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FULL PAPER

Ruthenium-alkylidene complexes with sterically rigid fluorinated NHC ligands

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Abstract: An efficient procedure for the preparation of novel olefin metathesis catalysts of Grubbs-Hoveyda type bearing sterically rigid NHC ligands has been developed. A preliminary evaluation of their catalytic activity has been performed on representative olefin metathesis reactions, such as RCM of malonates as well as self-metathesis of allylbenzene. As result, it was found that along with excellent robustness, new complexes demonstrate remarkable activity in metathesis of allylbenzene, outperforming commercially available Grubbs-Hoveyda catalyst in terms of yield and regioselectivity.

Introduction

Over the last two decades, olefin metathesis has experienced dramatic development to become a powerful and highly versatile method for the catalytic assembly of carbon-carbon bonds.[1] Ruthenium metathesis catalysts bearing *N*-heterocyclic carbene (NHC) ligands, commonly used for different synthetic purposes in academia, have begun to find nowadays industrial applications.[2] Despite prominent advances highlighting the great potential of these ligand sets, particularly attention is focused on complexes with unsymmetrical NHCs possessing unique opportunities for rapid fine-turning of their catalytic properties by modifying the NHC stereoelectronics.[3] The most attractive recent examples include the usage of chelating unsymmetrical NHC ligands in ruthenium-catalyzed *Z*-selective cross-metathesis.[4]

At the same time, fluorinated compounds have found widespread applications in life and material sciences.[5] Particular attention is focused on CF_3-containing compounds due to the strongly electron-withdrawing nature and large hydrophobic domain of CF_3 group.[6] Such a way modification often beneficially change the key physicochemical characteristics of molecules to bring them more desired properties such as increased lipophilicity or chemical stability.[7]

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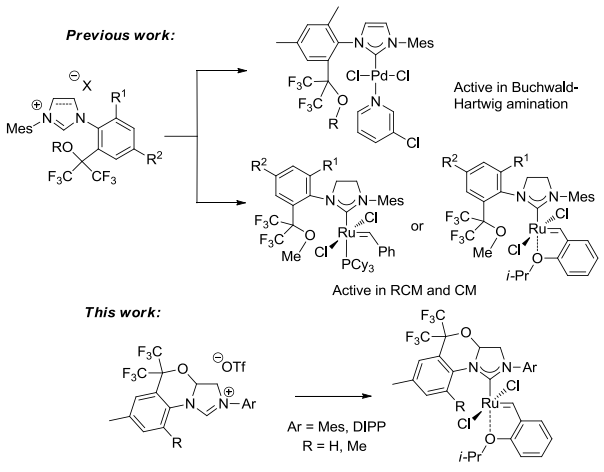
The impact of fluorinated groups on the performance of ruthenium-based olefin metathesis catalysts has been generally studied by using definitely modified phosphine,[8] benzylidene[9] ligands, as well as by the replacement of chlorine atoms at ruthenium, *e.g.* with perfluoroalkanoates.[10] Meanwhile, metathesis catalysts decorated with fluorinated NHC ligands are still quite rare.[11] Some beneficial features found for such complexes include increased solubility (*e.g.* in supercritical carbon dioxide),[12] rate acceleration in ring closing metathesis (RCM)[13] as well as a feasibility to apply fluorous separation technique for efficient catalyst recycling.[14] The development of new fluorinated NHC ligands, particularly unsymmetrical ones, to afford enhanced stability, improved reactivity and selectivity is therefore of interest.

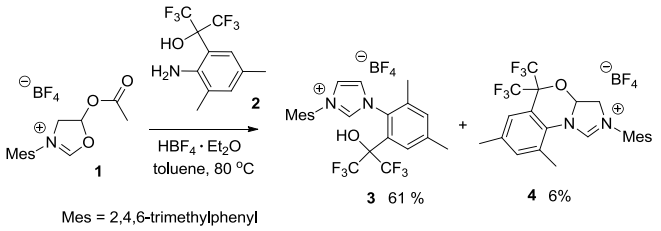
Recently we have developed an efficient route to the new family of unsymmetrical *N,N*-diaryl imidazolium[15] and imidazolinium[16] salts with bulky hexafluoroisopropylalkoxy [$(CF_3)_2$(OR)C-] group in one of the *N*-aryl substituents and investigated their potential as universal precursors of the corresponding NHC ligands for metal catalysis. Some of ruthenium-alkylidene complexes bearing these ligands demonstrated a good performance in olefin RCM and cross-metathesis (CM).[16] With the aim of further evaluating the effects of bulky fluorinated substituents installed in unsymmetrical NHC ligand on the activity of the resulting metathesis precatalysts, now we want to disclose the synthesis of novel imidazoline-based tricyclic NHC precursors and the corresponding ruthenium carbene complexes as well as preliminary evaluation of their catalytic activity (Scheme 1).



Scheme 1. Synthesis of metal complexes with fluorinated unsymmetrical NHC ligands.

Results and Discussion

Previously[15] we have described the heterocyclic interconversion of mesityl-substituted oxazolinium salt **1** [17] *via* the reaction with the binucleophilic fluorinated arylamine **2** mediated by tetrafluoroboric acid to afford a mixture of hydroxyl-containing imidazolium salt **3** along with unexpected tricyclic by-product **4** likely arising from additional heterocyclization upon the hydroxyl group under the reaction conditions (Scheme 2).



Scheme 2. Reaction of oxazolium salt **1** with fluorinated aniline **2**.

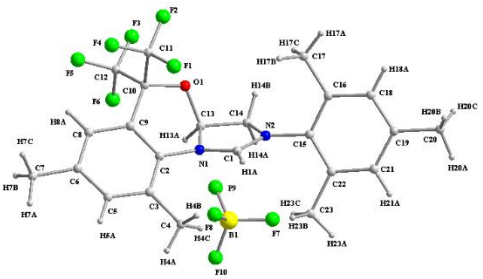
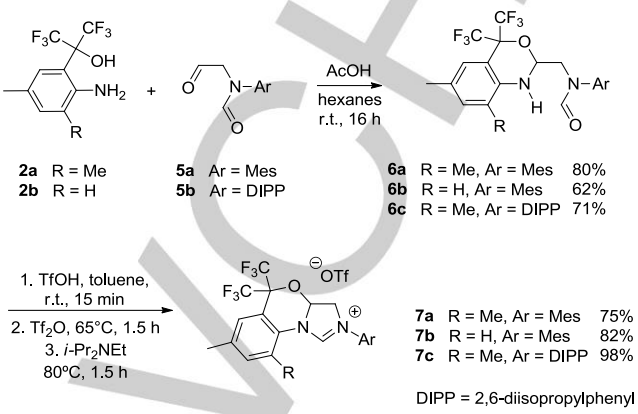


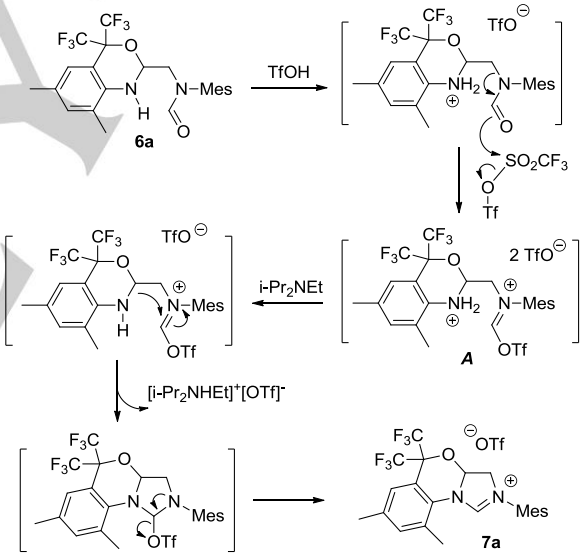
Figure 1. Molecular structure of salt **4**. Selected bonds[Å], angles[°] and dihedral angles [°]: O1-C13 1.424(1), O1-C10 1.425(1), N1-C1 1.327(1), N1-C2 1.419(1), N1-C13 1.458(1), N2-C1 1.305(1), N2-C14 1.482(1), C13-C14 1.524(1)Å, C13-O1-C10 115.02(8), C1-N1-C13 109.81(9), C1-N2-C14 110.08(9), N2-C1-N1 112.71(10), N1N2C1/C2C3C9 42.8, N1N2C1/C15C16C22 67.1.

The rigid tricyclic structure of **4** (Figure 1) has attracted our attention as a potential NHC precursor for the construction of the corresponding ruthenium olefin metathesis catalysts. After several unsuccessful attempts to redirect the reaction towards the preferential formation of tetrafluoroborate salt **4** we were pleased to find an alternative two-step route for the selective preparation of the desired compound as triflate salt **7a**. Thus, the synthetic sequence included the reaction of hydroxyl-containing aniline **2a** with readily available aryl-substituted amidoaldehyde **5a** [17,18] to afford benzoxazine-containing formamide **6a** followed by intramolecular heterocyclization *via* covalent activation of amide group of the latter under strong acidic conditions to furnish **7a** in good yield (Scheme 3).

To perform the key cyclization step (**6a** → **7a**) we have slightly modified the protocol recently developed by Organ[19] for sterically demanding imidazolinium salts. Thus, sequential addition of stoichiometric amounts of triflic acid (TfOH) and its anhydride (Tf_2O) to the formamide **6a** provided conditions for Vilsmeyer-Haack reaction. The use of Hünig's base has appeared to be optimal for heterocyclization of activated intermediate ***A*** to produce the desired imidazolinium triflate salt **7a** (Scheme 4). The final product can be easily purified by single recrystallization from hexanes.



Scheme 3. Preparation of tricyclic salts **7a-c**.

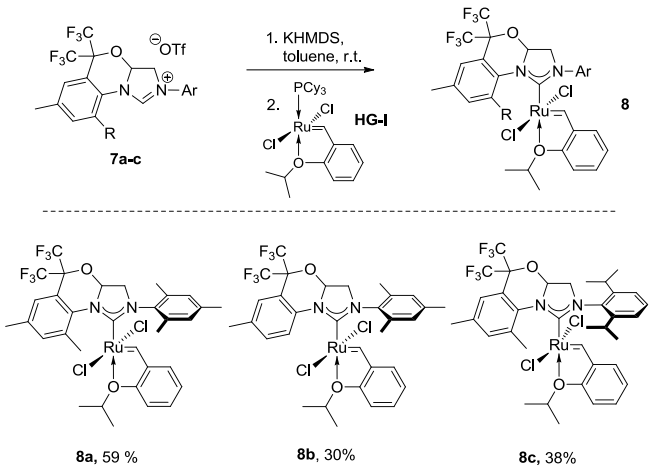


Scheme 4. Proposed mechanism for the formation of **7a**.

The found conditions have proved to be suitable for the preparation of two more tricyclic imidazolinium salts bearing substituents of different bulkiness. For these purposes fluorinated aniline **2b** [16] with free *ortho*-position (R = H) and amidoaldehyde **5b** with bulky 2,6-diisopropylphenyl group (Ar = DIPP) have been applied as starting materials. As result, the corresponding salts **7b** and **7c** were obtained in acceptable yields (Scheme 3). As a whole, the developed procedure gives good yields of **7a-c** in the range of 78-85 % for two steps even on a ten-gram scale (see Experimental Section).

With these fluorinated unsymmetrical NHC precursors **7a-c** in hand, we prepared the new ruthenium complexes **8a-c** in

moderate to good yields following the conventional route *via* the reaction of *in situ* generated carbene with commercially available Hoveyda-Grubbs complex $RuCl_2(PCy_3)(=CH(o\text{-}^iPrO\text{-}C_6H_4))$ **HG-I**[20] of first generation. Purification by silica gel chromatography afforded dark-green air stable solids **8a-c** (Scheme 5).



Scheme 5. Synthesis of ruthenium carbene complexes **8a-c**.

The complexes obtained were fully characterized by NMR spectroscopy and elemental analysis. In ^1H NMR spectra of **8a**, **8b** and **8c** measured at room temperature the absorptions of intrinsic benzylidene protons are observed around 16.9, 16.3 and 16.6 ppm, respectively, as singlets in each case. The ^{13}C NMR spectra of the NHCs display the corresponding resonances at 217.1(**8a**), 217.8(**8b**) and 221.1(**8c**) ppm for the carbene center, which are in the expected range for aryl-substituted imidazolidin-2-ylidenes (see Experimental section). In addition, single crystals of good quality for X-ray analysis from ruthenium complex **8a** and **8b** (Figures 2 and 3) were obtained by slow diffusion of hexane into concentrated solution of benzene and CH_2Cl_2 respectively.

Before testing of the activity of newly obtained complexes bearing unsymmetrical fluorinated NHC ligands, the thermal stability of these catalysts was examined. For this purpose, each of the ruthenium compounds was dissolved in deuterated benzene under an argon atmosphere and heated for one week at 50 °C. Degradation of the reference catalysts, with respect to 1,3,5-trimethoxybenzene utilized as an internal standard, was monitored by ^1H NMR spectroscopy. All new catalysts exhibited high stability under applied conditions (Figure 4). Even the least lasting of them **8a** decomposed by only 16% during one week (the scale covers the range 80−100%). As expected, complexes bearing a mesityl moiety were less stable than their 2,6-diisopropylphenyl analogues **8c**, which exhibited no signs of decomposition.

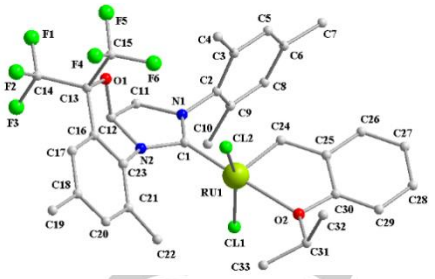


Figure 2. Structure of complex **8a**. Hydrogen atoms are omitted for clarity. *Selected bonds[Å], angles[°] and dihedral angles[°]: Ru1-C1 1.970(2), Ru1-Cl2 2.3420(5), Ru1-Cl1 2.3593(5), O1-C13 1.415(3), O1-C12 1.435(3), N1-C1 1.346(3), N1-C2 1.437(3), N1-C11 1.473(2), N2-C1 1.402(3), N2-C12 1.449(3), C11-C12 1.493,* ***Ru1…C22 3.121(2)****, C13-O1-C12 113.94(17), C1-N1-C2 129.32(17), Ru1N1N2C1$_{av}$/C2C3C9 88.7, Ru1N1N2C1$_{av}$/C16C21C23 44.5.*

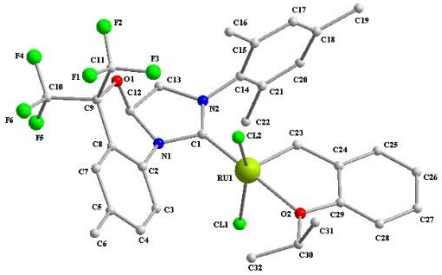


Figure 3. Structure of complex **8b**. Hydrogen atoms are omitted for clarity. Selected bonds[Å], angles[°] and dihedral angles[°]: Ru1-C1 1.965(2), Ru1-Cl2 2.3334(5), Ru1-Cl1 2.3412(5), O1-C9 1.420(2), O1-C12 1.437(2), N1-C1 1.388(2), N1-C12 1.441(2), N2-C1 1.335(2), N2-C13 1.472(2), **Ru1…C3 3.149(1)**, C9-O1-C12 116.32(15), C1-N1-C2 124.59(15), Ru1N1N2C1$_{av}$/C2C3C8 46.6, Ru1N1N2C1$_{av}$/C14C15C21 88.6.

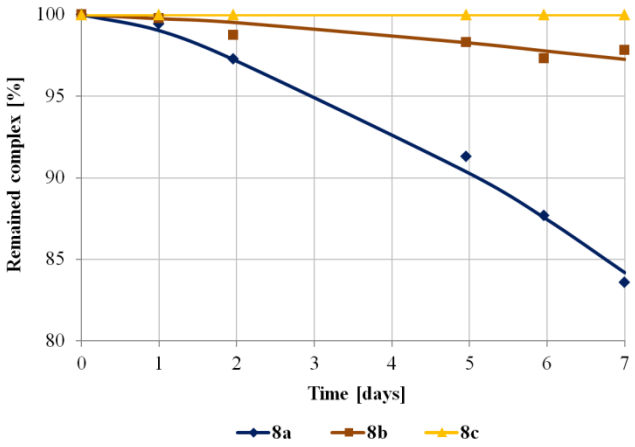


Figure 4. Thermal stability of complexes **8a-c** in benzene-d_6 solution at 50°C under argon monitored by ^1H NMR. Decomposition was determined based on the signal ratio between ruthenium compounds and internal standard 1,3,5-trimethoxybenzene.

Then we performed the initial investigation of catalytic activities of the prepared catalysts **8a-c** in RCM reactions with diallyl- and allylmetallylmalonates as well as in self-metathesis (SM) reaction of allylbenzene following standard conditions for evaluation of

olefin metathesis catalysts[21]. The commercially available complex $RuCl_2(H_2IMes)(=CH\text{-}(o\text{-}i\text{PrO-}C_6H_4))$ **HG-II**[22] (H_2IMes = 1,3-bis(mesityl)imidazolidin-2-ylidene) was used as reference catalyst to find out how modulating the electronic and steric changes of the fluoroalkyl-substituted NHCs might affect the catalytic activity. As a result, we found that the initiation rate of the catalyst **8a** in RCM of diethyl diallylmalonate (DEDAM) was almost the same as compared to **HG-II** (Figure 5). On the other hand, the initiation rates of catalysts **8b** and **8c** have proved to be distinctly lower than in the case of **8a** and **HG-II** displaying some initiation period (about 30 min). Nevertheless, the full conversion can be slowly achieved in 24 h, thus exhibiting high stability of the catalysts in solution.

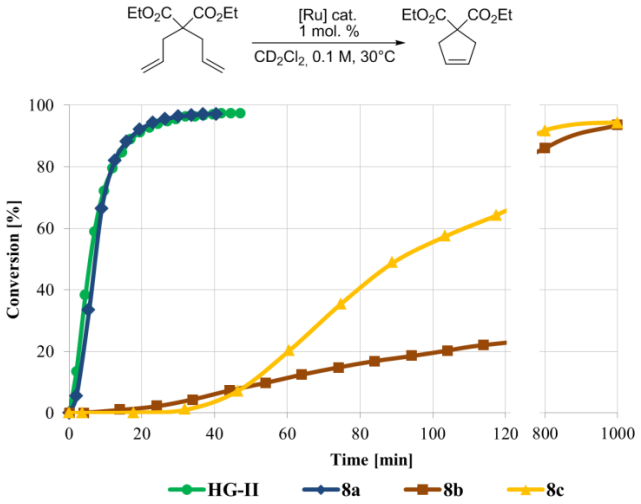


Figure 5. Catalytic activities of complexes **8a-c** and **HG-II** in RCM of DEDAM.

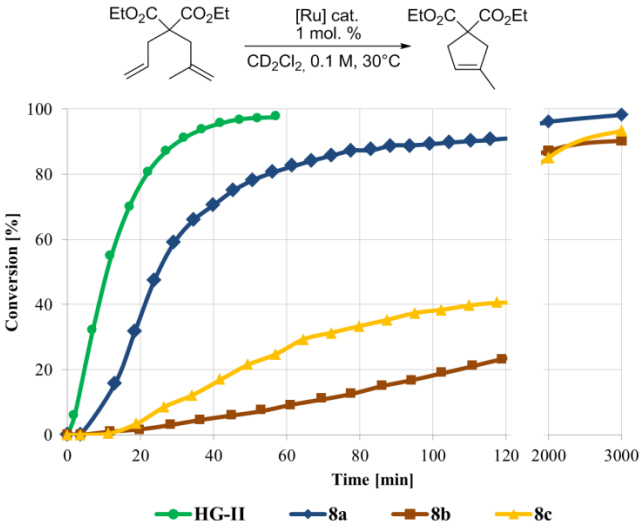


Figure 6. Catalytic activities of complexes **8a-c** and **HG-II** in RCM of DEAMM.

The ring-closing metathesis of the more sterically hindered diethyl allylmethallylmalonate was also achieved with the new catalysts **8a-c** (Figure 6). A similar reactivity profile as starting from DEDAM was observed, but the reaction rates were lower in all cases.

To estimate the efficiency of new complexes in cross-metathesis allylbenzene has been selected as a model substrate. As it is well known, the commercially available second generation Grubbs and Hoveyda-Grubbs catalysts in self-metathesis of allylbenzene usually induce isomerization of both starting compound and product[23] *via* double-bond migration to form the corresponding hard-separable mixture (Table 1, equation).

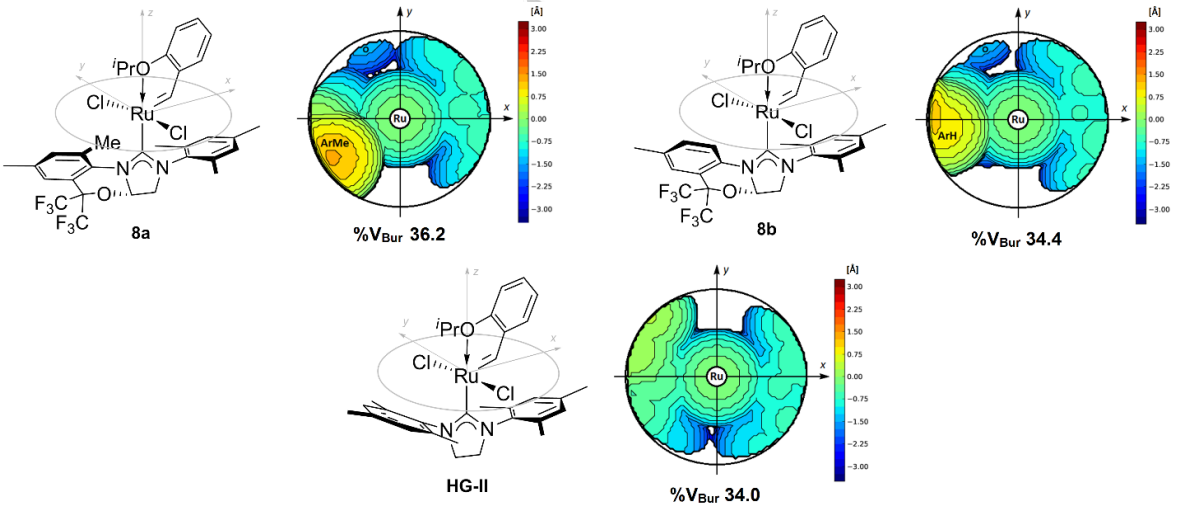


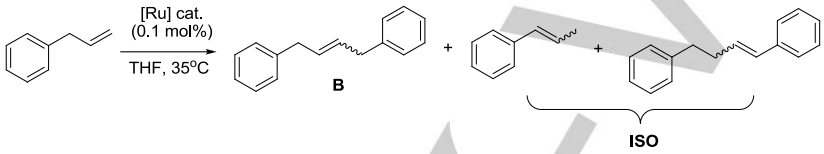
Figure 7. Steric maps of complexes **8a**, **8b**, and **HG-II**

We found that new complexes **8a-c** revealed in this reaction a good reactivity and much higher selectivity as compared with **HG-II** (Table 1). Thus, the yields of target self-metathesis product ***B*** were noticeably higher in all cases under catalysis with **8a-c** and the formation of undesirable isomerization by-products ***ISO*** did not succeed 1.0 % in most trials exhibiting two order higher ratios of ***B*** to ***ISO*** by comparing with **HG-II** (Table 1, entries 4, 7).

The observed selectivity could be addressed to the rigid structure of NHCs, which forces the more bulky aromatic fragment of the unsymmetrical ligand to locate in close proximity to ruthenium center. This in turn hampers the catalyst decomposition *via* ruthenium-hydride pathways and blocks any isomerization processes.[24] For proposed mechanism of preventing the isomerization process see Supporting Information.

In addition, the steric maps and buried volumes of catalytic pockets for **8a** and **8b** were calculated[25] and compared with analogous data obtained for **HG-II**[26] (Figure 7). Despite the fact that the resulting values of $\%V_{Bur}$ for **8a** and **8b** were only slightly higher than for **HG-II** (36.2 and 34.4 vs 34.0) namely the fixed location of tricyclic NHC ligand could be considered as a critical point for observed selectivity. Noteworthy, the absence of methyl group in **8b** does not significantly affect the distance of fused aromatic ring to ruthenium center (*Ru1…C22* = 3.12 Å for **8a**, *Ru1…C3* = 3.15 Å for **8b**, see Figure 2 and 3, respectively).

Table 1. Catalytic activity of complexes **8a-c** and **HG-II** in self-metathesis of allylbenzene[a]



Entry	[Ru] cat.	Time, h	Conversion, %	Yield **B**,[b] %	Yield **ISO**, %	Ratio **B/ISO**
1	**HG-II**	1	88.0	83.8	16.1	5
2	**HG-II**	2	89.9	83.3	16.7	5
3	**HG-II**	4	98.1	76.4	23.6	3
4	**8a**	1	76.1	**99.9**	0.1	**760**
5	**8a**	2	77.8	99.7	0.3	388
6	**8a**	4	81.3	99.6	0.4	270
7	**8b**	1	75.3	**99.9**	0.1	**752**
8	**8b**	2	77.7	99.3	0.7	154
9	**8b**	4	82.3	98.8	1.2	81
10	**8c**	1	74.3	99.2	0.8	123
11	**8c**	2	76.2	99.1	0.9	108
12	**8c**	4	80.1	98.9	1.1	88

[a] Conditions: THF; catalyst's loading 0.1 mol%; concentration of allylbenzene 3 M; reaction temperature 35 °C. Conversions and yields were determined by ^{1}H NMR spectroscopy and GC-MS analysis. [b] E/Z ratios in all cases were in a range of 4:1 to 5:1 respectively.

Conclusion

We have developed an efficient route to new tricyclic imidazolinium salts decorated with two geminal trifluoromethyl groups. The synthetic strategy is based on condensation of anilines containing bulky hexafluoroisopropoxy group in *ortho*-position with *N*-aryl-*N*-(2-oxoethyl) formamide followed by intramolecular heterocyclization under strong acidic conditions. The salts obtained were further successfully used as precursors of the corresponding NHC ligands for the preparation of three novel ruthenium carbene complexes of Grubbs-Hoveyda type. Their performance has been tested in representative olefin metathesis reactions. As a result, they have proved to be active in ring closing metathesis of diallyl- and allylmetallyl malonates.

The initiation rates in most cases were lower as compared to benchmark catalyst. Nevertheless, the full conversion can be slowly achieved in 1-2 days, thus exhibiting high stability of the catalysts in solution. On the other hand, new catalysts gave interesting results in self-metathesis of allylbenzene, outperforming commercially available Grubbs-Hoveyda catalyst in terms of yield and regioselectivity. In particular, the reaction with *N*-Mes-containing catalysts (**8a** and **8b**) led to remarkably low content of isomerization products (0.1%) in almost quantitative yield of desired self-metathesis product. The observed selectivity can be addressed to close proximity of fused aromatic ring in rigid tricyclic NHC ligand to ruthenium center that may hampering isomerization pathways during catalytic cycle. The data obtained can be useful in design and synthesis of new more selective olefin metathesis catalysts.

Experimental Section

All solvents were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. Syntheses of ruthenium complexes were performed under an argon atmosphere using a standard Schlenk technique. Analytical TLC was performed with Merck silica gel 60 F254 plates. Visualization was accomplished by UV light (254 and 366 nm), spraying by $Ce(SO_4)_2$ solution in 5% H_2SO_4 or $KMnO_4$ solution in water. Column chromatography was carried out using Merck silica gel 60 (230−400 mesh ASTM) and ethyl acetate/petroleum ether as eluent.

NMR spectra were recorded at room temperature on Bruker AC-200, AV-400, AV-500, AV-600 spectrometers operating at 200, 300, and 500 MHz for ^{1}H; 101, 126, and 151 MHz for ^{13}C; and 376 MHz for ^{19}F (CF_3CO_2H as reference). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks.

Mass spectra were measured on Agilent 5977A quadrupole instrument, using electron ionization (EI-MS) source with sample injection *via* Agilent 7890 gas chromatograph.[27] Measurements were performed in full-scan (scan range from m/z 35 to m/z 500) mode with ionization energy set at 70 eV, source temperature set at 230°C and transfer capillary temperature set at 300°C. Separation was carried out on Agilent HP-5ms fused silica capillary column (30 m length; 250 µm I.D.; 0.25 µm film thicknesses, (5% Phenyl)-methylpolysiloxane) using He (5.0 grade, NII KM) as carrier gas with average velocity at 30 cm/sec. Temperature program was started at 60°C and fixed for 2 min, then increased at a rate of 20ºC/min to 300ºC and held for 6 min. Injection port temperature was set at 300°C and operated in split mode at 10:1 ratio with sample injection volume of 1 µl. The spectra were processed using Bruker Data Analysis 4.0 software package with NIST 14 spectra database.

High-resolution mass spectra were obtained on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The experiments were performed in positive (+)MS ion mode (HV Capillary: 4500 V; Spray Shield Offset: –500 V) and negative (–)MS ion mode (HV Capillary: 2000 V; Spray Shield Offset: –500 V) with a scan range of *m/z* 50–1200 (or *m/z* 50–2000 for Ru complexes). External calibration of the mass spectrometer was achieved using a low-concentration tuning mix solution (Agilent Technologies). Direct syringe injection of solutions in DCM or MeCN was used at flow rate of 5 µL/min. For Ru complexes studied in DCM: nitrogen was used as the nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}, 180 °C). For organic compounds studied in MeCN: nitrogen was used as the nebulizer gas (1.2 bar) and dry gas (8.0 L min^{-1}, 200 °C). All the MS spectra were recorded with 1 Hz frequency and processed using Bruker Data Analysis 4.0 software package.

Purification of allylbenzene[24] and syntheses of 2-(2-amino-3,5-dimethylphenyl)-1,1,1,3,3,3-hexafluoro-propan-2-ol (**2a**),[16a] 2-(2-amino-5-methylphenyl)-1,1,1,3,3,3-hexafluoro-propan-2-ol (**2b**),[15] *N*-mesityl-*N*-(2-oxoethyl)formamide (**5a**),[17] *N*-(2,6-diisopropylphenyl)-*N*-(2-oxoethyl)formamide (**5b**)[18b] were carried out according to literature procedures.

General procedure for synthesis of compounds 6. The corresponding fluorinated aniline (1 eqiuv.) was added to a solution of *N*-mesityl-*N*-(2-oxoethyl)formamide or *N*-(2,6-diisopropylphenyl)-*N*-(2-oxoethyl)-formamide (1 equiv.) in petroleum ether (0.1 M). After complete dissolution of aniline 0.1 equiv. of glacial acetic acid was added. The reaction mixture was allowed to stir at room temperature overnight. Next day the reaction mixture was filtered to yield corresponding oxazine **6** as precipitate.

Synthesis of *N*-{[6,8-dimethyl-4,4-bis(trifluoromethyl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazin-2-yl]methyl}-*N*-mesitylformamide (6a). Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1H, C*H*O), 7.16 (s, 1H, H_{Ar}), 7.06 (s, 1H, H_{Ar}), 6.99 (s, 1H, H_{Ar}), 6.95 (s, 1H, H_{Ar}), 5.46 (br.s, 1H, N*H*), 4.87 (d, $J_{H,H}$ = 5.7 Hz, 1H, OC*H*N), 4.40 (dd, $J_{H,H}$ = 14.1, 8.0 Hz, 1H, CH_2), 3.54 (dd, $J_{H,H}$ = 14.1, 3.1 Hz, 1H, CH_2), 2.31 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.20 ppm (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.8 (*C*HO), 139.1 (C_{Ar}), 139.0 (C_{Ar}), 136.3 (C_{Ar}), 136.3 (C_{Ar}), 132.8 (C_{Ar}), 130.1 (C_{Ar}), 130.0 (C_{Ar}), 129.9 (C_{Ar}), 127.4 (C_{Ar}), 124.9 (C_{Ar}), 123.0 (q, $^1J_{C,F}$ = 290 Hz, CF_3), 122.3 (q, $^1J_{C,F}$ = 287 Hz, CF_3), 112.2 (C_{Ar}), 80.6 (NCO), 77.74 (hept, $^2J_{C,F}$ = 29 Hz), 50.1 (CH_2), 21.0 (CH_3), 21.0 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 16.8 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -72.17 (d, $^4J_{F,F}$ = 7.6 Hz, 3F, CF_3), -75.71 ppm (d, $^4J_{F,F}$ = 7.6 Hz, 3F, CF_3). IR (KBr): $\tilde{\nu}$ = 3367, 2950, 2921, 2880, 1671, 1497, 1354, 1262, 1233, 1207, 1178, 1110, 1097, 1057, 977, 961, 923, 862, 793, 752, 742, 709, 585, 538, 442 cm^{-1}. ESI-TOF: (+)MS calcd for $C_{23}H_{25}F_6N_2O_2$ $[M+H]^+$ *m/z* 475.1815, found *m/z* 475.1812, δ 0.6 ppm. Elemental analysis calcd for $C_{23}H_{24}F_6N_2O_2$ (%): C, 58.23; H, 5.10; N, 5.90; found C, 58.31; H, 5.17; N, 5.75.

Synthesis of *N*-mesityl-*N*-{[6-methyl-4,4-bis(trifluoromethyl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazin-2-yl]methyl}formamide (6b). Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1H, C*H*O), 7.29 (s, 1H, H_{Ar}), 7.15 (d, $^3J_{H,H}$ = 8.1 Hz, 1H, H_{Ar}), 6.98 (s, 1H, H_{Ar}), 6.95 (s, 1H, H_{Ar}), 6.83 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, H_{Ar}), 5.17 (br.s, 1H, N*H*), 4.91 (dd, $J_{H,H}$ = 7.0, 2.8 Hz, 1H, OC*H*N), 4.29 (dd, $J_{H,H}$ = 14.2, 7.1 Hz, 1H, CH_2), 3.59 (dd, $J_{H,H}$ = 14.2, 3.1 Hz, 1H, CH_2), 2.31 (s, 6H, CH_3), 2.22 ppm (s, 6H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.7 (CHO), 141.0 (C_{Ar}), 138.9 (C_{Ar}), 136.4 (C_{Ar}), 136.3 (C_{Ar}), 136.2 (C_{Ar}), 131.9 (C_{Ar}), 130.6 (C_{Ar}), 130.0 (C_{Ar}), 129.8 (C_{Ar}), 127.5 (C_{Ar}), 122.9 (q, $^1J_{C,F}$ = 290 Hz, CF_3), 122.2 (q, $^1J_{C,F}$ = 286 Hz, CF_3), 119.4 (C_{Ar}), 112.3 (C_{Ar}), 80.8 (NCO), 78.4-77.4 [m, $C(CF_3)_2$], 50.33(CH_2), 21.04 (CH_3), 21.01 (CH_3), 18.3 (CH_3), 18.2 ppm (CH_3); ^{19}F NMR (376 MHz, C_6D_6): δ = -72.30 – -72.40 (m, 3F, CF_3), -75.71 – -75.81 ppm (m, 3F, CF_3). IR (KBr): $\tilde{\nu}$ = 3353, 2946, 2923, 2876, 1672, 1619, 1511, 1474, 1424, 1355, 1277, 1262, 1231, 1183, 1100, 1087, 1012, 988, 966, 862, 823, 752, 746, 710, 584, 537 cm^{-1}. ESI-TOF: (+)MS calcd for $C_{22}H_{23}F_6N_2O_2$ $[M+H]^+$ *m/z* 461.1658, found *m/z* 461.1657, δ 0.2 ppm. Elemental analysis calcd for $C_{22}H_{22}F_6N_2O_2$ (%): C, 57.39, H, 4.82, N, 6.08, found C, 57.24, H, 5.12, N, 6.15.

Synthesis of *N*-(2,6-diisopropylphenyl)-*N*-{[6,8-dimethyl-4,4-bis(trifluoromethyl)-2,4-dihydro-1H-benzo[*d*][1,3]oxazin-2-yl]methyl}formamide (6c). Additional purification by column chromatography (petroleum ether/ethyl acetate 8:1) was required to obtain

the product of satisfactory quality. Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H, C*H*O), 7.40 (t, $J_{H,H}$ = 7.7 Hz, 1H, H_{Ar}), 7.26 (dd, $J_{H,H}$ = 7.7 Hz, 1.4, 1H, H_{Ar}), 7.21 (dd, $J_{H,H}$ = 7.8 Hz, 1.4, 1H, H_{Ar}), 7.16 (s, 1H, H_{Ar}), 5.51 (d, $J_{H,H}$ = 6.8 Hz, 1H, N*H*), 4.89-4.83 (m, 1H, NC*H*O), 4.64 (dd, $J_{H,H}$ = 13.9, 9.1 Hz, 1H, CH_2), 3.36-3.26 (m, 2H, CH_2, C*H*Me$_2$), 2.89 (hept, $^3J_{H,H}$ = 6.7 Hz, 1H, C*H*Me$_2$), 2.29 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.32 [d, $^3J_{H,H}$ = 6.9, 3H, CH(CH_3)$_2$], 1.16 [d, $^3J_{H,H}$ = 6.8, 3H, CH(CH_3)$_2$], 1.14 [d, $^3J_{H,H}$ = 6.9, 3H, CH(CH_3)$_2$], 1.02 ppm [d, $^3J_{H,H}$ = 6.8, 3H, CH(CH_3)$_2$]; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5 (*C*HO), 147.9 (C_{Ar}), 147.3 (C_{Ar}), 139.0 (C_{Ar}), 135.8 (C_{Ar}), 132.8 (C_{Ar}), 130.4 (C_{Ar}), 130.1 (C_{Ar}), 127.9 (C_{Ar}), 125.0 (C_{Ar}), 124.9 (C_{Ar}), 124.8 (C_{Ar}), 112.5 (C_{Ar}), 80.2 (N*C*O), 78.5-77.3 [m, *C*(CF$_3$)$_2$], 51.5 (CH_2), 28.7 (*C*Me$_2$), 27.9 (C*H*Me$_2$), 25.3 [C(*C*H$_3$)$_2$], 25.2 [C(*C*H$_3$)$_2$], 23.64 [C(*C*H$_3$)$_2$], 23.59 [C(*C*H$_3$)$_2$], 21.1 (*C*H$_3$), 16.8 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -72.29 (q, $^4J_{F,F}$ = 8.4 Hz, C*F*$_3$), -75.83 ppm (q, $^4J_{F,F}$ = 8.4 Hz, C*F*$_3$). IR (KBr): $\tilde{\nu}$ = 3356, 2969, 2951, 2932, 2866, 1674, 1499, 1461, 1368, 1277, 1257, 1221, 1205, 1179, 1147, 1094, 1056, 978, 965, 863, 811, 773, 749, 743, 712 cm^{-1}. ESI-TOF: (+)MS calcd for $C_{26}H_{31}F_6N_2O_2$ $[M+H]^+$ *m/z* 517.2284, found *m/z* 517.2288, δ 0.8 ppm. Elemental analysis calcd for $C_{26}H_{30}F_6N_2O_2$ (%): C, 60.46; H, 5.85; N, 5.42; found C, 60.61; H, 5.89; N, 5.20.

General procedure for synthesis of compounds 7. Triflic acid (120 µL, 1.37 mmol) was added to the solution of oxazine **6** (1.37 mmol) in toluene (30 mL), and the mixture was stirred at r.t. for 15 min. Then, triflic anhydride (230 µL, 1.37 mmol) was added, and the reaction mixture was heated at 65 °C for 1.5 h. DIPEA (720 µL, 4.11 mmol) was added, and the reaction mixture was heated at 80 °C for another 1.5 h. After cooling to r.t., solvents were removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (30 mL) and the solution was washed with water (3 × 20 mL). The organic layer was dried using $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was triturated in petroleum ether to yield **7** as beige solid.

Scaled-up one pot procedure for the synthesis of 7a-c. The corresponding fluorinated aniline (34.0 mmol) was added to a solution of *N*-mesityl-*N*-(2-oxoethyl)formamide or *N*-(2,6-diisopropylphenyl)-*N*-(2-oxoethyl)-formamide (1 equiv.) in petroleum ether (300 mL). After complete dissolution of aniline 0.2 mL of glacial acetic acid was added. The reaction mixture was allowed to stir at room temperature overnight. Next day the reaction mixture was filtered. The resulting precipitate was dissolved in 150 mL of toluene, then triflic acid (2.4 mL, 27.1 mmol) was added, and the mixture was stirred at r.t. for 15 min. Then, triflic anhydride (4.6 mL, 27.1 mmol) was added, and the reaction mixture was heated at 65 °C for 1.5 h. DIPEA (14.2 mL, 81.3 mmol) was added, and the reaction mixture was heated at 80 °C for another 1.5 h. After cooling to r.t., solvents were removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (150 mL) and the solution was washed with water (3 × 80 mL). The organic layer was dried using $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was triturated in petroleum ether to yield **7** (75-98%) as beige solid.

Synthesis of 2-mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3*H*-benzo[*d*]imidazo[5,1-*b*][1,3]oxazin-2-ium triflate (7a). Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.04 (s, 1H, NC*H*N), 7.34 (s, 1H, H_{Ar}), 7.29 (s, 1H, H_{Ar}), 6.96 (s, 2H, H_{Ar}), 6.13 (d, $J_{H,H}$ = 6.3 Hz, 1H, NCHO), 4.94 (dd, $J_{H,H}$ = 14.4, 6.5 Hz, 1H, CH_2), 4.08 (d, $J_{H,H}$ = 14.4 Hz, 1H, CH_2), 2.46 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.30 (s, 6H, CH_3), 2.19 ppm (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.0 (N*C*N), 141.3 (C_{Ar}), 139.0 (C_{Ar}), 135.3 (C_{Ar}), 135.2 (C_{Ar}), 134.7 (C_{Ar}), 132.1 (C_{Ar}), 130.1 (C_{Ar}), 129.3 (C_{Ar}), 128.5 (C_{Ar}), 125.8 (C_{Ar}), 121.9 (q, $^1J_{C,F}$ = 288 Hz, C*C*F$_3$), 121.3 (q, $^1J_{C,F}$ = 286 Hz, C*C*F$_3$), 120.4 (q, $^1J_{C,F}$ = 320 Hz, S*C*F$_3$), 117.5 (C_{Ar}), 85.6 (NCO), 78.2 [hept, $^2J_{C,F}$ = 30 Hz, *C*(CF$_3$)$_2$], 57.6 (*C*H$_2$), 21.4 (*C*H$_3$), 21.1 (*C*H$_3$), 17.4 (*C*H$_3$), 16.8 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -71.90 (q, $^4J_{C,F}$ = 8.5 Hz, 3F, CC*F*$_3$), -76.13 (q, $^4J_{C,F}$ = 8.4 Hz, 3F, CC*F*$_3$), -78.98 ppm (s, 3F, SC*F*$_3$). IR (KBr): $\tilde{\nu}$ = 3016, 2926, 1624, 1605, 1282, 1268, 1227, 1212, 1158, 1109, 1089, 1058, 1031, 973, 861, 750, 743, 712, 639, 570, 518 cm^{-1}. ESI-TOF: (+)MS calcd for $C_{23}H_{23}F_6N_2O$ $[M–OTf]^+$ *m/z* 457.1709, found *m/z* 457.1709, δ < 0.1 ppm; (–)MS calcd for CF_3O_3S $[OTf]^–$ *m/z* 148.9526, found *m/z* 148.9526, δ < 0.1. Elemental analysis calcd for $C_{24}H_{23}F_9N_2O_4S$ (%): C, 47.53; H, 3.82; N, 4.62; found C, 47.42; H, 3.93; N, 4.60.

Synthesis of 2-mesityl-7-methyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3*H*-benzo[*d*]imidazo[5,1-*b*][1,3]oxazin-2-ium triflate (7b). Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.24 (s, 1H, NC*H*N), 7.93 (d, $J_{H,H}$ = 8.2 Hz, 1H, H_{Ar}), 7.48 (s, 1H, H_{Ar}), 7.31 (d, $J_{H,H}$ = 7.9 Hz, 1H, H_{Ar}), 6.97 (s, 2H, H_{Ar}), 6.23 (d, $J_{H,H}$ = 6.3 Hz, 1H, NC*H*O), 4.98 (dd, $J_{H,H}$ = 14.3, 7.3 Hz, 1H, CH_2), 4.08 (dd, $J_{H,H}$ = 14.2, 2.4 Hz, 1H, CH_2), 2.43 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.18 ppm (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (NCN), 141.3 (C_{Ar}), 139.4 (C_{Ar}), 135.7 (C_{Ar}), 134.3 (C_{Ar}), 133.4 (C_{Ar}), 130.3 (C_{Ar}), 130.0 (C_{Ar}), 129.6 (C_{Ar}), 129.4 (C_{Ar}), 127.9 (C_{Ar}), 121.9 (q, $^1J_{C,F}$ = 289 Hz, C*C*F$_3$), 121.8 (C_{Ar}), 121.3 (q, $^1J_{C,F}$ = 286 Hz, C*C*F$_3$), 120.4 (q, $^1J_{C,F}$ = 289 Hz, S*C*F$_3$), 115.8 (C_{Ar}), 84.3 (NCO), 79.0-77.4 [m, *C*(CF$_3$)$_2$], 57.9 (*C*H$_2$), 21.5 (*C*H$_3$), 21.1 (*C*H$_3$), 17.4 (*C*H$_3$), 16.9 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -71.82 (q, $^4J_{F,F}$ = 7.6 Hz, 3F, CC*F*$_3$), -75.98 (q, $^4J_{F,F}$ = 7.2 Hz, 3F, CC*F*$_3$), -78.75 ppm (s, 3F, SC*F*$_3$). IR (KBr): $\tilde{\nu}$ = 3075, 2966, 2926, 2862, 1624, 1294, 1268, 1234, 1219, 1172, 1097, 1038, 971, 859, 821, 751, 744, 709, 701 cm^{-1}. ESI-TOF: (+)MS calcd for $C_{22}H_{21}F_6N_2O$ $[M–OTf]^+$ *m/z* 443.1553, found *m/z* 443.1551, δ 0.5 ppm; (–)MS calcd for CF_3O_3S $[OTf]^–$ *m/z* 148.9526, found *m/z* 148.9524, δ 1.3 ppm. Elemental analysis calcd for $C_{23}H_{21}F_9N_2O_4S$ (%): C, 46.63; H, 3.57; N, 4.73; found C, 46.40; H, 3.68; N, 4.74.

Synthesis of 2-(2,6-diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3*H*-benzo[*d*]imidazo[5,1-*b*][1,3]oxazin-2-ium triflate (7c). Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H, NC*H*N), 7.47 (t, $J_{H,H}$ = 7.8 Hz, 1H, H_{Ar}), 7.33 (s, 1H, H_{Ar}), 7.29-7.22 (m, 3H, H_{Ar}), 6.12 (d, $J_{H,H}$ = 6.0 Hz, 1H, NC*H*O), 4.95 (dd, $J_{H,H}$ = 14.7, 6.4 Hz, 1H, CH_2), 4.08 (d, $J_{H,H}$ = 14.6 Hz, 1H, CH_2), 3.00 (hept, $^3J_{H,H}$ = 6.7 Hz, 1H, C*H*Me$_2$), 2.79 (hept, $^3J_{H,H}$ = 6.6 Hz, 1H, C*H*Me$_2$), 2.41 (s, 3H, ArCH_3), 2.40 (s, 3H, ArCH_3), 1.28 [d, $^3J_{H,H}$ = 6.7 Hz, 3H C(CH_3)$_2$], 1.24 [d, $^3J_{H,H}$ = 6.7 Hz, 3H C(CH_3)$_2$], 1.19 [d, $^3J_{H,H}$ = 6.7 Hz, 3H C(CH_3)$_2$], 1.10 ppm [d, $^3J_{H,H}$ = 6.8 Hz, 3H C(CH_3)$_2$]; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.1 (N*C*N), 146.4 (C_{Ar}), 145.9 (C_{Ar}), 139.1 (C_{Ar}), 135.4 (C_{Ar}), 132.3 (C_{Ar}), 131.9 (C_{Ar}), 128.8 (C_{Ar}), 128.4 (C_{Ar}), 125.7 (C_{Ar}), 125.0 (C_{Ar}), 124.9 (C_{Ar}), 121.9 (q, $^1J_{F,F}$ = 289 Hz, CF$_3$), 121.4 (q, $^1J_{F,F}$ = 286 Hz, CF$_3$), 120.4 [m, *C*(CF$_3$)$_2$], 117.5 (C_{Ar}), 85.8 (N*C*O), 59.8 (*C*H$_2$), 28.5 (*C*Me$_2$), 28.5 (*C*Me$_2$), 24.8 [C(*C*H$_3$)$_2$], 24.2 [C(*C*H$_3$)$_2$], 23.8 [C(*C*H$_3$)$_2$], 23.6 [C(*C*H$_3$)$_2$], 21.5 (Ar*C*H$_3$), 16.6 ppm (Ar*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -71.91 – -72.01 (m, 3F, CC*F*$_3$), -76.39 – -76.48 (m, 3F, CC*F*$_3$), -78.82 ppm (s, 3F, SC*F*$_3$). IR (KBr): $\tilde{\nu}$ = 2971, 2934, 2876, 1623, 1284,1269, 1218, 1085, 1059, 973, 866, 809, 749, 743, 712 cm^{-1}. ESI-TOF: (+)MS calcd for $C_{26}H_{29}F_6N_2O$ $[M–OTf]^+$ *m/z* 499.2179, found *m/z* 499.2179, δ < 0.1 ppm; (–)MS calcd for CF_3O_3S $[OTf]^–$ *m/z* 148.9526, found *m/z* 148.9525, δ 0.7 ppm. Elemental analysis calcd for $C_{27}H_{29}F_9N_2O_4S$ (%): C, 50.00; H, 4.51; N, 4.32; found C, 50.26; H, 4.64; N, 4.38.

General procedure for synthesis of ruthenium complexes 8. In a flame-dried Schlenk flask, imidazolinium salt **7** (0.42 mmol) was mixed with 15 mL of anhydrous toluene. The resulting mixture was degassed three times and cooled to -5 °C; then KHMDS (0.45 mL of 1 M solution in THF, 0.45 mmol) was added to the mixture under an argon atmosphere. The reaction mixture was stirred for 2 min before Hoveyda catalyst **HG-I** (0.19 g, 0.32 mmol) was added. Then mixture was stirred for 100 min at r.t. During this time, the reaction mixture changed color from brown to green. Once complete, solvents were removed from the reaction mixture under reduced pressure, and the resulting substance was purified by column

chromatography using petroleum ether/ethyl acetate (3:1) as eluent to yield Hoveyda-type catalyst **8** as a green solid.

Synthesis of dichloro(2-isopropoxybenzylidene)[2-mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3*H*-benzo[*d*]imidazo[5,1-*b*][1,3]oxazin-1-ylidene]ruthenium(II) (8a). The product was additionally purified by recrystallization from methanol. Yield: 59%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 16.91 (s, 1H, C*H*Ar), 7.63 (ddd, J = 8.7, 7.1, 1.8, 1H, H_{Ar}), 7.43 (s, 1H, H_{Ar}), 7.41 (s, 2H, H_{Ar}), 7.21 (s, 1H, H_{Ar}), 7.07-6.98 (m, 4H, H_{Ar}), 5.62 (d, $J_{H,H}$ = 5.6 Hz, 1H, NC*H*O), 5.19-5.11 (m, 1H, C*H*Me$_2$), 4.50 (d, $J_{H,H}$ = 6.9 Hz, 1H, CH_2), 4.04 (d, $J_{H,H}$ = 13.0 Hz, 1H, CH_2), 3.37 (s, 3H, ArCH_3), 2.52 (s, 3H, ArCH_3), 2.51 (s, 3H, ArCH_3), 2.44 (s, 3H, ArCH_3), 2.40 (s, 3H, ArCH_3), 1.76-1.50 ppm [m, 6H, C(CH_3)$_2$]; ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 296.4 (Ru=*C*H), 217.1 (N*C*N), 153.1 (C_{Ar}), 144.9 (C_{Ar}), 140.0 (C_{Ar}), 138.9 (C_{Ar}), 138.0 (C_{Ar}), 137.4 (C_{Ar}), 137.1 (C_{Ar}), 134.3 (C_{Ar}), 131.2 (C_{Ar}), 130.6 (C_{Ar}), 129.6 (C_{Ar}), 125.8 (C_{Ar}), 123.4 (q, $^{1}J_{C,F}$ = 290 Hz, *C*F$_3$), 123.1 (C_{Ar}), 123.0 (C_{Ar}), 122.4 (q, $^{1}J_{C,F}$ = 287 Hz, *C*F$_3$), 119.1 (C_{Ar}), 114.0 (C_{Ar}), 84.9 (N*C*O), 78.4 [hept, $^{2}J_{C,F}$ = 31 Hz, *C*(CF$_3$)$_2$], 76.1 (O*C*Me$_2$), 59.8 (*C*H$_2$), 22.4 (Ar*C*H$_3$), 22.2 (Ar*C*H$_3$), 21.6 (Ar*C*H$_3$), 21.4 (Ar*C*H$_3$), 19.6 [C(*C*H$_3$)$_2$], 18.6 ppm [C(*C*H$_3$)$_2$]; ^{19}F NMR (376 MHz, CD_2Cl_2): δ = -72.52 (s, 3F, C*F*$_3$), -73.74 ppm (s, 3F, C*F*$_3$). ESI-TOF: (+)MS calcd for $C_{33}H_{34}Cl_2F_6N_2O_2Ru$ [M]$^{+\bullet}$ *m/z* 776.0943, found *m/z* 776.0934, δ 1.0 ppm. Elemental analysis calcd for $C_{33}H_{34}Cl_2F_6N_2O_2Ru$ (%): C, 51.04; H, 4.41; N, 3.61; found C, 50.84; H, 4.52; N, 3.84. Suitable for X-ray crystals of **8a** were grown by slow diffusion of hexane vapors in C_6H_6 solution.

Synthesis of dichloro(2-isopropoxybenzylidene)[2-mesityl-7-methyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3*H*-benzo[*d*]imidazo[5,1-*b*][1,3]oxazin-1-ylidene]ruthenium(II) (8b). Yield: 30%. ^{1}H NMR (400 MHz, C_6D_6): δ = 16.31 (s, 1H, C*H*Ar), 9.91 (d, $J_{H,H}$ = 7.9 Hz, 1H, H_{Ar}), 7.65 (s, 1H, H_{Ar}), 7.34 (dd, $J_{H,H}$ = 8.0, 1.8 Hz, 1H, H_{Ar}), 7.13-7.08 (m, 1H, H_{Ar}), 6.98 (dd, $J_{H,H}$ = 7.5, 1.6 Hz, 1H, H_{Ar}), 6.79 (s, 1H, H_{Ar}), 6.72 (s, 1H, H_{Ar}), 6.66 (t, $J_{H,H}$ = 7.3 Hz, 1H, H_{Ar}), 6.44 (d, $J_{H,H}$ = 8.3 Hz, 1H, H_{Ar}), 4.97 (d, $J_{H,H}$ = 6.7 Hz, 1H, NC*H*O), 4.65 (hept, $^{3}J_{H,H}$ =5.9 Hz, 1H, OC*H*Me$_2$), 3.54 (dd, $J_{H,H}$ = 13.0, 6.9 Hz, 1H, CH_2), 3.37 (dd, $J_{H,H}$ = 12.9, 1.7 Hz, 1H, CH_2), 2.33 (s, 3H, ArCH_3), 2.27 (s, 3H, ArCH_3), 2.17 (s, 3H, ArCH_3), 1.94 (s, 3H, ArCH_3), 1.81 [d, $^{3}J_{H,H}$ = 6.0 Hz, 3H, C(CH_3)$_2$], 1.56 ppm [d, $^{3}J_{H,H}$ = 6.0 Hz, 3H, C(CH_3)$_2$]; ^{13}C NMR (126 MHz, C_6D_6): δ = 294.4 (Ru=*C*H), 217.8 (N*C*N), 153.1 (C_{Ar}), 144.5 (C_{Ar}), 139.5 (C_{Ar}), 138.8 (C_{Ar}), 138.6 (C_{Ar}), 137.6 (C_{Ar}), 137.2 (C_{Ar}), 136.7 (C_{Ar}), 133.0 (C_{Ar}), 130.1 (C_{Ar}), 130.0 (C_{Ar}), 124.1 (C_{Ar}), 123.4 (q, $^{1}J_{C,F}$ = 290 Hz, *C*F$_3$), 122.8 (C_{Ar}), 122.7 (q, $^{1}J_{C,F}$ = 286 Hz, *C*F$_3$), 122.4 (C_{Ar}), 116.9 (C_{Ar}), 113.4 (C_{Ar}), 83.0 (N*C*O), 78.5 [hept, $^{2}J_{C,F}$ = 30 Hz, *C*(CF$_3$)$_2$], 75.1 (O*C*Me$_2$), 58.9 (*C*H$_2$), 22.5 (Ar*C*H$_3$), 22.3 (Ar*C*H$_3$), 21.1 (Ar*C*H$_3$), 18.2 [C(*C*H$_3$)$_2$], 17.7 ppm [C(*C*H$_3$)$_2$]; ^{19}F NMR (376 MHz, C_6D_6): δ = -71.61 (q, $^{4}J_{F,F}$ = 8.1 Hz, 3F, C*F*$_3$), -73.69 ppm (q, $^{4}J_{F,F}$ = 8.1 Hz, 3F, C*F*$_3$). ESI-TOF: (+)MS calcd for $C_{32}H_{32}Cl_2F_6N_2O_2Ru$ [M]$^{+\bullet}$ *m/z* 762.0786, found *m/z* 762.0783, δ 0.3 ppm. Elemental analysis calcd for $C_{32}H_{32}Cl_2F_6N_2O_2Ru$ (%): C, 50.40; H, 4.23; N, 3.67; found C, 50.44; H, 4.43; N, 3.86. Suitable for X-ray crystals of **8b** were grown by slow diffusion of hexane in DCM solution.

Synthesis of dichloro(2-isopropoxybenzylidene)[2-(2,6-diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-3a,5-dihydro-3*H*-benzo[*d*]imidazo[5,1-*b*][1,3]oxazin-1-ylidene]ruthenium(II) (8c). Yield: 38%. ^{1}H NMR (400 MHz, C_6D_6): δ = 16.59 (s, 1H, Ru=C*H*), 7.53 (s, 1H, H_{Ar}), 7.32 (t, $J_{H,H}$ = 7.7 Hz, 1H, H_{Ar}), 7.24 (dd, $J_{H,H}$ = 7.8, 1.7 Hz, 1H, H_{Ar}), 7.15-7.04 (m, 3H, H_{Ar}), 6.97 (dd, $J_{H,H}$ = 7.5, 1.7 Hz, 1H, H_{Ar}), 6.61 (t, $J_{H,H}$ = 7.4 Hz, 1H, H_{Ar}), 6.37 (d, $J_{H,H}$ = 8.3 Hz, 1H, H_{Ar}), 5.12 (d, $J_{H,H}$ = 5.6 Hz, 1H, NC*H*O), 4.57 (hept, $^{3}J_{H,H}$ = 6.2 Hz, 1H, OC*H*Me$_2$), 3.79 (dd, $J_{H,H}$ = 12.8, 5.6 Hz, 1H, CH_2), 3.65-3.53 (m, 5H, ArCH_3, ArC*H*Me$_2$), 3.41 (d, $J_{H,H}$ = 12.9 Hz, 1H, CH_2), 1.95 (s, 3H, ArCH_3), 1.66 [d, $^{3}J_{H,H}$ = 6.1 Hz, 3H, C(CH_3)$_2$], 1.42 [d, $^{3}J_{H,H}$ = 6.1 Hz, 3H, C(CH_3)$_2$], 1.33 [d, $^{3}J_{H,H}$ = 6.7 Hz, 3H, C(CH_3)$_2$], 1.20 [d, $^{3}J_{H,H}$ = 6.4 Hz, 3H, C(CH_3)$_2$], 1.12 [d, $^{3}J_{H,H}$ = 6.5 Hz, 3H, C(CH_3)$_2$], 1.01 ppm [d, $^{3}J_{H,H}$ = 6.8 Hz, 3H, C(CH_3)$_2$]; ^{13}C NMR (151 MHz, C_6D_6): δ = 292.5 (Ru=*C*H), 221.1 (N*C*N), 153.1 (C_{Ar}), 149.6 (C_{Ar}), 148.0 (C_{Ar}), 144.3 (C_{Ar}), 137.8 (C_{Ar}), 137.6 (C_{Ar}), 137.0 (C_{Ar}), 134.4 (C_{Ar}), 130.4 (C_{Ar}), 130.3 (C_{Ar}), 128.4 (C_{Ar}), 125.7 (C_{Ar}), 125.4 (C_{Ar}), 125.1 (C_{Ar}), 122.8 (C_{Ar}), 122.4 (C_{Ar}), 119.1 (C_{Ar}), 113.6 (C_{Ar}), 84.9 (N*C*O), 75.3 (O*C*Me$_2$), 61.9 (*C*H$_2$), 28.6 (Ar*C*Me$_2$), 27.6 (Ar*C*Me$_2$), 27.1 [ArC(CH$_3$)$_2$], 25.6 [ArC(CH$_3$)$_2$], 24.0 [ArC(*C*H$_3$)$_2$], 23.6 [ArC(*C*H$_3$)$_2$], 23.3 (Ar*C*H$_3$), 22.4 (Ar*C*H$_3$), 21.9 [OC(CH$_3$)$_2$], 21.0 ppm [OC(*C*H$_3$)$_2$]; ^{19}F NMR (376 MHz, C_6D_6): δ = -71.84 (q, $^{4}J_{C,F}$ = 11.5 Hz, 3F, C*F*$_3$), -72.89 ppm (q, $^{4}J_{C,F}$ = 11.0 Hz, 3F, C*F*$_3$). ESI-TOF: (+)MS calcd for $C_{36}H_{40}Cl_2F_6N_2O_2Ru$ [M]$^{+\bullet}$ *m/z* 818.1413, found *m/z* 818.1403, δ 1.2 ppm. Elemental analysis calcd for $C_{36}H_{40}Cl_2F_6N_2O_2Ru$ (%): C, 52.81; H, 4.92; N, 3.42; found C, 52.96; H, 5.01; N, 3.22.

CCDC 1850675 (for **4**), 1850674 (for **8a**) and 1854390 (for **8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

Ring-closing metathesis of diethyl diallylmalonate or diethyl allylmethallylmalonate. An NMR tube with a screw-cap septum top was charged with starting material (60 μmol) solution in CD_2Cl_2 (0.5 mL) under argon atmosphere. The sample was equilibrated at 30°C in the NMR probe before 6 mM catalyst solution in CD_2Cl_2 (0.1 mL, 0.6 μmol) was added *via* syringe. Data points were collected every 2-3 minutes. The conversion to RCM product was determined by comparing the ratio of the integrals of the methylene protons in the starting materials, δ 2.61 (dt, $J_{H,H}$ = 7.4, 1.1 Hz, 4H) for DEDAM and 2.72-2.61 (m, 4H) for DEAMM, with those in the products, δ 2.98 (s, 4H) and 2.98-2.85 (m, 4H) respectively.

Self-metathesis of allylbenzene. A flame-dried Schlenk flask was charged with allylbenzene (355 mg, 3.0 mmol) in anhydrous degassed THF (0.4 mL) under argon atmosphere. The mixture was stirred at 35°C before 15 mM catalyst solution in THF (0.2 mL, 3 μmol) was added *via* syringe. Data points were collected over an appropriate period of time by taking the probes (~0.1 mL) from the reaction mixture. The reaction was quenched using excess of ethyl vinyl ether (0.5 mL). The conversion to CM product was determined by GCMS and NMR.

Thermal Stability Test. An NMR tubes with a screw-cap septum top were charged with solutions of complexes **8a-c** (12.9 μmol) and 1,3,5-trimethoxybenzene (internal standard, 2.2 mg, 12.9 μmol) in C_6D_6 (0.6 mL) under argon atmosphere. The samples were equilibrated at 50°C for one week. Data points were collected after appropriate time intervals. The rate of decomposition of complexes was determined by comparing the ratio of the integrals of methyl protons the internal standard, δ 3.31 (s, 9H) with those for the characteristic Ru=C*H*Ar, δ 17.00 (for **8a**), 16.31 (for **8b**) and 16.59 (for **8c**) (s, 1H).

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Keywords: N-Heterocyclic carbenes • unsymmetrical imidazolium salts • fluorinated NHC ligands • alkene metathesis

[1] *Handbook of Metathesis*, ed. R. H. Grubbs and A. G. Wenzel, Wiley-VCH, Weinheim, **2015**.

[2] a) *Olefin Metathesis-Theory and Practice*, ed. K. Grela, Wiley, Hoboken, NJ, **2014**; b) C. S. Higman, J. A. M. Lummiss, D. E. Fogg, *Angew. Chem. Int. Ed.*, **2016**, *55*, 3552-3565; *Angew. Chem.*, **2016**, *128*, 3612-3626.

[3] a) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705-2733; b) J. Tornatzky, A. Kannenberg, S. Blechert, *Dalton Trans.* **2012**, *41*, 8215-8225; c) F. B. Hamad, T. Sun, S. Xiao, F. Verpoort, *Coord. Chem. Rev*. **2013**, *257*, 2274-2292; d) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723-6753.

[4] a) S. Shahane, C. Bruneau, C. Fischmeister, *ChemCatChem* **2013**, *5*, 3436-3459; b) T. P. Montgomery, A. M. Johns, R. H. Grubbs, *Catalysts* **2017**, *7*, 87; c) A. Dumas, R. Tarrieu, T. Vives, T. Roisnel, V. Dorcet, O. Baslé, M. Mauduit, *ACS Catal.* **2018**, *8*, 3257-3262.

[5] a) R.E. Banks, B.E. Smart, J.C. Tatlow, *Organofluorine Chemistry: Principles and Commercial Applications*, Plenum Press, New York, **1994**; b) H. Hiyama, *Organofluorine Compounds: Chemistry and Applications*, Springer, Berlin, **2000**; c) S. Purser, P.R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev*. **2008**, *37*, 320-330; d) P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*, second ed., Wiley-VCH, Weinheim, **2013**; e) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881-1886; f) F. Giornal, S. Pazenok, L. Rodefeld, N. Lui, J.-P. Vors, F.R. Leroux, *J. Fluorine Chem*. **2013**, *152*, 2-11; g) J. Wang, M. Sánchez-Roselló, J.L. Aceña, C. del Pozo, A.E. Sorochinsky, S. Fustero, V.A. Soloshonok, H. Liu, *Chem. Rev*. **2014**, *114,* 2432-2506.

[6] a) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, UK, **2006**; b) M. Jagodzinska, F. Huguenot, G. Candiani, M. Zanda, *ChemMedChem*, **2009**, *4*, 49-51.

[7] a) M. Schlosser, *Angew. Chem. Int. Ed.* **1998**, *37*, 1496-1513; *Angew. Chem.* **1998**, *110*, 1538-1556; b) D. O'Hagan, *Chem. Soc. Rev*. **2008**, *37*, 308-319.

[8] a) R. C. Da Costa, J. A. Gladysz, *Chem. Commun*. **2006**, 2619-2621; b) R. C. Da Costa, J. A. Gladysz, *Adv. Synth. Catal*. **2007**, *349*, 243-254; c) R. Tuba, R. C. Da Costa, H. S. Bazzi, J. A. Gladysz, *ACS Catal.* **2012**, *2*, 155-162; d) R. Tuba, E. N. Brothers, J. H. Reibenspies, H. S. Bazzi, J. A. Gladysz, *Inorg. Chem*. **2012**, *51*, 9943-9949.

[9] a) M. Matsugi, Y. Kobayashi, N. Suzumura, Y. Tsuchiya and T. Shioiri, *J. Org. Chem*., 2010, **75**, 7905-7908; b) J. Kvíčala, M. Schindler, V. Kelbichova, M. Babuněk, M. Rybáčková, M. Kvičalova, J. Cvačka, A. Březinova, *J. Fluorine Chem*., **2013**, *153*, 12-25; c) J. Lim, S. S. Lee, J. Y. Ying, *Chem. Commun*., **2008**, 4312-4314; d) Q. Yao, Y. Zhang, *J. Am. Chem. Soc*., **2004**, *126*, 74-75; e) Y. Duan, T. Wang, Q. Xie, X. Yu, W. Guo, J. Wang, G. Liu, *Dalton Trans*. **2016**, *45*, 19441-19448.

[10] a) L. Yang, M. Mayr, K. Wurst and M. R. Buchmeiser, *Chem. Eur. J*., **2004**, *10*, 5761-5770; b) T. S. Halbach, S. Mix, D. Fischer, S. Maechling, J. O. Krause, C. Sievers, S. Blechert, O. Nuyken, M. R. Buchmeiser, *J. Org. Chem*., **2005**, *70*, 4687-4694; *c*) S. Monfette, K. D. Camm, S. I. Gorelsky, D. E. Fogg, *Organometallics*, **2009**, *28*, 944-946.

[11] a) S. Fustero, A. Simón-Fuentes, P. Barrio, G. Haufe, *Chem. Rev*. **2015**, *115*, 871-930; b) V. Siano, I. d'Auria, F. Grisi, C. Costabile, P. Longo, *Cent. Eur. J. Chem.* **2011**, *9*, 605-609; c) J. Hošek, M. Rybáčková, J. Čejka, J. Cvačka, J. Kvíčala, *Organometallics* **2015**, *34*, 3327-3334.

[12] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236-3253.

[13] a) T. Ritter, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2006**, *128*, 11768-11769; b) D. R. Anderson, D. J. O'Leary, R. H. Grubbs, *Chem. Eur. J.* **2008**, *14*, 7536-7544.

[14] J. Hošek, O. Šimůnek, P. Lipovská, V. Kolaříková, K. Kučnirová, A. Edr, N. Štěpánková, M. Rybáčková, J. Cvačka, J. Kvíčala *ACS Sustainable Chem. Eng.*, **2018**, *6*, 7026-7034.

[15] M. A. Topchiy, M. A. Zotova, S. M. Masoud, A. K. Mailyan, I. V. Ananyev, S. E. Nefedov, A. F. Asachenko, S. N. Osipov, *Chem. Eur. J.* **2017**, *23*, 6663-6674.

[16] a) S. M. Masoud, A. K. Mailyan, V. Dorcet, T. Roisnel, P. H. Dixneuf, C. Bruneau, S. N. Osipov, *Organometallics*, **2015**, *34*, 2305-2313; b) S. M. Masoud, M. A. Topchiy, A. S. Peregudov, T. Roisnel, P. H. Dixneuf, C. Bruneau, S. N. Osipov, *J. Fluorine Chem.* **2017**, *200*, 66-76; c) S. M. Masoud, T. R. Akmalov, O. I. Artyushin, C. Bruneau, S. N. Osipov, *Russ. Chem. Bull.*, **2017**, *9*, 1601-1606.

[17] A. Fürstner, M. Alcarazo, V. César, C. W. Lehmann, *Chem. Commun.* **2006**, 2176-2178.

[18] a) D. Katayev, Y.-X. Jia, A. K. Sharma, D. Banerjee, C. Besnard, R. B. Sunoj, E. P. Kündig, *Chem. Eur. J.* **2013**, *19*, 11916-11927; b) A. Schumacher, M. Bernasconi, A. Pfaltz, *Angew. Chem. Int. Ed.*, **2013**, *52*, 7422-7425; *Angew. Chem. Int. Ed.*, **2013**, *125*, 7570-7573; c) G. A. Price, A. R. Bogdan, A. L. Aguirre, T. Iwai, S. W. Djuric, M. G. Organ, *Catal. Sci. Technol*., **2016**, *6*, 4733-4742; d) R. Kyan, K. Sato, N. Mase, N. Watanabe, T. Narumi, *Org. Lett*. **2017**, *19*, 2750-2753.

[19] M. Tsimerman, D. Mallik, T. Matsuo, T. Otani, K. Tamao, M. G. Organ, *Chem. Commun.,* **2012**, *48*, 10352-10354.

[20] J. S. Kingsbury, J. P. A. Harrity, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791-799.

[21] T. Ritter, A. Hejl, A. G. Wenzel, T. W. Funk, R. H. Grubbs, *Organometallics*, **2006**, *25*, 5740-5745.

[22] S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168-8179.

[23] a) A. M. Lozano Vila, S. Monsaert, R. Drozdzak, S. Wolowiec, F. Verpoort, *Adv. Synth. Catal.* **2009**, *351*, 2689-2701; b) M. Shao, L. Zheng, W. Qiao, J. Wang, J. Wang, *Adv. Synth. Catal.*, **2012**, *354*, 2743-2750; c) G. Liu, L. Zheng, M. Shao, H. Zhang, W. Qiao, X. Wang, B. Liu, H. Zhao, J. Wang, *Tetrahedron* **2014**, *70*, 4718-4725.

[24] J. Engel, W. Smit, M. Foscato, G. Occhipinti, K. W. Törnroos, V. R. Jensen, *J. Am. Chem. Soc.*, **2017**, *139*, 16609-16619.

[25] a) L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics*, **2016**, *35*, 2286-2293; b) SambVca 2.0: a web application for analyzing catalytic pockets. https://www.molnac.unisa.it/OMtools/sambvca2.0/.

[26] M. Barbasiewicz, M. Bieniek, A. Michrowska, A. Szadkowska, A. Makal, K. Woźniak, K. Grela, *Adv. Synth. Catal.*, **2007**, *349*, 193-203.

[27] A. M. Tsedilin, A. N. Fakhrutdinov, D. B. Eremin, S. S. Zalesskiy, A. O. Chizhov, N. G. Kolotyrkina, V. P. Ananikov, *Mend. Comm*., **2015**, *25*, 454-456.

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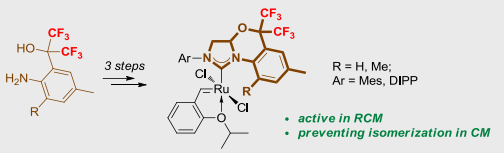

Novel ruthenium-alkylidene complexes with sterically rigid fluorinated NHC ligands were synthesized and evaluated in representative olefin metathesis reactions. Along with excellent robustness, they demonstrate remarkable activity in self-metathesis of allylbenzene, outperforming commercially available Grubbs-Hoveyda catalyst in terms of yield and regioselectivity.

Key Topic: metathesis catalysts

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Page No. – Page No.

Ruthenium-alkylidene complexes with sterically rigid fluorinated NHC ligands