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Synthesis and catalytic activity of ruthenium complexes modified with chiral racemic per- and polyfluorooxaalkanoates

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ABSTRACT

Silver salts of racemic 2*H*-perfluoro(3-oxahexanoic) (**3a**), perfluoro(2-methyl-3-oxahexanoic) (**3b**) and 2,3,3,3-tetrafluoro-2-methoxypropanoic acid (**3c**) gave with Hoveyda-Grubbs 2nd generation catalyst **4** or its bis(polyfluoroalkylated) analogue **5** the corresponding bis(polyfluoroacylated) ruthenium complexes **1a**–**1c** or **2a**, **2b** as mixtures of three diastereoisomers. Their catalytic activity in model ring-closing metathesis (RCM) reactions decreased in the order **1b–2b** > **1a–2a** > **1c** due to increased steric hindrance around the catalytic centre in complexes **1a**, **1c** and **2a**, as well as due to lower acidity of acid **3c** resulting in lower electrophilicity of the complex **1c**. Thus, the complexes **1b** and **2b** displayed high activity in RCM of bis-unsaturated malonates forming disubstituted (RCM2) or trisubstituted (RCM3) double bond and were even significantly active in the formation of tetrasubstituted bond (RCM4), while complexes **1a**, **1c** were active in RCM2 but inactive in RCM3. Moreover, the yield of RCM2 catalyzed with complex **1c** was rather low.

1. Introduction

Grubbs and Hoveyda-Grubbs complexes belong to the most efficient precatalysts of alkene metathesis. The popularity of this reaction was triggered by its excellent tolerance to functional groups, ability to form medium-size rings and high variability of structures obtained [1]. Notably, Hoveyda-Grubbs 2nd generation precatalyst **4** containing an NHC ligand, chlorines and chelating alkoxybenzylidene ligand became extremely popular due to high activity, stability and ability to be recycled by column chromatography [2]. Hence, its framework opened multiple possibilities of modifications with per- or polyfluoroalkyl groups with different aims [3]. Thus, in contrast to Grubbs 2nd generation precatalyst, whose phosphine ligand was modified with polyfluoroalkyl groups resulting in significant acceleration of the initiation phase of metathesis by heavy fluorous removal of the ligand into perfluoroalkane in a heavy fluorous two-phase system [4], the alkoxybenzylidene ligand of complex **4** was modified with a polyfluoroalkyl group in the aromatic ring allowing its light fluorous recycle using fluorous solid phase extraction (FSPE) [5]. An analogous modification with a strong electron-accepting perfluoroalkyl group accelerated the initiation phase of metathesis due to the easier decoordination of the alkoxy group from ruthenium [5], as was supported by DFT calculations [5]. Synthetically challenging are the modifications of the NHC ligand. Thus, aryl groups of the NHC ligand were modified with linear [5,6] or branched [7] ponytails. In another approach, the direct polyfluoroalkylation of imidazolidinylidene ring was achieved [6] with the aim of improving the fluorophilicity of complex **4**.

Most attention has been focused on the substitution of chloride ligands on ruthenium complex **4** with silver per- or polyfluoroalkanoates, which proceeds smoothly and, hence, was exploited for various purposes. Thus, the modifications with short perfluoroalkanoates mostly served as precatalysts for model reactions and ring opening or diyne metathesis polymerizations, while modification with perfluoroglutaric acid was employed for tethering the catalyst to polymeric network [8]. On the other hand, the use of long silver perfluoroalkanoates resulted in the formation of a precatalyst with amphiphilic properties [9]. Similarly, the chelating analogue of precatalyst **4** was modified with perfluorononanoic acid with the aim of forming emulsions [10].

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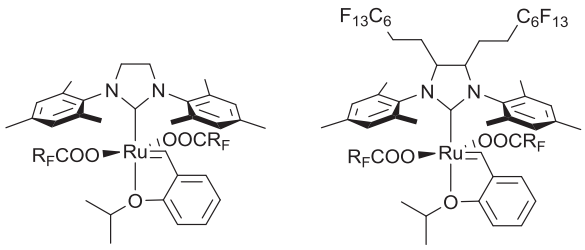


Fig. 1. Target complexes **1**,**2** modified with racemic fluorinated oxaalkanoates **3**.

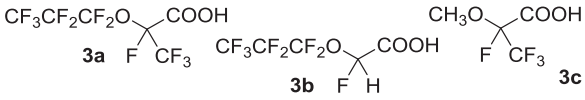


Fig. 2. Racemic fluorinated acids **3** employed as ligands.

In contrast to perfluorinated ponytails, much less attention was devoted to perfluoropolyether-based modifications, probably due to lower availability of the corresponding building blocks. Their stability is analogous [11] and they were successfully employed in the synthesis of fluorous phosphines, copper, ruthenium and rhodium complexes, and metallaphthalocyanines [12]. We recently reported that modification of imidazolium salts, as well as palladium, silver or ruthenium complexes with perfluoropolyoxaalkyl ponytails resulted in higher fluorophilicity compared with analogous substitutions with perfluoroalkyl ponytails [13]. Furthermore, catalytic activity of Hoveyda-Grubbs precatalyst **4** analogues substituted with perfluoropolyoxaalkanoates was superior to their analogues containing perfluoroalkanoate chains [14].

In contrast to achiral alkene metathesis, its enantioselective variants enable the formation of new stereogenic centres in the substrate molecule. Consequently, this process is still attracting more attention due to its potential use in the synthesis of chiral biologically active molecules with potential pharmacochemical applications. As catalysts, apart from more sensitive Schrock precatalysts, several variants of ruthenium complexes have been developed based on chiral NHC ligands. However, their synthesis is tedious, expensive and requires multiple steps, which prevents their practical application [15].

Some racemic per- or polyfluorooxaalkanoic acids are commercially available or can be synthesized. Hence, we envisioned that their resolution to enantiomerically pure fluoro acids [16] followed by their exchange for chloride ligands in ruthenium precatalyst **4** could lead to a new class of easily available chiral precatalysts of enantioselective alkene metathesis.

Before synthesizing expensive chiral catalysts, the knowledge about the influence of substitution in the fluoroalkanoate chain on the stability and activity of these catalysts would be desirable. We therefore report here the synthesis of precatalyst **4** analogues **1**, **2** modified with racemic per- or polyfluorooxaalkanoates, as well as their activity in model alkene metatheses (Fig. 1).

2. Results and discussion

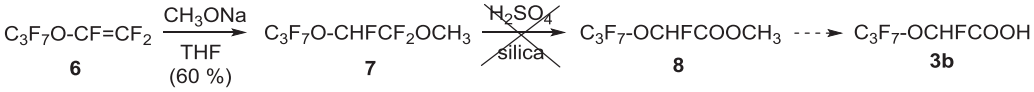
2.1. Starting racemic fluoroalkanoic acids

Commercially available racemic polyfluoroalkanoic acids are rather scarce. We had already synthesized a complex **4** analogue bearing two racemic perfluoropolyoxaalkanoate ligands based on hexafluoropropylene oxide (HFPO) trimer. However, these ligands contained two stereogenic centres and, thus, a complex mixture of diastereoisomers was formed. Hence, our first choice of polyfluorinated acid bearing one stereogenic centre was the compound derived from HFPO dimer, perfluoro(2-methyl-3-oxahexanoic) acid (**3a**, Fig. 2), which is commercially available.

From the experiments with metathesis precatalysts containing HFPO trimer based branched perfluoropolyoxaalkanoate, we knew that their catalytic activity is significantly reduced compared to the analogous linear perfluoropolyoxaalkanoates. Our second choice of racemic acid was, therefore, 2*H*-perfluoro(3-oxahexanoic) acid (**3b**, Fig. 2), which has a similar length of polyfluorooxaalkyl chain, but significantly reduced steric hindrance. However, acid **3b** is not available commercially and had to be synthesized.

Our first approach was based on the paper of Larsen [17], who on analogous systems transformed a CF_2OCH_3 group to a $COOCH_3$ group using concentrated H_2SO_4 with silica as an HF scavenger. Perfluoro(propyl vinyl ether) (**6**) is a common fluorinated monomer and reacts easily with methanol to the corresponding fluorinated ether **7** [18]. However, subsequent reaction with sulfuric acid and silica, according to [17] failed to give ester **8** and only the starting compound was isolated (Scheme 1).

We therefore decided to follow the procedure reported in patent [19], which employed the direct addition of water followed by basic hydrolysis in a two phase diethyl ether/water system. Surprisingly, reaction with a 3 fold excess of aqueous NaOH at 35 °C gave, after acidification, 26% of a 7:1 mixture of target acid **3b** and perfluoropropanoic acid (PFPA, Table 1 Entry 1). When, under analogous conditions, 5% of 18-crown-6 ether was added as a

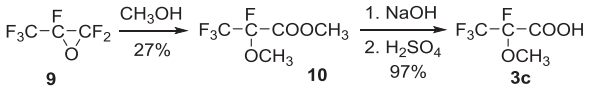


Scheme 1. Attempted synthesis of fluoro acid **3b** by acidic hydrolysis.

Table 1
Optimization of preparation of fluoro acid **3b.**

Entry	Base	Catalyst	Solvent	Temp. (°C)	Product composition' (%)			Isolated yield (%)[a]
					3b	PFPA	Other	
1	NaOH	–	diethyl ether	35	87	13	0	26
2	KOH	18-C-6	diethyl ether	35	0	78	22	0
3	KOH	18-C-6	diethyl ether	25	100	0	0	10
4	KOH	NMe_4OH	diethyl ether	35	92	8	0	51
5	KOH	–	1,4-dioxane	35	100	0	0	56[b]

[a] After acidic work up.
[b] Sealed system (autoclave) used.



Scheme 2. Preparation of polyfluorinated acid **3c**.

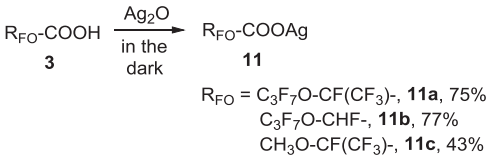
phase transfer catalyst, mainly PFPA was formed together with smaller amounts of other side-products (fluoromalonic acid, Table 1 Entry 2). Lowering the temperature to 25 °C gave exclusively target acid **3b**, however, the conversion was low and only a 10% yield was reached (Table 1 Entry 3). Further improvement was achieved when we used tetramethylammonium hydroxide as a phase transfer catalyst at 35 °C, yielding 51% of a 9:1 mixture of acid **3b** and perfluoropropanoic acid (Table 1 Entry 4). The by-product, PFPA, was removed by repeated extraction of the ether solution of the product mixture with water, yielding 22% of pure acid **3b**. Finally, the best results were achieved when diethyl ether was substituted for 1,4-dioxane and a sealed system (an autoclave) was used to minimize loses of starting volatile fluoroalkene, giving 56% yield of pure acid **3b** without the need of extractive treatment (Table 1 Entry 5).

A third acid, 2,3,3,3-tetrafluoro-2-methoxypropanoic acid (**3c**, Fig. 2), was chosen to compare how the electron donor properties of the methoxy group influenced the activity of the precatalyst **1c** made therefrom. Acid **3c** was synthesized by opening hexafluoropropylene oxide (HFPO, **9**) with methanol under safe pressure-free conditions [20], followed by alkaline hydrolysis of the ester **10** formed and acidification of the carboxylate salt with sulfuric acid (Scheme 2).

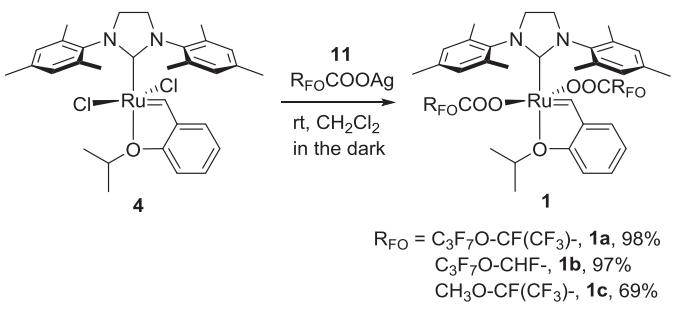
2.2. Synthesis of modified precatalysts *1*, *2*

The first group of precatalyst **1** was prepared according to our previously published procedure from commercial precatalyst **4** and silver salts **11a**–**11c** of the corresponding acids **3a**–**3c**. Among several methods for obtaining silver salts **11**, the reaction with Ag_2O in diethyl ether or acetone in the dark gave the best results (Scheme 3).

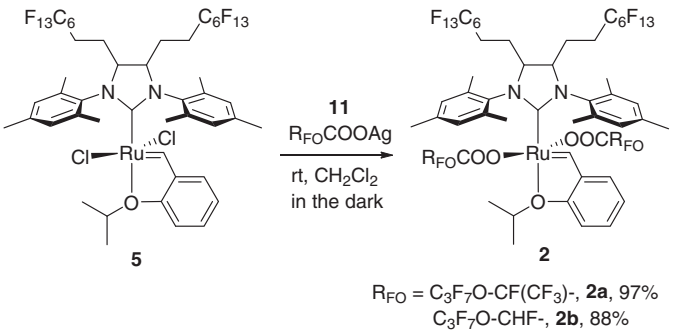
In a glove box, we then mixed silver salts **11a–11c** with Hoveyda-Grubbs 2nd generation precatalyst **4**, added anhydrous degassed CH_2Cl_2 and stirred the mixture in the dark at room temperature for 3 h, during which time the originally green solution quickly turned deep violet. Crystalline precatalysts **1** were obtained by filtration of the solution through a Celite layer and



Scheme 3. Preparation of silver salts **11**.



Scheme 4. Synthesis of bis(polyfluorooxaalkylated) precatalysts **1**.



Scheme 5. Synthesis of tetrakis(polyfluoroalkylated) precatalysts **2**.

evaporation of the solvent in moderate to excellent yields (Scheme 4).

We have recently become interested in recycling polyfluorinated catalysts using fluorous separation methods, which use a two layer system of perfluorinated and nonfluorinated solvent. After reaction, organic products are separated into a non-fluorinated solvent (e.g. toluene), while the catalyst is recycled in a perfluorinated solvent. For this, the fluorous partition coefficient P_i(FBS), i.e. the ratio of the content of the catalyst in perfluorinated/nonfluorinated solvent should be larger than 0.2. However, for catalysts **1** the P_i(FBS) is lower than 0.1 and, hence, more fluorinated catalysts were required.

For their synthesis, rather than the commercial precatalyst **4**, we used its bis(polyfluoroalkylated) analogue **5** reported recently by us [6]. Its reaction with silver salts **11a**, **11b** using the conditions described above gave excellent yields of the more fluorophilic precatalysts **2** (Scheme 5).

2.3. Stereochemistry and NMR spectroscopy of precatalysts *1*

The characteristic feature of ^{1}H NMR spectra of ruthenium complexes bearing the alkoxybenzylidene ligand is the signal of the benzylidene hydrogen with a strongly downfield shift above 17 ppm. While for complexes bearing only achiral chloride or perfluoroalkanoate ligands this signal is a simple singlet, three signals in an approximate ratio of 1: 2: 1 were observed for complexes **1,** implying the existence of three diastereoisomers (Fig. 3). For complex **1b**, two more small signals were additionally observed.

Indeed, stereochemical analysis of precatalyst **1a** modified with two racemic alkanoates revealed that they consist of four distinct structures, namely two achiral diastereoisomers and two chiral

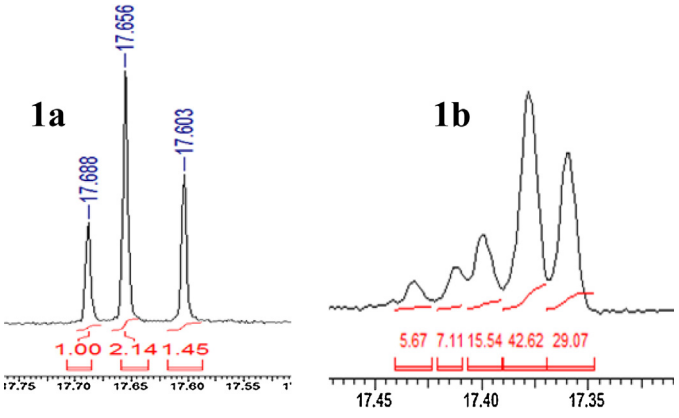


Fig. 3. ^{1}H NMR signals of the Ru=CH group of complexes **1a** and **1b**.

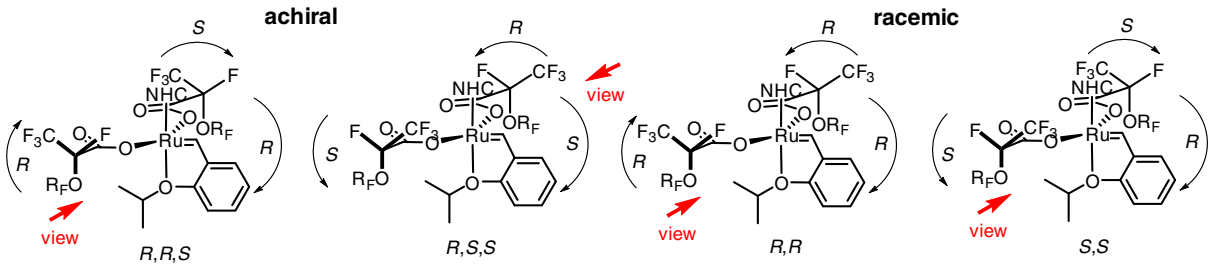


Fig. 4. Four distinct stereoisomers of precatalyst **1a**.

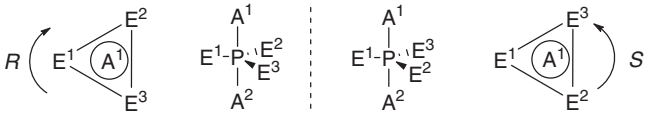


Fig. 5. Stereochemical assignment of chiral pentacoordinated compounds.

enantiomers (in analogy to a book example, pentane-2,3,4-diol, central Ru atom bearing two identical *R* or *S* ligands in the chiral complexes is achiral). As enantiomeric structures cannot be distinguished by NMR spectroscopy, overall three diastereomeric structures were observed in the NMR spectra in agreement with the experiment (Fig. 4).

The assignment of absolute configuration of the four distinct stereoisomers was based on the provisional of Martin et al., originally developed for chiral λ^4-sulfanes or other pentacoordinated compounds [21]. In this approach, the pentacoordinated compound is oriented from the apical substituent with a higher priority according to the CIP rules to the apical substituent with a lower priority. When the equatorial ligands are then arranged according to CIP rules in the clockwise manner, the pentacoordinated compound is assigned stereodescriptor *R*, while the counterclockwise arrangement is assigned stereodescriptor *S* (Fig. 5).

For the precatalysts **1** bearing central pentacoordinated Ru atom, polyfluorooxaalkanoates represent the apical substituents and, according to IUPAC rules, for two identical structures with the opposite absolute configuration, the structure with the *R* configuration has a higher priority than that with the *S* configuration.

The appearance of two more signals in the NMR spectrum of complex **1b** was a surprise to us. We first excluded that the two small additional peaks could belong to the complex of different formula, because no signals belonging to different species were observed neither in MS spectra nor in HPLC. Hence, we assumed that the two additional signals could belong to another conformation of **1b**, sufficiently stable on the NMR time scale. Indeed, computational analysis of complex **1b** found three main conformations. Two of them (major **1bA** with about 87% of abundance at r.t. and minor **1bB** with about 6%) have standard *trans*-orientation of the fluoroalkanoate ligands with expected rapid conformational interchange on the NMR time scale. However, the third conformation **1bC** bears both fluoroalkanoate ligands in the *cis*-orientation with the alkoxybenzylidene ligand coordinated in the equatoreal plane of the complex. Providing the conformational

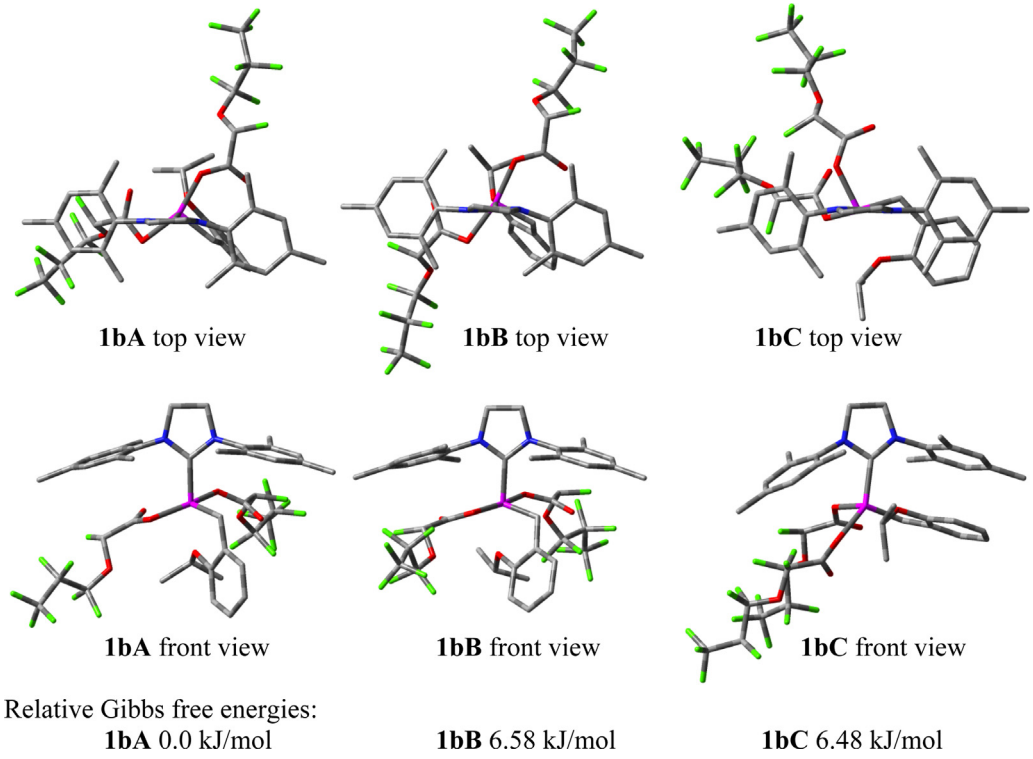


Fig. 6. Geometries and relative Gibbs free energies of three dominant conformations of complex **1b**. Hydrogens are omitted for clarity.

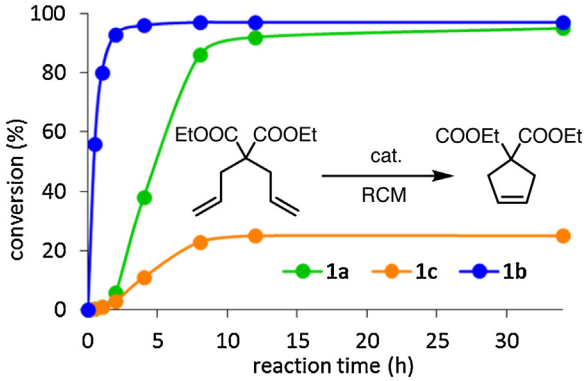


Fig. 7. Catalytic activity of precatalysts **1** (5 mol%) in the RCM of DEDAM at 40 °C.

change of this coordination is sufficiently slow, this could explain the presence of the two additional signals of the benzylidene proton in the NMR spectrum of **1b** with roughly expected integral ratio (see Fig. 6).

2.4. Catalytic activity of complexes *1, 2*

We first tested all three precatalysts **1** in the ring closing metathesis (RCM) of diethyl diallylmalonate (DEDAM, Fig. 7). While precomplexes **1a** and **1b** gave nearly 100% conversion to the product, precomplex **1c** bearing the electron donor methoxy group was significantly less active. Fig. 7 also shows that precatalyst **1b** is more active than precatalysts **1a**, **1c**, modified with sterically hindered branched polyfluoropolyoxaalkanoates.

The role of steric hindrance is even more emphasized in the RCM of the more demanding substrate, diethyl allylmethallylmalonate (DEAMM, Fig. 8), where precatalysts **1a** and **1c** were inactive, while **1b** gave more than 70% conversion after 28 h. Comparison with precatalyst **2b** bearing two polyfluorinated ponytails in the NHC ligand showed that the role of the fluorinated chains in the NHC ligand on the precatalyst activity is neglibible. Both reactions gave more than 80% conversion after prolonged reaction times (8 days).

Both precatalysts were slightly less active than previously published [14] precatalyst **1d** bearing perfluoropolyoxaalkanoate ligands probably due to higher electronegativity of ligands in **1d**, but significantly more active than precatalyst **1e** bearing perfluoroalkanoate ligands. This gave under identical conditions conversion below 30% after 28 h, emphasizing deactivating role of

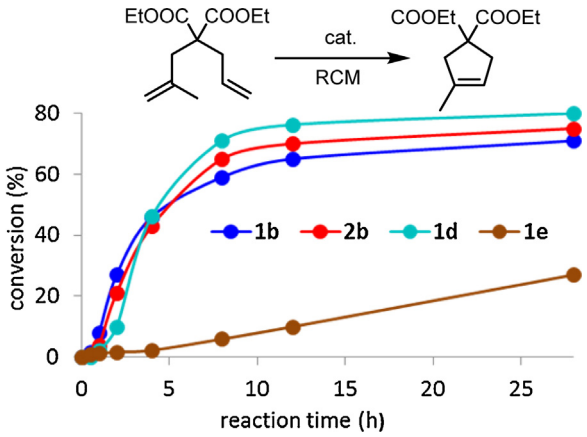


Fig. 8. Catalytic activity of precatalysts **1b** and **2b** (5 mol%) in the RCM of DEAMM at 40 °C and comparison with analogous precatalysts bearing perfluoro-3,6-dioxaheptanoate (**1d**) and perfluoroheptanoate (**1e**) ligands.

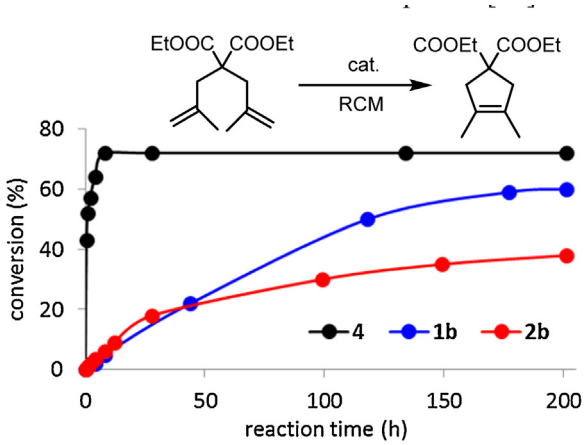


Fig. 9. Catalytic activity of precatalysts **1b** and **2b** (5 mol%) in the RCM of DEDMM at 110 °C.

higher steric hindrance, caused by lower flexibility of the perfluoroalkyl chains [14] compared to perfluoropolyether chains.

RCM of diethyl dimethallylmalonate (DEDMM), forming a tetrasubstituted double bond, belongs to the most demanding metathesis processing, pushing standard ruthenium metathesis precatalysts as Hoveyda-Grubbs 2nd generation complex (**4**) to its limits with conversion not exceeding 58% [2]. Thus, special precatalysts [22] or reaction solvents [23] had to be used to enable high conversions of this reaction. We recently found that with precatalyst **4**, raising the reaction temperature of DEDMM metathesis to 110 °C improved its conversion to 72%. Regarding precatalysts bearing fluoroalkanoate ligands, only very low yield and TON equal to 10 of DEDMM metathesis was reported [24].

Surprisingly, precatalysts **1b** and **2b** were markingly active in this highly demanding metathesis at 110 °C, reaching the respective 60% and 38% conversion after sufficiently long (8 days) reaction time (Fig. 9). Lower activity of **2b** can be attributed to lower flexibility of the mesityl groups of its NHC ligand, caused by the presence of polyfluoroalkylated chains in the imidazolidinylidene ring. This can further increase steric hindrance around the Ru centre. Finally, with the perspective aim to perform enantioselective RCM, we decided to compare the activity of modified precatalysts **1a**, **2a** and **2b** in the RCM of prochiral trienes. Previous reports using prochiral trienes formed chiral cyclic compounds with the formation of trisubstituted [25] or tetrasubstituted [26] bond. Because we found that branched polyfluorooxaalkanoate modified precatalysts **1a**, **2a** are inactive in these RCM, we

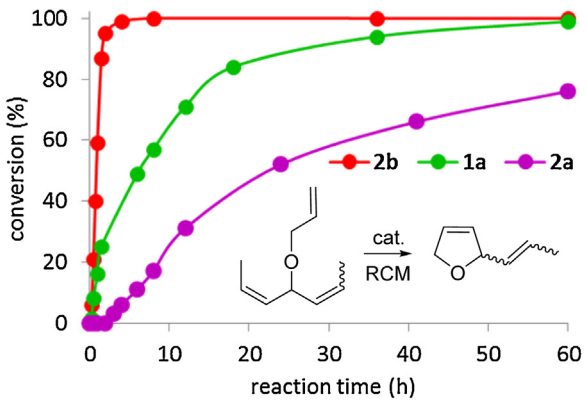


Fig. 10. Catalytic activity of precatalysts **1a**, **2a** and **2b** (5 mol%) in the RCM of AHD at 40 °C.

employed analogous reaction forming disubstituted double bond using 4-(allyloxy)hepta-2,5-diene (AHD) as a substrate (Fig. 10).

The results showed that all precatalysts tested are substantially active in the reaction. Comparison of the activity of precatalyst **2b** bearing two polyfluoroalkyl groups in the NHC ligand and linear polyfluorooxaalkanoate ligands with that of precatalyst **1a** containing non-modified NHC ligand and branched polyfluorooxaalkanoate ligands showed that the branching is more negatively influencing the catalytic activity. Nevertheless, the RCM using both precatalysts reached nearly total conversion after 60 h. Still, the attachment of the polyfluoroalkylated chains on the NHC ligands lowers somewhat the catalytic activity, as can be seen from the comparison of precatalysts **1a** and **2a**, where the RCM catalyzed by the latter precatalyst reached only 76% conversion after 60 h.

The differences in the activity of the three precatalysts tested are even more emphasized when the rate of the initiation phase of the RCM is compared, as can be seen from the more detailed view on the first 8 h of the RCM (Fig. 11).

We recently reported successful and ecologically advantageous recycling of polyfluorinated alkene metathesis precatalysts using a mixture of HFE-7100 ether and dichloromethane at −20 °C [6]. We were hence quite satisfied to find that highly fluorinated precatalysts **2a**, **2b** could be successfully recycled after RCM reaction of DEAMM for four consecutive cycles without significant loss of activity (the details of our medium fluorous recycling methodology will be given in our successive prepared manuscript).

3. Conclusion

Silver salts of commercially available or synthesized chiral racemic per- and polyfluorooxaalkanoic acids were successfully employed in the synthesis of diastereomeric ruthenium precatalysts of alkene metathesis. Model RCM reactions showed that catalytic activity of the precatalysts decreased with increasing steric hindrance and decreasing electron-acceptor strength of the fluorooxaalkanoate ligand backbone, $C_3F_7OCHF- > C_3F_7O(CF_3)CF- > CH_3O(CF_3)CF-$. Surprisingly, the most active precatalyst even succeeded in the demanding formation of tetrasubstituted double bond in the RCM of diethyl dimethallylmalonate. Although the catalytic activity of the synthesized precatalysts is lower than that of commercially available precatalysts, it is still sufficient for most metathesis reactions. With the herein reported approach and simultaneously developed enantiomerically pure fluorooxaalkanoic acids, we expect to obtain new easily accessible chiral precatalysts of enantioselective alkene and enyne metathesis.

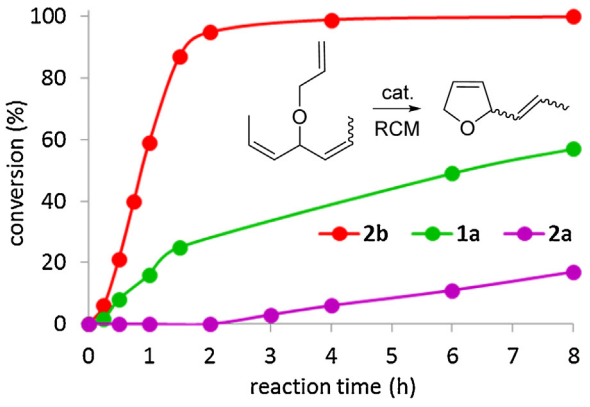


Fig. 11. First 8 h of the RCM of AHD catalyzed by **1a**, **2a** and **2b** (5 mol%) at 40 °C.

4. Experimental

4.1. General description of methods and materials

Temperature data were uncorrected. NMR spectra were recorded with a Varian MercuryPlus spectrometer, ^{1}H NMR spectra at 299.97 MHz, ^{19}F NMR spectra at 282.23 MHz and ^{13}C NMR spectra at 75.44 MHz, or with a Agilent 400-MR DDR2, ^{1}H NMR spectra at 399,94 MHz, ^{19}F NMR spectra at 376,29 MHz and ^{13}C NMR spectra at 100,58 MHz pro ^{13}C NMR, using residual deuterated solvent signals as the internal standards for the ^{1}H and ^{13}C NMR spectra or CCl_3F as the internal standard for the ^{19}F NMR spectra. Chemical shifts are given in parts per million, coupling constants in hertz. Mass spectra (ESI, APCI) were measured with a LCQ Fleet (Finnigan) instrument and HRMS spectra (ESI, APCI, FAB) with a LTQ Orbitrap XL (Thermo Fisher Scientific) or ZAB-EQ (VG Analytical) instrument.

All reactions were performed in a dry inert atmosphere (Ar) in an oven-dried flasks. Solid compounds were introduced into the reaction flasks in a dry box. All reactions including silver salts were performed in the dark. Perfluoro(2-methyl-3-oxahexanoic) acid were purchased from Apollo Scientific, [1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene](dichloro)(2-isopropoxybenzylidene)ruthenium(IV) (**4**, Hoveyda-Grubbs 2nd generation precatalyst), diethyl diallylmalonate and silver(I) oxide were purchased from Sigma-Aldrich. 4,5-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene](dichloro)(2-isopropoxybenzylidene)ruthenium(IV) (**5**), diethyl allylmethallylmalonate and diethyl dimethallylmalonate according to [26a,26c]. Perfluoro(3-oxahex-1-ene) was kindly gifted by Asahi Glass. 2,3,3,3-Tetrafluoro-2-methoxypropanoic acid was synthesized according to [20b], 4-allyloxyhepta-2,5-diene by Kolaříková et al. [27]. Dichloromethane was dried over CaH_2, distilled, and stored over molecular sieves, acetone was dried by distillation from P_2O_5 and diethyl ether was distilled from the solution of diphenyl ketyl radical.

4.2. Preparation of 2,4,4,5,5,6,6,6-octafluoro-3-oxahexanoic acid (*3b*)

250 mL autoclave was charged with KOH (12 g, 500 mmol), H_2O (20 mL), 1,4-dioxane (100 mL) and perfluoro(3-oxahex-1-ene) (**6**, 20 g, 75 mmol) and stirred 3 days at 35 °C. After cooling to room temperature, the reaction mixture was acidified with 6 M H_2SO_4 (25 mL) and extracted with diethyl ether (3 × 300 mL). Combined extracts were washed with water (2 × 300 mL) and dried with $MgSO_4$. Solvents were removed on a rotary vacuum evaporator (40 °C, 1 h, 25 kPa) and then on an oil vacuum pump (20 °C, 2 h, 2 kPa) to yield 12.5 g (56%) of the target acid **3b** (95% purity, brownish liquid). ^{1}H NMR (299,97 MHz, $CDCl_3$) [28]: δ 6.2 (d, $^2J_{H-F}$ = 54.2 Hz, 1H, C**H**F), 9.2 (bs, 1H, COO**H**) ppm. ^{19}F NMR (282,23 MHz, $CDCl_3$) [28]: δ -81.8 (t, $^4J_{F-F}$ = 7 Hz, 3F, C**F**$_3$), −85.5 (dm, $^2J_{F-F}$ = 146 Hz, 1F, CF_3CF_2CF**F**), −87.4 (dm, $^2J_{F-F}$ = 147 Hz, 1F, CF_3CF_2CF**F**), −130.2 (m, 2F, CF_3CF_2), −136.4 (dm, $^2J_{H-F}$ = 54 Hz, 1F, CH**F**) ppm.

4.3. Preparation of silver perfluorocarboxylates *11*. general procedure

A light protected flask was charged with Ag_2O (1 equiv.) and anhydrous acetone (3 mL/equiv.). Polyfluorooxaalkanoic acid **3** (2 equiv.) was added and the mixture was stirred for 5 h at r.t. The reaction mixture was then filtered in the absence of light through a Celite layer, the solids were washed with anhydrous acetone and the solvent removed on a light protected rotary vacuum evaporator (40 °C, 1 h, 25 kPa) and finally at oil pump vacuum (25 °C, 1 h, 1 kPa) yielding the target silver salt **11**.

*4.4. Silver(I) perfluoro(3-oxa-2-methylhexanoate) (**11a**)*

According to the general procedure, Ag_2O (0.7 g, 3.0 mmol) and perfluoro(2-methyl-3-oxahexanoic) acid (**3a**, 2.0 g, 6.1 mmol) gave salt **11a** 2.0 g, 75%, white crystals, m.p. 286.5–305 °C (decomposition). ^{19}F NMR (282.23 MHz, acetone-d_6): δ −80.7 (dm, $^2J_{F-F}$ = 146 Hz, 1F, $CF_3CF_2CF\mathbf{F}$), −81.0 (s, 3F, $C\mathbf{F}_3$), −81.9 (s, 3F, $C\mathbf{F}_3$), −84.6 (dm, $^2J_{F-F}$ = 145 Hz, 1F, $CF_3CF_2C\mathbf{F}F$), −124.1 (m, 1F, C**F**), −129.5 (m, 2F, $CF_3C\mathbf{F}_2$) ppm. HRMS (ESI^-): $[M-Ag]^-$ calcd. for $C_6F_{11}O_3$ 328.9677, found 328.9675.

*4.5. Silver(I) 2,4,4,5,5,6,6,6-octafluoro-3-oxahexanoate (**11b**)*

According to the general procedure, Ag_2O (0.88 g, 3.8 mmol) and 2,4,4,5,5,6,6,6-octafluoro-3-oxahexanoic acid (**3b**, 2.0 g, 7.6 mmol) gave salt **11b** (2.2 g, 77%, light yellow crystals, m.p. 124.4 °C (decomposition)). ^1H NMR (299,97 MHz, acetone-d_6): δ 6.41 (d, $^2J_{H-F}$ = 55.9 Hz, 1H, C**H**F) ppm. ^{19}F NMR (282,23 MHz, acetone-d_6): δ −81.0 (t, $^4J_{F-F}$ = 8 Hz, 3F, $C\mathbf{F}_3$), −84.2 (dm, $^2J_{F-F}$ = 148 Hz, 1F, $CF_3CF_2CF\mathbf{F}$), −85.3 (dm, $^2J_{F-F}$ = 149 Hz, 1F, $CF_3CF_2C\mathbf{F}F$), −128.8 (dm, $^2J_{H-F}$ = 60 Hz, 1F, CH**F**), −129.3 (m, 2F, $CF_3C\mathbf{F}_2$) ppm. HRMS (ESI^-): $[M-Ag]^-$ calcd. for $C_5HF_8O_3$ 260.9803, found 260.9802.

*4.6. Silver(I) 2,3,3,3-tetrafluoro-2-methoxypropanoate (**11c**)*

According to the general procedure, Ag_2O (0.17 g, 0.74 mmol) and 2,3,3,3-tetrafluoro-2-methoxypropanoic acid (**3c**, 0.24 g, 1.4 mmol) gave salt **11c** (0.17 g, 43%, white crystals, m.p. 230–245 °C (decomposition)). ^1H NMR (299.97 MHz, acetone-d_6): δ 3.53 (s, 3H, $CF_3CF(OC\mathbf{H_3})COOAg$) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −80.8 (d, $^3J_{F-F}$ = 3.4 Hz, 3F, $C\mathbf{F_3}CF(OCH_3)COOAg$), −126.9 (m, 1F, $CF_3C\mathbf{F}(OCH_3)COOAg$) ppm. ^{13}C NMR (100.58 MHz, acetone-d_6): δ 54.2 (d, $^3J_{C-F}$ = 2.0 Hz, 1C, $\mathbf{C}H_3$), 107.8 (dq, $^1J_{C-F}$ = 244 Hz, $^2J_{C-F}$ = 35 Hz, 1C, **C**F), 120.9 (dq, $^1J_{C-F}$ = 244 Hz, $^2J_{C-F}$ = 35 Hz, 1C, $\mathbf{C}F_3$), 166.6 (d, $^2J_{F-F}$ = 33 Hz, 1C, **C**OO) ppm. MS (ESI^-) *m*/*z* (%): 373.1 [2x(M-Ag)+Na]$^-$ (84), 217.0 [M-Ag+MeCN]$^-$ (100), 175.0 $[M-Ag]^-$ (85). HRMS (ESI^-): $[M-Ag]^-$ calcd. for $C_4H_3F_4O_3$ 175.0021, found 175.0021.

*4.7. Preparation of ruthenium complexes **1**, **2**. general procedure*

In a glove box, a flask was charged with Ru complex **4** or **5** and Ag salt **3**. Anhydrous degassed CH_2Cl_2 was then added and the resulting mixture was stirred at room temperature for 3 h in the dark. The solids were filtered off through a Celite layer and washed with anhydrous (2 mL). The solution was diluted with anhydrous hexane (10 mL) and remaining precipitated Ag salt was again filtered off. Evaporation of the solvents on a rotary vacuum evaporator (40 °C, 1 h, 25 kPa) and finally at oil pump vacuum (25 °C, 1 h, 1 kPa) gave the products **1** or **2**.

*4.8. [1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene](2-isopropoxybenzylidene)-bis[perfluoro(2-methyl-3-oxahexanoyl)oxy] ruthenium(IV)(**1a**)*

According to the general procedure, silver salt **3a** (20 mg, 0.047 mmol) and complex **4** (**HG2**, 11.6 mg, 0.019 mmol) gave the target complex **1a** (22 mg, 98%, deep violet crystals). ^1H NMR (399,94 MHz, CD_2Cl_2): δ 0.95 + 0.97 + 0.97 (3 × d, $^3J_{H-H}$ = 5.9 Hz, 6H, $OCH(C\mathbf{H}_3)_2$), 2.06 (m, 6H, Ar'C**H**$_3$-*p*), 2.43 (m, 12H, Ar'C**H**$_3$-*o*), 4.09 + 4.11 + 4.12 (3 × s, 4H, C**H**$_2$), 4.46 (m, 1H, O**C**H$(CH_3)_2$), 6.63 (m, 1H, Ar**H**), 6.96 (m, 1H, Ar**H**), 7.11 (dd, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, Ar**H**), 7.19 (m, 4H, Ar'**H**), 7.37 (m, 1H, Ar**H**), 17.58 + 17.63 + 17.68 (3 × bs, 1H, Ru = C**H**) ppm. ^{19}F NMR (376.29 MHz, CD_2Cl_2): δ −80.7 + (-81.2) (2 × dm, $^2J_{F-F}$ = 150 Hz, 1F, $CF\mathbf{F}CF_2CF_3$), −81.2 + (−81.3) + (−81.6) + (−81.8) (4 × m, $^4J_{F-F}$ = 13 Hz, 3F, $C\mathbf{F}_3CF$), −81.5 + (−81.7) + (−81.7) (4 × t, $^4J_{F-F}$ = 10 Hz, 3F, $C\mathbf{F}_3CF_2$), −83.5 + (−83.6) + (84.4) + (−84.6) (4 × dm, $^2J_{F-F}$ = 150 Hz, 1F, $CF\mathbf{F}CF_2CF_3$), −128.4 + (−128.9) (2 × m, 1F, $CF_3C\mathbf{F}$), −129.9 + (−130.2) + (−130.3) (3 × m, 2F, $CF_3C\mathbf{F}_2$) ppm, ^{13}C NMR (100.58 MHz, CD_2Cl_2): δ 17.0 (m, 4C, Ar'**C**H_3 − *o*), 18.3 (m, 2C, Ar'**C**H_3 − *p*), 19.8 + 19.9 + 20.8 (3 × s, 2C, $OCH(\mathbf{C}H_3)_2$), 50.1 (s, 2C, **C**H_2N), 75.0 + 75.1 + 75.2 (3 × s, 1C, O**C**H$(CH_3)_2$), 106–120 (m, 22C, **C**F_3, **C**F_2, **C**F), 110.8 + 111.1 + 111.3 (3 × s, 1C, $\mathbf{C}_{Ar}HC_{Ar}OiPr$), 122.2 + 122.3 + 122.3 (3 × s, 1C, $\mathbf{C}_{Ar}H$), 123.7 + 123.8 + 123.9 (3 × s, 1C, $\mathbf{C}_{Ar}H$), 129.5 (m, 4C, $\mathbf{C}_{Ar}H$), 130.1 + 130.2 + 130.3 (3 × s, 1C, $\mathbf{C}_{Ar}H$), 136.5 + 137.2 + 137.4 (3 × m, 2C, $\mathbf{C}_{Ar'}CH_3$), 139.0 + 140.2 + 140.7 (3 × m, 4C, o-$\mathbf{C}_{Ar'}CH_3$), 142.6 + 142.8 + 143.0 (3 × s, 1C, $\mathbf{C}_{Ar}CH$ = Ru), 153.5 (s, 1C, $\mathbf{C}_{Ar}$-OiPr), 159.2 + 159.4 + 162.8 (3 × d, $^2J_{C-F}$ = 25 Hz, 1C, **C**OO), 209.1 + 209.3 + 209.6 (3 × s, 1C, N**C**N), 319.4 (m, **C**H = Ru) ppm. MS (ESI^+) *m*/*z* (%): 929.2 $[M+Na]^+$ (100), 731.2 (59), 441.3 (88). HRMS (ESI^+): $[M+Na]^+$ calcd. for $C_{39}H_{44}F_8N_2NaO_7Ru$ 929.1956, found 929.1965.

*4.9. [1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene](2-isopropoxybenzyli-dene)bis[(2,4,4,5,5,6,6,6-octafluoro-3-oxahexanoyl)oxy])ruthenium(IV) (**1b**)*

According to the general procedure, silver salt **3b** (53 mg, 0.14 mmol) and complex **4** (**HG2**, 30 mg, 0.048 mmol) gave the target complex **1b** (50 mg, 97%, deep violet crystals, m.p. 71–73 °C). ^1H NMR (399,94 MHz, CD_2Cl_2): δ 0.93 + 0.94 + 1.32 + 1.40 + 1.49 (5 × d, $^3J_{H-H}$ = 5.9 Hz, 6H, $OCH(C\mathbf{H}_3)_2$), 2.24 + 2.25 + 2.26 + 2.28 (4 × bs, 12H, *o*-C**H**$_3$), 2.45 (s, 6H, *p*-C**H**$_3$), 4.10 + 4.11 (2 × bs, 4H, C**H**$_2$), 4.58 + 4.71 (m + septet, $^3J_{H-H}$ = 5.87 Hz, 1H, O**C**H$(CH_3)_2$), 5.65 (dm, $^2J_{H-F}$ = 57.5 Hz, 1H, C**H**F), 6.67 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, Ar**H**), 6.88 + 6.97 (2 × t, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar**H**), 7.08 (dd, $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, Ar**H**), 7.16 (m, 4H, Ar'**H**), 7.26 + 7.38 (2 × m, 1H, Ar**H**), 17.37 + 17.39 + 17.41 + 17.42 + 17.44 (5 × bs, 1H, Ru = C**H**) ppm. ^{19}F NMR (282,23 MHz, CD_2Cl_2): δ −81.5 (m, 3F, $C\mathbf{F}_3$), −84.1 + (-84.7) + (-85.3) (3 × m, 2F, $CF_3CF_2C\mathbf{F}F$), −86.6 + (−86.7) + (−86.9) (3 × dm, $^3J_{F-F}$ = 148 Hz, 2F, $CF_3CF_2CF\mathbf{F}$), −129. 5 (m, 2F, CH**F**), −129.7 + (−129.8) + (-129.9) (3 × s, 4F, $CF_3C\mathbf{F}_2CF_2$) ppm. ^{13}C NMR (100,58 MHz, CD_2Cl_2): δ 17.60 + 17.62 + 17.64 (3 × s, 4C, Ar'**C**H_3-*o*), 19.87 + 19.90 + 19.93 (3 × s, 2C, Ar'**C**H_3-*p*), 20.74 + 20.76 + 20.78 (3 × s, 2C, $OCH(\mathbf{C}H_3)_2$), 52.00 (s, 2C, **C**H_2N), 74.98 + 74.99 + 75.05 (3 × s, 1C, O**C**H$(CH_3)_2$), 96.62 + 99.06 (2 × dm, $^3J_{C-F}$ = 25 Hz, 2C, **C**HF), 103.00 − 122.00 (2 × m, 6C, $\mathbf{C}F_3$, $\mathbf{C}F_2$), 111.59 + 111.61 + 111.63 + 111.64 (4 × s, 1C, $\mathbf{C}_{Ar}HC_{Ar}OiPr$), 122.91 + 122.95 + 122.99 (3 × s, 1C, $\mathbf{C}_{Ar}H$), 123.78 + 123.79 + 123.85 + 123.91 (4 × s, 1C, $\mathbf{C}_{Ar}H$), 130.13 (s, 4C, $\mathbf{C}_{Ar'}H$), 130.17 + 130.23 + 130.30 (3 × s, 1C, $\mathbf{C}_{Ar}H$), 135.27 (bs, 2C, $\mathbf{C}_{Ar'}CH_3$), 139.34 + 139.37 + 139.40 + 139.42 (4 × s, 4C, $\mathbf{C}_{Ar'}CH_3$), 139.98 + 140.00 + 140.02 (3 × s, 2C, $\mathbf{C}_{Ar'}N$), 143.97 (m, 1C, $\mathbf{C}_{Ar}CH$ = Ru), 153.77 (m, 1C, $\mathbf{C}_{Ar}OiPr$), 164.96 + 165.07 (2 × d, $^2J_{C-F}$ = 26 Hz, 2C, **C**OO), 210.47 (m, 1C, N**C**N), 313.23 + 313.66 (2 × m, 1C, **C**H = Ru) ppm. MS (ESI), *m*/*z* (%) 1101 $[M+Na]^+$ (100); 817 $[M-C_5HF_8NaO_3]^+$ (57). HRMS (ESI): calcd. for $C_{41}H_{40}F_{16}N_2NaO_7Ru$ ($[M+Na]^+$) 1101.1517, found 1101.1516.

*4.10. [1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene](2-isopropoxybenzylidene)-bis[(2,3,3,3-tetrafluoro-2-methoxypropanoyl)oxy]ruthenium(IV)(**1c**)*

According to the general procedure, silver salt **3c** (14 mg, 0.049 mmol) and complex **4** (**HG2**, 10 mg, 0.016 mmol) gave the target complex **1c** (10 mg, 69%, ochre crystals, m.p. 75-80 °C). ^1H NMR (299.97 MHz, CD_2Cl_2): δ 0.97 + 0.98 + 1.02 (3 × d, $^3J_{H-H}$ = 6.2) Hz, 6H, 0.84 + 2.87 + 3.23 + 3.26 (4 × s, 6H, C**H**$_3$O), 4.08 + 4.09 + 4.11 (3 × s, 4H, C**H**$_2$N); 4.46 (m, 1H, O**C**H$(CH_3)_2$), 6.61 (m, 1H, Ar**H**3), 6.97 (m, 1H, Ar**H**5), 7.12 (m, 1H, Ar**H**6), 7.17 (s, 4H, Ar'**H**), 7.35 (m, 1H, Ar**H**4), 17.49 + 17.51 + 17.54 (3 × s, 1H, Ru = C**H**) ppm. ^{19}F NMR (376.29. CD_2Cl_2): δ −80.5 + (−80.6) + (-80.8) + (-80.9) (5 × d, $^3J_{F-}$

$_F$ = 3 Hz, 3F), −129.2 + (−131.3) + (−131.3) + (−131.4) + (−131.6) (5 × m, 1F). ^{13}C NMR (100.58 MHz, CD_2Cl_2): δ 19.8 (bs, 4C, Ar'**C**H_3-*o*), 20.1 + 20.1 (2 × s, 2C, Ar'**C**H_3-*p*), 20.8 (s, 2C, OCH(**C**H_3)$_2$), 52.3 (m, 2C, **C**H_2N), 52.9 + 52.9 + 53.0 (3 × s, 1C, O**C**H_3), 74.9 + 75.0 (2 × s, 1C, O**C**H(CH_3)$_2$), 106–120 (m, 22C, **C**F_3, **C**F_2, **C**F), 114.2 (s, 1C, **C**$_{Ar}$HC$_{Ar}$OiPr), 122.0 + 122.3 + 122.6 (3 × s, 1C, **C**$_{Ar}$H), 123.3 + 123.7 + 124.1 (s, 1C, **C**$_{Ar}$H), 129.4 + 129.4 + 129.5 + 129.5 (4 × s, 4C, **C**$_{Ar'}$H), 129.6 + 129.7 + 129.7 (3 × s, 1C, **C**$_{Ar}$H), 134.6 (m, 2C, **C**$_{Ar'}$$CH_3$), 139.3 (bs, 4C, **C**$_{Ar'}$$CH_3$), 139.4 (m, 2C, **C**$_{Ar'}$N), 142.7 + 143.0 + 143.2 (3 × s, 1C, **C**$_{Ar}$CH = Ru), 153.3 + 153.5 + 153.6 (3 × s, 1C, **C**$_{Ar}$OiPr), 162.3 (m, 2C, **C**OO), 210.3 + 210.4 (2 × s, 1C, N**C**N), 315.2 (m, 1C, **C**H = Ru) ppm. MS (ESI$^+$) *m*/*z* (%): 929.2 [M+Na]$^+$ (100), 731.2 (59), 441.3 (88). HRMS (ESI$^+$): [M+Na]$^+$ calcd. for $C_{39}H_{44}F_8N_2NaO_7Ru$ 929.1956, found 929.1965.

*4.11. [4,5-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1,3-bis (2,4,6-trimethylphenyl)-imidazolidin-2-ylidene](2-isopropoxybenzylidene)bis[perfluoro(2-methyl-3-oxahexanoyl)-oxy] ruthenium(IV) (**2a**)*

According to the general procedure, silver salt **3a** (36 mg, 0.083 mmol) and complex **5** (**HG2**, 14 mg, 0.011 mmol) gave the target complex **2a** (19.4 mg, 97%, deep violet wax). ^{1}H NMR (299.97 MHz, CD_2Cl_2): δ 0.82–0.93 (m, 3H, (C**H**$_3$)CH(CH_3)O), 0.94–1.96 (m, 3H, (CH_3)CH(C**H**$_3$)O), 1.88 (br m, 6H, C**H**$_2$), 2.14 (br m, 2H, C**H**$_2$), 1.97–2.14 (m, 6H, *p*-C**H**$_3$), 2.35 + 2.39 + 2.43 + 2.46 + 2.49 + 2.51 (6 × s, 12H, *o*-C**H**$_3$), 4.06 (m, 2H, NC**H**), 4.48 (m, 1H, C**H**(CH_3)$_2$), 6.64 (m, 1H, Ar**H**), 6.97 (m, 1H, Ar**H**), 7.09 (m, 1H, Ar**H**), 7.25 (m, 4H, Ar'**H**), 7.38 (m, 1H, Ar**H**), 17.46 + 17.50 + 17.56 + 17.57 (4 × bs, 1H, Ru = C**H**) ppm. ^{19}F NMR (282.23 MHz, CD_2Cl_2): δ −81.7 (m, 6F, C**F**$_3$CF$_2$CF$_2$), −80.5–(−82.4) (m, 2F, CF$_3$CF$_2$C**F**F), −81.8–(−82.5) (m, 12F, **C**F$_3$), −83.1–(−83.8) (m, 2F, CF$_3$CF$_2$C**F**F), −115.4 (m, 4F, C**F**$_2$CH$_2$), −122.6 (m, 4F, C**F**$_2$CF$_2$CH$_2$), −123.6 (m, 4F, C**F**$_2$CF$_2$CF$_2$CH$_2$), −124.7 (m, 4F, CF$_3$CF$_2$C**F**$_2$), −126.9 (m, 4F, CF$_3$C**F**$_2$CF$_2$), −129.1 (m, 2F, C**F**), −130.7 (m, 4F, CF$_3$C**F**$_2$CF$_2$) ppm. ^{13}C NMR (75,44 MHz, CD_2Cl_2): δ 18.27 + 18.51 + 18.73 (3 × s, 4C, Ar'**C**H_3-*o*), 20.02 + 20.16 + 20.60 (3 × bs, 2C, OCH(**C**H_3)), 21.29 + 21.39 (2 × s, 2C, *p*-**C**H_3), 25.74 (m, 2C, CF$_2$CH$_2$**C**H$_2$), 28.09 (t, $^2J_{C-F}$ = 21.4 Hz, 2C, CF$_2$**C**H$_2$CH$_2$), 68.19 + 69.99 (2 × s, 2C, CF$_2$CH$_2$CH$_2$**C**H), 75.76 (m, 1C, O**C**H(CH_3)), 98.22–129.17 (m, 20C, **C**F$_3$, **C**F$_2$), 111.57 + 111.78 (2 × s, 1C, **C**$_{Ar}$H), 122.90 (s, 1C, **C**$_{Ar}$H), 124.67 + 124.82 (2 × s, 1C, **C**$_{Ar}$H), 130.44 (2 × s, 4C, **C**$_{Ar'}$H), 131.06 + 131.35 + 131.61 + 131.68 (4 × s, 1C, **C**$_{Ar}$H), 135.68 (bs, 2C, **C**$_{Ar'}$$CH_3$), 137.63 + 137.78 + 138.79 + 138.98 (4 × s, 4C, **C**FCF$_3$), 140.46 + 140.63 + 140.77 + 140.90 + 140.97 (5 × s, 4C, **C**$_{Ar'}$$CH_3$), 141.60 (s, 2C, **C**$_{Ar'}$N), 143.33 (m, 1C, **C**$_{Ar}$CH = Ru), 154.14 (m, 1C, **C**$_{Ar}$OiPr), 159.85 + 160.20 (2 × s, 2C, **C**OO), 214.49 + 214.79 (2 × s, 1C, Ru = **C**NN), 320.75 (m, 1C, Ru = **C**H) ppm. MS (ESI), *m*/*z* (%) 1929 [M+Na]$^+$ (100); 1577 [M-($C_6F_{11}O_3$)]$^+$ (28); 1247 [M-(2 × $C_6F_{11}O_3$)]$^+$ (33); 999 (28). HRMS (ESI): calcd. for $C_{59}H_{44}F_{48}N_2NaO_7Ru$ ([M+Na]$^+$) 1929.1322, found 1929.1318.

*4.12. [4,5-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1,3-bis (2,4,6-trimethylphenyl)-imidazolidin-2-ylidene](2-isopropoxybenzylidene)bis[(2,4,4,5,5,6,6,6-octafluoro-3-oxahexanoyl)oxy)ruthenium(IV)(**2b**)*

According to the general procedure, silver salt **3b** (21 mg, 0.057 mmol) and complex **5** (**HG2**, 37 mg, 0.028 mmol) gave the target complex **2b** (44 mg, 88%, deep violet wax). ^{1}H NMR (399.94 MHz, CD_2Cl_2): δ 0.87 (d, $^3J_{H-H}$ = 6.2 Hz, 3H, (C**H**$_3$)CH(CH_3)O), 0.95 (d, $^3J_{H-H}$ = 6.2 Hz, 3H, (CH_3)CH(C**H**$_3$)O), 1.75–1.97 (br m, 6H, C**H**$_2$), 2.12–2.25 (br m, 2H, C**H**$_2$), 2.20 + 2.21 (2 × s, 6H, *o*-C**H**$_3$), 2.32 + 2.33 + 2.34 + 2.35 (4 × s, 6H, *o*-C**H**$_3$), 2.45 (s, 6H, *p*-C**H**$_3$), 4.05 (m, 2H, NC**H**), 4.59 (m, 1H, C**H**(CH_3)$_2$), 5.62 (dm, $^2J_{H-F}$ = 58.0 Hz, 2H, C**H**F), 6.67 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar**H**), 6.97 (tm, $^3J_{H-H}$ = 7.5 Hz, 1H, Ar**H**), 7.05 (m, 1H, Ar**H**), 7.17 (m, 2H, Ar'**H**), 7.22 (m, 2H, Ar'**H**), 7.35 (tm, 1H, Ar**H**), 17.17 + 17.21 + 17.22 + 17.26 + 17.27 (5 × bs, 1H, Ru = C**H**) ppm. ^{19}F NMR (282,23 MHz, CD_2Cl_2): δ −81.1 (t, $^3J_{F-F}$ = 8 Hz, 6F, C**F**$_3$), −81.6 (m, 6F, C**F**$_3$CF$_2$CF$_2$), −83.9–(−85.5) (m, 2F, CF$_3$CF$_2$C**F**F), −86.1–(−87.2) (m, 2F, CF$_3$CF$_2$C**F**F), −114.9 (m, 4F, C**F**$_2$CH$_2$), −122.1 (m, 4F, C**F**$_2$CF$_2$CH$_2$), −123.1 (m, 4F, C**F**$_2$CF$_2$CF$_2$CH$_2$), −124.1 (m, 4F, CF$_3$CF$_2$C**F**$_2$), −126.4 (m, 4F, CF$_3$C**F**$_2$CF$_2$), −129.3 (dm, $^2J_{H-F}$ = 60 Hz, 2F, CH**F**), −129.8 (m, 4F, CF$_3$C**F**$_2$CF$_2$O) ppm. ^{13}C NMR (100,58 MHz, CD_2Cl_2): δ 18.90 + 19.50 (2 × s, 4C, Ar'**C**H_3-*o*), 20.60 (bs, 2C, OCH(**C**H_3)), 21.30 (s, 2C, *p*-**C**H_3), 25.69 (m, 2C, CF$_2$CH$_2$**C**H$_2$), 28.13 (t, $^2J_{C-F}$ = 21 Hz, 2C, CF$_2$**C**H$_2$CH$_2$), 69.14 (s, 2C, CF$_2$CH$_2$CH$_2$**C**H), 75.00 (m, 1C, O**C**H(CH_3)), 96.58 + 99.05 (2 × m, 2C, **C**HF), 107.08–119.69 (m, 18C, **C**F$_3$, **C**F$_2$), 111.52 (s, 1C, **C**$_{Ar}$H), 122.36 (s, 1C, **C**$_{Ar}$H), 123.45 (s, 1C, **C**$_{Ar}$H), 130.05 (s, 4C, **C**$_{Ar'}$H), 130.45 (s, 1C, **C**$_{Ar}$H), 133.41 (bs, 2C, **C**$_{Ar'}$$CH_3$), 138.82 + 139.13 + 139.28 (3 × s, 4C, **C**$_{Ar'}$$CH_3$), 140.19 (s, 2C, **C**$_{Ar'}$N), 143.26 (m, 1C, **C**$_{Ar}$CH = Ru), 153.08 (m, 1C, **C**$_{Ar}$O*i*Pr), 163.65 + 163.84 (2 × s, 2C, **C**OO), 214.85 (s, 1C, Ru = **C**NN), 313.53 (m, 1C, Ru = **C**H) ppm. MS (ESI), *m*/*z* (%) 1793 [M+Na]$^+$ (48); 1509 [M-($C_5HF_8O_3$)]$^+$ (51); 1247 [M-(2 × $C_5HF_8O_3$)]$^+$ (100); 999 (28). HRMS (ESI): calcd. for $C_{57}H_{46}F_{42}N_2NaO_7Ru$ ([M+Na]$^+$) 1793.1570, found 1793.1571.

4.13. Study of catalytic activity. general procedure

An NMR tube was charged with catalyst (5.0 μmol, 5 mol%) and solvent (CD_2Cl_2, 0.65 mL). The substrate (0.100 mmol) was added and the mixture was heated to the given temperature. The progress of the reaction was monitored by ^{1}H NMR spectroscopy.

4.14. Diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate

^{1}H NMR (299.97 MHz, $CDCl_3$) [29]: δ 1.22 (t, $^3J_{H/H}$ = 7.0 Hz, 6H, CH_2C**H**$_3$), 1.70 (s, 3H, C**H**$_3$), 2.87 (m, 2H, C**H**$_2$), 2.93 (m, 2H, C**H**$_2$), 4.16 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, C**H**$_2$$CH_3$), 5.18 (m, 1H, C**H**) ppm.

4.15. Diethyl 3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate

^{1}H NMR (299.97 MHz, toluene-d_8) [30]: δ 0.95 (t, $^3J_{H/H}$ = 7.3 Hz, 6H, CH_2C**H**$_3$), 1.62 (s, 6H, C**H**$_3$), 3.10 (s, 4H, C**H**$_2$), 3.97 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, C**H**$_2$$CH_3$) ppm.

4.16. 2-(Prop-1-enyl)-2,5-dihydrofuran

^{1}H NMR (299.97 MHz, CD_2Cl_2) [31]: *δ* 1.69 (dd, $^3J_{H-H}$ = 5.7 Hz, ^4JH − H = 1.3 Hz, 3H, CHC**H**$_3$), 4.59 (m, 2H, OCH$_2$C**H**C**H**), 5.08–5.16 (bs, 1H, OC**H**), 5.43 (ddq, ^3JH − H = 15.0 Hz, ^3JH − H = 7.5 Hz, ^4JH − H = 1.3 Hz, 1H, CH_3CHC**H**), 5.64–5.76 (m, 2H, OC**H**$_2$), 5.91 (dq, $^3J_{H-H}$ = 6.2 Hz, ^4JH − H = 1.8 Hz, 1H, CH_3C**H**) ppm.

4.17. Computational details

DFT calculations were performed using Gaussian 09W program suite [32] using the resolution-of-identity approach [33], recent Minnesota MN12L pure functional [34], def2-SVP basis set [35] and universal def2 auxiliary basis set [36]. Vibrational frequencies were calculated for all species to characterize them as minima or transition states. Vizualizations of the molecules were performed with the GaussView program [37]. The geometries of all calculated structures and their energies are listed in Supporting information of this article.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2016.09.005.

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