH_2=CH−NHC carbene followed by the intramolecular activation of a vinyl sp^2 C−H bond on coordination to a ruthenium(II) center.

Nitrogen-containing heterocyclic carbene (NHC) metal complexes[1] 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 metathesis,[3] 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 functional carbenes containing a weakly coordinating lateral group allowing its reversible coordination to the metal center, 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 [RuCl(PCy_3)(indenylidene)(arene)]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 *N*−CH_2CH_2OMe chain to [$RuCl_2$(*p*-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** (X = OMe (**a**), Cl (**b**)) and addition of the expected resulting NHC ligand to [$RuCl_2$(*p*-cymene)]$_2$ (**1**) does not lead to the expected $RuCl_2$(*p*-cymene)(NHC) complex but to the new chelating mixed carbene alkenyl complex **3** (eq 1). The evidence for intramolecular vinyl sp^2 CH bond activation is presented.



1 **2** **3**

(1)

We have shown recently that the allenylidene−ruthenium complex [Ru=C=C=CPh_2(Cl)(PCy_3)(*p*-cymene)]OTf (**5**), readily obtained from $RuCl_2$(PCy_3)(*p*-cymene) (**4**), is active in alkene metathesis[7] and proceeds via a rearrangement leading to the corresponding indenylidene−ruthenium complex **6** either by heating[8] or more readily and quantitatively on addition of acid.[6]

---

* To whom correspondence should be addressed. Tel: + 33 2 23 23 62 80. Fax: + 33 2 23 23 69 39. E-mail: pierre.dixneuf@univ-rennes1.fr.

[†] Institut des Sciences Chimiques de Rennes.

[‡] Groupe Matière Condensée.

(1) For reviews on N-heterocyclic carbenes see: (a) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247. (b) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (c) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181. (d) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (e) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913.

(2) (a) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229 and references therein. (b) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165. (c) Navarro, O.; Kelly, R. A.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194 and references therein. (d) Hadei, N.; Kantchev, E.-A. B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 3805.

(3) (a) Connon, S. J.; Blechert, S. In *Topics in Organometallic Chemistry*; Dixneuf, P. H., Bruneau, C., Eds.; Springer-Verlag: Berlin, 2004; Vol. 11 (Ruthenium Catalysts and Fine Chemistry), p 93. (b) Astruc, D. *New J. Chem.* **2005**, *29*, 42. (c) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117. (d) Connon, S. J.; Blechert, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900. (e) Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Adv. Synth. Catal.* **2002**, *344*, 1. (f) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (g) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (h) Maier, M. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2073.

(4) (a) César, V.; Bellemin-Laponnaz, S.; Gade, L. *Chem. Soc. Rev.* **2004**, *33*, 619. (b) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534. (c) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951.

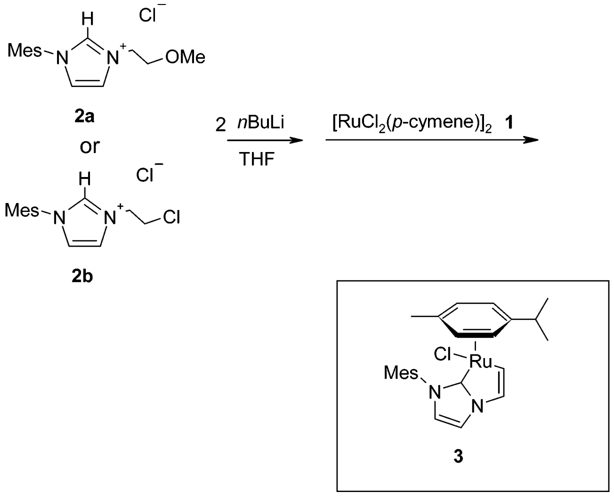
(5) (a) Cetinkaya, B.; Demir, S.; Ozdemir, I.; Toupet, L.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Chem. Eur. J.* **2003**, *9*, 2323. (b) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, 248, *2239*. (c) Poyatos, M.; Mas-Marzà, E.; Sanaú, M.; Peris, E. *Inorg. Chem.* **2004**, *43*, 1793. (d) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340. (e) Hermann, W. A.; Schwarz, J.; Gardiner, M. G. *Organometallics* **1999**, *18*, 4082. (f) McManus, H. A.; Guery, P. J. *Chem. Rev.* **2004**, *104*, 4151. (g) Schneider, N.; César. V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2005**, *24*, 4886.

(6) (a) Castarlenas, R.; Dixneuf, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4524. (b) Castarlenas, R.; Vovard, C.; Fischmeister, C.; Dixneuf, P. H. *J. Am. Chem. Soc.*, in press.

(7) (a) Fürstner, A.; Liebl, M.; Lehmann, C. W.; Picquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem. Eur. J.* **2000**, *6*, 1847. (b) Castarlenas, R.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *J. Mol. Catal. A: Chem.* **2004**, *213*, 31.

10.1021/om060087i CCC: $33.50

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 the precursor **4** by the electron-donating, bulky, and chelating NHC ligand with a *N*-CH_2CH_2OMe 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 $ClCH_2CH_2OMe$ 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 $[RuCl_2(p\text{-cymene})]_2$ (**1**) in THF at room temperature. The expected product $[RuCl_2(NHC)(p\text{-cymene})]$ (**7**) was not formed. The ^1H NMR analysis of the resulting complex showed the absence of the CH_2CH_2OMe branch and the presence of the *p*-cymene ligand, with four different aromatic protons, suggesting its coordination to a chiral ruthenium center. An alkenyl group was observed with deshielded protons (δ 8.65 (d), 7.06 (d), $^3J_{HH} = 5.6$ 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 favor of the complex **3** (eq 2). The same complex **3** was also obtained by starting from the chlorinated salt **2b** instead of **2a** in a slightly better yield (37% vs 30% from **2a**).



(2)

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

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 and 1.349 Å, respectively, are consistent with C═C double bonds. It is noteworthy that the NHC carbene ligand and the five-membered ruthenacycle Ru1−C11−C12−N1−C15 are coplanar, as the sum of the angles (C13N1C15), (C15N1C12), and (C12N1C13) reaches 360.0° and the torsion angle (C12N1C15N2) equals 179.45°. The Ru−C15 bond length (2.03 Å) is slightly shorter than typical ruthenium−carbon bonds of various (arene)ruthenium−monodentate NHC complexes (typically 2.06−2.09 Å).[5a,9] This feature was previously observed for a ruthenium complex containing a chelating (NHC) carbene arene ligand, $[RuCl_2\{(\eta^1\text{-CN}[CH_2(\eta^6\text{-}C_6H_2Me_3\text{-}2,4,6)])CHCHN\text{-}(CH_2(\eta^6\text{-}C_6H_2Me_3\text{-}2,4,6)\}]$, with a Ru−C bond length of 2.04 Å.[5a]

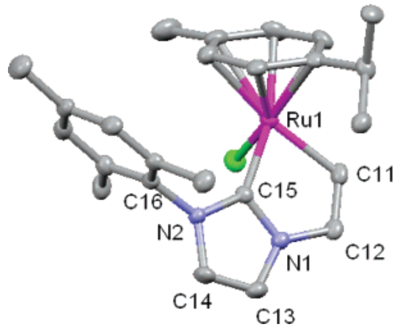
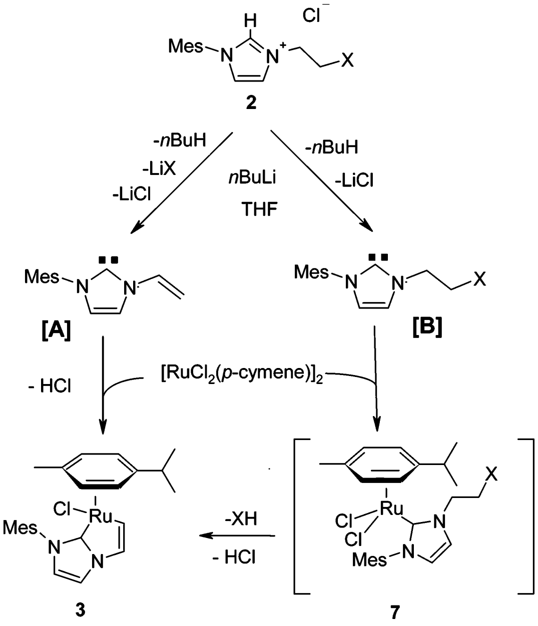


Figure 1. Molecular structure of complex **3** (50% probability ellipsoids). H atoms and the CH_2Cl_2 molecule of crystallization are omitted for clarity. Selected bond lengths (Å): Ru1−C15 = 2.028(4), Ru1−C11 = 2.071(5), C11−C12 = 1.350(7), N1−C12 = 1.424(6), N2−C16 = 1.456(6), C13−C14 = 1.350(7).

Scheme 1



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 the vinylcarbene **[A]** followed by elimination of HCl on coordination to the ruthenium(II) center. The second possibility is the formation of the carbene **[B]**, leading to complex **7**, followed by the elimination of XH and HCl (Scheme 1).

The deprotonation of **2b** by *n*Buli has been followed by ^1H NMR at low temperature by the observation of the imidazole NCH═CHN 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 and 6.5 ppm showed two important features. First, we note the presence of four NCH═CHN vinylic protons at 5.61 and 6.21 ppm and at 5.71 and 6.13 ppm, showing the presence of two carbene species.[10−12] The second information comes from the signals at about 5 and 6.5 ppm characteristic

---

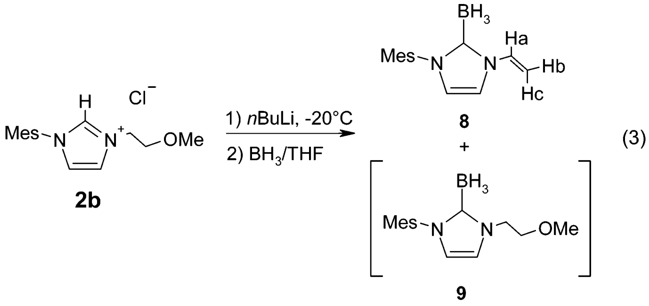
(8) Bassetti, F.; Centola, F.; Séméril, D.; Bruneau, C.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 4459.

(9) Ozdemir, I.; Yigit, B.; Cetinkaya, B.; Ulku, D.; Tahir, M. N.; Arici, C. *J. Organomet. Chem.* **2001**, *633*, 27.

(10) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523.

of a $CH_2{=}CH{-}$ 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 BH_3 or BF_3.[13] Thus, **2a** was deprotonated at − 20 °C and then the formed species were trapped by BH_3. When 1 equiv of *n*Buli was used at −20 °C, the ^{1}H 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 3). The second species was not clearly identified, but NMR data support derivative **9** (eq 3). However, when 2 equiv of *n*Buli was added to **2a**, as in the formation of **3**, only species **8** was observed. Its ^{1}H NMR spectrum shows a vinyl group linked to a heteroatom, as three doublets of doublets were observed (^{1}H NMR (200 MHz): 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).



(3)

These observations support the in situ formation of both intermediates **[A]** and **[B]** by deprotonation of salt **2**. However in the formation of **3**, 2 equiv of *n*BuLi is 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** and that its coordination to the ruthenium atom of **1** favors the intramolecular activation of a vinyl sp^2 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 NEt_3 to the reaction mixture did not increase the yield of **3**. The addition of HBF_4 to **3** led to its decomposition rather than to the formation of a $CH{=}CH_2$ group or the formation of an alkylidene ligand, as observed by Werner[14] 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 established,[15] the reaction presented here reveals an unprecedented example of C−H bond activation of an NHC vinyl group by a ruthenium(II) species. Previous C−H bond activations by ruthenium(II) complexes were discovered in the ortho metalation of phosphites[16] 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 has been performed with osmium polyhydrides[19] and the mixed pyridine−N-heterocyclic carbene on reaction with $IrH_5(PPh_3)_2$[20] is known to “abnormally” bind to iridium via imidazolium (NCH═CHN)C−H bond activation. These metal polyhydride complexes generate a coordinatively unsaturated metal moiety on loss of hydrogen before C−H bond activation.[19,20] The hypothesis is made here that, for both ortho metalation and the present reaction, the coordination of the substrate (arylamine, aryl phosphite, or vinyl NHC) takes place first, followed by C−H bond activation by the 18-electron ruthenium(II) center.

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 five-membered ruthenacycle. Low-temperature NMR observations are consistent with the initial formation of an *N*-vinyl *N*-mesityl imidazolylidene carbene, and thus, the formation of the complex implies an intramolecular activation of an usually inert vinyl sp^2 C−H bond.

Acknowledgment. We are grateful to the CNRS, the University of Rennes, and the European Network IDECAT for financial support.

Supporting Information Available: Text and figures giving experimental details and crystallographic data for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference number 276178 also contains 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.

OM060087I

---

(11) Although the resolution of the low-temperature NMR experiments was not very good, the ratio of the two carbene species could be estimated as 1/1.

(12) The involvement of an electron-rich olefin as the carbene source (Wanzlick equilibrium) was discarded, since experiments designed to prepare and use this type of intermediate failed to produce any complex. The experimental conditions used were those reported in ref 5a.

(13) Ramnial, T.; Jong, H.; McKenzie, I. D.; Jennings, M.; Clyburne, J. A. C. *Chem. Commun*. **2003**, 1722.

(14) Jung, S.; Brandt, C. D.; Wolf, J.; Werner, H. *Dalton Trans*. **2004**, 375.

(15) (a) Kakiuchi, F.; Murai, S. Activation of unreactive bonds and organic synthesis. In *Topics in Organometallic Chemistry*; Springer-Verlag: Berlin, 1999; Vol. 3, p 47. (b) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826. (c) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731.

(16) Lewis, L. N.; Smith, J. F. *J. Am. Chem. Soc*. **1986**, *108*, 2728.

(17) (a) Ritleng, V.; Sutter, J. P.; Pfeffer, M.; Sirlin, C. *Chem. Commun.* **2000**, 129. (b) Ritleng, V.; Pfeffer, M.; Sirlin, C. *Organometallics* **2003**, *22*, 347.

(18) (a) Paneque, M.; Pérez, P. J.; Pizzano, A.; Poveda, M. L.; Taboada, S.; Trujillo, M.; Carmona, E. *Organometallics* **1999,** 18, 4304. (b) Paneque, M.; Poveda, M. L.; Salazar, V.; Taboada, S.; Carmona, E. *Organometallics* **1999,** 18, 139.

(19) Recently Esteruelas et al. have reported the activation of an olefinic sp^2 CH bond of vinylpyridine promoted by the osmium polyhydride complexes $OsH_3(SnPh_2Cl)(P^iPr_3)_2$[19a] and $OsH_6(P^iPr_3)_2$:[19b] (a) Eguillor, B.; Esteruelas, M. E.; Olivan, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428. (b) Barrio, P.; Esteruelas, M. E.; Oñate, E. *Organometallics* **2004**, *23*, 3627.

(20) (a) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274. (b) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461.