

## Facile Migratory Insertion of a N-Heterocyclic Carbene into a Ruthenium–Carbon Double Bond: A New Type of Reaction of a NHC Ligand

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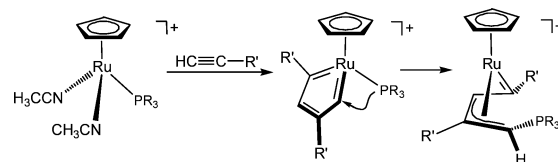
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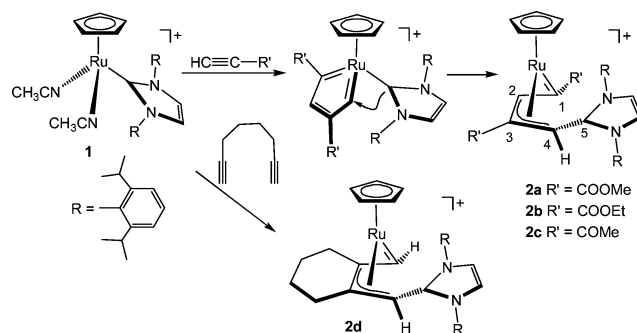
In recent years, there has been much interest in the application of N-heterocyclic carbenes (NHC) as *noninterfering* supporting ligands in various stoichiometric and catalyzed reactions of transition metal complexes.<sup>1</sup> The role of the carbene ligands is similar to that of ubiquitous tertiary phosphine ligands, but they are considered to be much more strongly bound to a metal center than phosphines and thus less likely to participate in rearrangements within the metal coordination sphere. However, several recent reports clearly show that NHC–metal bonds are not inert, and NHC ligands are able to participate in various inter- and intramolecular reactions.<sup>2</sup> This includes migration of a methyl group to a coordinated NHC ligand,<sup>2c</sup> the reductive elimination of alkylimidazolium salts from NHC alkyl complexes,<sup>2f</sup> and various examples of substitutions of NHC ligands by trialkylphosphines.<sup>2h,i</sup> Our studies of the interactions between the [RuCp(PR<sub>3</sub>)]<sup>+</sup> moiety, derived from labile [RuCp(PR<sub>3</sub>)(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup>, and alkynes have revealed that the PR<sub>3</sub> ligand rapidly migrates onto the carbene carbon atom of a highly electrophilic biscarbene intermediate, affording allyl carbene complexes (Scheme 1).<sup>3,4</sup> In this context, we found it interesting to switch over to the bulky NHC ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr<sup>r</sup>) in order to see whether similar transformations take place. Herein we report the first example of a NHC migration from a formally Ru(VI) center to the carbene carbon of a metallacyclopentatriene moiety.

Treatment of [RuCp(IPr<sup>r</sup>)(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> (**1**) with 2 equiv of the terminal alkynes HC≡CR (R = COOMe, COOEt, COMe) and 1 equiv of 1,7-octadiene in CH<sub>2</sub>Cl<sub>2</sub> for 30 min results in the formation of the deep purple allyl carbene complexes [RuCp(=C(R)-η<sup>3</sup>-CHC(R)CH-IPr<sup>r</sup>)]PF<sub>6</sub> (**2a–c**) and [RuCp(=CH-η<sup>3</sup>-C(CH<sub>2</sub>)<sub>4</sub>-CCH-IPr<sup>r</sup>)]PF<sub>6</sub> (**2d**), respectively, in essentially quantitative yield as monitored by <sup>1</sup>H NMR spectroscopy (Scheme 2). These reactions proceed via an electrophilic metallacyclopentatriene similarly to the reactions with PR<sub>3</sub> and SbR<sub>3</sub> as co-ligands reported previously.<sup>5,6</sup> The involvement of such an intermediate is evident from <sup>1</sup>H and <sup>1</sup>H–<sup>13</sup>C HSQC NMR measurements at –20 °C in CD<sub>2</sub>Cl<sub>2</sub>. While, with terminal alkynes, no intermediates could be detected, with 1,7-octadiene, a characteristic low-field resonance at 17.08 ppm was observed, assignable to the carbene hydrogens of a metallacyclopentatriene intermediate. This resonance is correlated with a signal at 298.0 ppm which can be associated with the C<sub>α</sub> ring carbons (see Supporting Information, Figure S1). For comparison, the analogous cationic phosphine and stibine-based ruthenacyclopentatriene complexes, [RuCp(=C<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>)(PCy<sub>3</sub>)]<sup>+</sup> and [RuCp(=C<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>)(SbPh<sub>3</sub>)]<sup>+</sup>, show resonances of the C<sub>α</sub> ring carbons at 325.6 and 330.3 ppm, respectively.<sup>5,6</sup> The C–C coupling of the terminal alkynes was highly regioselective in head-to-tail

Scheme 1



Scheme 2



fashion, with the substituents ending up exclusively in the 1 and 3 position. In the course of this process, the IPr<sup>r</sup> ligand has migrated onto the unsubstituted carbene carbon atom of the metallacyclopentatriene moiety with concomitant cleavage of the NHC ruthenium bond. The identity of **2** was established by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and by elemental analysis.

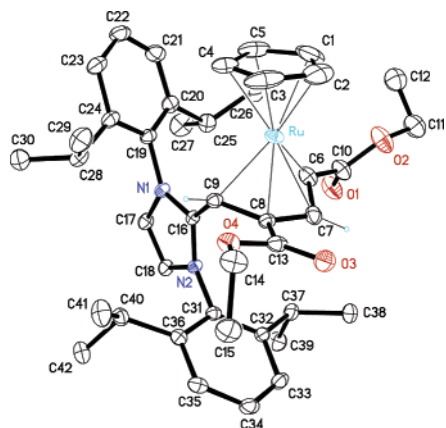
The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2a** exhibits a characteristic low-field resonance at 237.4 ppm and a resonance at 30.3 ppm, assignable to the carbene carbon atom C<sup>1</sup> and the terminal allyl carbon atom C<sup>4</sup> bearing the IPr<sup>r</sup> substituent. The carbenium carbon atom C<sup>5</sup> gives rise to a signal at 153.6 ppm. Concurrent NMR spectra are observed for **2b**, **2c**, and **2d**.

DFT/B3LYP calculations have been performed to shed light on the detailed mechanism of this unusual rearrangement. The results of this study are shown in Figure 2. On the basis of our experimental findings, starting point and key intermediate is obviously the metallacyclopentatriene complex **A** (with 1,3-dimethylimidazol-2-ylidene as model NHC ligand). The conversion of the metallacyclopentatriene **A** into the final allylcarbene complex **C** proceeds with relatively small activation barriers, the rate-limiting step being an initial distortion to produce the intermediate **B**. What happens is bending of the metallacycle, approaching the C<sub>β</sub> carbon atoms to the metal. Conversely, at the other side of the molecule, the Ru–C<sub>α</sub> bond stretches, and this carbon atom starts to form a new C<sub>α</sub>–C(NHC) bond. This feature is already obvious in the transition state **TS<sub>AB</sub>**, where the C–C(NHC) distance is 2.71 Å. The free activation energy is 23.1 kcal mol<sup>–1</sup>. **TS<sub>AB</sub>** is much closer to **B** than to **A**. The final transformation involves complete Ru–C(NHC) bond breaking and formation of the C<sub>α</sub>–C(NHC) bond, with simultaneous

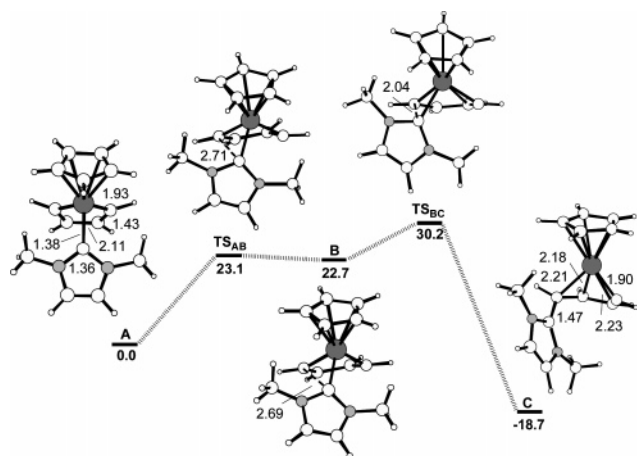
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**Figure 1.** Structural view of  $[\text{RuCp}(=\text{C}(\text{COOEt})-\eta^3\text{-CHC}(\text{COOEt})\text{CH-IPr}')\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$  (**2b** $\cdot\text{CH}_2\text{Cl}_2$ ) showing 40% thermal ellipsoids ( $\text{PF}_6^-$ ,  $\text{CH}_2\text{-Cl}_2$ , and most atoms omitted for clarity). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ru–C(1–5)<sub>av</sub> 2.215(2), Ru–C(6) 1.917(3), Ru–C(7) 2.208(2), Ru–C(8) 2.124(2), Ru–C(9) 2.144(2), C(6)–C(7) 1.406(3), C(7)–C(8) 1.429(3), C(8)–C(9) 1.439(3), C(9)–C(16) 1.475(3), C(16)–N(1) 1.346(2), C(16)–N(2) 1.354(3), C(6)–C(7)–C(8) 115.2(2), C(7)–C(8)–C(9) 119.2(2), C(8)–C(9)–C(16) 121.9(2).



**Figure 2.** Reaction profile of the computed relative Gibbs free energies (in kcal/mol) for the migratory insertion of a 1,3-dimethylimidazol-2-ylidene ligand into the Ru–C double bond of the ruthenacyclopentatriene intermediate (A) to give the allyl carbene complex (C) (bond distances in  $\text{\AA}$ ).

formation of the allyl carbene and the adjustments of the carbon chain, namely, formation of the Ru–C $_{\beta}$  bonds. The overall reaction from A to C is exergonic by  $-18.7$  kcal/mol.

An alternative pathway to afford allyl carbenes has also been considered involving intramolecular nucleophilic attack of the NHC ligand at a coordinated HC $\equiv$ CH ligand to give an intermediate 1-metallacyclopentatriene complex. In the case of Mo and Re, it has been demonstrated that such complexes are able to react with a further alkyne molecule to give allyl carbenes.<sup>8</sup> DFT calculations, however, revealed that the formation of a 1-metallacyclopentatriene is kinetically less favorable than the oxidative coupling of two alkynes to give A (see Supporting Information, Figure S2).

In conclusion, our experimental and theoretical data provide for the first time clear evidence that a N-heterocyclic carbene is able to migrate from a ruthenium center to an electrophilic alkylidene

ligand. This process is accompanied by Ru–C bond cleavage and is another example of the finding that a N-heterocyclic carbene ligand needs not necessarily be just a spectator ligand but can switch over to an actor ligand.

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**Supporting Information Available:** Detailed experimental procedures for the synthesis and characterization of **1**, **2a–d**, and complete crystallographic data and technical details in CIF format for **2b** $\cdot\text{CH}_2\text{-Cl}_2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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