Novel olefin metathetis catalysts with fluorinated *N*-alkyl-*N*′-arylimidazolin-2-ylidene ligands*

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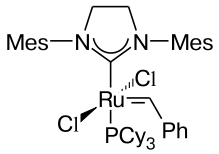
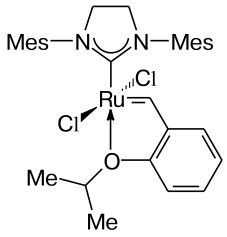
Novel ruthenium carbene complexes bearing unsymmetrical *NHC*-ligands based on *N*-alkyl-*N*′-arylimidazoline with hexafluoroisopropylmethoxy group in *para*-position of *N*-aryl moiety have been synthesized. Catalytic activity of complexes obtained was investigated on model reactions of intra- and intermolecular olefin metathesis.

Key words: fluorinated *N*-heterocyclic carbenes, ruthenium carbene complexes, olefin metathesis, catalysis.

Recent advances in development of novel ruthenium-based metathesis catalysts are associated mostly with modification of *N*-heterocyclic carbene (*N*-HC) ligand in commercially available Grubbs **G-II** and Hoveyda **H-II** complexes allowing for a direct tuning of the catalyst efficiency.[1—8] For example, varying electronic and steric properties of substituents at the nitrogen atoms located in direct proximity to a carbene center, one can significantly alter the catalytic activity, stability, and selectivity in many types of metathesis transformations.



G-II

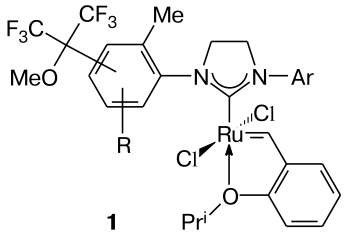


H-II

Therefore, unsymmetrical *N*-heterocyclic carbenes have currently assumed a new importance, since desymmetrization enables the further rapid tuning of catalytic properties. Introduction of functional groups having chelating, chirality or shielding effects can have a dramatic impact on stability, reactivity, and selectivity of a catalyst, encouraging the researches to search for novel efficient catalytic systems.[9]

At the same time it is common knowledge that organofluorine compounds are widely used today in almost all fields of science and technology including medicine and manufacturing of novel materials. The reason is that fluorine atoms or organofluorine substituents introduced in an organic molecule significantly alter its physico-chemical properties. This particularly holds true for trifluoromethylated compounds as CF_3 moiety is one of the most lypophilic groups in organic chemistry, as well as highly electronegative and bulky.[10—15] As for ruthenium-based metathesis catalysts, steric and electronic effects of fluorinated substituents on their catalytic activity has been studied mainly for fluorine-modified phosphine and styrene ligands as well as in the case of substituting chlorine atoms bonded to ruthenium, *e.g.* for fluoroalkoxy moieties.[16—27] Presently, just a few examples of catalysts bearing fluorinated *N*-HC-ligands are reported in literature.[28—32]

Recently, we developed synthetic procedures to obtain novel metathesis catalysts with *N,N*′-diarylsubstituted imidazolinilydene ligands having hexafluoroisopropylmethoxy group ($(CF_3)_2(OMe)C$—) in the *N*-aryl substituent (**1**) and demonstrated high activity of these com-



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* Dedicated to Academician of the Russian Academy of Sciences G. A. Abakumov on the occasion of his 80th birthday.

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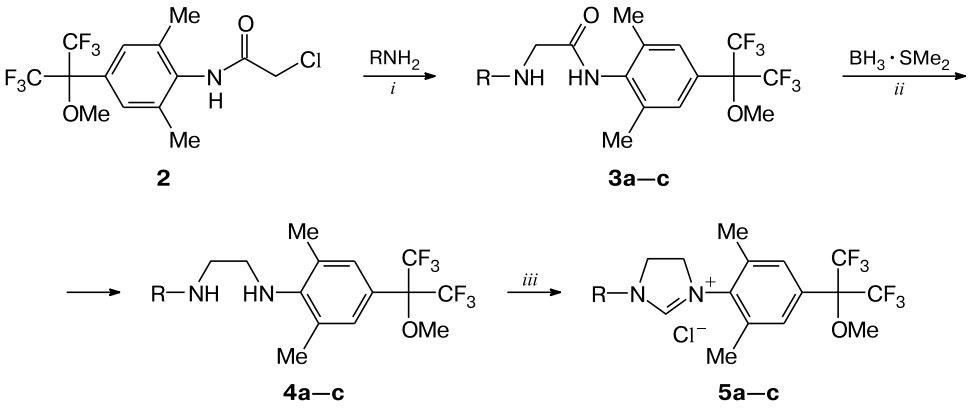
Scheme 1



Reagents and conditions: *i*. 20 °C, 24—48 h; *ii*. toluene, 80 °C, 8 h; *iii*. 1) MeOH/HCl, 2) $HC(OEt)_3$, 100 °C

Compound	R	Product yields (%) 3	4	5
a	Bu^t	95	99	80
b	Pr^i	96	79	99
c	Cy	98	87	99

* Cy is cyclohexyl.

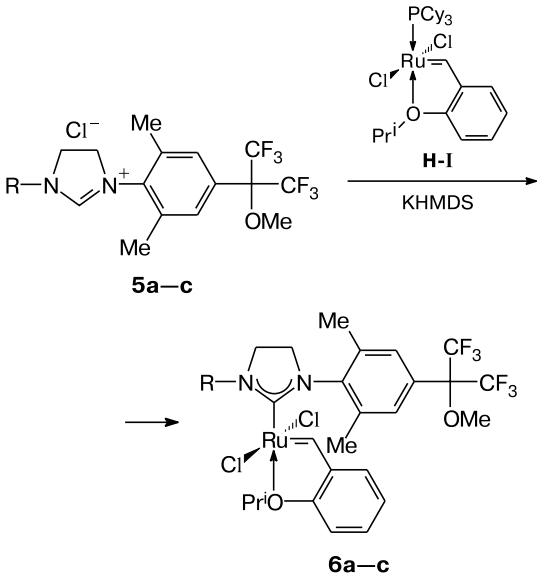
plexes in reactions of intra- and intermolecular olefin metathesis.[33—35]

To elucidate the effect of more donor *N*-alkyl substituents in the fluorinated *N*-HC-ligand on activity of the catalyst, in the present study we have synthesized the corresponding ruthenium carbene complexes and performed the preliminary catalytic activity testing thereof.

Primarily, our efforts were focused on the synthesis of unsymmetrical *N*-alkyl-*N*′-arylimidazolinium salts. For this purpose, fluorinated anilide **2** was used as a starting compound (Scheme 1) which is readily obtainable according to our previous procedure[36] starting from commercially available 2,6-dimethylaniline, hexafluoroacetone hydrate, and chloroacetyl chloride. Thus, it was established that reaction of anilide **2** with primary amines such as *tert*-butylamine, isopropylamine, and cyclohexylamine proceeds smoothly at room temperature without solvent with an excess of amine and is completed within 1—3 days (TLC control) to produce the corresponding aminoamides **3a—c** in nearly quantitative yields (see Scheme 1). Subsequent reduction of the amide keto group in compounds **3a—c** proceeds effectively using dimethylsulfide complex of BH_3 in toluene at 80 °C to give high yields of diamines **4a—c**. The latter readily undergo intramolecular heterocyclization during the conventional treatment using triethyl orthoformate to afford the desired imidazolinium salts **5a—c** (see Scheme 1).

The salts **5a—c** thus obtained were further used as precursors for the corresponding *N*-heterocyclic ruthenium complexes **6a—c** (Scheme 2). Carbenes were generated *in situ* by treating the parent salts **5a—c** with potassium hexamethyldisylazide (KHMDS) in anhydrous toluene under argon at 0 °C followed by the addition of the commercially available first-generation Hoveyda complex **H-I** (see Ref. 36) to the reaction mixture. Generally, slight heating during 30—40 min was needed for the ligand exchange reaction (PCy_3 for *N*-HC) to be completed. Resulting complexes **6a—c** were isolated by column chromatography on silica gel as dark-green powders characteristic for phosphine-free Hoveyda-type complexes (**H-II**).

Scheme 2

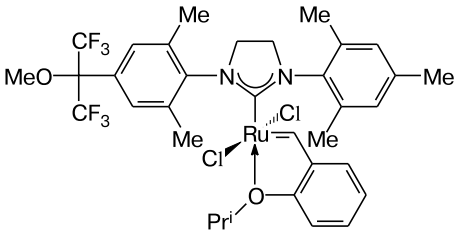


Reagents and conditions: KHMDS, toluene, 0 °C→40 °C.

Yields (%): 70 (**6a**), 39 (**6b**), 25 (**6c**).

The complexes obtained were completely characterized by NMR-spectroscopy (^{1}H, ^{13}C, ^{19}F), and elemental analysis data. In the ^{1}H NMR spectra of all compounds characteristic signals of benzylidene protons (Ru=C—H) are observed in the range of 16.5—17.1 ppm, with the corresponding carbon atoms (Ru=C—H) ranging from 208—209 ppm in the ^{13}C NMR spectra. Also, the ^{13}C NMR spectra show characteristic signals of carbene atoms (N—C—N) at 306, 285, and 286 ppm for compounds **6a**, **6b**, and **6c** respectively.

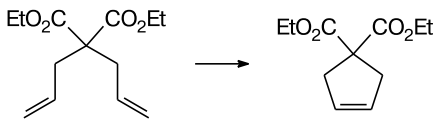
Catalytic activity of complexes **6a**—**c** synthesized was tested in benchmark ring-closing metathesis reactions using diethyldiallyl malonate (DEDAM) and cross metathesis of allylbenzene with 1,4-diacetoxybut-2-ene. Commercially available second-generation Hoveyda catalyst **H-II** as well as an unsymmetrical complex having bisaryl *N*-HC-ligand **1a** obtained by us earlier,[33] were used as reference compounds.



1a

As a result, it was found that initiation rate for catalysts **6b** and **6c** in reaction with DEDAM proved to be far lower compared to catalysts **H-II** and **1a**; the highest conversion (80%) was reached in reaction with isopropyl derivative **6b** for 48 h. Catalyst **6a** bearing a bulky *tert*-Bu substituent at the nitrogen atom did not catalyze this process (Scheme 3, Fig. 1).

Scheme 3



Reagents and conditions: Ru-catalyst (1 mol %), 0.1 *M* CH_2Cl_2, 30 °C.

The similar tendency was observed for the cross metathesis reaction of allylbenzene with 1,4-diacetoxybut-2-ene (Scheme 4, Fig. 2). In this case, catalyst **6b** was the most active, having reached the conversion values close to those for **H-II** and **1a**, however for a more prolonged period of time (3 h). Similar to the reaction with DEDAM, complex **6a** proved to be absolutely inert.

To summarize, in the present study we have synthesized three novel unsymmetrical fluorinated ruthenium carbene complexes having alkyl substituents at one of the nitrogen atoms, and tested their catalytic activity in model reactions of intra- and intermolecular olefin metathesis. It was found that replacing an aryl substituent by an alkyl one decreases significantly the activity of the above complexes in the metathesis reactions studied. However the moderate reactivity of isopropyl derivative **6b** allows one to expect its application in other types of metathesis such as metathesis polymerization of bicyclic monomers where the low initiation rate improves the polymer structure.[8]

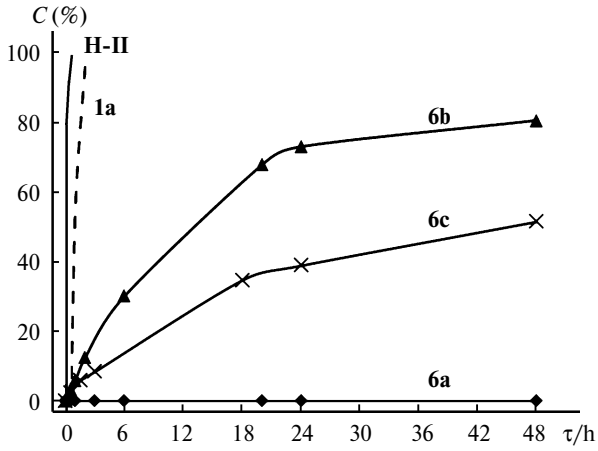
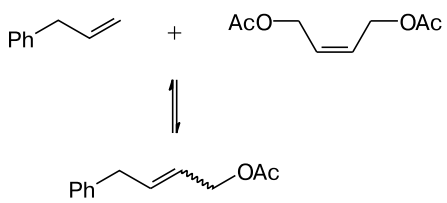


Fig. 1. Time dependency of DEDAM conversion of a catalyst nature.

Scheme 4



Reagents and conditions: Ru-catalyst (2.5 mol %), 0.1 *M* CH_2Cl_2, 25 °C.

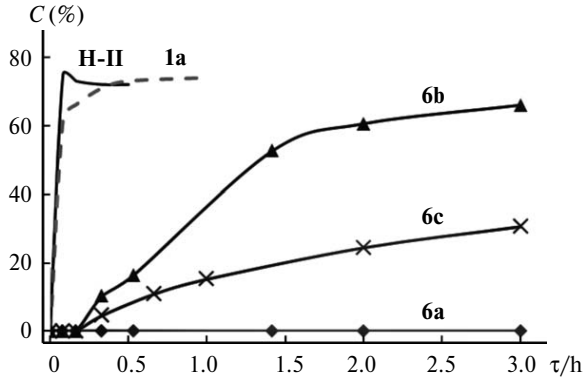


Fig. 2. Time dependency of allylbenzene conversion of a catalyst nature.

Experimental

Solvents used in reactions were dried according to standard procedures. Other reagents were recrystallized or distilled if necessary. Ruthenium complexes were synthesized under argon atmosphere using standard Schlenk techniques. The reactions were monitored by TLC on Merck 60 F_{254} plates. The plates were visualized using UV irradiation (254 and 366 nm), solutions of $Ce(SO_4)_2$ in 5% H_2SO_4 or $KMnO_4$ in water. Column chromatography was performed using silica gel Merck 60 (230 400 mesh ASTM) eluting with ethyl acetate—petroleum ether. NMR spectra were measured at room temperature on Bruker AV-300 and Bruker AV-400 instruments at an operating frequences of 300 and 400 MHz for ^{1}H; 75 and 101 MHz for ^{13}C, and 282 and 376 MHz for ^{19}F ($CFCl_3$ was used as a standard) respectively. The chemical shifts were referenced relative to the residual undeuterated solvent peaks.

Synthesis of aminoamides 3 (general procedure). 2-Chloro-*N*-[4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]acetamide (**2**) (1.5 g, 4.0 mmol) was dissolved in 20-fold excess of the corresponding amine (80 mmol). The reaction mixture was stirred at room temperature until starting compound **2** had been completely consumed (TLC control), then the mixture was treated with 10% aqueous $NaHCO_3$ solution (20 mL) and extracted with ethyl acetate (3×20 mL). The combined organic layer was washed with saturated aqueous sodium chloride and water, then dried over $MgSO_4$ and evaporated under reduced pressure. An excess of RNH_2 was distilled off *in vacuo*. The resulting solid was recrystallized from petroleum ether.

2-(*tert*-Butylamino)-*N*-[4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]acetamide (3a). The reaction was completed within 3 days. Yield 95%, m.p. 126—128 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.19 (s, 1 H, NHCO); 7.27 (s, 2 H, H_{arom}); 3.48 (s, 3 H, OMe); 3.43 (s, 2 H, CH_2); 2.28 (s, 6 H, 2 Me); 1.70 (br. s, 1 H, N<u>H</u>CH_2); 1.17 (s, 9 H, C—<u>Me</u>$_3$). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 171.2, 136.3, 135.7, 128.1, 126.1, 122.5 (q, CF_3, $^1J_{C,F}$ = 290 Hz); 83.7—82.1 (m, <u>C</u>$(CF_3)_2$); 54.4, 51.4, 46.3, 29.2, 19.2. ^{19}F NMR ($CDCl_3$), δ: −70.79. Found (%): C, 51.94; H, 5.89; N, 6.72. $C_{18}H_{24}F_6N_2O_2$. Calculated (%): C, 52.17; H, 5.84; N, 6.76.

***N*-[4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-2-(isopropylamino)acetamide (3b).** The reaction was completed within 1 day. Yield 96%, m.p. 74—76 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.13 (s, 1 H, NHCO); 7.26 (s, 2 H, H_{arom}); 3.47 (s, 5 H, CH_2, OMe); 2.92 (hept, 1 H, C<u>H</u>Me_2, J = 6.1 Hz); 2.27 (s, 6 H, 2 Me); 2.21 (br. s, 1 H, N<u>H</u>CH_2); 1.14 (d, 6 H, CH<u>Me</u>$_2$, J = 6.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 170.5, 136.5, 135.7, 128.0, 126.2, 122.5 (q, CF_3, $^1J_{C,F}$ = = 289 Hz); 83.7—82.1 (m, <u>C</u>$(CF_3)_2$); 54.4, 50.3, 50.0, 23.0, 19.1. ^{19}F NMR ($CDCl_3$), δ: −70.80. Found (%): C, 50.87; H, 5.59; N, 6.94. $C_{17}H_{22}F_6N_2O_2$. Calculated (%): C, 51.00; H, 5.54; N, 7.00.

***N*-[4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-2-(cyclohexylamino)acetamide (3c).** The reaction was completed within 1 day. Yield 98%, m.p. 96—98 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.11 (br. s, 2 H, NHCO); 7.26 (s, 2 H, H_{arom}); 3.47 (s, 5 H, CH_2, OMe); 2.52—2.47 (m, 1 H, $H_{cyclohexyl}$); 2.27 (s, 6 H, 2 Me); 1.96—1.06 (m, 10 H, $H_{cyclohexyl}$). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 170.8, 136.2, 135.7, 128.0, 126.1, 122.5 (q, CF_3, $^1J_{C,F}$ = 290 Hz); 83.7—82.1 (m, <u>C</u>$(CF_3)_2$); 57.8, 54.4, 50.1, 34.0, 26.0, 25.1, 19.1. ^{19}F NMR ($CDCl_3$), δ: −70.79. Found (%): C, 54.51; H, 5.85; N, 6.32. $C_{20}H_{26}F_6N_2O_2$. Calculated (%): C, 54.54; H, 5.95; N, 6.36.

Synthesis of diamines 4 (general procedure). Aminoamide **3** (2.9 mmol) was dissolved in anhydrous toluene (18 mL), then $BH_3 \cdot SMe_2$ (7 mL of 2 *M* solution in THF, 13.0 mmol) was added dropwise at room temperature under argon atmosphere. The resulting mixture was stirred at 80 °C for 8 h. Then it was cooled to room temperature and 10 mL of methanol and 20 mL of 10% aqueous HCl were added slowly, followed by extraction with ethyl acetate (2×30 mL). The aqueous solution was treated with $NaHCO_3$ and extracted with ethyl acetate (2×30 mL). Combined organic layer after two extractions was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated under reduced pressure.

***N*^{1}-*tert*-Butyl-*N*^{2}-[4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]ethane-1,2-diamine (4a).** Yield 99%, m.p. 58—60 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.11 (s, 2 H, H_{arom}); 4.09 (br. s, 2 H, NH); 3.45 (s, 3 H, OMe); 3.17 (t, 2 H, CH_2, J = 5.6 Hz); 2.79 (t, 2 H, CH_2, J = 5.6 Hz); 2.32 (s, 6 H, 2 Me); 1.12 (s, 9 H, C—<u>Me</u>$_3$). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 148.6, 128.7, 127.8, 122.8 (q, CF_3, $^1J_{C,F}$ = 291 Hz); 118.7, 83.9—82.2 (m, <u>C</u>$(CF_3)_2$); 54.1, 50.4, 48.7, 42.7, 29.3, 19.5. ^{19}F NMR ($CDCl_3$), δ: −70.99. Found (%): C, 54.17; H, 6.85; N, 7.18. $C_{18}H_{26}F_6N_2O$. Calculated (%): C, 53.99; H, 6.55; N, 7.00.

***N*^{1}-[4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-*N*^{2}-isopropylethane-1,2-diamine (4b).** Yield 79%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.12 (s, 2 H, H_{arom}); 3.97 (br. s, 2 H, NH); 3.45 (s, 3 H, OMe); 3.21 (t, 2 H, C<u>H</u>$_2$, J = 5.6 Hz); 2.93—2.84 (m, 3 H, C<u>H</u>$_2$, C<u>H</u>Me_2); 2.32 (s, 6 H, 2 Me); 1.12 (d, 6 H, CH<u>Me</u>$_2$, J = 6.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 148.4, 128.7, 128.3, 122.8 (q, CF_3, $^1J_{C,F}$ = 291 Hz); 119.1, 83.0 (hept, <u>C</u>$(CF_3)_2$, $^2J_{C,F}$ = 28 Hz); 54.1, 49.0, 47.5, 47.2, 22.7, 19.4. ^{19}F NMR ($CDCl_3$), δ: −70.98. Found (%): C, 52.68; H, 6.26; N, 7.40. $C_{17}H_{24}F_6N_2O$. Calculated (%): C, 52.85; H, 6.26; N, 7.25.

***N*^{1}-[4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-*N*^{2}-cyclohexylethane-1,2-diamine (4c).** Yield 87%, m.p. 171—173 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.11 (s, 2 H, H_{arom}); 4.07 (br. s, 2 H, NH); 3.45 (s, 3 H, OMe); 3.25 (t, 2 H, CH_2, J = 5.6); 2.92 (t, 2 H, CH_2, J = 5.7 Hz); 2.61—2.52 (m, 1 H, $H_{cyclohexyl}$); 2.33 (s, 6 H, 2 Me); 2.04—1.10 (m, 10 H, $H_{cyclohexyl}$). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 148.3, 128.7, 128.3, 122.8 (q, CF_3, $^1J_{C,F}$ = 291 Hz); 119.2, 83.0 (hept, <u>C</u>$(CF_3)_2$, $^2J_{C,F}$ = 28 Hz); 57.0, 54.1, 47.1, 46.7, 32.9, 25.9, 25.0, 19.5. ^{19}F NMR ($CDCl_3$), δ: −70.97. Found (%): C, 56.62; H, 6.75; N, 6.69. $C_{20}H_{28}F_6N_2O$. Calculated (%): C, 56.33; H, 6.62; N, 6.57.

Synthesis of imidazolinium salts 5 (general procedure). Concentrated hydrochloric acid (1 mL, 12 mmol) was added to a solution of **4** (1.1 mmol) in MeOH (10 mL) and stirred for 10 min, followed by evaporation of the mixture at the reduced pressure. The resulting solid dihydrochloride was dissolved in the absolute *ortho*-xylene (60 mL), the mixture was refluxed under argon for 10 min to remove the remaining water, then it was cooled to room temperature and triethyl orthoformate (200 μL, 1.1 mmol) was added. The resulting mixture was stirred at 90 °C for 8 h. After the reaction was completed (TLC control), all volatiles were removed under reduced pressure,

the solid residue was rinsed with tetrahydrofurane and petroleum ether.

1-*tert*-Butyl-3-[4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-4,5-dihydro-1*H*-imidazol-3-ium chloride (5a). Yield 80%, m.p. 220—222 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.32 (s, 1 H, NCHN); 7.29 (s, 2 H, H_{arom}); 4.34 (s, 4 H, 2 CH_2); 3.46 (s, 3 H, OMe); 2.44 (s, 6 H, 2 Me); 1.59 (s, 9 H, C—$\underline{Me}_3$). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 157.5, 136.8, 135.4, 129.5, 128.8, 122.07 (q, CF_3, $^1J_{C,F}$ = 289 Hz); 83.5—81.3 (m, $\underline{C}(CF_3)_2$); 58.0, 54.6, 51.2, 46.7, 28.3, 18.8. ^{19}F NMR ($CDCl_3$), δ: −70.57. Found (%): C, 51.22; H, 5.79; N, 6.22. $C_{19}H_{25}ClF_6N_2O$. Calculated (%): C, 51.07; H, 5.64; N, 6.27.

3-[4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-1-isopropyl-4,5-dihydro-1*H*-imidazol-3-ium dichloride (5b). Yield 99%, m.p. 210—215 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.00 (s, 1 H, NCHN); 7.43 (s, 2H, H_{arom}); 4.28—4.15 (m, 4 H, 2 CH_2); 4.01 (hept, 1 H, C$\underline{H}Me_2$, J = 6.5 Hz); 3.47 (s, 3 H, OMe); 2.41 (s, 6 H, 2 Me), 1.34 (d, 6 H, CH$\underline{Me}_2$, J = 6.6 Hz). ^{13}C NMR (101 MHz, DMSO-d_6), δ: 157.4, 137.6, 136.3, 128.1, 127.8, 122.1 (q, CF_3, $^1J_{C,F}$ = 292 Hz); 82.2 (hept, $\underline{C}(CF_3)_2$, $^2J_{C,F}$ = 28 Hz); 54.6, 50.3, 49.9, 46.5, 20.4, 17.8. ^{19}F NMR (DMSO-d_6,), δ: −70.07. Found (%): C, 50.13; H, 5.45; N, 6.45. $C_{18}H_{23}ClF_6N_2O$. Calculated (%): C, 49.95; H, 5.36; N, 6.47.

3-[4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-1-cyclohexyl-4,5-dihydro-1*H*-imidazol-3-ium chloride (5c). Yield 99%, m.p. 224—226 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.09 (s, 1 H, NCHN); 7.42 (s, 2 H, H_{arom}); 4.24 (s, 4 H, 2 CH_2); 3.71—3.61 (m, 1 H, $H_{cyclohexyl}$); 3.47 (s, 3 H, OMe); 2.41 (s, 6 H, 2 Me); 1.57 (m, 10 H, $H_{cyclohexyl}$). ^{13}C NMR (101 MHz, DMSO-d_6), δ: 157.4, 137.6, 136.3, 128.1, 127.7, 122.1 (q, CF_3, $^1J_{C,F}$ = 290 Hz); 82.2 (hept, $\underline{C}(CF_3)_2$, $^2J_{C,F}$ = 28 Hz); 57.0, 54.6, 49.8, 47.0, 30.4, 24.6, 24.3, 17.8. ^{19}F NMR (DMSO-d_6,), δ: −70.10. Found (%): C, 53.13; H, 5.84; N, 5.65. $C_{21}H_{27}ClF_6N_2O$. Calculated (%): C, 53.34; H, 5.75; N, 5.92.

Synthesis of ruthenium complexes 6 (general procedure). In a flame dried Schlenk vial imidazolinium salt **5** (0.40 mmol) was dispersed in anhydrous toluene (9 mL). The resulting mixture was cooled to 0 °C and degassed thrice, then KHMDS (420 μL of 1 *M* solution in THF, 0.42 mmol) was added under argon. The reaction mixture was stirred for 10 min at room temperature and complex **H-I** (0.20 g, 0.33 mmol) was added, the reaction mixture was stirred at 40 °C for 40 min. During this time the mixture turned from brown to the dark-blue. After completion of the reaction solvents were evaporated under reduced pressure and green crystalline product was isolated using column chromatography (eluting with petroleum ether—ethyl acetate, 3 : 1).

{1-*tert*-Butyl-3-[4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-4,5-dihydro-1*H*-imidazol-2-ylidene}(dichloro)(2-isopropoxybenzylidene)ruthenium(II) (6a). Yield 70%. ^{1}H NMR (400 MHz, C_6D_6), δ: 17.10 (s, 1 H, C=H); 7.54 (s, 2 H, H_{arom}); 7.18 (t, 1 H, H_{arom}, J = 8.0 Hz); 7.13 (d, 1 H, H_{arom}, J = 7.7 Hz); 6.73 (t, 1 H, H_{arom}, J = 7.3 Hz); 6.45 (d, 1 H, H_{arom}, J = 8.1 Hz); 4.58 (hept, 1 H, C$\underline{H}Me_2$, $^3J_{H,H}$ = 5.9 Hz); 3.21 (s, 3 H, OMe); 3.15—3.01 (m, 4 H, 2 CH_2); 2.29 (s, 6 H, 2 Me), 2.08 (s, 9 H, C—$\underline{Me}_3$); 1.53 (d, 6 H, CH($C\underline{H}_3$)$_2$, J = 6.0 Hz). ^{13}C NMR (101 MHz, C_6D_6), δ: 306.0, 209.1, 153.0, 146.2, 144.5, 140.1, 130.5, 128.9, 123.4 (q, CF_3, $^1J_{C,F}$ = 291 Hz); 123.4, 122.6, 113.7, 84.0—82.9 (m, $\underline{C}(CF_3)_2$); 74.6, 56.3, 54.2, 51.1, 45.8, 29.7, 22.4, 18.9. ^{19}F NMR (C_6D_6), δ: −70.20. Found (%): C, 47.87; H, 5.11; N, 3.86. $C_{29}H_{36}Cl_2F_6N_2O_2Ru$. Calculated (%): C, 47.68; H, 4.97; N, 3.83.

Dichloro {3-[4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-1-isopropyl-4,5-dihydro-1*H*-imidazol-2-ylidene}(2-isopropoxybenzylidene)ruthenium(II) (6b). Yield 39%. ^{1}H NMR (400 MHz, C_6D_6), δ: 16.46 (s, 1 H, C=H); 7.59 (s, 2 H, H_{arom}); 7.23—7.15 (m, 2 H, H_{arom}); 6.79 (t, 1 H, H_{arom}, J = 7.4 Hz); 6.49 (d, 1 H, H_{arom}, J = 8.2 Hz); 5.84 (hept, 1 H, NC$\underline{H}Me_2$, J = 5.8 Hz); 4.72 (hept, 1 H, OC$\underline{H}Me_2$, J = 5.8 Hz); 3.29 (s, 3 H, OMe); 3.16—3.04 (m, 4 H, CH_2); 2.25 (s, 6 H, 2 Me); 1.78 (d, 6 H, NCH$\underline{Me}_2$, J = 5.9 Hz); 1.56 (d, 6 H, OCH$\underline{Me}_2$, J = 6.3 Hz). ^{13}C NMR (101 MHz, C_6D_6), δ: 285.8, 208.1, 152.9, 144.8, 143.1, 140.3, 129.2, 128.8, 128.5, 123.3 (q, CF_3, $^1J_{C,F}$ = 290 Hz); 122.6, 122.2, 113.3, 83.5 (hept, $\underline{C}(CF_3)_2$, $^2J_{C,F}$ = 29 Hz); 75.1, 54.2, 52.9, 50.8, 41.8, 22.0, 20.7, 18.7. ^{19}F NMR (C_6D_6), δ:−70.22. Found (%): C, 46.87; H, 4.89; N, 3.99. $C_{28}H_{34}Cl_2F_6N_2O_2Ru$. Calculated (%): C, 46.93; H, 4.78; N, 3.91.

Dichloro {1-cyclohexyl-3-[4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl]-4,5-dihydro-1*H*-imidazol-2-ylidene}(2-isopropoxybenzylidene)ruthenium(II) (6c). Yield 24%. ^{1}H NMR (400 MHz, C_6D_6), δ: 16.41 (s, 1 H, C=H); 7.52 (s, 2 H, H_{arom}); 7.20—7.07 (m, 2 H, H_{arom}), 6.72 (t, 1 H, H_{arom}, J = 7.2 Hz); 6.43 (d, 1 H, H_{arom}, $J_{H,H}$ = 8.1 Hz); 5.35—5.23 (m, 1 H, $H_{cyclohexyl}$); 4.65 (hept, 1 H, C$\underline{H}Me_2$, $^3J_{H,H}$ = 5.6 Hz); 3.21 (s, 3 H, OMe); 3.12 (s, 4 H, CH_2); 2.78—2.67 (m, 2 H, $H_{cyclohexyl}$); 2.19 (s, 6 H, 2 Me); 1.93—1.64 (m, 5 H, $H_{cyclohexyl}$); 1.74 (d, 6 H, CH$\underline{Me}_2$, J = 5.5 Hz); 1.42—1.00 (m, 3 H, $H_{cyclohexyl}$). ^{13}C NMR (101 MHz, C_6D_6), δ: 286.0, 208.4, 152.9, 144.9, 143.0, 140.4, 129.1, 128.8, 128.5, 123.4 (q, CF_3, $^1J_{C,F}$ = 291 Hz); 122.6, 122.2, 113.3, 83.20 (hept, $\underline{C}(CF_3)_2$, $^2J_{C,F}$ = 28 Hz); 74.9, 61.2, 54.2, 50.9, 43.3, 31.2, 26.3, 25.9, 22.1, 18.7. ^{19}F NMR (C_6D_6), δ: −70.18. Found (%): C, 48.95; H, 4.98; N, 3.83. $C_{31}H_{38}Cl_2F_6N_2O_2Ru$. Calculated (%): C, 49.21; H, 5.06; N, 3.70.

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