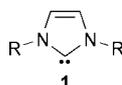


N-Heterocyclic carbenes can coexist with alkenes and C–H acidic sites

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First published as an Advance Article on the web 18th October 2001**The isolation of compounds 3 and 7a,b proves that a singlet carbene center can coexist with alkenes or C–H acidic sites in proximity without spontaneous annihilation.**Among the nucleophilic carbenes that can be isolated in pure form,¹ N-heterocyclic carbenes (NHC's) of the general structure **1**² are rapidly gaining importance as electron-donating ligands

for transition metal centers in different oxidation states.³ Applications of NHC-complexes to catalysis have recently met with considerable success, olefin metathesis⁴ and cross coupling chemistry⁵ being the most convincing cases.⁶ Usually, NHC ligands bearing simple alkyl or aryl substituents R on their N-atoms are employed, although *functionalized* ones may be of even greater preparative appeal. A pertinent example is the ruthenium complex **5** which serves as a 'designer' catalyst for olefin metathesis capable of regenerating itself once the substrate is depleted.⁷ The reported synthesis of **5** involves the *in situ* generation of carbene **3** as a *transient* species which is immediately trapped by admixed (PCy₃)₂Cl₂Ru=CHPh⁸ to form product **4**; though easy to carry out, this *in situ* protocol turned out to be rather low yielding (41%). Heating **4** in an inert solvent then effects the intramolecular metathesis of the tethered olefin to form the metallacyclic complex **5**.

To improve the synthesis of this promising catalyst, we were pursuing the *isolation* of compound **3** containing an alkene next to the carbene center. Although cyclopropanation of olefins is a prototype carbene reaction with low activation barrier,^{9–11} the preparation of **3** is surprisingly simple. This compound is obtained in essentially quantitative yield as a crystalline solid by treatment of the imidazolium salt **2** with KOt-Bu in THF at 0 °C followed by a standard work-up.¹² The spectral data and the molecular structure in the solid state (Fig. 1) show the *presence of a carbene center in proximity to the intact alkene group*.[†] Difference maps clearly reveal the location of all hydrogen atoms; the volume element adjacent to the carbene C-atom has

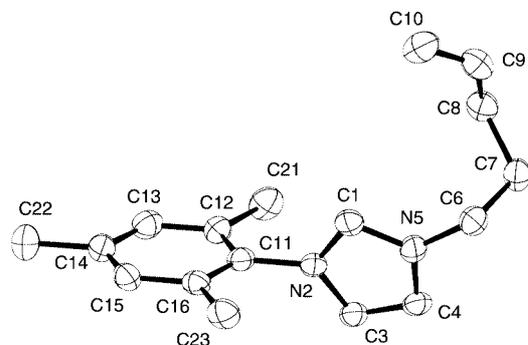
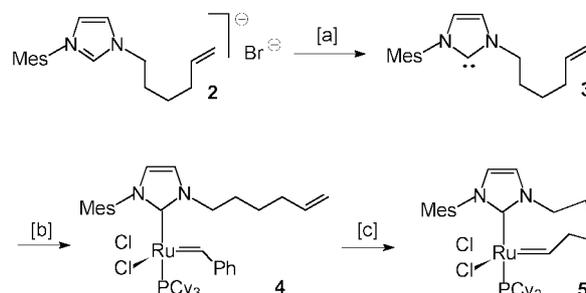


Fig. 1 Molecular structure of **3**.[‡] Anisotropic displacement parameters are shown at 50% probability level. There are two independent molecules in the asymmetric unit. The major difference is found in the conformation of the alkyl chain. The torsion angle C6–C7–C8–C9 is 67.6(5)° compared to 177.1(4)° in the second molecule. The difference of the dihedral angles formed between the mesityl and the NHC is 15.8°.

no significant electron density. To the best of our knowledge, this is the first example of an isolated carbene that coexists with an olefin in its vicinity.

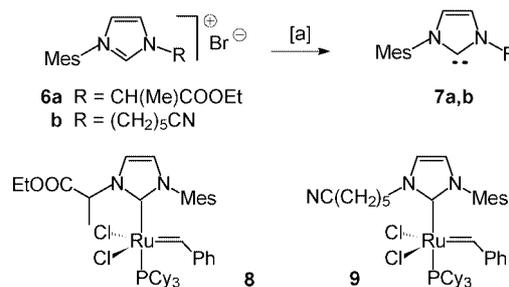
With **3** in hand, it was possible to improve the synthesis of the targeted ruthenium complex **5** (Scheme 1). Thus, reaction of (PCy₃)₂Cl₂Ru=CHPh with isolated **3** in toluene affords complex **4** in 86% yield which cyclizes upon heating to form the desired product **5**. The use of toluene instead of *n*-pentane in the latter reaction is beneficial for solubility reasons and constitutes a noteworthy improvement over our original procedure.⁷



Scheme 1 Reagents and conditions: [a] KOt-Bu, THF, 0 °C, 98%; [b] (PCy₃)₂Cl₂Ru=CHPh, toluene, 0 °C, 86%; [c] *n*-pentane (reflux) or toluene (65 °C), 41–77%; Mes = 2,4,6-trimethylphenyl (= mesityl).

Next, we investigated if other functional groups that are generally believed to be incompatible with free carbenes can similarly be incorporated into NHC's. The insertion of carbenes into acidic C–H bonds is known to be a facile process;⁹ therefore the preparation of compounds **7a,b** bearing an ester or a nitrile group seemed challenging, in particular since Arduengo¹³ has previously reported that closely related dihydroimidazol-2-ylidenes rapidly insert into the acidic C–H bonds of MeCN, MeSO₂Ph, HCCl₃ or HC≡CH.¹⁴

Gratifyingly, however, carbenes **7a,b** are obtained in excellent yields by deprotonation of the corresponding imidazolium salts **6a,b** (Scheme 2),[†] although they were found to deteriorate within hours even at 0 °C. Reaction of (PCy₃)₂Cl₂Ru=CHPh⁸ with these functionalized carbenes in toluene at ambient temperature provides the novel ruthenium complexes **8** (74%) and **9** (38%).[§] The X-ray structure of **8** (Fig. 2) shows the characteristic π–π stacking between the benzylidene ligand and the mesityl group which was previously recognized as a highly



Scheme 2 Reagents and conditions: [a] KOt-Bu, THF, –10 °C, 95% (**7a**), 89% (**7b**); Mes = 2,4,6-trimethylphenyl (= mesityl).

