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New olefin metathesis catalysts with fluorinated unsymmetrical imidazole-based ligands

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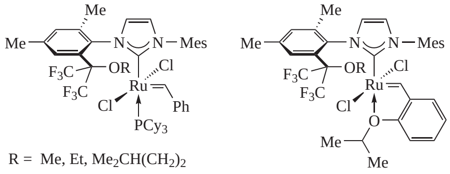
New olefin metathesis catalysts, unsaturated analogues of the Grubbs II and Hoveyda–Grubbs II ones, bearing bulky (alkoxy)hexafluoroisopropyl groups in one of the aryl substituent of NHC ligand provide high conversions in model ring closing metathesis of diallyl- and allylmethallylmalonates.

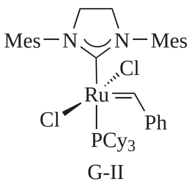

R = Me, Et, $Me_2CH(CH_2)_2$

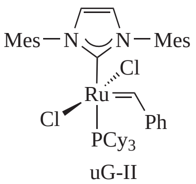
The last two decades have witnessed significant advances in chemistry of alkene metathesis,[1] mostly due to the development of robust and highly efficient ruthenium catalytic systems with N-heterocyclic carbene (NHC) ligands[2] [*e.g*. Grubbs II (G-II) and Hoveyda–Grubbs II (HG-II) as well as their unsaturated analogues uG-II and uHG-II], which have found broad application.[3] Despite substantial progress in this area, particular attention during the past few years has been focused on complexes with unsymmetrical NHCs possessing unique opportunities for rapid fine-turning of their catalytic properties by modifying the NHC stereoelectronics.[4] The most attractive recent examples include the usage of chelating unsymmetrical NHC ligands in ruthenium-catalyzed *Z*-selective cross-metathesis.[5] The further development of new catalytic systems bearing unsymmetrical NHC ligands is therefore of current interest.

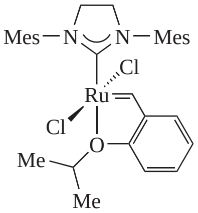
We have recently developed an efficient route to the new family of ruthenium complexes of G-II and HG-II type bearing unsymmetrical *N*,*N'*-diarylimidazolinium ligands with bulky (alkoxy)hexafluoroisopropyl [$(CF_3)_2(RO)C$] group in one of the *N*-aryl substituents, and demonstrated their good performance in olefin ring-closing metathesis (RCM) and cross-metathesis (CM).[6] It was also found that the replacement of *N*-aryl moiety by more electron-donating *N*-alkyl group in NHC ligand notably reduces activity of the complexes.[7]

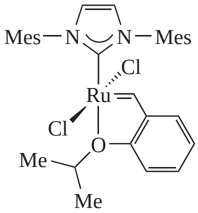
Taking into account that G-II and HG-II analogues bearing unsymmetrical unsaturated NHCs (*i.e*., imidazolin-2-ylidenes) are still scarce[8] due to a lack of synthetic procedures to access imidazolinium salts with two different aryl groups,[9] here we aimed to disclose the synthesis of novel ruthenium carbene complexes comprising unsaturated imidazole-based NHC ligands with bulky fluorinated substituent in one of the *N*-aryl moieties as well as preliminary evaluation of their efficiency in RCM of diethyl diallyl- and allylmethallylmalonates.

For this purpose, based on our previous findings[10] comprising transformation of a Mes-substituted oxazolinium tetrafluoroborate salt **1**[11] *via* the reaction with the binucleophilic fluoroalkyl-substituted aniline **2** followed by selective O-alkylation of intermediate salt **3**, the desired NHC precursors **4a**–**c** were obtained in good yields (Scheme 1).

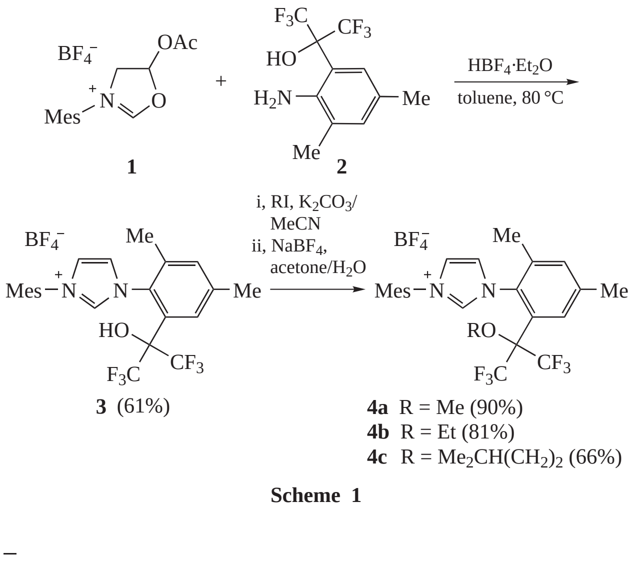

G-II


uG-II


HG-II


uHG-II

Mes = 2,4,6-$Me_3C_6H_2$


1 **2**

3 (61%)

4a R = Me (90%)
4b R = Et (81%)
4c R = $Me_2CH(CH_2)_2$ (66%)

Scheme 1

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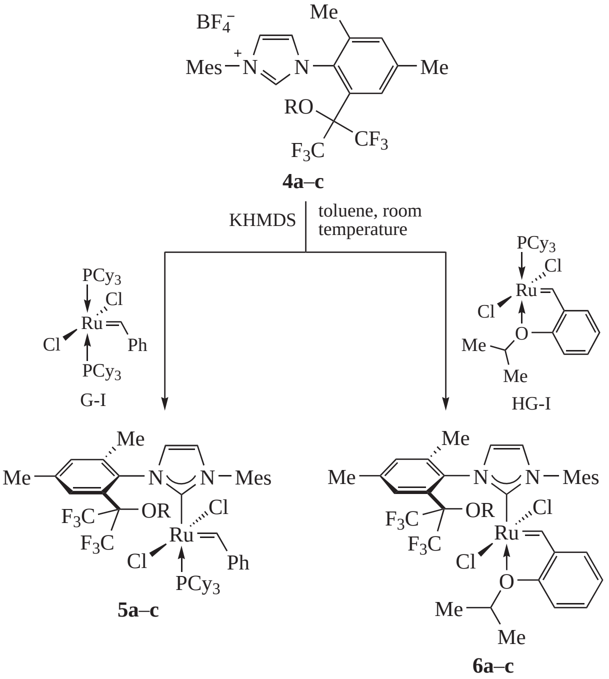
With these fluorinated NHC salts in hands, we synthesized six new ruthenium complexes **5a–c** and **6a–c**. Thus, following the conventional route by the reaction of *in situ* generated carbene with commercially available G-I[12] and HG-I,[13] these complexes were obtained in reasonable yields (Scheme 2). Purification by silica gel chromatography and further crystallization from a CH_2Cl_2–pentane mixture afforded dark-brown (**5**) and dark-green (**6**) air stable solids. Complexes **5a–c** and **6a–c** were completely characterized by NMR spectroscopy and elemental analysis (see Online Supplementary Materials).

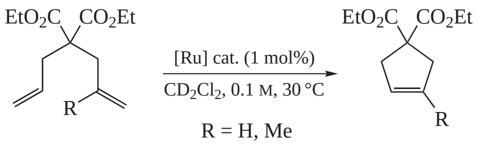


	R	Yield of **5** (%)	Yield of **6** (%)
a	Me	53	57
b	Et	52	51
c	$Me_2CH(CH_2)_2$	46	50

Scheme 2

In addition, single crystals **6a**,**b** of good quality for X-ray analysis (Figure 1)[†] were obtained by slow diffusion of hexane vapors into CH_2Cl_2 solution.

Catalytic activities of the prepared precatalysts **5a–c** and **6a–c** were investigated in RCM reactions with diethyl diallylmalonate and its more sterically hindered methallyl analogue (Scheme 3). The available complexes uG-II[14] and uHG-II[‡] were used as reference catalysts.



Scheme 3

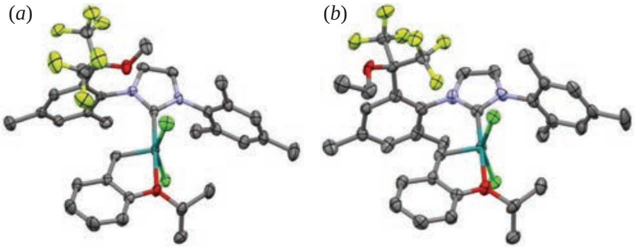


Figure 1 Molecular structure of complexes (*a*) **6a** and (*b*) **6b**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

We have found that initiation rates of Grubbs type complexes **5a–c** were noticeably higher in RCM of diethyl diallylmalonate as compared to uG-II [Figure 2(*a*)]. Phosphine free complexes **6a–c** demonstrated similar tendency with respect to reference catalyst uHG-II, exhibiting some initiation period (particularly for **6c**) before they could achieve full conversion in longer reaction times (2 h).

The ring-closing metathesis of the more sterically hindered diethyl allylmethallylmalonate was also achieved with new catalysts **5a–c** and **6a–c**. A similar reactivity profile as starting from diallylmalonate was observed for **5a–c** exceeding reaction rate found for uG-II. On the other hand, the Hoveyda type catalysts

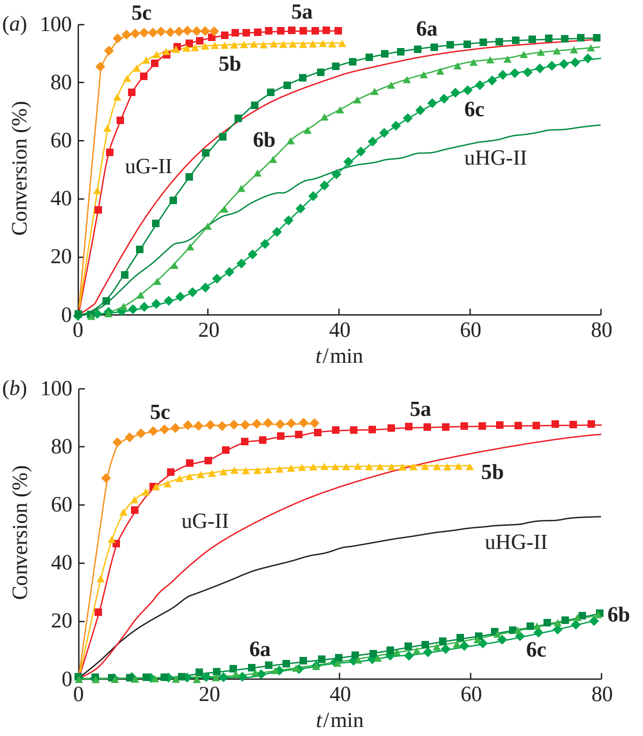


Figure 2 RCM of (*a*) diethyl diallylmalonate and (*b*) diethyl allylmethallylmalonate with catalysts **5a–c** and **6a–c** as compared to uG-II and uHG-II.

[†] The X-ray measurements were made on a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromator, MoKα radiation, λ = 0.71073 Å, ω-scanning). The semi-empirical method SADABS was applied for the absorption correction. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms in the complexes were placed geometrically and included in the structure factors calculation in the riding motion approximation. All the data reduction and further calculations were performed using the SAINT and SHELXTL-97.

Crystal data for **6a**: $C_{34}H_{36}Cl_2F_6N_2O_2Ru$, $CHCl_3$, M = 909.98, at 150(2) K, monoclinic, space group $P2_1/c$ (no. 14), a = 30.353(3), b = 12.8878(13) and c = 20.147(2) Å, V = 7723.1(14) Å^3, Z = 8, d_{calc} = 1.565 g cm^{-3}, μ = = 0.815 mm^{-1}.

Crystal data for **6b**: $2(C_{35}H_{38}Cl_2F_6N_2O_2Ru)$, $CHCl_3$, M = 1728.65, at 150(2) K, monoclinic, space group $C2/c$ (no. 15), a = 62.202(16), b = = 12.330(3) and c = 21.325(5) Å, V = 16142(7) Å^3, Z = 8, d_{calc} = 1.423 g cm^{-3}, μ = 0.680 mm^{-1}.

CCDC 1847041 and 1847042 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[‡] This complex was specially prepared from uG-II by styrene ligand exchange (see Online Supplementary Materials).

6a–c showed much lower activity in this reaction compared to reference catalyst uHG-II [Figure 2(*b*)].

In conclusion, we prepared six new olefin metathesis catalysts bearing unsymmetrical imidazole-based NHC ligands with bulky (alkoxy)hexafluoroisopropyl groups in *ortho*-positions of *N*-aryl substituent. Their performance has been evaluated in model ring closing metathesis reactions of diallyl- and allylmethallylmalonates. New phosphine-containing catalysts **5** demonstrated higher reaction rates and yields of cyclization products in all cases in comparison with reference catalysts. In contrast, new Hoveyda type phosphine free catalysts **6** have proved to be less active in RCM of allylmethallylmalonate.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.11.015.

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