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Fluorine-containing ruthenium-based olefin metathesis catalysts

Salekh M. Masoud,[a] Daria V. Vorobyeva,[a] Dmitry A. Petropavlovskikh,[a] Christian Bruneau,[b] Sergey N. Osipov [a, c]

[a] A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation
[b] University of Rennes 1, Institute of Chemical Sciences, UMR CNRS 6226, Campus de Beaulieu, Bât. 10C, 263 Avenue de Général Leclerc, 35042 Rennes Cedex, France
[c] Peoples' Friendship University of Russia (RUDN University), ul. Miklukho-Maklaya 6, 117198 Moscow, Russian Federation

The review summarizes literature data on the methods for the introduction of fluorine atoms and fluoralkyl groups into different ligands to construct metathesis-active ruthenium carbene complexes. It also analyzes the influence of fluorinated ligands on the catalytic activity of the complexes. The choice, structure and positions of fluorinated substituents in NHC ligands are generally dictated by the desire to increase the electrophilicity of the ruthenium atom due to the electron-withdrawing effect of fluorine atoms and fluoroalkyl groups, resulting, as a rule, in an increase in the activity of the ruthenium complex. In catalysts with unsymmetrical fluorine-containing NHC ligands, there is a possibility of additional Ru – F coordination, making the complexes much more stable and, consequently, more active. The presence of fluorine in chelating alkylidene ligands provides an increase in the catalyst initiation rate due to a weakening of the ruthenium – heteroatom bond. Besides, the introduction of polyfluoroalkyl groups into ligands solves the problem of catalyst recovery using fluorous biphasic systems for reuse.
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Dedicated to Professor Pierre H. Dixneuf from the University of Rennes (France) for his outstanding contribution to organometallic chemistry and catalysis.

1. Introduction

In recent years, the alkene metathesis has become one of the most important tools for the carbon – carbon double bond formation in the synthesis of diverse molecules, from simple alkenes [1] to biologically active compounds [2–4] and macromolecules.[5] The importance of the development of the metathesis method in organic synthesis has been recognized by the award of the 2005 Nobel Prize in Chemistry jointly to Y.Chauvin (France), R.Grubbs (USA) and R.Schrock (USA). Ruthenium,[6] molybdenum and tungsten carbene complexes [7] are the most efficient alkene metathesis catalysts.

Numerous types of metathesis catalysts are currently known. However, ruthenium carbene complexes, commonly known as Grubbs catalysts, (Fig. 1) are the most popular due to high air and moisture stability combined with tolerance to a wide range of functional groups (*e.g.*, hydroxy, carboxy, carbonyl, *etc.*) in substrates.[8] The first

S.M.Masoud. PhD in Chemistry, Researcher at the Laboratory for Ecological Chemistry, INEOS RAS.
E-mail: skh.masoud@gmail.com
Current research interests: organic and organometallic chemistry, homogeneous catalysis.
D.V.Vorobyeva. PhD in Chemistry, Senior Researcher at the same Laboratory.
E-mail: d-20@mail.ru
Current research interests: organic, organofluorine and organometallic chemistry, homogeneous catalysis.
D.A.Petropavlovskikh. PhD student at the same Laboratory.
E-mail: dmitrypetrpavl@gmail.com
Current research interests: organic, organofluorine and organometallic chemistry, homogeneous catalysis.
Christian Bruneau. PhD, Professor, Director of the Green Chemistry and Catalysis Department at the Institute of Chemical Sciences at the University of Rennes.
E-mail: christian.bruneau@univ-rennes1.fr
Current research interests: organometallic chemistry, green catalysis.
S.N.Osipov. Doctor of Chemical Sciences, Head of the Laboratory for Ecological Chemistry, INEOS RAS.
E-mail: osipov@ineos.ac.ru
Current research interests: organic, organofluorine and organometallic chemistry, homogeneous catalysis.

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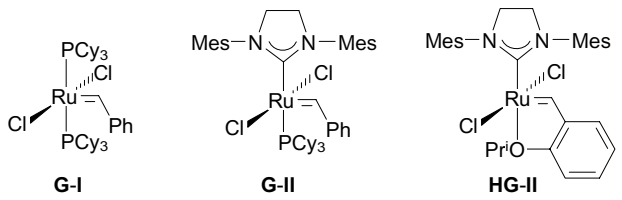


Figure 1. Commercially available ruthenium metathesis catalysts: the first-generation Grubbs catalyst (**G-I**), the second-generation Grubbs catalyst (**G-II**) and the second-generation Hoveyda–Grubbs catalyst (**HG-II**).

ruthenium-based metathesis catalyst with the known structure was synthesized in 1992.[9] Since that time a large number of different modifications were described.[10] This area of research has attracted great attention of chemists and, despite significant advances, the design of novel, more efficient and selective metathesis catalysts is still of great interest.

Hérisson and Chauvin[11] were the first to suggest the mechanism of metal-catalyzed olefin metathesis, according to which the [2 + 2]-cycloaddition of the starting olefin to the carbene centre of the metal complex giving a metallacyclobutane intermediate and the subsequent retro-[2 + 2]-cycloaddition (Scheme 1) are key steps in the metathesis. It is worth noting that each step of this catalytic cycle is reversible.

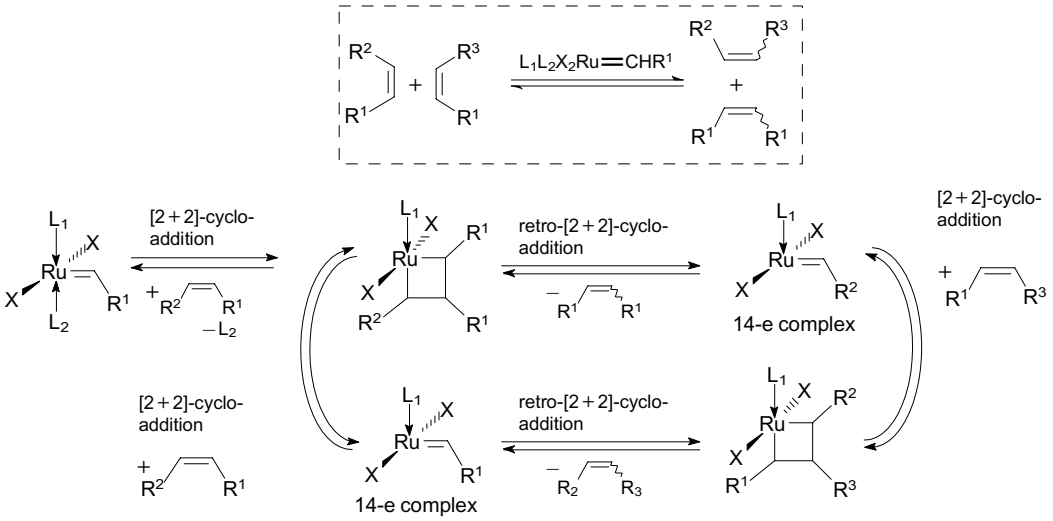
In the general case, the reaction affords an equilibrium mixture of all possible metathesis products. Therefore, the metathesis can be successfully applied as a preparative method only if the equilibrium is shifted in a particular direction, for instance, *via* the opening of strained rings or, on the contrary, the closure of stable five- or six-membered carbon rings or heterocycles. Depending on the structure of the starting substrates, several main types of metathesis were described, such as the cross-metathesis (CM), ring-closing metathesis (RCM) of diolefins, ring-closing enyne metathesis (RCEYM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET), *etc*. Among these types of catalytic reactions, RCM, ROMP and CM have the most practical value. The outcome of the cross-metathesis is the most difficult to predict because of the absence of strong thermodynamic restrictions associated with the irreversibility of the reaction and *E*/*Z*-product selectivity. Despite the fact that the *E* isomer of the alkene product is thermodynamically favourable, the cross-metathesis generally does not afford this isomer in pure form, and the impurity of the *Z* isomer is often hard to separate. On the other hand, many biologically active and natural compounds contain carbon–carbon double bonds in the Z configuration. Therefore, the synthesis of new selective catalysts capable of providing the formation of pure *E* or *Z* isomers of alkenes is one of the challenging problems in the methodological development of metathesis reactions.

The chemistry of fluorine-containing compounds is a rapidly growing field of research.[12] Due to the unique properties of the fluorine atom, such as low polarizability, the small atomic radius, high electronegativity, the ability to form hydrogen bonds and coordinate to transition metals[13] and a strong carbon–fluorine bond, organofluorine compounds often exhibit properties significantly different from those of the non-fluorinated parent compounds. High fluorine abundance in the Earth's crust and the easy detection of fluorine by ^{19}F NMR spectroscopy (due to the high gyromagnetic ratio and monoisotopic nature[14]) makes the chemistry of organofluorine compounds highly attractive for synthetic chemists. Hence, organofluorine compounds are widely used in different fields, such as medicinal chemistry, materials science and agriculture. Finally, of special attention are organoperfluorine derivatives capable of forming a non-polar fluorous phase that is immiscible with most organic solvents and thereby facilitating the recovery of catalysts or isolation of reaction products from the reaction mixture.[15]

In addition to the above-mentioned fluorophilicity, which is caused by the presence of perfluoroalkyl substituents, the introduction of fluorine atoms into ligands of ruthenium catalysts can result in the formation of an intramolecular Ru–F bond, enhance the electron-withdrawing properties or increase the steric bulkiness of the ligands. The changes caused by the introduction of fluorine into the ligand can significantly alter the catalyst activity and selectivity.

In the general case, Grubbs catalysts contain several different ligands (Fig. 2). In these catalysts, the reactive carbene ligand (most often arylidene) plays a key role, being directly involved in the [2 + 2]-cycloaddition step in the

Scheme 1



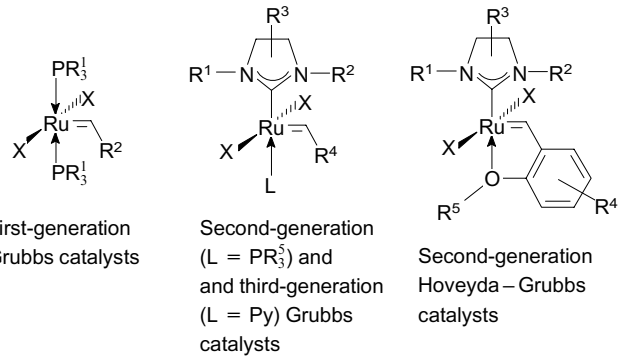


Figure 2. Grubbs and Hoveyda – Grubbs catalysts.

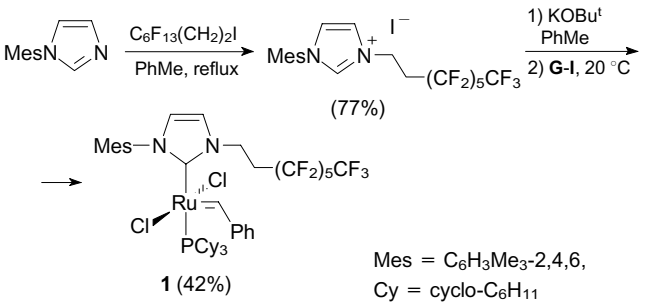
metathesis. Second- and third-generation catalysts contain an *N*-heterocyclic carbene (NHC) ligand. Due to the unique steric and electronic properties of the latter, catalysts bearing this ligand have high stability and activity. The phosphine (first- and second-generation Grubbs catalysts) or pyridine (third-generation Grubbs catalysts) ligands are most often employed as L-type ligands; a chloride ion is used as an X-type ligand in the majority of complexes.

All the above-mentioned ligands (alkylidene, NHC, L, X) can be modified in different ways depending on the task at hand. In recent years, various modifications of Grubbs catalysts were described,[10,14] the main goals of which were to increase the catalyst selectivity and stability, improve catalyst recyclability and recoverability and simplify product isolation. However, some of these problems are still challenging. Certain problems can be addressed using fluorine-containing substituents. The present review summarizes available methods for the synthesis of fluorine-containing ruthenium alkene metathesis catalysts, their structural features and catalytic activity. The review is divided into sections according to the type of fluorine-containing ligands. The data in each section are presented in chronological order.

2. Fluorine in NHC ligands

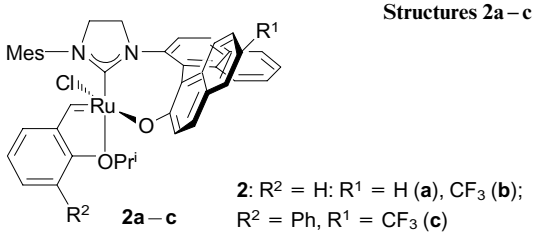
Complex **1**, synthesized by A.Fürstner group[16] in 2001 (Scheme 2), was the first example of second-generation Grubbs catalysts bearing a fluorinated group in the NHC ligand. The fluorine-containing precursor of this ligand was synthesized by the alkylation of easily accessible *N*-mesitylimidazole.[17] Complex **1** was synthesized by a standard procedure involving the deprotonation with potassium *tert*-butoxide. Due to the presence of a perfluoroalkyl substituent, catalyst **1** has good solubility and shows high catalytic activity in the ring-closing metathesis of *N*,*N*-dimethallyl-*N*-tosylamide in supercritical carbon dioxide.

Scheme 2



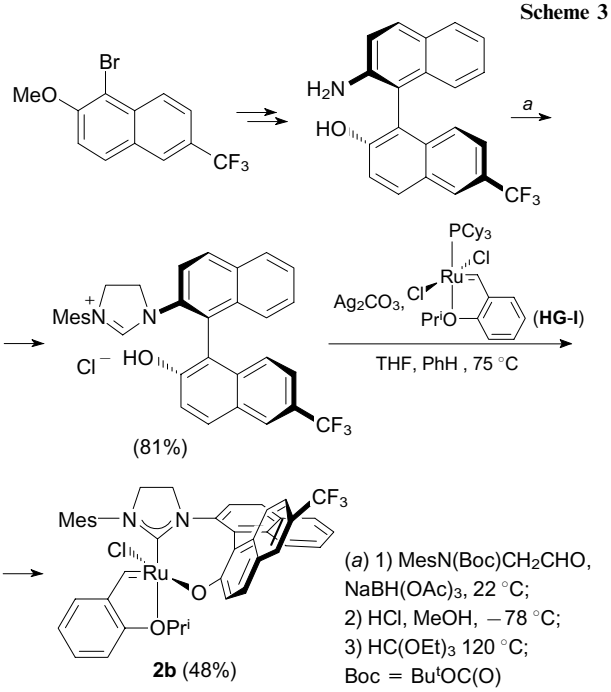
In 2002, A.Hoveyda and co-workers[18] reported a method for the synthesis of catalyst **2a** bearing a chiral bidentate binaphthyl NHC ligand. Catalyst **2a** proved to be air-stable and exhibited high activity in asymmetric metathesis reactions (> 98% *ee*). More recently (in 2003), this research group described the synthesis and catalytic activity of six further modifications of catalyst **2**, two of which (**2b**,**c**) contained a CF_3 group.[19]

Structures 2a – c



A fluorinated binaphthyl NHC ligand for complexes **2b**,**c** was prepared by a multistep procedure starting from a substrate that already contained fluorine (Scheme 3). Target complex **2b** was synthesized by transmetalation of the appropriate silver NHC complex, which was generated *in situ* from the trifluoromethyl-containing binaphthyl-bridged imidazolinium salt and Ag_2CO_3.

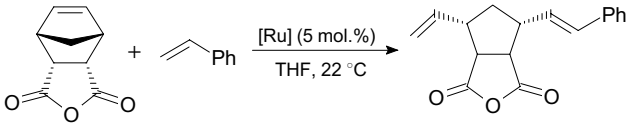
Scheme 3



The presence of the trifluoromethyl group causes a significant increase in the efficiency of the catalysts. For example, the rate of asymmetric AROCM of norbornenedicarboxylic anhydride and styrene increases three- and 160-fold in the presence of catalysts **2b** and **2c**, respectively, compared to non-fluorinated catalyst **2a** (Table 1).

In 2006, Grubbs and co-workers[20] characterized complexes **3a**,**b** containing fluorine in the *ortho* positions of aryl substituents of the NHC ligand (Scheme 4). Catalyst **3a**

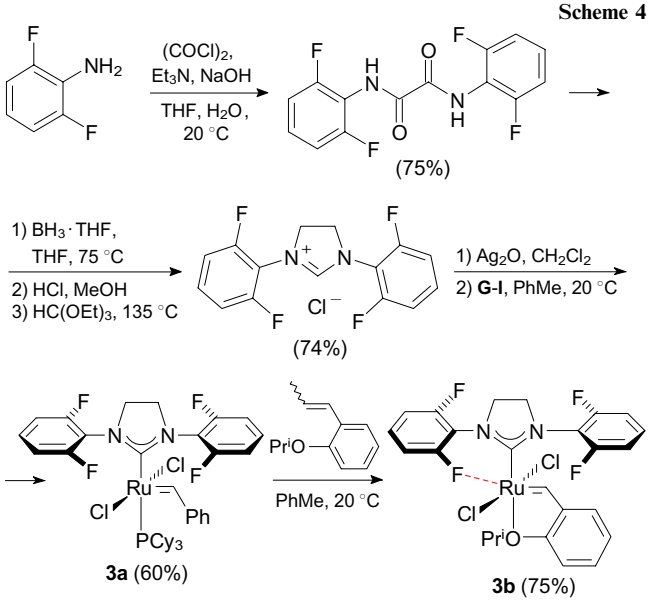
Table 1. AROCM of norbornenedicarboxylic anhydride and styrene.[16]



Catalyst	Time	Conversion (%)	Yield (%)
2a	66 h	> 99	35
2b	22 h	> 99	55
2c	25 min	> 99	85

exhibited higher activity in RCM of diethyl diallylmalonate (DEDAM) compared to the related catalyst **G-II**. Meanwhile, catalyst **3b** proved to be less active than **HG-II**. This significant difference in the activity was attributed to the Ru···F coordination established by X-ray diffraction. This coordination leads to an increase in the stability of the 14-electron complex in the step of initiation of catalyst **3a**; however, in the case of catalyst **3b**, this coordination bond hinders the access of an alkene molecule to the metal centre. Despite relatively low activity, catalyst **3b** proved to be efficient in RCM reactions giving tetrasubstituted alkenes.[21] The corresponding fluorine-containing ligand was synthesized from commercially available 2,6-difluoroaniline.

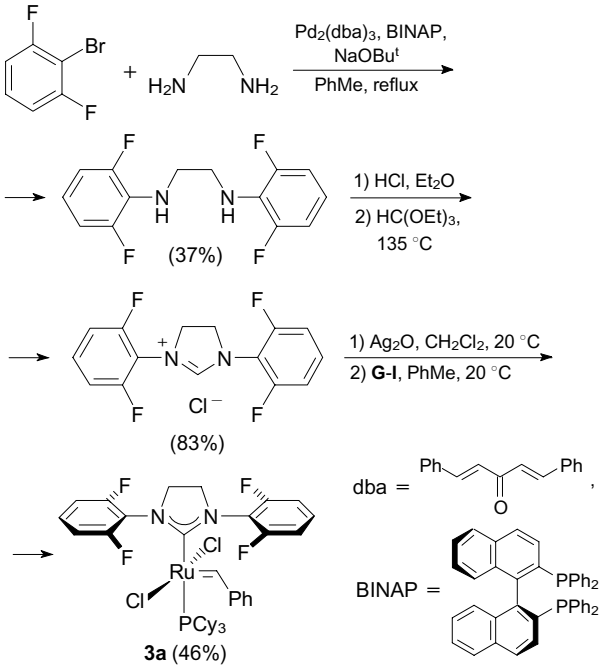
Scheme 4



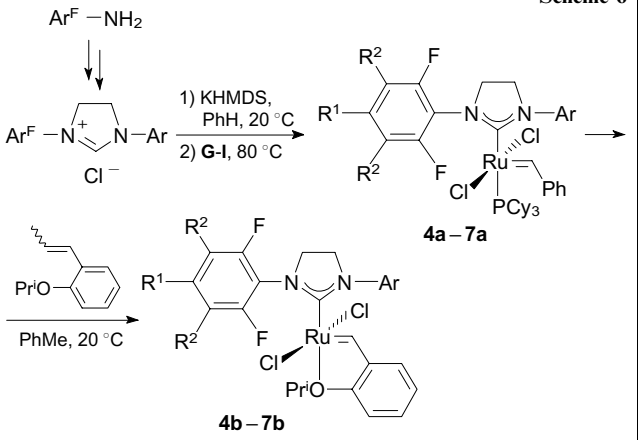
An alternative approach to the synthesis of complex **3a** using 1-bromo-2,6-difluorobenzene as the starting compound was proposed by Costabile and co-workers[22] (Scheme 5). The resulting complex was tested in different RCM, ROMP and CM reactions.

Similar trends in the above-mentioned reactions were found for related unsymmetrical complexes **4**–**7**; in all cases, phosphine-containing catalysts **4a**–**7a** exhibited higher activity than phosphine-free catalysts **4b**–**7b** (Scheme 6).[23,24] In the cross-metathesis of allylbenzene with *cis*-1,4-diacetoxy-2-butene, catalysts **5**–**7** showed higher *E*/*Z* selectivity with a conversion of > 60%. Precursors of NHC ligands were synthesized starting from appropriate anilines by a procedure involving the following steps:

Scheme 5



Scheme 6

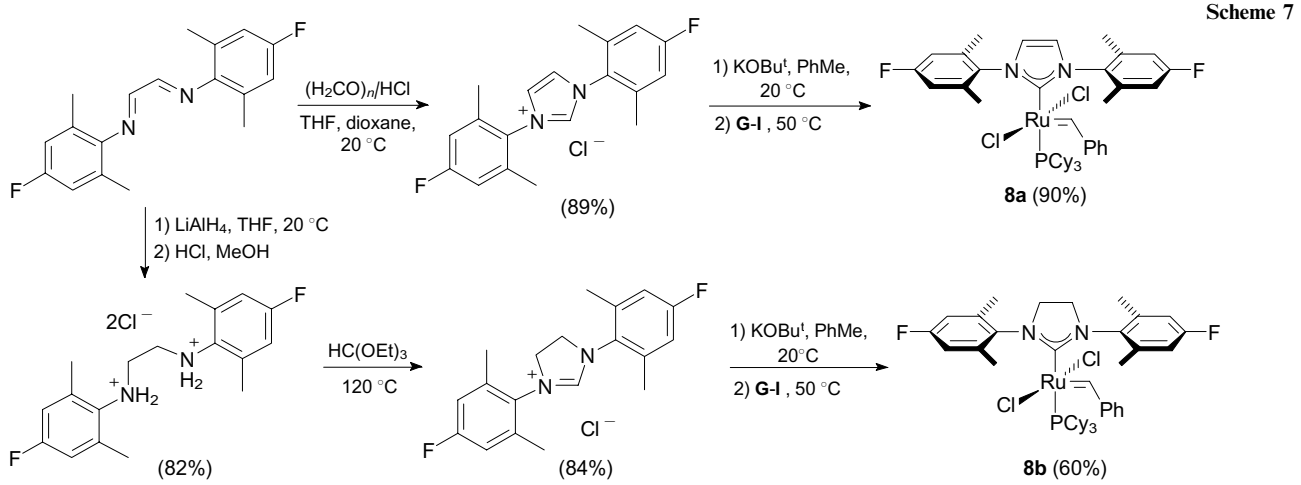


Ar = Mes: $R^1 = R^2 = H$ (**4a** 83%, **4b** 74%),
$R^1 = F$, $R^2 = H$ (**5a** 80%, **5b** 85%), $R^1 = R^2 = F$ (**6a** 76%, **6b** 57%);
Ar = DIPP, $R^1 = R^2 = H$ (**7a** 44%, **7b** 85%);
KHMDS = $K[N(SiMe_3)_2]$, DIPP = $C_6H_3Pr^i$-2,6

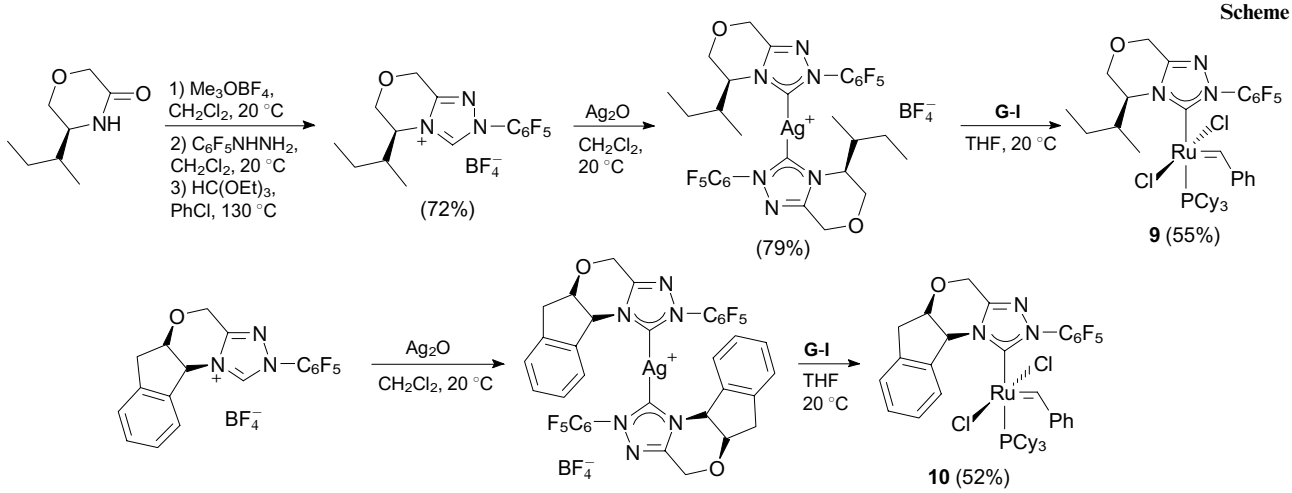
1) the treatment of fluorine-containing aniline with oxalyl chloride or its monoesters; 2) the addition of a second aniline molecule giving oxalyl amides; 3) the reduction of carbonyl groups with $BH_3 \cdot THF$ and 4) the cyclization to the unsymmetrical imidazolinium salt upon the treatment with triethyl orthoformate. The deprotonation of imidazolinium salts with potassium hexamethyldisilazide afforded complexes **4a**–**7a**, the ligand-exchange reaction of which under standard conditions gave phosphine-free complexes **4b**–**7b** (see Scheme 6).

Plenio and co-workers[25] synthesized second-generation Grubbs complexes with NHC ligands containing a fluorine atom in the *para* position of *N*-aryl moieties (**8a** and **8b**, Scheme 7). However, the catalytic activity of the new complexes was not evaluated and only some physicochem-

Scheme 7



Scheme 8

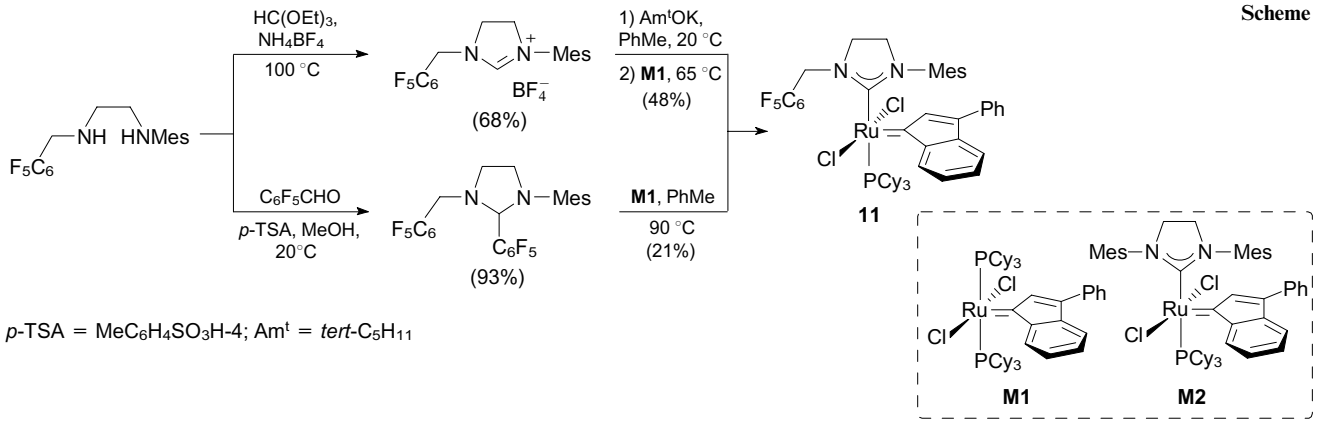


ical properties were studied. Fluorine atoms were introduced into the aromatic ring by the Schiemann reaction.

Grela and co-workers [26] synthesized catalysts **9** and **10** bearing chiral 1,2,4-triazol-5-ylidene ligands with pentafluorophenyl groups and evaluated their activity in ARCM and AROCM reactions (Scheme 8). Complexes **9** and **10** showed high enantioselectivity in AROCM of norbornenedicarboxylic anhydride with styrene, but the product yields and stability of these complexes were lower compared to the non-fluorinated analogues. Besides, because of low stability, these complexes were generated *in situ* for all catalytic tests.

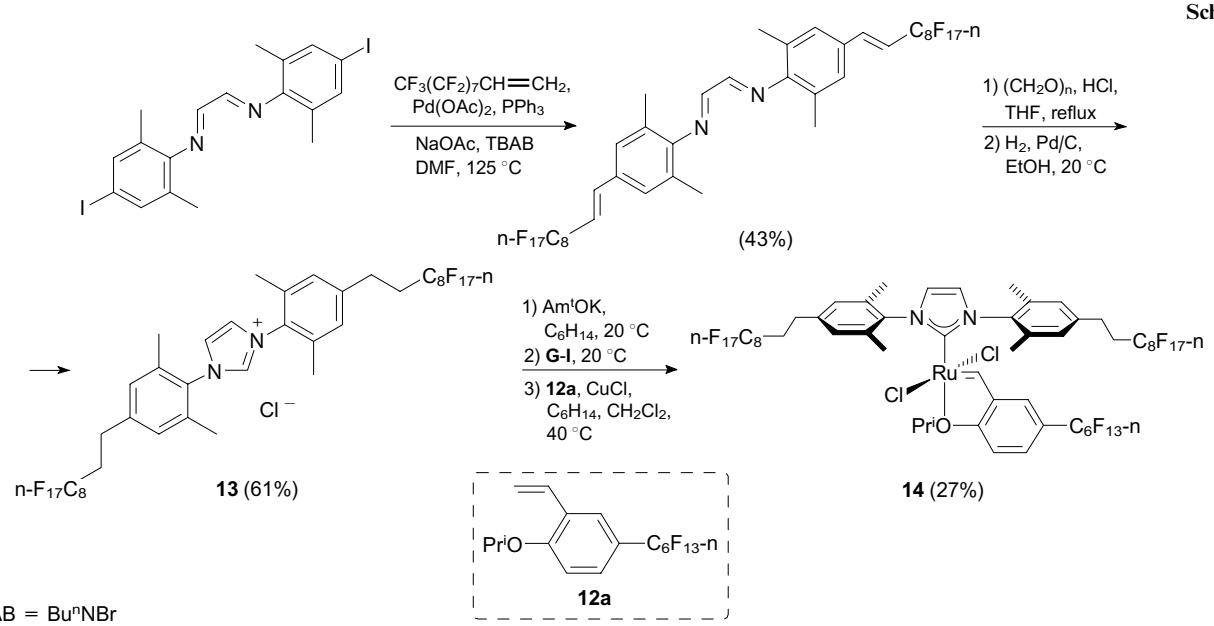
This research group also reported the synthesis of an indenylidene catalyst bearing an unsymmetrical NHC ligand with a pentafluorophenyl group (**11**, Scheme 9).[27] In RCM of DEDAM performed in air,[28] catalyst **11** proved to be more active but less stable than commercially available **M2** (trade name, by Umicore). The ligand was synthesized starting from pentafluorobenzaldehyde. Complex **11** was prepared using two different approaches: 1) the deprotonation of the corresponding imidazolium tetrafluorobo-

Scheme 9



p-TSA = $MeC_6H_4SO_3H$-4; Am^t = *tert*-C_5H_{11}

Scheme 10

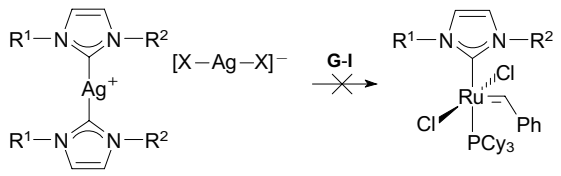


rate and 2) the decomposition of the pentafluorophenyl adduct. The former approach was found to be more efficient.

Kvíčala *et al.*[29] reported the modification of a second-generation Hoveyda – Grubbs catalyst with perfluoroalkyl moieties to increase its fluorophilicity. The mesityl groups of NHC ligands and the benzylidene ligands were replaced with perfluoroalkyl groups (see the next Section). A perfluoroalkyl-containing moiety was introduced by the Heck reaction of iodine-containing diimine with perfluorooctylethylene followed by the closure of the imidazolium ring and the catalytic double-bond hydrogenation (Scheme 10).

Despite the presence of three polyfluoroalkyl substituents in complex **14**, the partition coefficient P_i(FBS) [the ratio of the concentrations of the substance in each phase of the fluorous biphasic system (FBS)] between perfluoro(methylcyclohexane) (PFMC) and toluene was as low as 0.16, which is too small for the catalyst regeneration. The catalytic activity of complex **14** in RCM of DEAMM was not higher than the activity of available **HG-II**. It is worth noting that attempts to coordinate a ruthenium atom to *N*,*N*′-dipolyfluoroalkyl NHC ligands lacking the mesityl moiety failed due apparently to low stability of sterically unhindered NHC complexes (Scheme 11).[30]

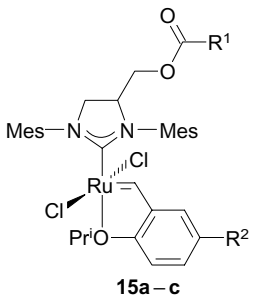
Scheme 11



R^1, R^2 = $(CH_2)_n(CF_2)_mCF_3$ (n = 1, 2; m = 6, 8);
$CH_2CF_2(OCF_2CF_2)_nOCF_3$ (n = 1, 2), X = I, OTf, ONf;
Tf = CF_3SO_2, Nf = n-$C_4F_9SO_2$

Grela and co-workers[31, 32] made efforts to synthesize fluorous metathesis catalysts. However, perfluoroalkyl-containing complexes **15a – c**[31] also showed low fluorophilicity.

Structures 15a – c



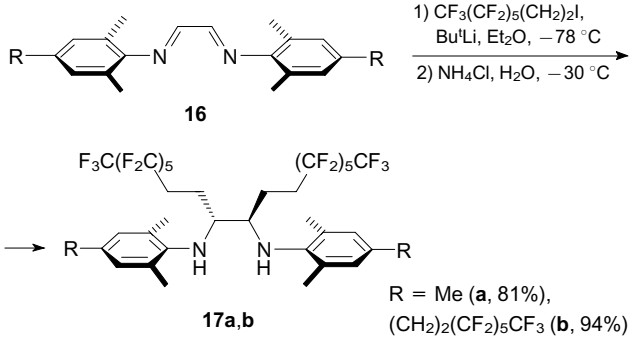
R^1 = $(CF_2)_7CF_3$: R^2 = H (**a**), $S(CF_2)_7CF_3$ (**b**);
R^1 = C_6F_5, R^2 = H (**c**)

Thus, complex **15a** was insoluble in PFMC, and complex **15b** formed only a stable emulsion.[31] Complexes **15** were not tested as catalysts because of low fluorophilicity.

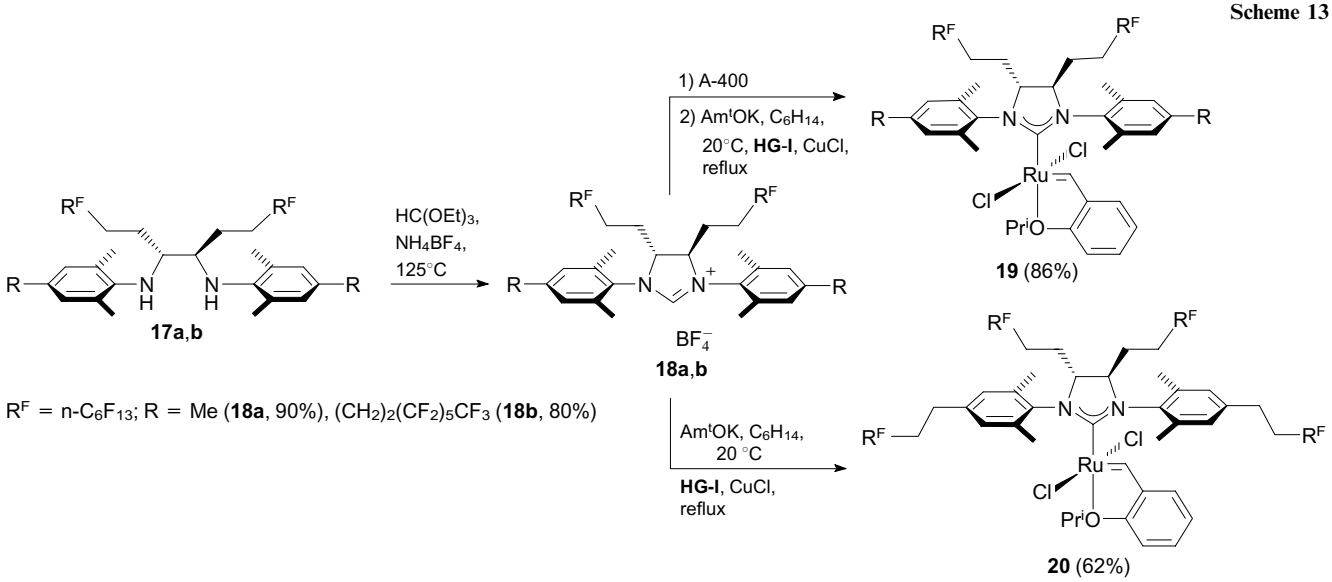
Another approach to increase the fluorophilicity was described by Kvíčala and co-workers[33] in 2015. They were the first to introduce a fluorine-containing substituent directly into the imidazolium ring using the reaction of 2-(perfluorohexyl)ethyllithium with diimines **16** (Scheme 12). The reaction resulted in the selective formation of the *threo* isomer (an enantiomeric mixture) in high yields.

Diamines **17a**,**b** were used to prepare a series of second-generation Hoveyda – Grubbs catalysts containing fluorine

Scheme 12



Scheme 13



R^F = n-C_6F_{13}; R = Me (**18a**, 90%), $(CH_2)_2(CF_2)_5CF_3$ (**18b**, 80%)

substituents in NHC ligands (**19** and **20**, Scheme 13). Catalyst **19** was synthesized *via* the replacement of tetrafluoroborate with a chloride ion on an Amberlite 400 (A-400) ion-exchange column.

The partition coefficient for catalyst **19** was low [P_i(FBS) = 0.055], while it was higher than unity for **20** [P_i(FBS) = 1.1]. Therefore, a heavy fluorous Grubbs catalyst bearing fluorinated substituents only in the NHC ligand was synthesized for the first time. Both complexes showed activity in RCM of DEAMM and DEDMM comparable with that of commercially available **HG-II**. It should be noted that complex **19** can be reused for five cycles with a slight loss of activity (from 86 to 81% within 1 h in RCM of DEAMM) in a mixture of dichloromethane and highly fluorinated ethers HFE-7100 (a mixture of methyl perfluorobutyl and methyl perfluoroisobutyl ethers).

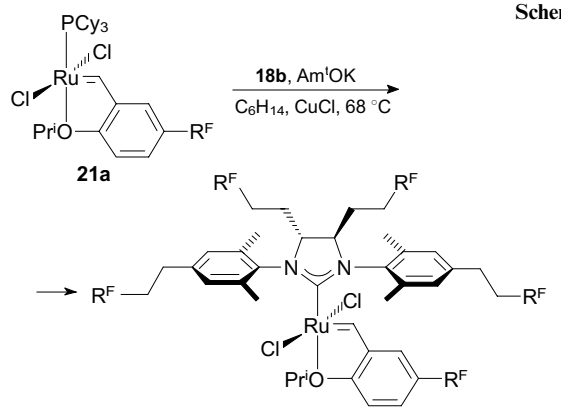
Recently, Kvíčala and co-workers[34] reported the synthesis of three new fluorous complexes **22** – **24** (Schemes 14, 15). Complex **22** was prepared by a standard procedure from the previously known ligand **18b** and appropriate **HG-I**-type catalyst **21a** (see Section 3, Scheme 53).

Complexes **23** and **24** (Scheme 15) were synthesized by a special procedure assuming that the $-CF_2CH_2-$ unit is a potential source of instability. The authors replaced the linear substituent $CF_3(CF_2)_5(CH_2)_2$ with the more stable tertiary moiety $CF_3(CF_2)_4CMe_2$, which was synthesized by the reaction of trimethylaluminium with a perfluorohexyl group.

Complex **22** exhibited high fluorophilicity [P_i(FBS) = 14], good activity in RCM of DEDAM and reusability (the yield of the metathesis product was 89% over five cycles). The fluorophilicity of complex **23** [P_i(FBS) = 0.5] was much lower; however, this complex showed high activity in RCM of sterically hindered DEDMM. Besides, Kvíčala and co-workers[34] described fluorous modifications of Grubbs catalysts bearing perfluoroalkyl substituents in arylidene ligands and X-type ligands. These complexes are considered in Sections 3 and 4, respectively.

In 2016, Togni and co-workers[35] reported the synthesis of a series of new catalysts **25a** – **f** containing an N-CF_3 group in the benzimidazole-based NHC ligand (Scheme 16).

Scheme 14



R^F = n-C_6F_{13}

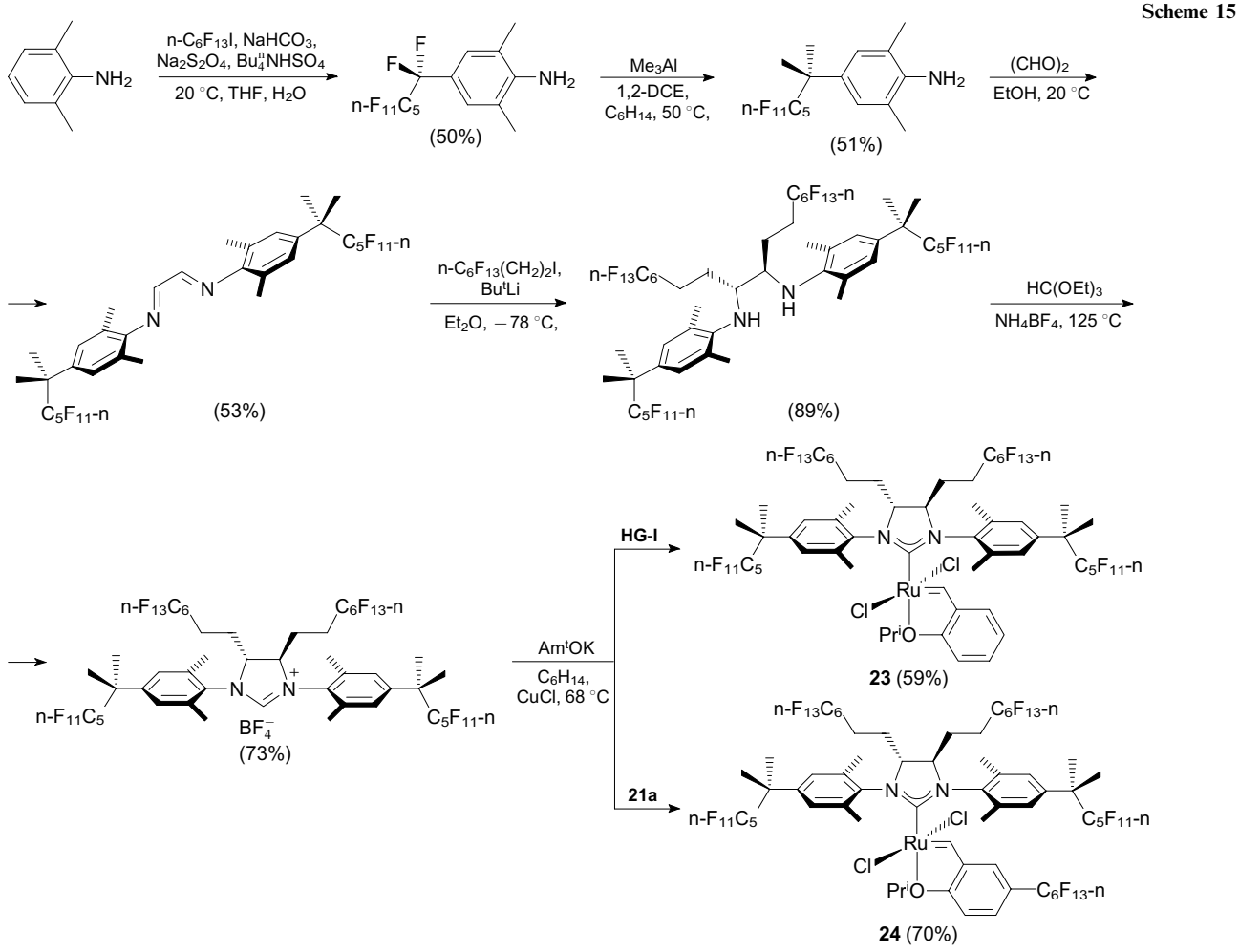
The synthesis of the corresponding benzimidazolium salts is based on the electrophilic arylation or alkylation of *N*-CF_3-benzimidazole. Target complexes **25a** – **f** were prepared by the deprotonation of the salts with NaHMDS *in situ* in toluene in the presence of a stoichiometric amount of **G-I** [$RuCl_2(=CHPh)(PCy_3)_2$].

All complexes were tested in RCM of DEDAM and in CM of allylbenzene with 1,4-diacetoxybut-2-ene. However, these complexes were found to be somewhat less active than the commercial catalyst **G-II**. On the other hand, these complexes showed excellent chemoselectivity (up to 97% alternating dyads) in alternating norbornene – cyclooctene copolymerization and unusually high selectivity (80 – 90%) to terminal olefins in the ethenolysis of ethyl oleate.

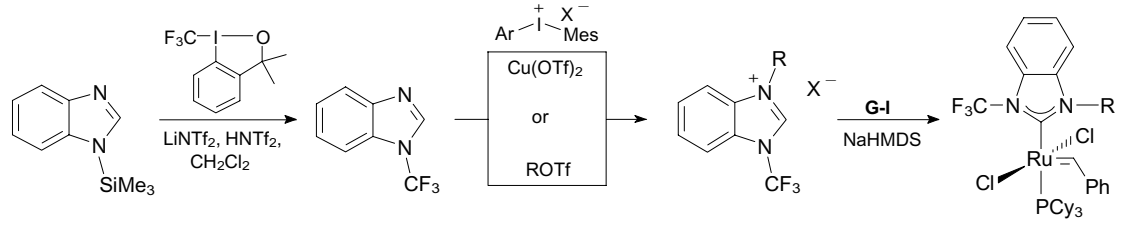
The authors suggested that the activity of the complexes can be associated with the electronic and steric effects of the *N*-CF_3 group in the NHC ligand, the more so that the X-ray diffraction data for complexes **25a**,**b** and **25d** provide evidence for the existence of a Ru – F interaction, which is similar to that found by Grubbs for **3b** (see Scheme 4) and is responsible for its high initiation rate and activity in RCM.

In the subsequent study,[36] these authors tested the activity of complexes **25a** – **f** and other ruthenium benzylidene complexes with different NHC ligands in the ethenolysis of cyclic alkenes, resulting in the selective formation of α,ω-dienes. It is worth noting that this metathesis trans-

Scheme 15



Scheme 16



X = BH_4, OTf; R = $C_6H_4CF_3$-4 (**25a**, 60%), $C_6H_3(CF_3)_2$-3,5 (**25b**, 33%), Bu^n (**25c**, 41%), Ph (**25d**, 46%), $C_6H_4NO_2$-4 (**25e**, 43%); Pr^i (**25f**, 41%)

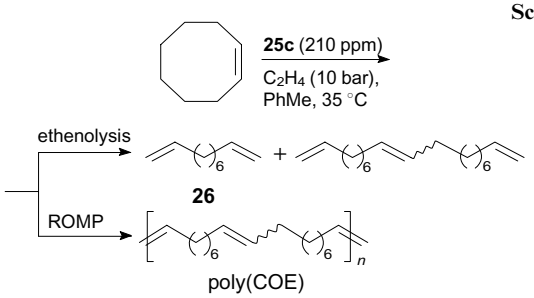
25a–f

formation involving ruthenium initiators is usually accompanied by the competing ROMP reaction, giving mainly polymeric products and low yields of the target terminal dienes. Among all the N-CF_3 systems under study, complex **25c** proved to be the most efficient in the ethenolysis of cyclooctene, providing a high conversion (96%) and good selectivity for the formation of ethenolysis product **26** (53%) (Scheme 17).

Moreover, **25c** did not show the formation of even trace amounts of polycyclooctene [poly(COE)] in ROMP in the absence of ethylene. On the contrary, the use of the commercial catalyst **G-II** resulted in the formation of poly(COE) as the major product, while the target product was obtained in 12% yield.

These authors also evaluated the activity of **25c** in the ethenolysis of challenging substrates, such as norbornene derivatives, which are the most popular monomers in

Scheme 17



ROMP due to high strain of their bicyclic structures. An efficient method was developed for the synthesis of valuable functionalized α,ω-dienes in yields higher than 70%.[36] Quantum chemical calculations were performed in order to account for the observed selectivity in the ethenolysis. These

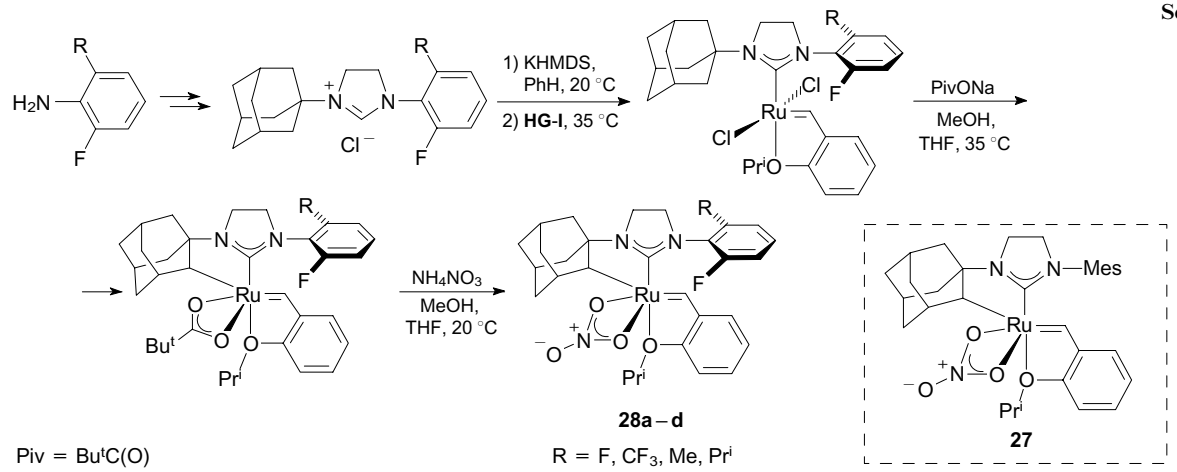
calculations confirmed the authors' hypothesis that the control of the selectivity is determined mainly by the π-acceptor properties of the unsymmetrical N-CF_3-containing NHC ligand, which increase the relative rate of degenerate metathesis and increase the selectivity of the ethenolysis of cyclic alkenes.

In general, the presence of an unsymmetrical NHC ligand bearing the strongly electron-withdrawing CF_3 group in complexes **25** and the Ru–F interaction are key factors providing high selectivity in the above-described transformations, which can be used to modulate the desired catalytic properties.

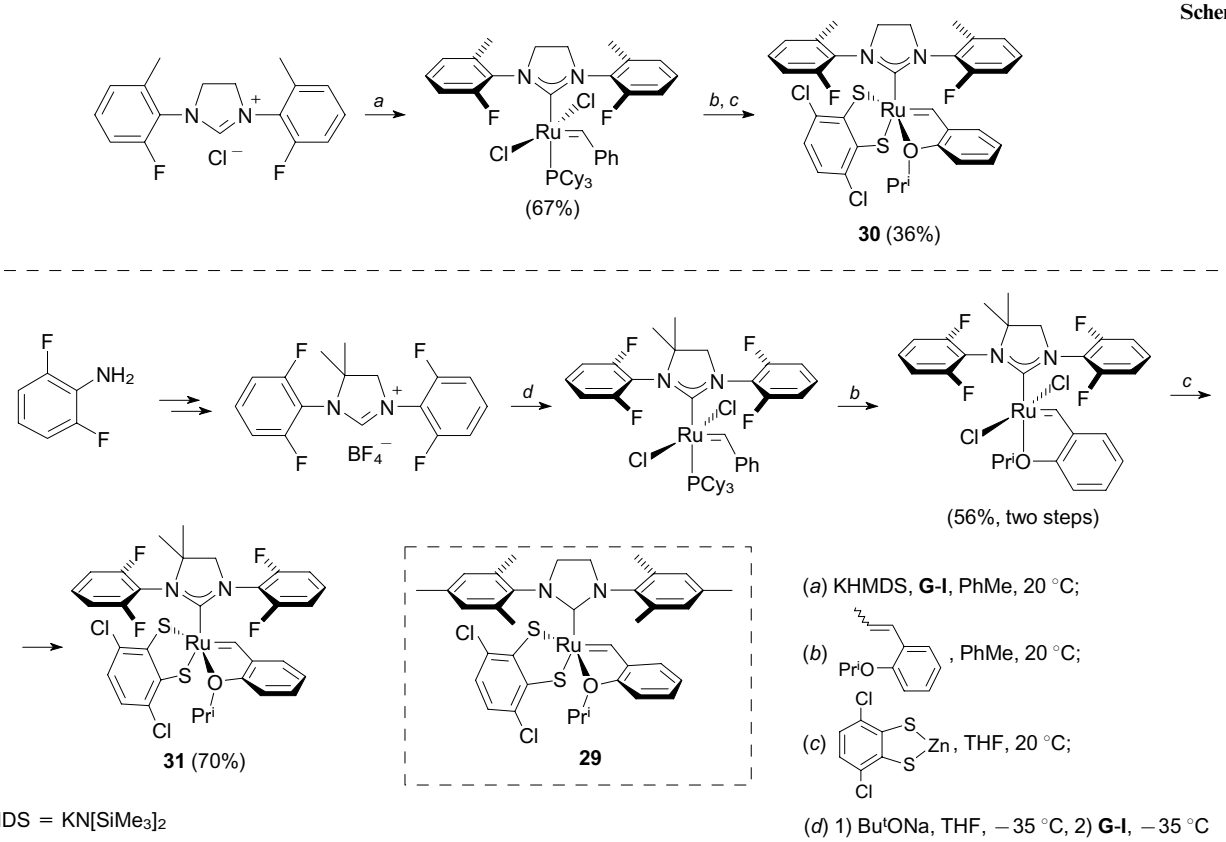
As mentioned above, the key step in the metathesis affords a metallacyclobutane intermediate, and the orientation of the substituents in the latter has a decisive effect on the stereochemical outcome of the reactions, particularly, of cross-metathesis reactions. The control of the geometry of this intermediate is an important condition for both stereoselective and stereoretentive olefin metathesis.[37,38] Recently, Endo and Grubbs[39] described the synthesis of fluorine-containing derivatives of *Z*-selective catalyst **28** (Scheme 18) with a chelating (through CH activation) adamantyl-based NHC ligand and catalyst **31**[40,41] with a dithiolate ligand (Scheme 19). All complexes were synthesized starting from appropriate commercially available fluorine-containing anilines. Adamantyl complexes **28a–d** were tested in cross-metathesis and homodimerization reactions, in which they showed high activity and *Z*-selectivity; however, these parameters are not better than those of non-fluorinated analogue **27**.[42]

The replacement of methyl groups in the *ortho* positions of *N*-aryl substituents in thiolate complex **29** with fluorine

Scheme 18



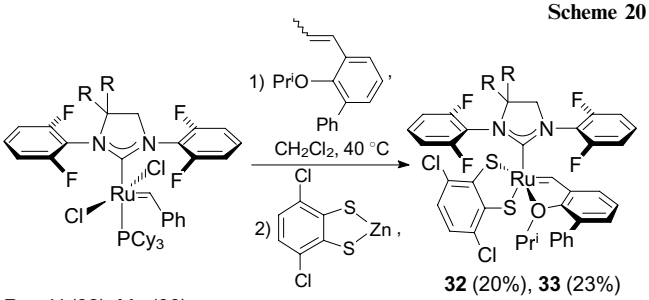
Scheme 19



atoms (catalysts **30** and **31**, see Scheme 19) led to an increase in the yields in the metathesis of *trans*-alkene substrates[43] and high *Z*- and *E*-selectivity in the synthesis of trisubstituted allyl alcohols and ethers in the cross-metathesis.[44] Dithiolate ligands in complexes **30** and **31** were introduced by the transmetalation of zinc dithiolate.

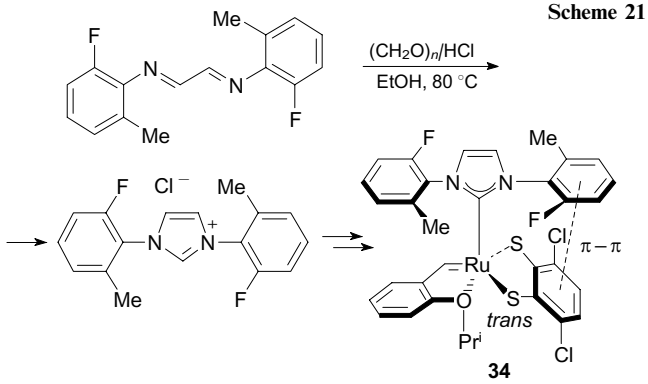
The introduction of an additional phenyl group into the benzylidene ligand of catalysts **30** and **31** (catalysts **32** and **33**, Scheme 20) resulted in an increase in the rates of formation of *Z* isomers.[45]

Scheme 20



In 2019, Hoveyda and co-workers[46] synthesized complex **34** (Scheme 21), an unsaturated analogue of **32**, and evaluated its catalytic activity in the *Z*-selective cross-metathesis in order to prepare (*Z*)-α,β-unsaturated esters, carboxylic acids and their amides highly valuable in medicinal chemistry.

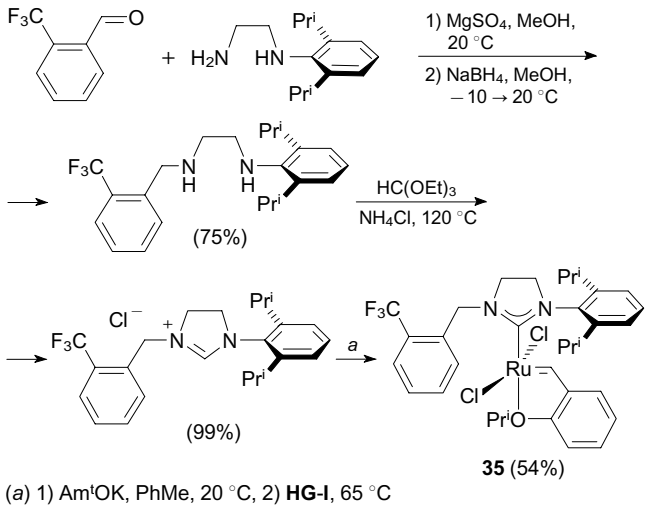
Scheme 21



Complex **34** proved to have much higher catalytic activity and *Z*-selectivity than complex **32**, providing the *Z*/*E* isomer ratios >98 : 2. Based on the calculated and experimental data, the authors concluded that the observed activity of **34** is associated with a π–π interaction between the *N*-fluoroaryl substituent and the catecholthiolate ligand due to a shortening of the Ru–C^{NHC} and Ru–S(*trans*) bonds. Apparently, this provides the optimal stereochemical configuration of the substituents in the key ruthenacyclobutane intermediate.

Grela and co-workers[47] reported the synthesis of complex **35** containing a trifluoromethyl group in the NHC ligand (Scheme 22). Complex **35** was prepared in three steps from commercially available *N*-(2,6-diisopropylphenyl)-ethane-1,2-diamine and *o*-(trifluoromethyl)benzaldehyde. Despite high stability in solution, complex **35** was found to be somewhat less active in benchmark RCM reactions than structurally similar non-fluorinated catalysts.

Scheme 22



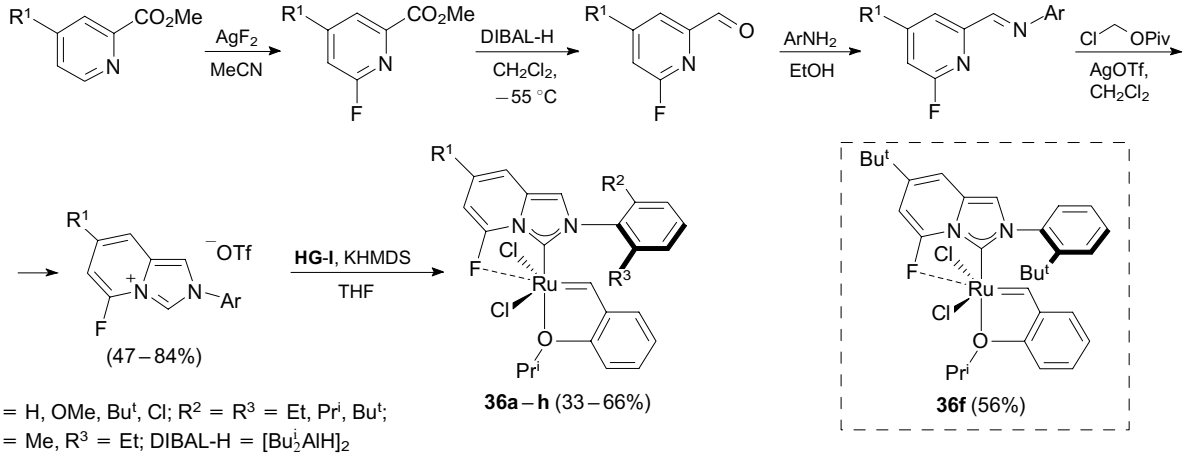
A series of ruthenium-based complexes **36** bearing unsymmetrical fluorinated imidazo[1,5-a]pyridin-3-ylidene ligands were recently synthesized and evaluated in the ethenolysis of methyl oleate.[48] The synthesis of the imidazopyridinium precursor of the NHC ligand includes: 1) the selective Hartwig's fluorination of pyridine-2-carboxylate;[49] 2) the reduction of carboxylate to aldehyde followed by the reaction with anilines giving the corresponding imines and 3) the cyclization of the latter with chloromethyl pivalate and silver triflate to form the desired NHC precursors (Scheme 23). The target ruthenium carbene complexes were synthesized under standard ligand-exchange conditions using the first-generation Grubbs–Hoveyda catalyst **HG-I**.

These authors studied the effect of the NHC ligand structure on the catalytic activity, selectivity and thermal stability of the catalysts. According to the X-ray diffraction, the complexes are stabilized in the solid state by a Ru–F interaction. Complex **36f** containing the *ortho*-(*tert*-butyl)-phenyl substituent at the nitrogen atom and the σ-donor Bu^t group in the pyridine moiety was found to be the most efficient catalyst. It showed a high turnover number (TON ⩽ 6700) and high selectivity (up to 86%) to the formation of terminal olefins in the ethenolysis of methyl oleate. This catalyst also proved to be very efficient in the most challenging transformations, such as the ethenolysis of *cis*-cyclooctene and the natural carotenoid squalene.

Osipov and co-workers[50, 51] developed methods for the introduction of the hexafluoroisopropylalkoxy group in the *ortho* position of one of the *N*-aryl substituents in the NHC ligand in order to increase the stability and selectivity of unsymmetrical ruthenium complexes. At first it was expected that the presence of a bulky fluorine-containing group bearing an anionic centre in the vicinity of the ruthenium atom can enhance the stability of the complex through an additional Ru···O coordination, and the presence of two trifluoromethyl groups can improve solubility in industrially important monomers or alkanes.

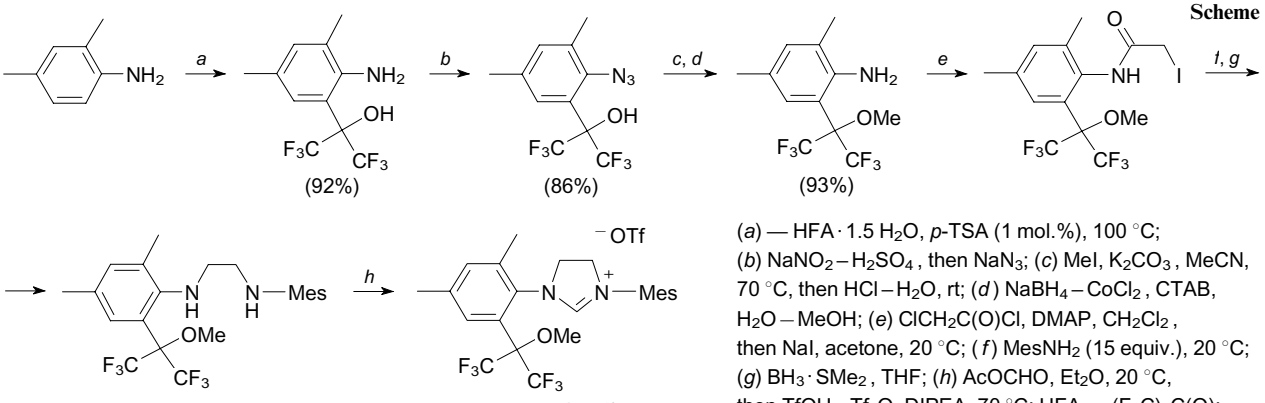
First, diamines **37** were prepared by conventional methods of organic synthesis, and their subsequent heterocyclization to desired imidazolinium salts **38** (see Ref. 50) was successful only after the selective formylation of the sterically more accessible *N*-arylamino group followed by the

Scheme 23



R^1 = H, OMe, Bu^t, Cl; R^2 = R^3 = Et, Pr^i, Bu^t;
R^2 = Me, R^3 = Et; DIBAL-H = $[Bu^i_2AlH]_2$

Scheme 24

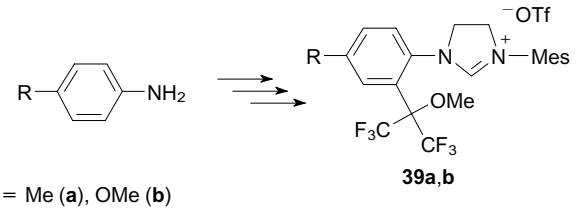


(*a*) — HFA · 1.5 H_2O, *p*-TSA (1 mol.%), 100 °C; (*b*) $NaNO_2 – H_2SO_4$, then NaN_3; (*c*) MeI, K_2CO_3, MeCN, 70 °C, then $HCl – H_2O$, rt; (*d*) $NaBH_4 – CoCl_2$, CTAB, H_2O – MeOH; (*e*) $ClCH_2C(O)Cl$, DMAP, CH_2Cl_2, then NaI, acetone, 20 °C; (*f*) $MesNH_2$ (15 equiv.), 20 °C; (*g*) $BH_3 \cdot SMe_2$, THF; (*h*) AcOCHO, Et_2O, 20 °C, then TfOH – Tf_2O, DIPEA, 70 °C; HFA = $(F_3C)_2C(O)$; *p*-TSA = $MeC_6H_4SO_3H$-4; DIPEA = Pr$^i_2$EtN; DMAP = 4-Me_2NPy; CTAB = (n-$C_{16}H_{33}$)NMe_3Br

intramolecular Vilsmeier – Haack cyclization (Scheme 24, step *h*).

This method was applicable to the synthesis of salts **39a**,**b**,[50] lacking the methyl group at the *ortho* position, starting from *para*-toluidine and *para*-anisidine (Scheme 25).

Scheme 25



R = Me (**a**), OMe (**b**)

Salts **38** and **39a**,**b** were used to synthesize ruthenium complexes **40** and **41** (Scheme 26). Appropriate NHC ligands were generated *in situ* using KHMDS or Am^{t}OK in toluene in the presence of first-generation Grubbs (**G-I**) and Hoveyda – Grubbs (**HG-I**) complexes to accomplish the ligand exchange.

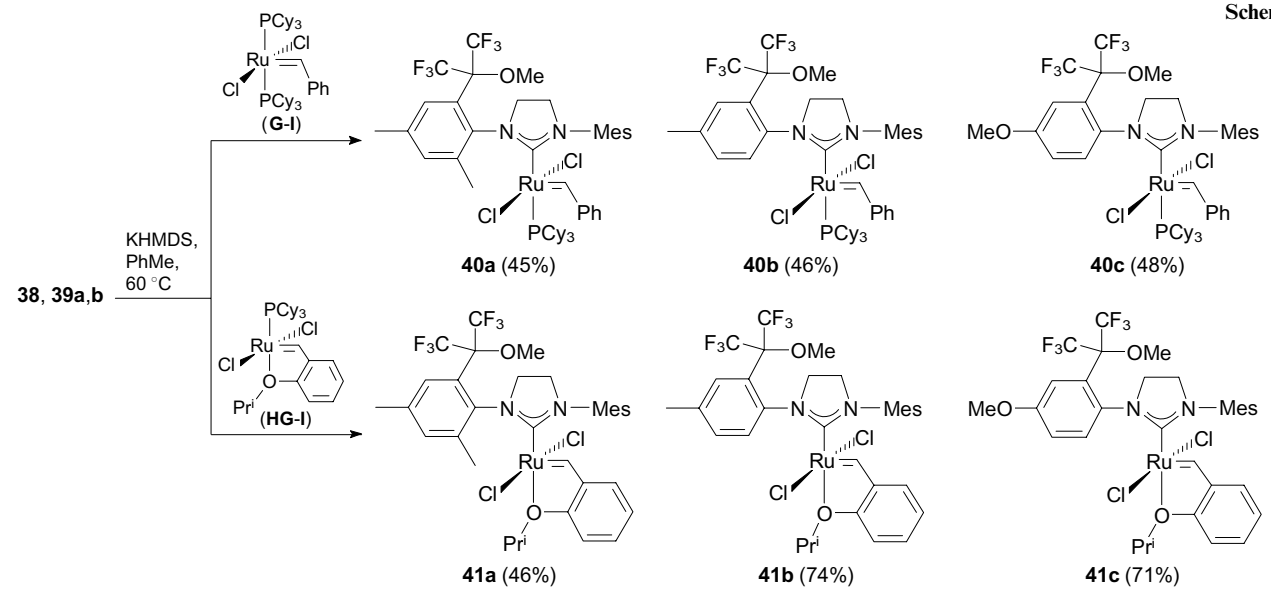
Compounds **40** and **41** were evaluated for catalytic activity in RCM and CM reactions. It was found that the activity of these compounds is comparable with and sometimes even higher than that of the catalysts **G-II** and **HG-II**.[50,51] For instance, fluoroalkyl-containing Hoveyda – Grubbs-type complexes **41b**,**c** bearing a mono-*ortho*-aryl-substituted NHC ligand exhibit unusually high initiation rate in the cross-metathesis of 1,3-diacetoxybut-2-ene with allylbenzene, resulting in the conversion more than 10% higher than that achieved with **HG-II**.[51]

This research group also developed an efficient approach to the synthesis of similar ruthenium complexes **45** and **46** bearing unsaturated *N*,*N*′-diarylimidazolyl-2-ylidene NHC ligands (see Scheme 28).[52] The method for the preparation of NHC precursors is based on an original strategy for the synthesis of sterically hindered imidazolium salts[53] involving the heterocyclic interconversion of oxazolinium salts on treatment with substituted anilines. This strategy is also applicable to fluorine-substituted arylamines containing two nucleophilic centres. Thus, the reaction of Fürstner's oxazolinium salt with *ortho*-hexafluoroisopropoxyaniline resulted in the selective formation of desired hydroxy-containing imidazolium salt **42** (Scheme 27); this reaction also afforded an insignificant amount of tricyclic compound **43**, which is apparently due to the heterocyclization at the hydroxy group. In pure form, salt **42** can be isolated by a single crystallization from a chloroform – diethyl ether mixture in good yields even at high loads.[54]

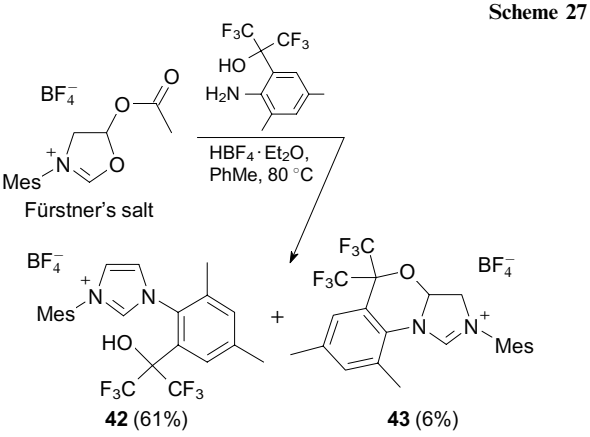
The free hydroxy group in compound **42** can be directly functionalized *via O*-alkylation in the presence of potassium carbonate giving salts **44a** – **c** in high yields. The latter proved to be suitable NHC precursors in the synthesis of complexes **45** and **46** (Scheme 28).

Grubbs-type complexes **45a** – **c** were found to be much more active in RCM reactions of diallyl- and allyl methallyl

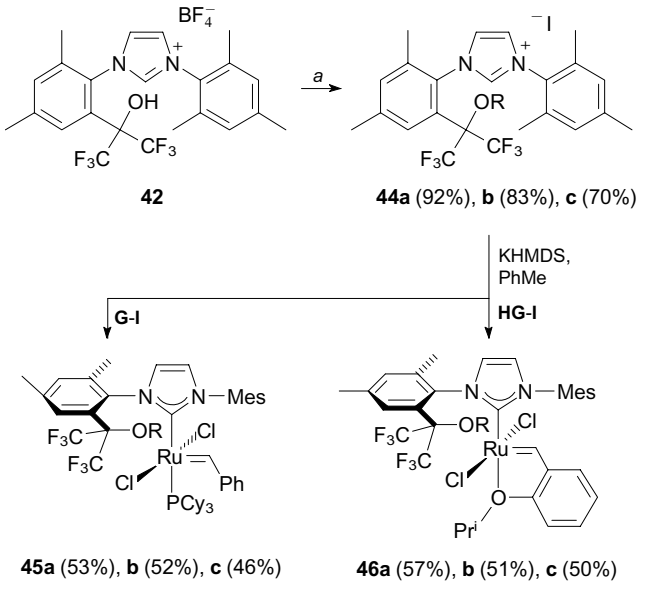
Scheme 26



Scheme 27



Scheme 28



(*a*) RI, K_2CO_3, MeCN, 20 °C; **44** – **46**: R = Me (**a**), Et (**b**), Am^i (**c**)

malonates [52] compared to non-fluorinated unsaturated symmetrical analogue of the complex **G-II**.

The reaction of Fürstner's oxazolinium salt with fluorinated binucleophilic aniline affords OH-substituted imidazolium salt **42** as the target product along with unusual by-product **43** (see Scheme 27). Due to the rigid tricyclic structure, the latter compound is of interest for the preparation and evaluation of catalytic activity of the corresponding ruthenium complexes. For this purpose, a route to the selective synthesis of these compounds as triflate salts was specially developed. The synthetic sequences included the reaction of fluorine-containing anilines with readily accessible *N*-aryl dialdehydes [53, 55 – 58] giving the corresponding benzoxazines. The subsequent intramolecular heterocyclization *via* activation of the formyl group under the conditions found for the synthesis of salts **38** and **39** (see Schemes 24 and 25) gave desired tricyclic products **47a** – **c** in high yields (Scheme 29).

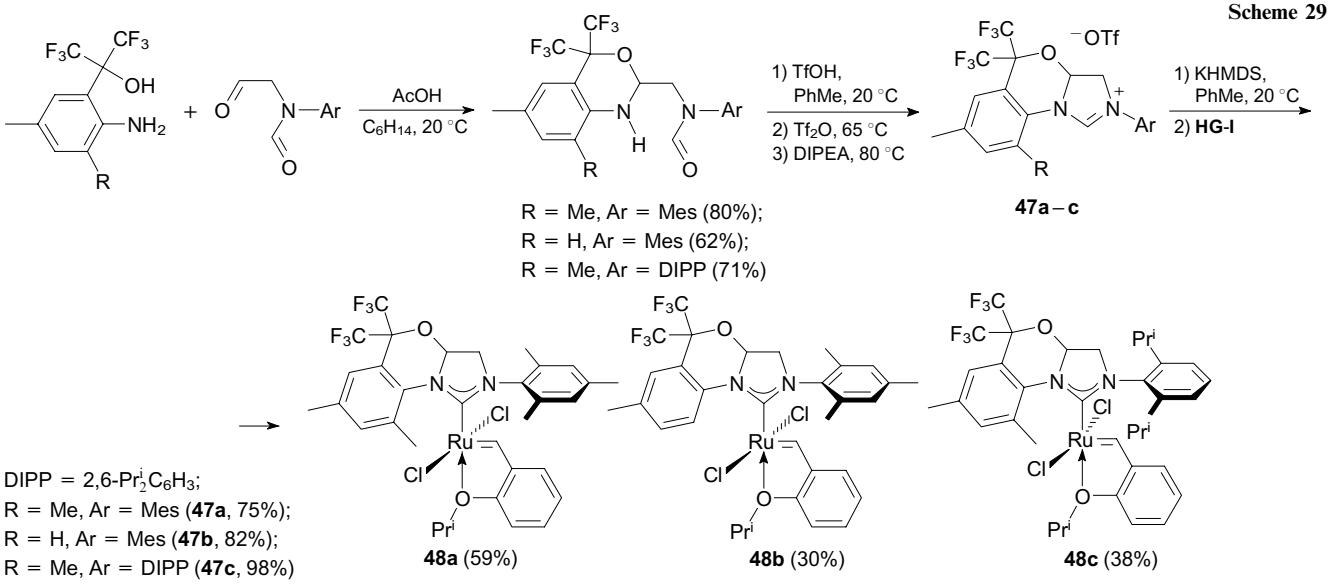
Stable ruthenium complexes **48a** – **c** bearing sterically rigid NHC ligands were synthesized *via* a standard route from salts **47a** – **c** and evaluated for catalytic activity. It was found that allylbenzene complexes **48a** – **c** caused almost no isomerization in the self-metathesis (SM) and provided high yields of the target self-metathesis product and excellent selectivity.[54] Apparently, the observed selectivity is attributed to the rigid structure of the NHC ligand, resulting in the close arrangement of the *ortho* substituent of the aromatic moiety and the ruthenium centre, which interferes with the isomerization *via* the most probable hydride mechanism.[59 – 61]

In order to design new metathesis catalysts capable of inducing *Z*/*E* selectivity, complexes **48a**,**b** were used in the synthesis of monothiolate derivatives **49a**,**b** (Scheme 30). However, despite moderate activity in RCM and CM reactions, these compounds did not induce significant *Z*-selectivity in the self-metathesis of allylbenzene.[62]

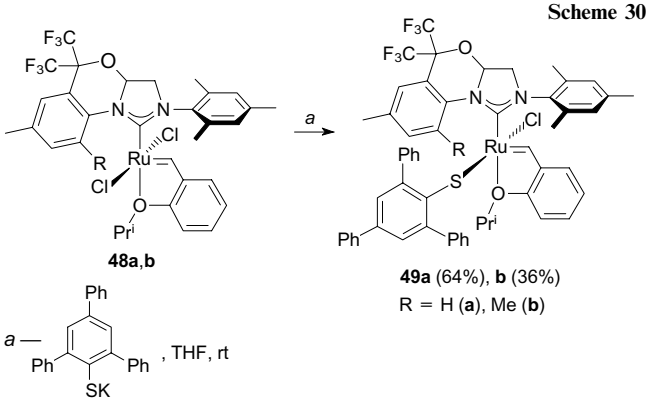
3. Fluorine in arylidene ligands

The first **G-I**-type catalyst bearing a fluorinated arylidene ligand **50** was synthesized in 1996 by Grubbs and co-workers [63] from the diazo derivative of commercially available *p*-fluorobenzaldehyde (Scheme 31). The presence of a fluo-

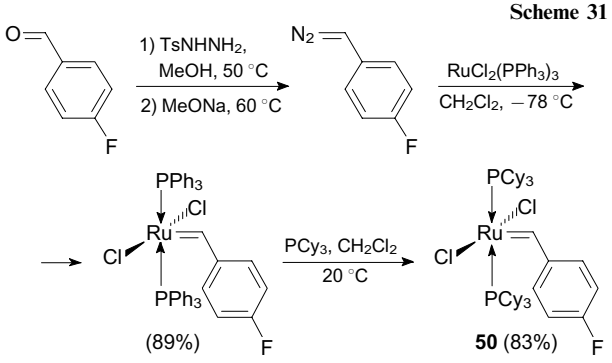
Scheme 29



Scheme 30



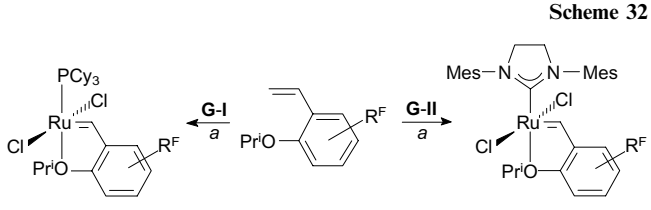
Scheme 31



rine atom at the *para* position of the benzylidene ligand was found to have a weak influence on the kinetic profile of the catalyzed reaction.

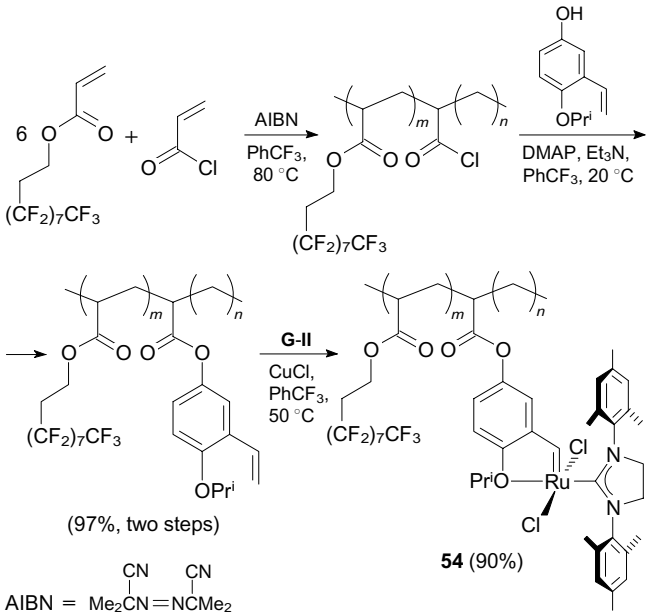
Blechert and co-workers [64] synthesized catalysts **51** – **53** bearing a fluorine-substituted arylidene ligand by the replacement of styrene ligands in complexes **G-I** and **G-II** with the corresponding fluorinated styrene derivatives (Scheme 32). The phosphine-containing catalysts (**51a**, **52a** and **53a**) exhibited higher activity compared to **HG-I**, whereas the phosphine-free complexes (**51b**, **52b** and **53b**) showed activity very similar to that of **HG-II**.

Scheme 32

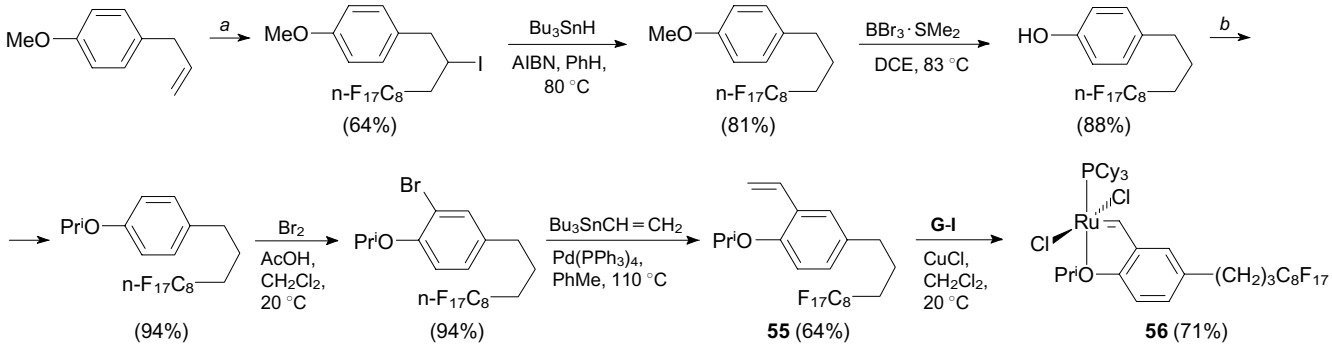


Yao and Zhang [65] described a Hoveyda – Grubbs catalyst immobilized *via* an arylidene ligand on a perfluoroalkyl-containing polymer. The polymer was synthesized from commercially available heptadecafluorodecyl acrylate (Scheme 33). The synthesized catalyst **54** not only showed

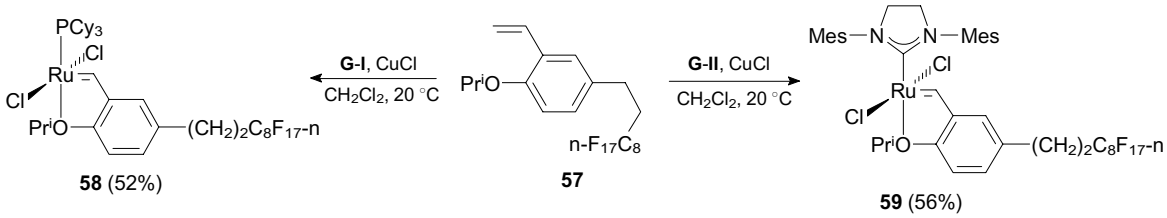
Scheme 33



Scheme 34



(*a*) $CF_3(CF_2)_7I$, Me_3Al, $Pd(PPh_3)_4$, CH_2Cl_2, 20 °C; (*b*) 1) NaH, THF, 0 °C; 2) Pr^iBr, DMF – THF, 20 °C



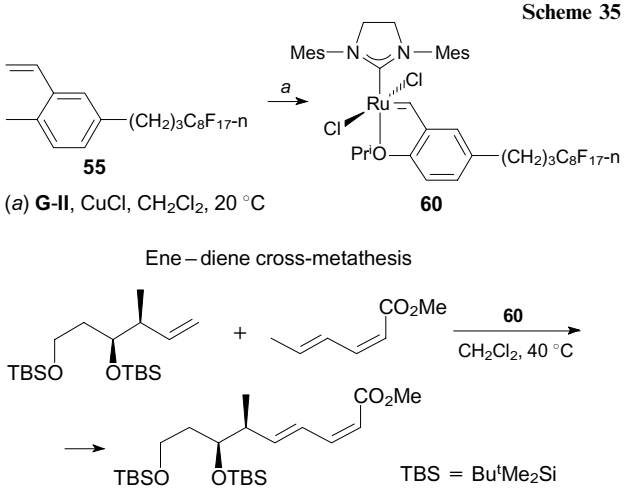
excellent solubility in perfluorohexane and trifluoromethylbenzene and high activity in RCM with a number of substrates but also exhibited high recyclability. For example, high activity of this catalyst in RCM of *N*,*N*-diallyltosylamide was maintained even after 20 cycles.

In 2005, Matsugi and Curran [66] described light fluorous versions of first- and second-generation Hoveyda-type catalysts. Styrene **55** was synthesized by the trimethylaluminium-induced addition of perfluoro-n-octyl iodide at the double bond followed by the dehalogenation with tributyltin hydride (Scheme 34).[67] Complexes **58** and **59** were synthesized from commercially available styrene **57**. Catalysts **56**, **58** and **59** were evaluated for activity in RCM reactions. The complexes exhibited activity similar to that of their non-fluorinated analogues **HG-I** and **HG-II** and showed good recyclability.

Compound **60** homologous to complex **56** was prepared in a similar way, and its activity was evaluated in the ene–diene cross-metathesis (Scheme 35).[68] Complex **60** retained activity similar to that of **HG-II** after three reuses. The catalyst was recovered from the reaction mixture by fluorous solid-phase extraction (F-SPE).

Besides, complex **60** was used in the intramolecular metathesis to prepare a series of heterocyclic compounds,

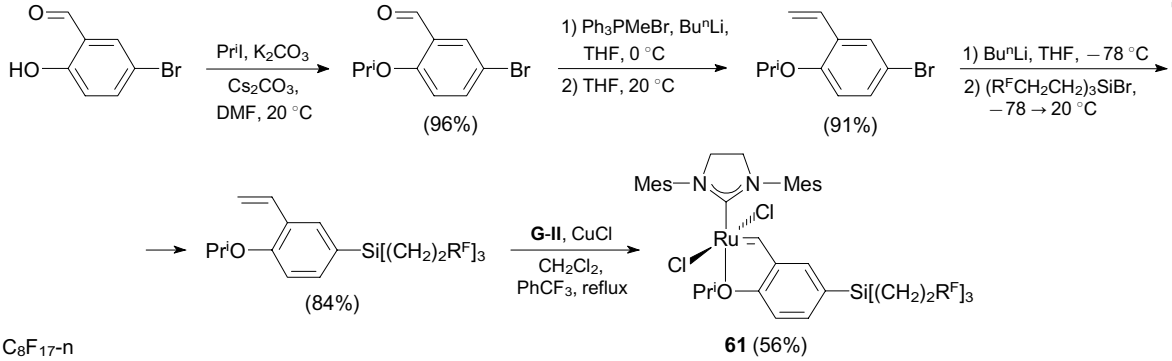
Scheme 35



including macrocycles, followed by the application of F-SPE for the catalyst regeneration.[69,70]

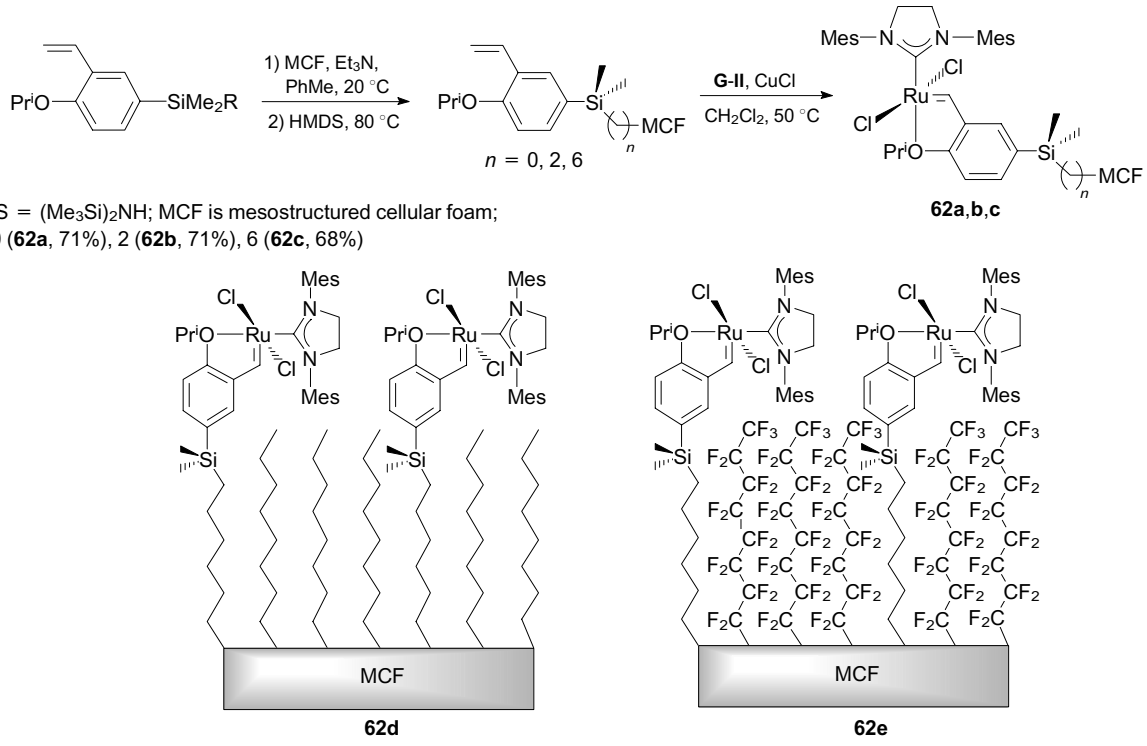
Michalek and Bannwarth [71] developed a method for the synthesis of an **HG-II**-type complex (**61**) containing a perfluorooctyl group for non-covalent immobilization on fluorous silica gel (Scheme 36). The catalytic activity of the

Scheme 36



R^F = C_8F_{17}-n

Scheme 37



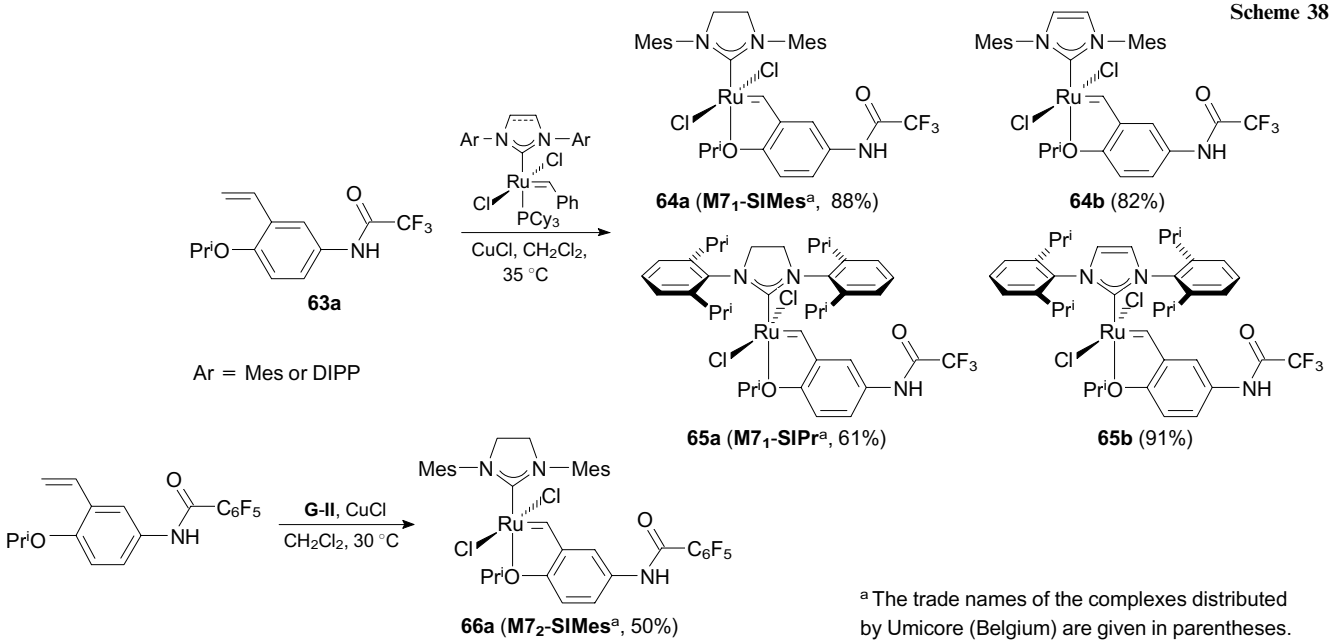
HMDS = $(Me_3Si)_2NH$; MCF is mesostructured cellular foam;
n = 0 (**62a**, 71%), 2 (**62b**, 71%), 6 (**62c**, 68%)

synthesized catalyst was evaluated in different RCM reactions. The immobilization of catalyst **61** on an amphiphilic polymer conetwork (APCN) made it possible to perform RCM in an aqueous medium.[72] The appropriate perfluoroalkyl-containing styrene was synthesized using trialkylbromosilane.[73]

The covalent immobilization of a Hoveyda – Grubbs-type catalyst on mesostructured cellular foam (MCF) containing perfluoroalkyl groups (**62e**, Scheme 37) as the fluorous solid support was performed through silyl linkages of arylidene ligands. Immobilized catalysts **62a** – **e** showed good recyclability in RCM reactions.[74]

A series of trifluoroacetamide-containing Hoveyda – Grubbs complexes **64** and **65** were synthesized by Nolan's and Mauduit's groups (Scheme 38).[75,76] Starting styrene **63a** was prepared by the acylation of 4-isopropoxy-3-vinylaniline with trifluoroacetic acid. Catalysts **64a**,**b** and **65a**,**b** exhibited high activity in a wide range of metathesis transformations (RCM, RCEYM and CM), including large-scale reactions with alkene substrates. Pentafluorophenyl-containing complex **66a** was found to be less active than **64a** in RCM of DEDAM.[77] In all cases, the $NHC(O)CF_3$ group had a beneficial effect on the catalytic activity of the complexes. Catalysts **65** with 2,6-diisopropylphenyl-containing ligands proved to be more efficient with sterically

Scheme 38

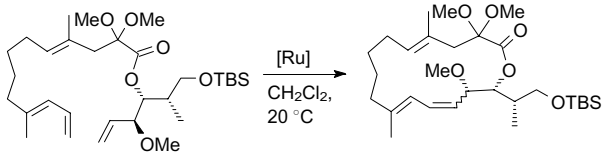


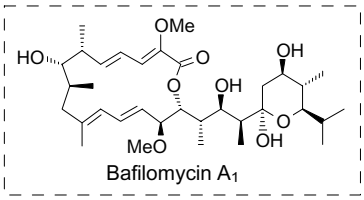
[a] The trade names of the complexes distributed by Umicore (Belgium) are given in parentheses.

non-hindered substrates. Besides, the purification of reaction mixtures by silica gel column chromatography resulted in very low residual ruthenium contamination in the reaction products (less than 2.5 ppm). Such high degree of purification was possible due to the formation of hydrogen bonds between oxygen atoms of trifluoroacetamide groups and silica gel.

Subsequently, the activity of catalysts **64a** and **65a** was tested in different RCM,[78,79] CM[80,81] and ethenolysis reactions.[82,32] In all cases, these catalysts were found to be more active than their non-fluorinated analogues. They also showed satisfactory results in the metathesis macrocyclization for the construction of the 16-membered bafilomycin macrolactone core on the model substrate (Table 2).[83]

Table 2. Synthesis of bafilomycin-type macrolactone and the results of catalysis.

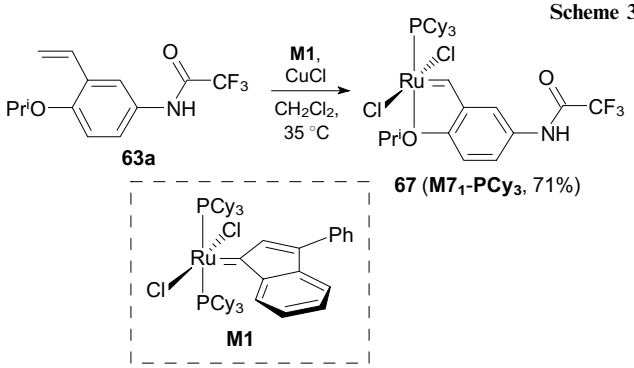




[Ru]	mol.%	Conversion (%)	*Z*/*E*	Yield (%)
G-I	20	~10	1 : 1	–
G-I	20 + 20	>90	7 : 3	–
64a	5	~35	7 : 3	–
65a	5	~35	7 : 3	–
67	5	~35	7 : 3	–
67	10 + 10	>90	7 : 3	48%

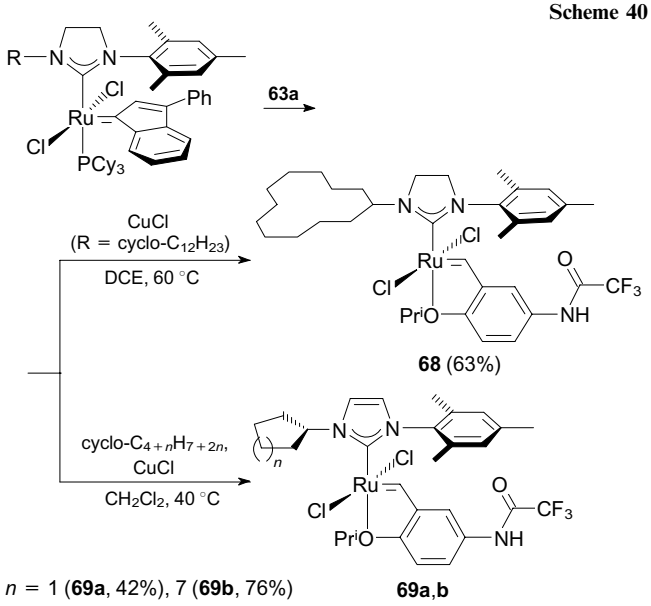
However, the best results were achieved using fluorine-containing first-generation catalyst **67**, which was synthesized from the commercially available indenylidene catalyst **M1** (Scheme 39).[83]

Scheme 39



Catalysts **68** and **69a**,**b** bearing a trifluoroacetamide-substituted benzylidene ligand and a cycloalkyl-substituted NHC moiety were synthesized in 2014 (Scheme 40). However, these catalysts showed lower stability and exhibited lower activity in RCM of DEDMM compared to **64a**,**b**[84] (see Scheme 38).

Scheme 40

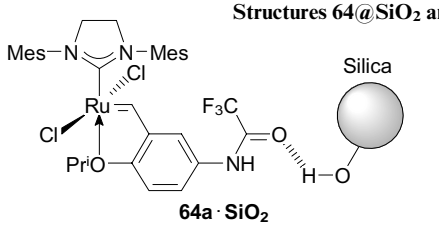


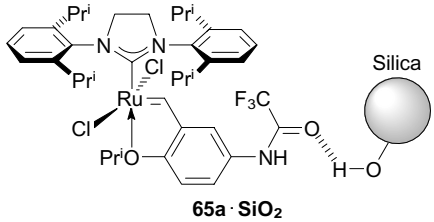
The synthesis of heterogeneous analogues of catalyst **64a** was described in several publications in 2014–2016. For instance, complex **70** containing the anthracenyl group was immobilized on modified silica *via* the formation of a charge-transfer complex, in which the anthracenyl group served as a donor and the electron-deficient 2,4,7-trinitrofluoren-9-one moiety acted as an acceptor (Scheme 41).[85] The immobilized catalyst **70**@SiO_2 retained high activity in RCM of DEDAM after four reuses, and it was also tested for recyclability in different types of metathesis reactions (RCM, RCEYM, CM), where it showed high reaction yields and selectivity.

The ability to form hydrogen bonds between trifluoroacetamide-containing complexes and silica gel was employed to prepare heterogeneous systems. Compounds **64a** and **65a** were immobilized on silica without surface pretreatment.[86,87] Immobilized catalytic systems **64a**@SiO_2 and **65a**@SiO_2 showed high activity in RCM, CM and RCEYM reactions in flow conditions. A significant decrease in the catalytic activity was observed after the fifth cycle.

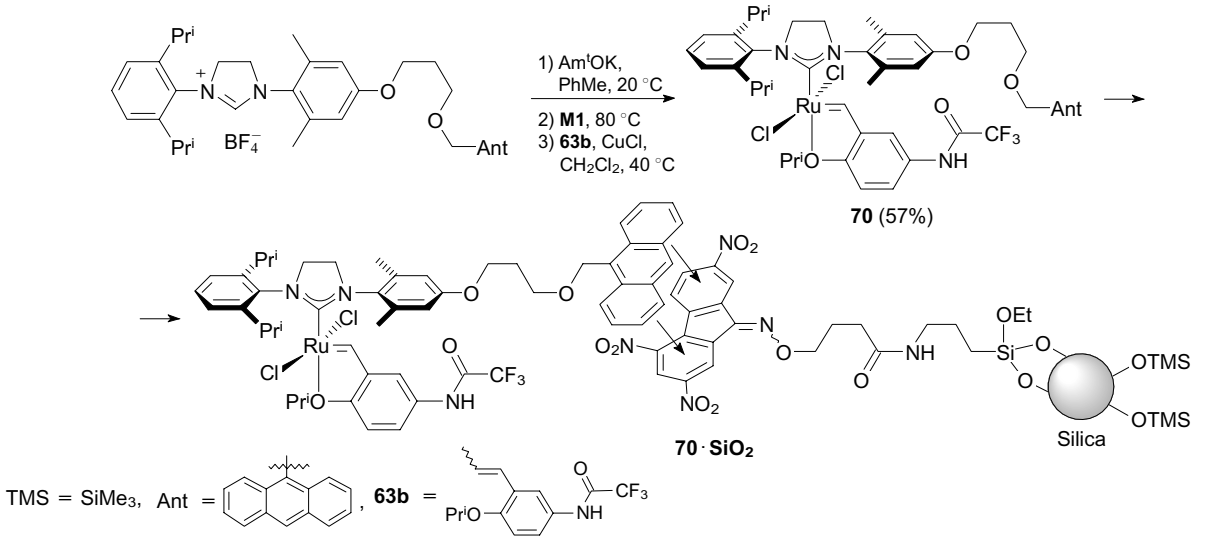
Recently, the immobilization of catalysts bearing the trifluoroacetamide-based styrene ligand onto reduced graphene oxide (RGO) (Scheme 42) was reported.[88] The cata-

Structures 64@SiO_2 and 65@SiO_2

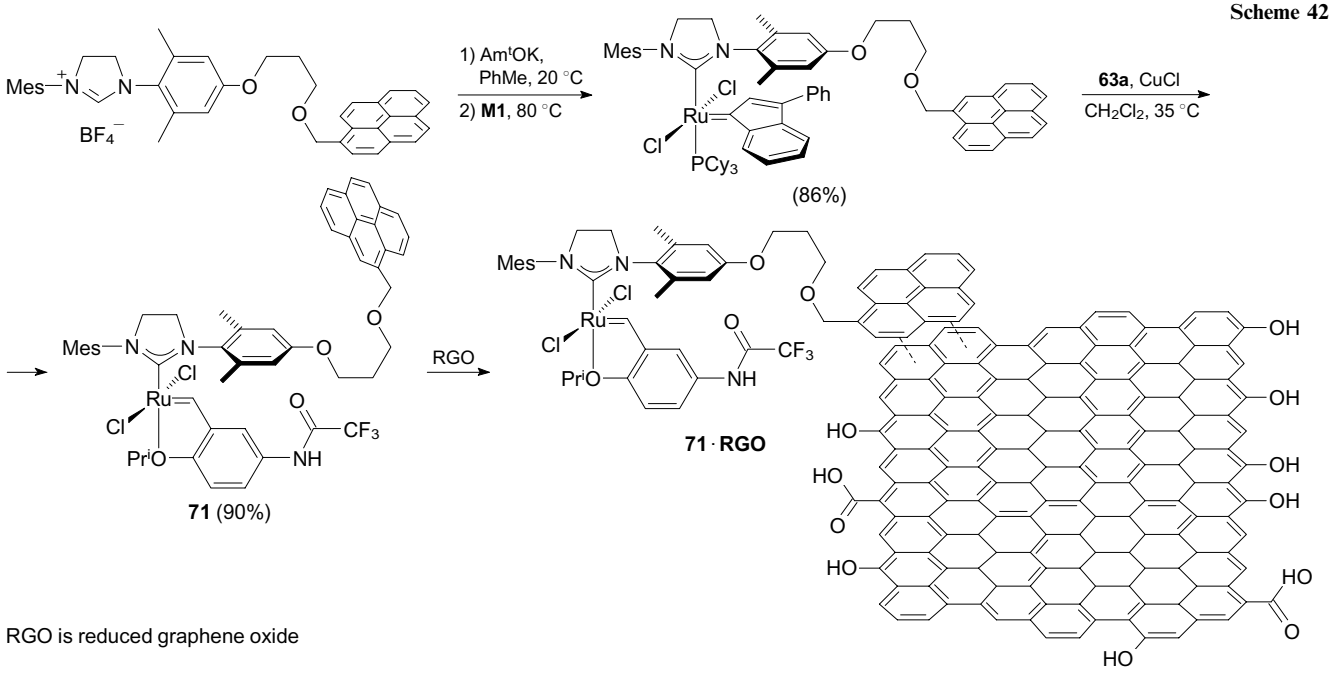




Scheme 41



Scheme 42



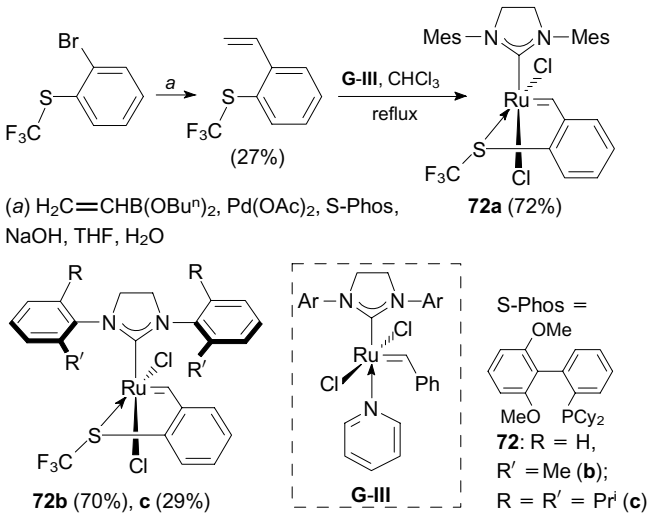
lyst **71**@RGO proved to be active in RCM of DEDAM, but a significant loss of activity was already observed after the second cycle.

In the past decade, several latent fluorine-containing metathesis catalysts were described. Lemcoff and co-workers[89,90] synthesized complexes **72a**–**c** bearing the benzylidene ligand with the chelating trifluoromethylthio group in two steps starting from commercially available 2-bromophenyl trifluoromethyl sulfide (Scheme 43).

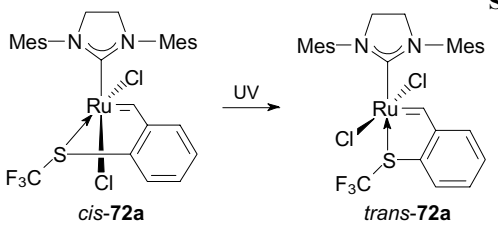
These complexes exist in the *cis*-dichloro configuration, which is inactive under standard conditions in RCM, CM and ROMP reactions; however, they isomerize to the active *trans* conformation under UV irradiation or heating (Scheme 44).

Complexes **72b**,**c** containing the *ortho*-tolyl and 2,5-diisopropylphenyl substituents, respectively, in the NHC ligand[91] were tested in RCM and CM reactions. Complex **72b** showed high activity towards sterically hindered DEDMM or *N*,*N*-dimethallyltosylamide under thermal or

Scheme 43



Scheme 44



UV activation conditions. Complex **72c** proved to be the most active towards unhindered substrates.

Besides, Lemcoff and co-workers described the application of complexes **72a** in the two-step photochemical synthesis of coumarins,[92] butenolides and levulinates[93] (Scheme 45). The UV-activated cross-metathesis was a key step in all cases.

The introduction of electron-withdrawing substituents in the *para* position of the styrene ligand leads to a significant decrease in the donor properties of the oxygen atom in catalysts **HG-II**, resulting in an increase in the initiation rate of the complex due to acceleration of the ligand dissociation. In order to further improve the properties of the leaving group, electron-withdrawing substituents can also be introduced in the *ortho*-ester function of styrene. Generally, this modification leads to a significant increase in the conversion of RCM, the reaction rate and the product yields with a minimum catalyst load.

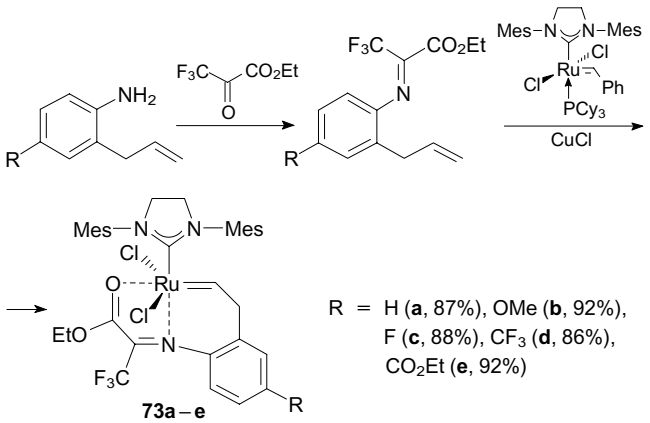
Taking into account these facts, Duan *et al.*[94] designed catalytic systems based on trifluoropyruvate imines, where the chelation occurs through double coordination with imine nitrogen and ester oxygen atoms (Scheme 46). The double coordination was established by X-ray diffraction.

Complexes **73d**,**e** containing additional electron-withdrawing groups (R = CF_3, CO_2Et) in the *para* position of the styrene ligand were found to have the highest activity and showed high conversion, initiation rates and yields in RCM reactions with a wide range of functionalized substrates.

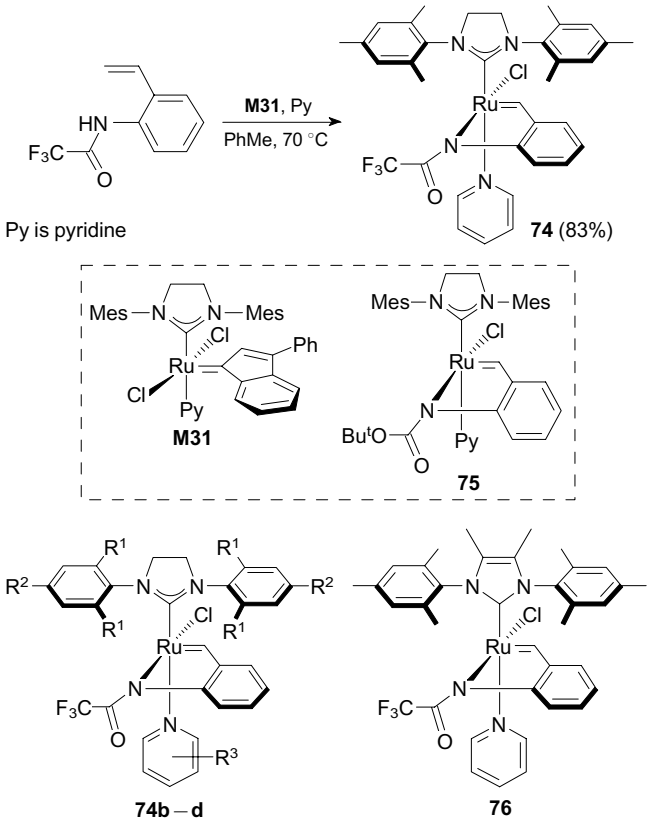
Grela and co-workers[95] synthesized catalyst **74** with a covalent chelating trifluoroamide ligand by the replacement of the ligand in the complex **M31** (Umicore) in the presence of pyridine (Scheme 47). Catalyst **74** was tested in RCM of DEDAM and DEAMM. Its activity was low in neutral medium, but a significant increase in the activity was observed upon activation with an ethereal solution of HCl. Fluorine-containing catalyst **74** was found to be more active in RCM of DEDAM compared to its non-fluorinated analogue **75**.

Complexes **74b**–**d** and **76** were prepared in a similar way. Upon activation with HCl or Me_3SiCl, these complexes can be used as efficient catalysts in different RCM

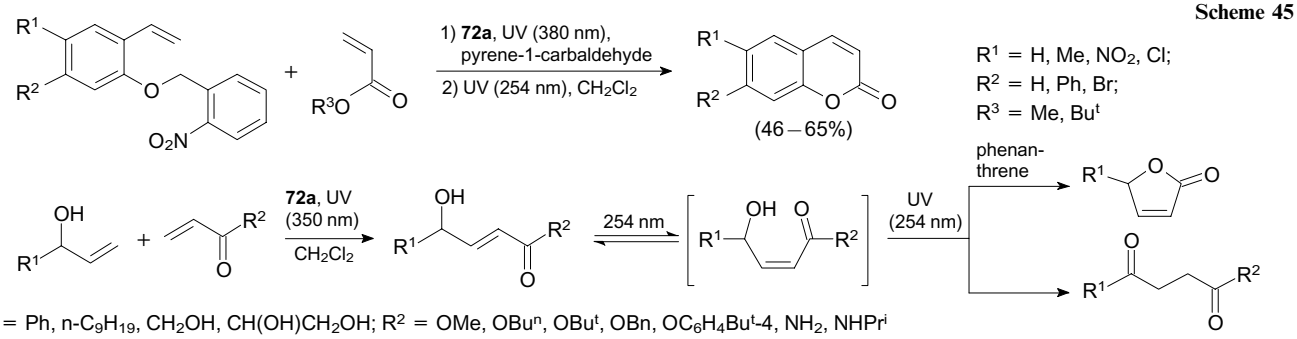
Scheme 46



Scheme 47



Scheme 45



reactions, enyne cycloisomerization and CM, in particular, with multifunctional substrates. Moreover, due to their latency and possibility of on-demand activation, fluorine-containing amide complexes **74a** – **d** and **76** can be employed in ROMPs of dicyclopentadiene (DCPD) and *endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid. However, low solubility of these complexes in non-polar solvents limits their commercial applications.[96]

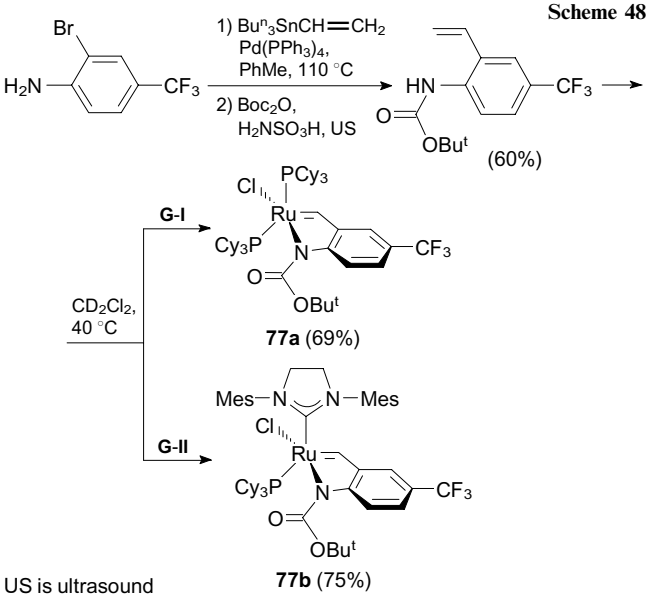
Structurally similar carbamate complexes **77** bearing a *para*-CF_3 group in the styrene ligand (Scheme 48) were synthesized by Pietraszuk and co-workers[97] and were tested in RCM of DEDAM and DEAMM, in ROMP of COD and in CM. In all cases, the complexes showed latent behaviour. Two equivalents of HCl were required for their activation. The presence of the electron-withdrawing trifluoromethyl group promotes an increase in the activity compared to their non-fluorinated analogues.

In 2008 – 2010, Matsugi *et al.*[98,99] reported the synthesis of catalysts **78** containing a perfluoroalkyl group directly bonded to the aromatic ring of the benzylidene ligand (Scheme 49). The perfluoroalkylation of salicylaldehyde was performed in the presence of the radical initiator V-70L [a fraction of the commercially available initiator V-70, m.p. = 58 °C,[100] (±)-2,2′-azobis(2,4-dimethyl-4-methoxyvaleronitrile)[101]] and caesium carbonate as a soft base. These conditions made it possible to perform the reaction at room temperature.

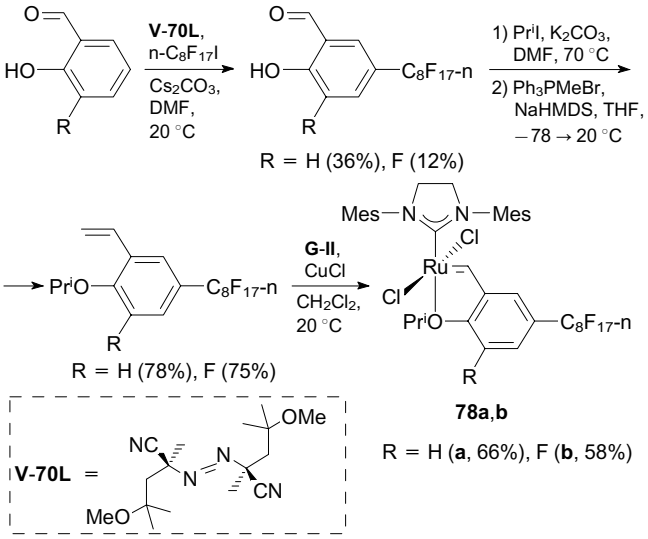
Compared to **HG-II** and **59** (see Scheme 34), catalysts **78a**,**b** showed higher activity in RCM of DEDAM, DEAMM and *N*,*N*′-diallyltosylamide. Catalyst **78a** was recovered using F-SPE in each iteration. It was demonstrated that this catalyst can be reused up to five times, with excellent yields of both the recovered catalyst and the reaction products. Meanwhile, complex **78b** was not recoverable.

Mauduit and co-workers[102] reported the synthesis of complexes **79a** – **c** bearing fluorinated sulfonamide groups. In this approach, the corresponding styrenes were prepared by the sulfonation of 4-isopropoxy-3-vinylaniline with trifluoromethanesulfonic anhydride or aryl sulfonyl chlorides (Scheme 50). Catalysts **79a** – **c** showed low activity in RCM of DEAMM and in CM with different substrates.

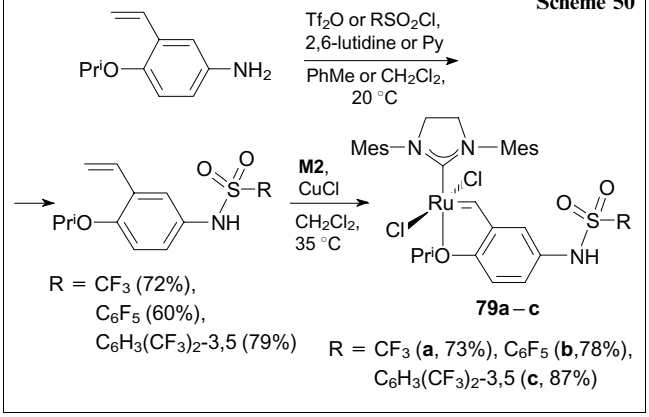
Scheme 48



Scheme 49



Scheme 50

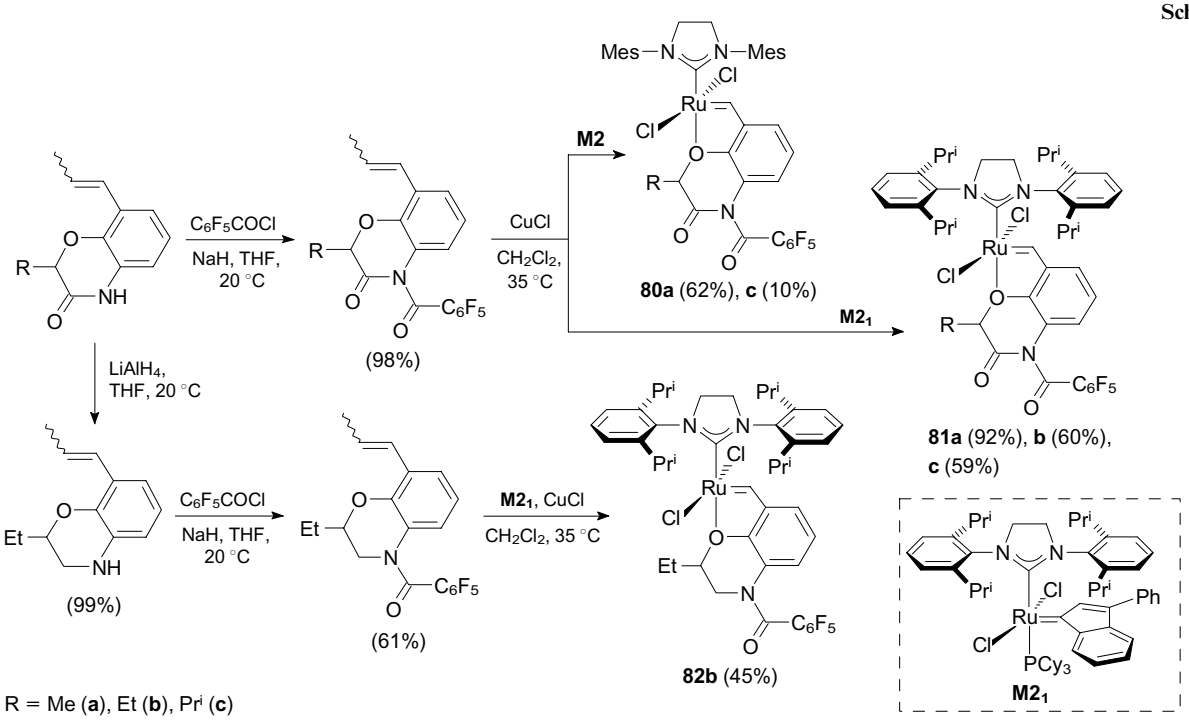


Caijo and Mauduit[103] patented the synthesis of new catalysts **80a**, **81a** – **c** and **82b** bearing the 1,4-oxazine moiety in the benzylidene ligand (Scheme 51). This modification provides an approach to the further synthetically facile fine tuning of the complexes. A fluorine-containing moiety was introduced *via* acylation of the appropriate amine with pentafluorobenzoyl chloride. The commercial indenylidene catalysts **M2** and **M2$_1$** (Umicore) were employed as the starting ruthenium complexes.

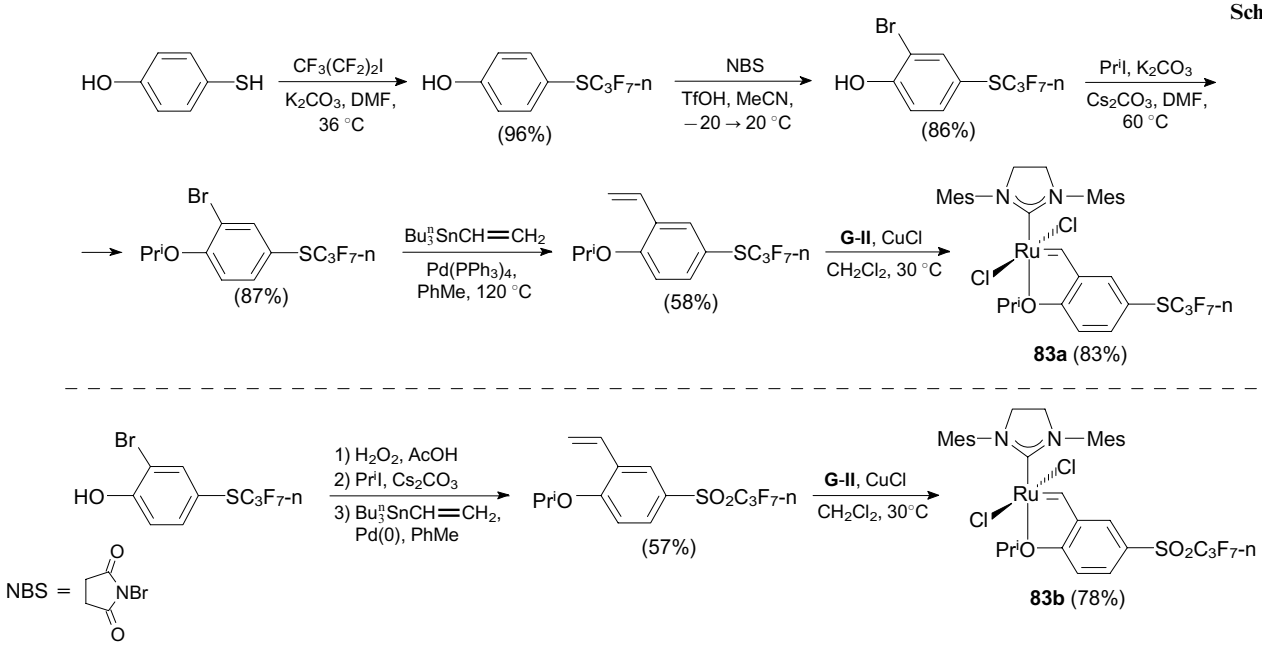
In RCM of DEAMM, catalysts **81b**[104] and **82b**[105] showed high activity and initiation rates. It was found that the replacement of mesityl groups in complexes **80a**,**c** by the diisopropylphenyl moiety (**81a**,**c**) leads to a significant decrease in the initiation rate with a simultaneous increase in the stability of these complexes in solution. It was also demonstrated that the structure of the benzylidene ligand plays a key role in high activity of catalyst **81c**.[106]

In 2013, Grela and co-workers[107] reported the synthesis and catalytic properties of a series of Hoveyda – Grubbs-type catalysts containing different electron-withdrawing groups. The catalytic properties were fine-tuned using the weak electron-withdrawing perfluoro-n-propylthio group (**83a**) and the strong electron-withdrawing perfluoro-n-propylsulfonyl group (**83b**) (Scheme 52). Perfluoroalkyl groups were introduced *via* the nucleophilic substitution of perfluoropropyl iodide in the presence of potassium carbonate. As expected, the initiation rate of catalyst **83b** was high, but

Scheme 51



Scheme 52



the catalyst was found to be unstable even at low temperatures.

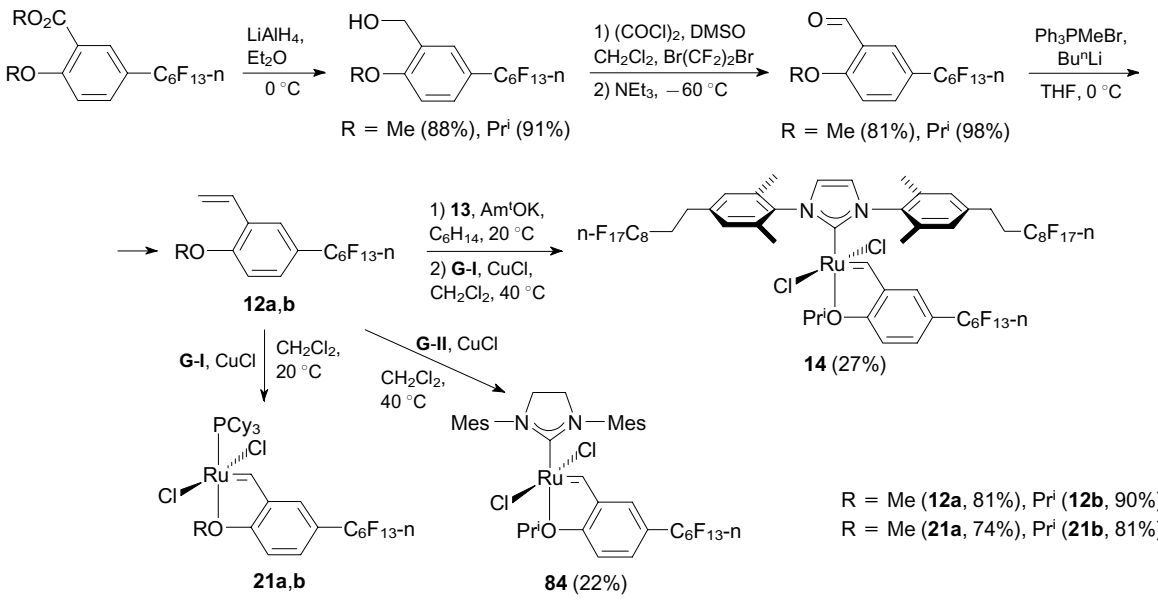
Kvíčala *et al.*[29] described, apart from the synthesis of imidazolium salt **13** containing two perfluoroalkyl groups (see Scheme 10), the synthesis of perfluoroalkyl-containing styrenes **12a**,**b** and **85** and the corresponding light fluorous catalysts **14**, **21a**,**b**, **84** and **86** (Schemes 53 and 54). In all cases, the Ullmann reaction was used to introduce a perfluoroalkyl group capable of increasing the activity of the catalysts and fluorophilicity. Catalysts **14**, **21a**,**b** and **84** showed high activity in RCM reactions.

Bis-perfluoroalkyl-containing styrene **85** proved to be inactive in the reaction giving complex **86** (Scheme 54) and was not capable of coordinating to the ruthenium atom through an oxygen atom. For Hoveyda–Grubbs-type catalysts, the inability for chelation of benzylidene ligands with low electron density at the oxygen atom was described for the first time by Grela and co-workers[108] in 2004.

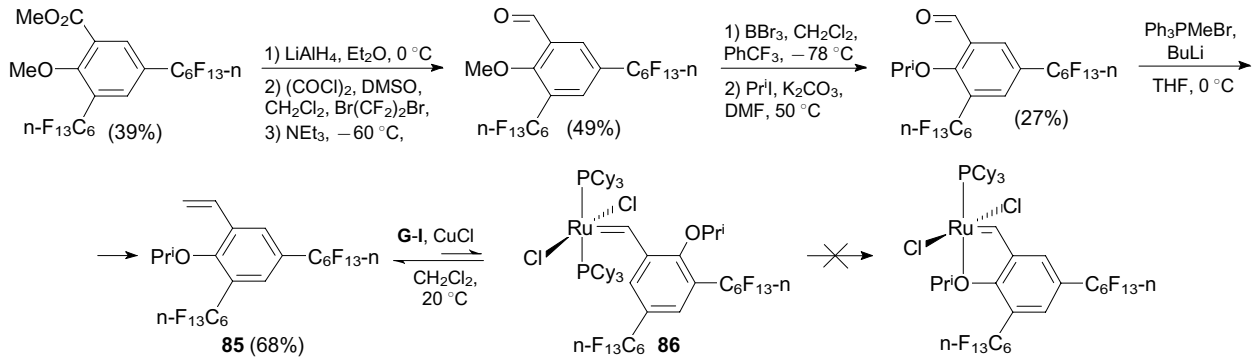
More recently, Kvíčala and co-workers[33] synthesized complex **87** containing perfluoroalkyl substituents both in NHC and benzylidene ligands (Scheme 55). However, the new complex did not act as a heavy fluorous catalyst and was less active in RCM reactions than **HG-II**.

The possibility of immobilization of perfluoroalkyl-containing Hoveyda-type catalysts on a polytetrafluoroethylene support was described by Matsugi and co-workers[109] in 2015. Complex **88** containing the perfluorodecyl group was the first example of Hoveyda–Grubbs-type

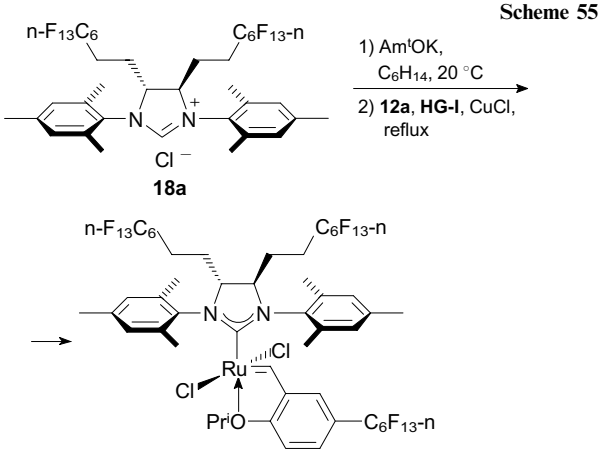
Scheme 53



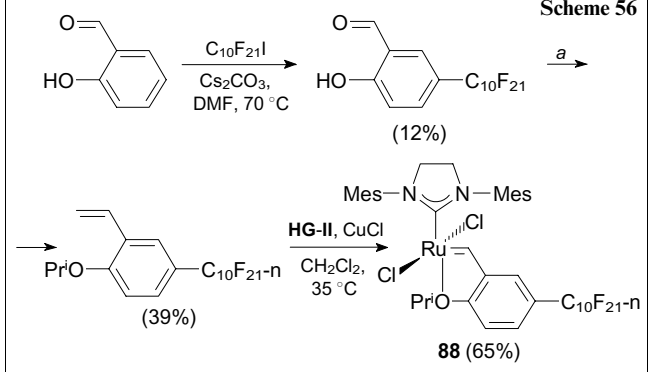
Scheme 54



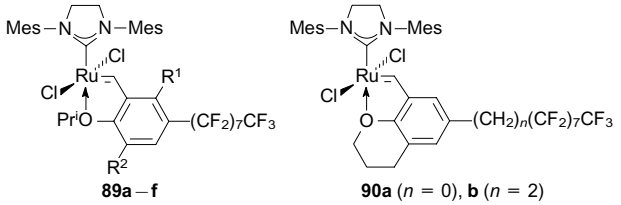
Scheme 55



Scheme 56



Structures 89, 90



89: R^1 = H: R^2 = OPr^i (**a**), OMe (**b**), Ph (**c**), 1-Naph (**d**), 2-Naph (**e**), H (**f**); Naph is naphthyl

complexes that can transfer between the liquid and solid phases in RCM reactions (Scheme 56), unlike complex **78a** synthesized previously. Complex **88** provided excellent yields of both the reaction products and the recovered catalyst in RCM with different substrates.

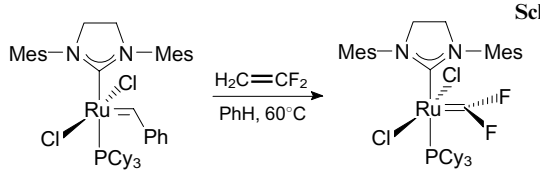
In the subsequent study, this research group [110] reported the synthesis of new perfluoroalkyl-containing catalysts **89a – f** and **90a**,**b** and their catalytic activity in RCM.

Fluorinated substituents were introduced into aromatic substrates by the above-mentioned methods. 1-Naphthyl-containing catalyst **89d** showed the highest activity in the metathesis.

4. Fluorine in indenylidene, allenylidene and methylidene ligands

In 2001, Grubbs and co-workers[111] synthesized the first ruthenium difluorocarbene complex **91** (Scheme 57) when studying the metathesis of 1,1-difluoroethylene as one of the challenging substrates in the presence of catalyst **G-II**. It was found that this reaction was not catalytic because secondary metathesis products, such as ethylene and tetrafluoroethylene, were not detected. However, the double bond in difluoroethylene is initially cleaved in a metathesis fashion and, consequently, it is the first example of difluoroalkene metathesis. Complex **91** was tested in ROMP of cyclooctadiene, in which it showed low catalytic activity.

Scheme 57

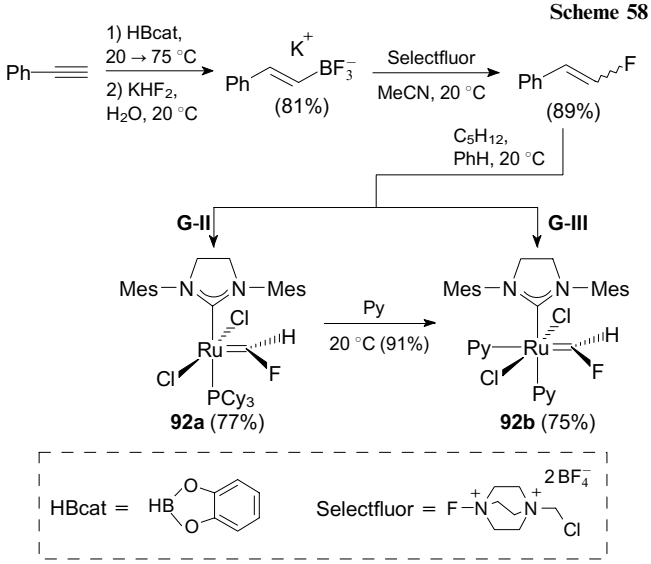


91 (86%)

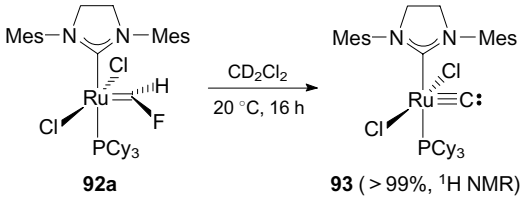
Six years later, Johnson and co-workers[112] reported the synthesis of second- and third-generation monofluoromethylidene catalysts (**92a** and **92b**, Scheme 58). β-Fluorostyrene was prepared under mild conditions by the electrophilic fluorination of potassium alkenyltrifluoroborate in the presence of Selectfluor.[113] The catalytic activity of complexes **92a** and **92b** was higher than that of related difluorocarbene compound **91** but it was still rather low. Catalyst **92b** was less stable in solution and had a higher initiation rate than **92a**.

Despite rather high stability in the solid state, complex **92a** is prone to form carbide complex **93** in solution (Scheme 59). The reaction occurs slowly in dichloromethane with a long induction period.

Scheme 58

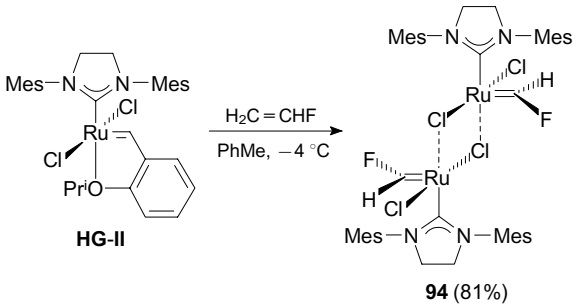


Scheme 59



92a **93** (> 99%, ^{1}H NMR)

Scheme 60

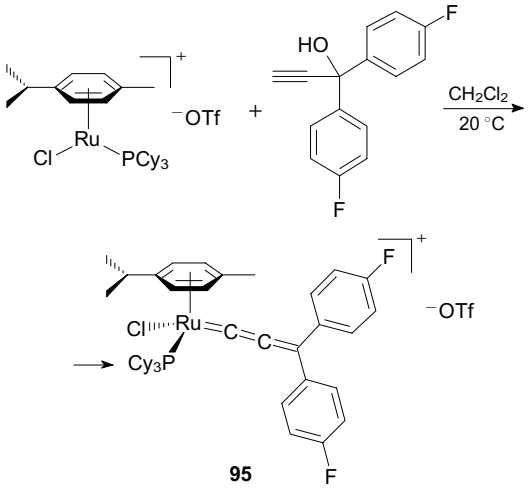


94 (81%)

The most recently available ruthenium monofluoromethylidene complex **94** (Scheme 60) was described in 2009.[114] Initially, it was identified as an intermediate in CM reactions of disubstituted alkenes and vinyl fluoride in the presence of **HG-II**. Subsequently, this catalyst was synthesized as the target product in high yield by the reaction of an excess of vinyl fluoride with **HG-II**. The dinuclear structure of the complex was established by X-ray diffraction. In CM of 5-decene and vinyl fluoride, complex **94** showed TON = 1.2.

Dixneuf and co-workers[115] were the first to synthesize cationic allenylidene complex **95** containing fluorine atoms in the *para* positions of phenyl groups of the allenylidene ligand (Scheme 61).

Scheme 61

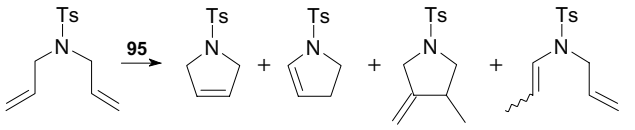


95

In RCM of *N*,*N*-diallyltosylamide, complex **95** showed higher activity than the non-fluorinated analogue but it was less selective. The by-products generated in the reaction are shown in Scheme 62.

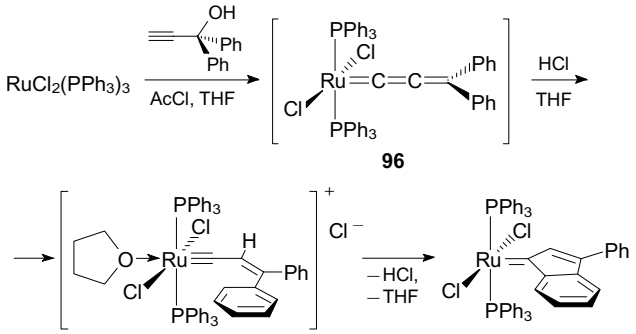
Ruthenium indenylidene complexes are also efficient catalysts for the olefin metathesis, which are rather resistant

Scheme 62



to severe conditions. An important advantage of such catalysts is that they are readily accessible. Thus, the indenylidene complex was synthesized by the reaction of 1-arylpropargyl alcohol with tris(triphenylphosphine)ruthenium(II) chloride in the presence of Lewis acid (Scheme 63). The reaction proceeds through the formation of allenylidene complex **96**, which can also be isolated from the reaction mixture. The method is general for the synthesis

Scheme 63



Ac = MeC(O)

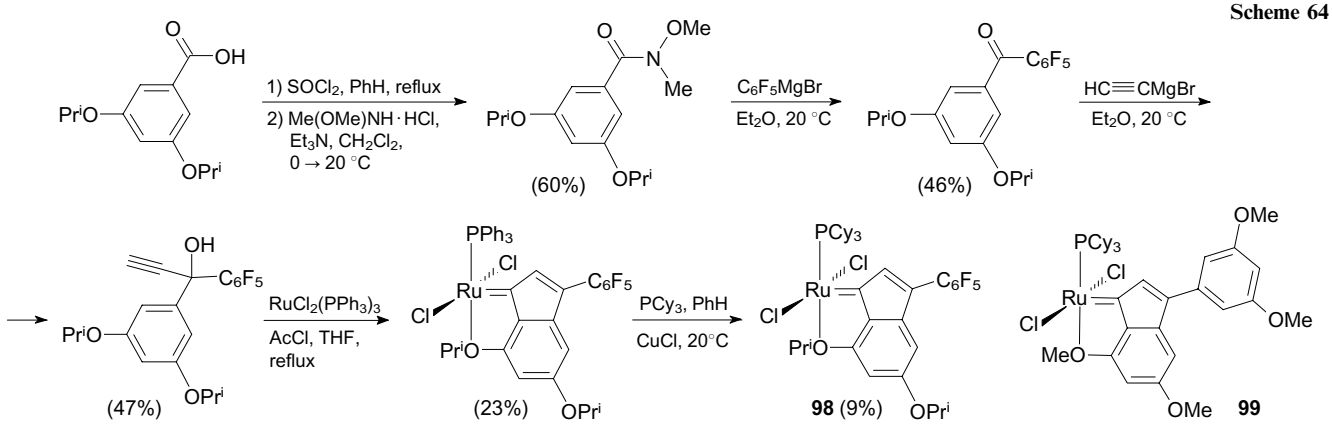
of indenylidene complexes of not only ruthenium but also other transition metals.[116] Generally, the subsequent transformations of complex **97** involve the replacement of the triphenylphosphine ligand with the tricyclohexylphosphine one using an excess of tricyclohexylphosphine.

In the patent, Holtcamp and co-workers[117] described the synthesis of indenylidene catalyst **98** bearing the pentafluorophenyl group (Scheme 64). The fluorinated group was introduced *via* the reaction of 3,5-diisopropoxy-*N*-methoxy-*N*-methylbenzamide with pentafluorophenylmagnesium bromide. Catalyst **98** showed a high turnover number in the ethenolysis of methyl oleate (TON = 4300), whereas, *e.g.*, methoxy-containing catalyst **99** had TON = 1800. This large difference can be attributed to the strong electron-withdrawing properties of the pentafluorophenyl group, resulting in a decrease in the strength of the ruthenium–oxygen coordination bond and an increase in the rate of the initiation step of the metathesis.[118]

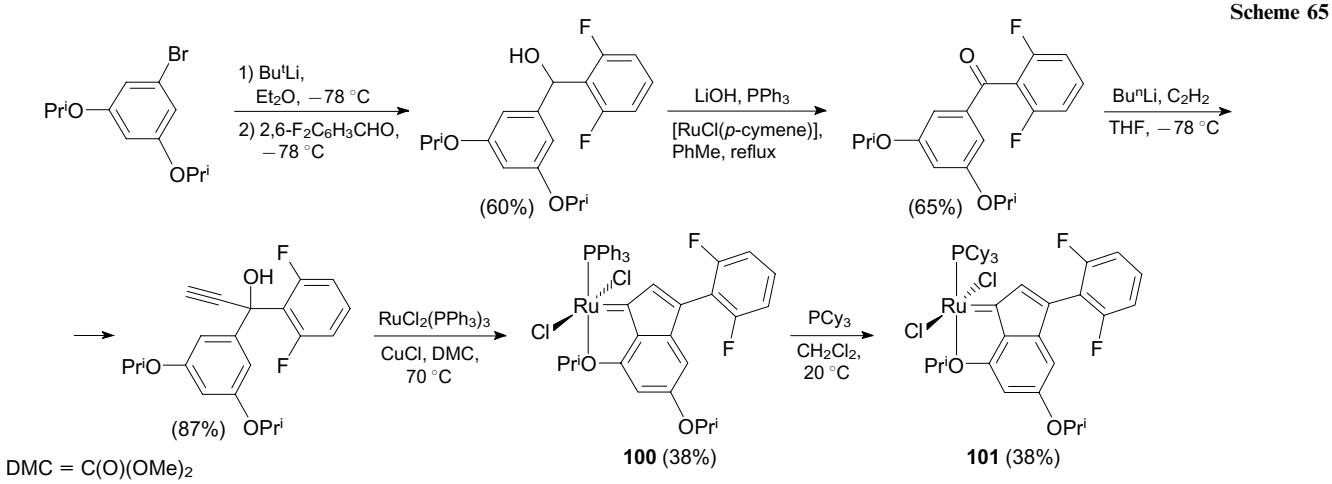
Bruneau and co-workers[119] described another modification of the chelating indenylidene ligand. A fluorine atom was introduced into the substrate by the reaction of 2,6-difluorobenzaldehyde with 3,5-diisopropoxyphenyllithium (Scheme 65). Carbene complex **100** was prepared in the green solvent dimethyl carbonate. The synthesized complex **101** proved to be efficient in RCM of DEDAM and DEAMM and was found to be thermally stable.

Indenylidene complexes **102a**,**b** containing one fluorine atom in the *para* position of the benzene ring of the indenylidene ligand were described by Verpoort and co-workers[120,121] (Scheme 66). The corresponding propargyl alcohol was prepared from commercially available *p*-fluo-

Scheme 64

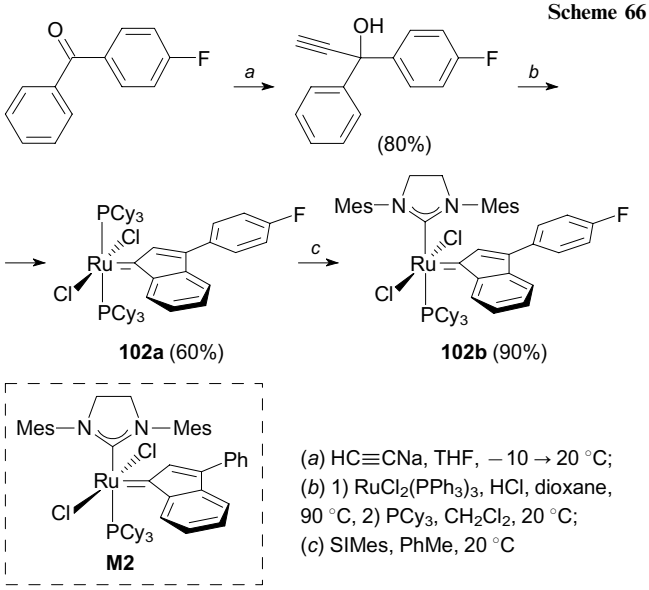


Scheme 65



DMC = C(O)(OMe)$_2$

Scheme 66



robenzophenone according to a literature procedure.[122] Complexes **102a**,**b** were evaluated for catalytic activity in RCM, RCEYM and ROMP reactions. In all cases, catalysts **102a**,**b** showed activity similar to that of the non-fluorinated analogue **M2**.

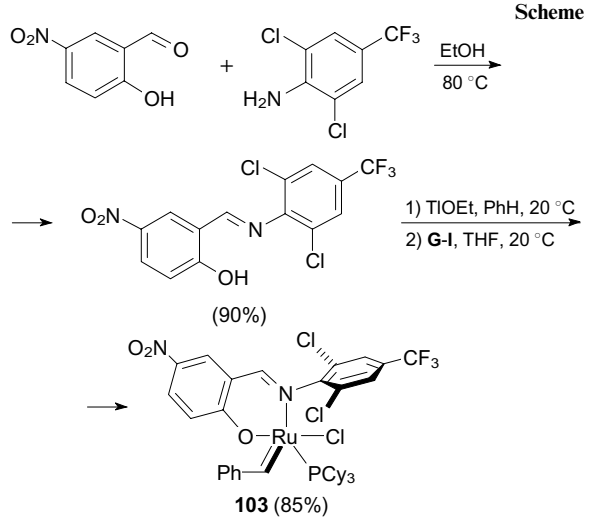
5. Fluorine in L-type ligands

In 1998, Grubbs and co-workers[123] synthesized a series of ruthenium complexes bearing a mixed-type (L and X) salicylaldimine ligand. In particular, they prepared complex **103** containing a fluorinated substituent in the L-type moiety (Scheme 67). The activity of catalyst **103** was similar to that of its analogues, the efficiency of which was low at room temperature but significantly increased upon heating.

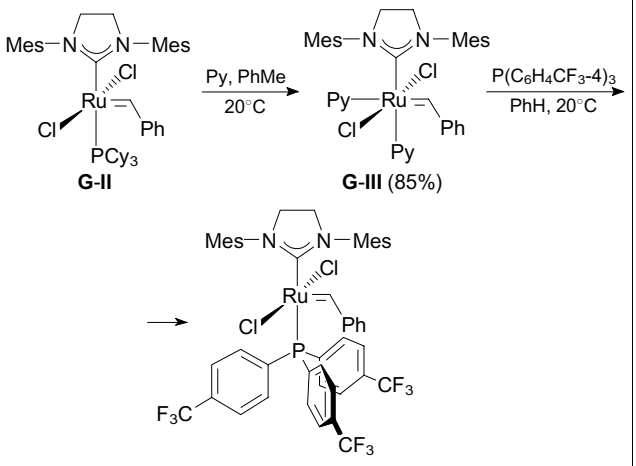
Non-chelating L-type ligands in ruthenium complexes are generally rather labile. Hence, the replacement of an L-type ligand with another one is usually performed by the treatment with an excess of the latter and occurs quite rapidly under mild conditions.

In 2001, Grubbs and co-workers[124] described the first synthesis of a third-generation catalyst (**G-III**) by the reaction of complex **G-II** with an excess of pyridine

Scheme 67



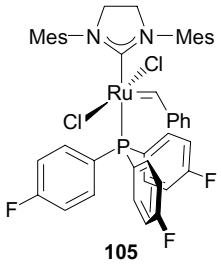
Scheme 68



(Scheme 68). Although **G-III** does not contain fluorine atoms, in this Section it is considered as an important starting compound for the synthesis of other complexes, in particular of those modified with fluorine-containing phosphine ligands. For instance, commercially available electronically pure tris[*p*-(trifluoromethyl)phenyl]phosphine, with low electron density at the phosphorus atom, was used to synthesize complex **104**, which proved to be more active than **G-II** in the CM reaction of acrylonitrile and allylbenzene and showed a high initiation rate and activity in ROMP of cyclooctadiene (see Scheme 68).[125]

Fluorous phosphine complex **105** was synthesized in a similar way.[126] This complex showed lower activity in RCM of diethyl 2-allyl-2-cinnamylmalonate and in ROMP of cyclooctadiene compared to complex **104**. Tris(pentafluorophenyl)phosphine was inactive in the reaction with **G-III**.[125]

Structure 105



In 2006 – 2012, Gladysz and co-workers[127, 128] published a series of studies on Grubbs-type catalysts **107a** – **d** bearing fluorous phosphine ligands. Previously, this research group reported the synthesis of phosphines **106a** – **d** (Scheme 69).[128] The introduction of perfluoroalkyl substituents was performed in two steps. Initially, phosphine was added to the appropriate perfluoroalkylethylene in the presence of azobisisobutyronitrile to form a mixture of the target compound (~90%) with primary and secondary phosphines $PH_x(CH_2CH_2(CF_2)_nCF_3)_{3-x}$ (x = 1, 2; n = 5, 7, 9). The addition was completed in the presence of the less active initiator 1,1′-azobis(cyclohexylcarbonitrile) to prevent polymerization. Phosphines **106a** – **d** exhibited very high fluorophilicity with a partition coefficient between toluene and PFMC P_i(FBS) > 80 (Table 3). The catalysts were synthesized by the replacement of the ligand

Scheme 69

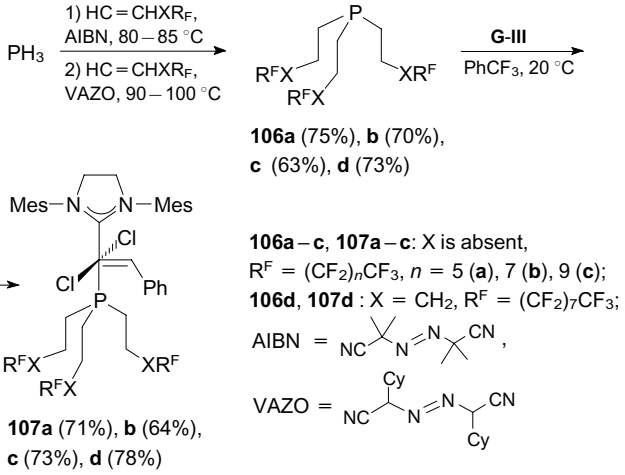


Table 3. Partition coefficients (PFMC/PhMe) of phosphines **106a** – **d** and complexes **107a** – **d**.

Phosphine	P_i (FBS)	[Ru]	P_i (FBS)
106a	82.3	**107a**	0.15
106b	> 300	**107b**	0.66
106c	> 300	**107c**	3.46
106d	82.3	**107d**	0.13

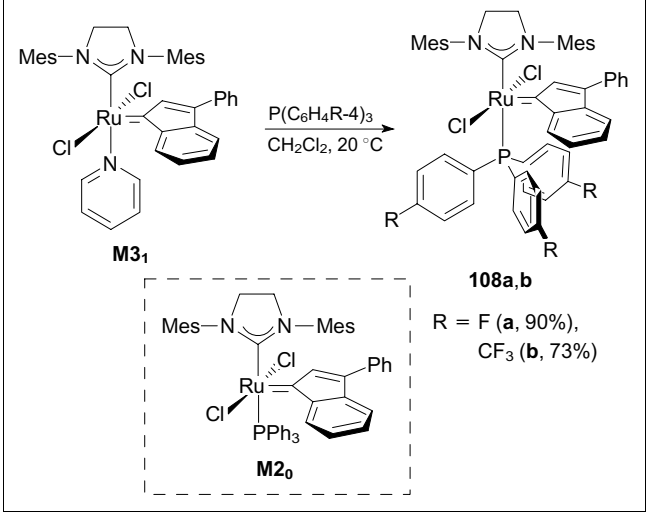
in complex **G-III** in a solution in trifluoromethylbenzene.[127] Table 3 presents the partition coefficients for phosphines **106a** – **d** and the corresponding catalysts **107a** – **d**.

Due to high fluorophilicity, catalyst **107c** was almost inactive in dichloromethane. Catalysts **107a**,**b** were tested in a series of benchmark RCM reactions. The initiation rate in dichloromethane – fluorous solvent biphasic systems was much higher than that in pure dichloromethane. This acceleration is associated with the phase transfer of the fluorous phosphine ligand to a fluorous solvent. The catalyst activation *via* phase transfer of the ligand (phase-transfer activation) was also found in ROMP of norbornene in the presence of catalyst **107b**.[129] It was shown that complex **107b** can be reused for three cycles in RCM of DEDAM.[130]

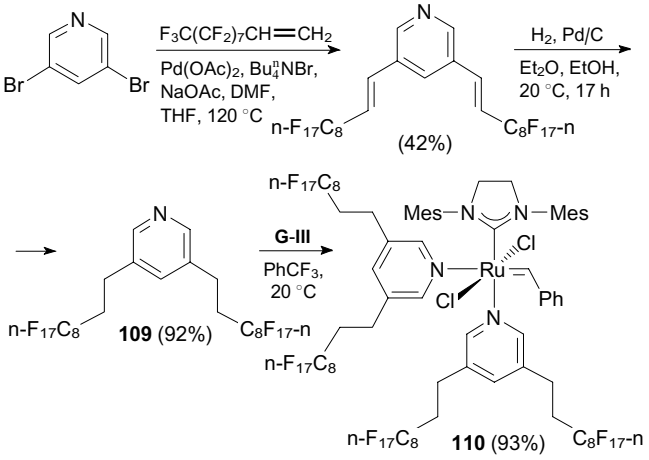
Indenylidene catalysts **108a**,**b**, analogues of complexes **104** and **105**, were described by Nolan and co-workers.[131] Complexes **108** were also synthesized from pyridine-containing indenylidene precursor $\mathbf{M3_1}$ (Scheme 70). Their catalytic activity was tested in a wide range of CM, RCM, RCEYM and RRM (ring-rearrangement metathesis) reactions. In most cases, complex **108b** showed higher activity compared to the non-fluorinated analogue $\mathbf{M2_0}$ (see Scheme 70).

Gladysz and co-workers[132] proposed another approach to the synthesis of ruthenium catalysts bearing fluorous L-type ligands. They prepared third-generation catalyst **110** containing two fluorous pyridine ligands (Scheme 71). Fluorous pyridine **109** was synthesized by the Heck reaction of 3,5-perfluoroalkylethylene with dibromopyridine followed by the double bond hydrogenation under mild conditions. The reaction of **109** with complex **G-III** afforded complex **110**.[133] Pyridine was completely removed from the reaction mixture by a series of freezing, evacuating and thawing cycles.

Scheme 70



Scheme 71

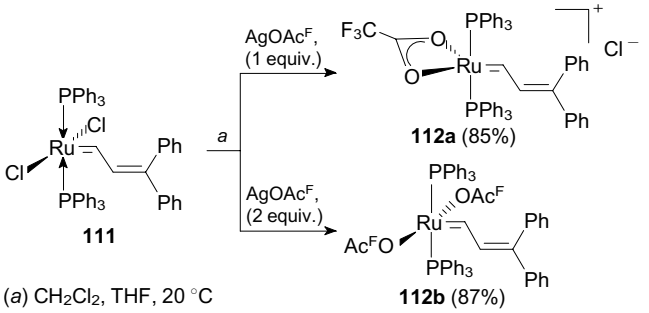


As in the case of catalysts **107a** – **d**, the activity of catalyst **110** in RCM was significantly higher in dichloromethane – fluorous solvent biphasic systems.

6. Fluorine in X-type ligands

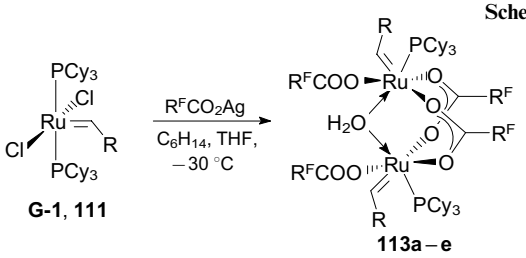
First ruthenium-based metathesis catalysts containing fluorine in an X-type ligand were described in 1993.[134] The synthesis involved the replacement of chlorine in Grubbs complex **111** with trifluoroacetate mediated by the appropriate silver salt (Scheme 72). Cationic catalyst **112a** showed high activity in ROMP of norbornene.[135,136]

Scheme 72



It is worth noting that this reaction in hexane affords water-bridged dinuclear complex **113a** bearing two trifluoroacetate groups (Scheme 73). Related compounds were synthesized using complex **G-I** as the starting compound.[137, 138]

Scheme 73

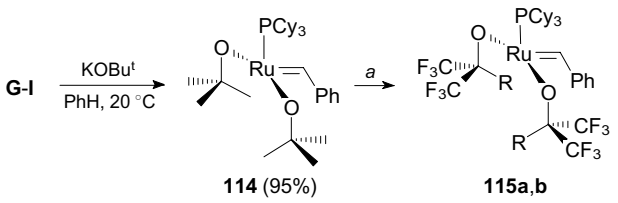


R = Ph (**G-I**), CH=CPh$_2$ (**111**);
113: R = Ph: R^F = CF_3 (**a**, 98%), C_2F_5 (**b**, 57%), C_6F_5 (**c**, 85%);
R = CH=CPh$_2$: R^F = CF_3 (**d**, 54%), C_6F_5 (**e**, 63%)

Catalysts **113a**,**b**,**d** were tested in self-metathesis reactions of internal olefins, in which they exhibited moderate activity. Catalysts **113c**,**e** with pentafluorobenzoate ligands proved to be inactive in these reactions.

Stable four-coordinate complexes **114** and **115a**,**b** were synthesized using bulky X-type ligands (Scheme 74).[139] Non-fluorinated complex **114** was prepared by the reaction of potassium *tert*-butoxide with complex **G-I** and then it was treated with an excess of fluorinated alcohol.

Scheme 74



(*a*) R(CF$_3$)$_2$COH, C_5H_{12}, 80°C; R = Me (**115a**, 40%), CF_3 (**115b**, 37%)

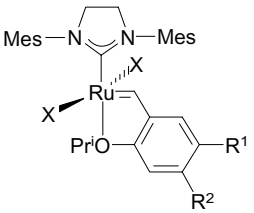
Complexes **115a**,**b** showed moderate activity even upon heating (60 °C), but they were highly active upon the addition of hydrochloric acid to the reaction mixture.

The method developed previously for the replacement of X-type ligands mediated by silver salts was used by Buchmeiser and co-workers[140–148] in 2004–2011. In this period of time, a series of catalysts (**116**–**121**), mainly Hoveyda-type catalysts, bearing different fluorinated X-type ligands were synthesized.

Complex **116b** exhibited high activity in a wide range of metathesis transformations. Catalyst **116a** was less active.[140] Complexes **116b**[141] and **116c**,**d**[143] catalyzed the cyclopolymerization of diethyl dipropargylmalonate (DEDPM, Scheme 75) but did not induce polymerization in a living manner.

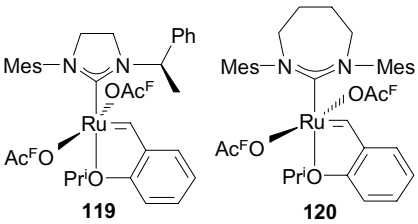
The cyclopolymerization of 1,6-heptadiynes in a living fashion can be performed in the presence of catalysts **117a**–**c** and **118a**–**c**.[141, 142] An elongation of the perfluoroalkyl chain of the catalyst led to a narrower molecular mass distribution of the resulting polyene.[143] Catalyst **117a** was found to be efficient in the cyclopolymerization of heptadiynes containing free hydroxy groups, in contrast to molybdenum-derived Schrock catalysts.[144] Besides, com-

Structures 116–121



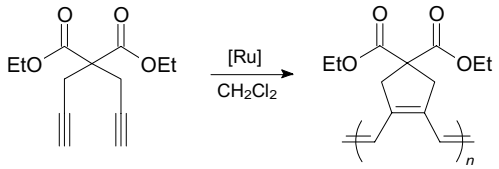
116a–**g**, **117a**–**c**, **118a**–**c**

116: R^1 = R^2 = H: X = OTf (**a**), O_2CCF_3 (**b**), $O_2CC_2F_5$ (**c**), $O_2CC_3F_7$-n (**d**), $O_2CC_6F_5$ (**e**), OC_6F_5 (f), $(CF_2)_3(CO_2)_2$ (**g**);
117: R^1 = R^2 = OMe;
118: R^1 = NO_2, R^2 = H:
X = O_2CCF_3 (**a**), $O_2CC_2F_5$ (**b**), $O_2CC_3F_7$-n (**c**)



Y = OTf: X = OTf (**a**), NCO (**b**), OAc^F (**c**)

Scheme 75



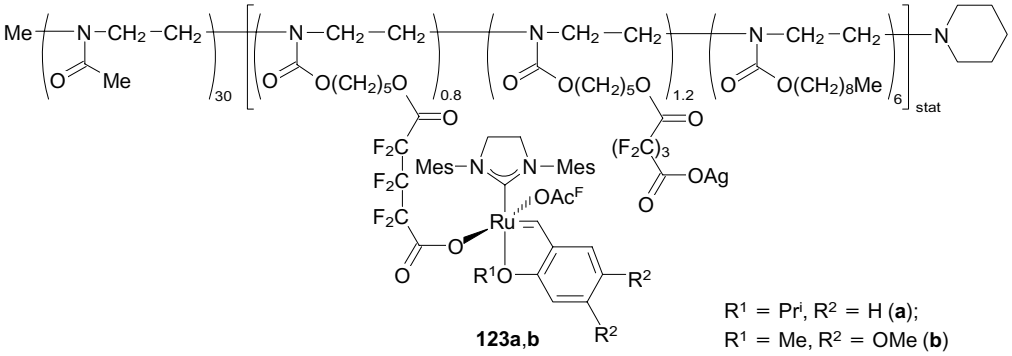
pounds **116b**, **117a** and **118a** were tested in the cyclopolymerization of *N*,*N*-dipropargylamines, where they showed high efficiency in the catalysis of polymerization processes.[145] Catalysts **116e** and **119** were synthesized with the goal to determine the effect of the ligand bulkiness on the catalytic properties, in particular on the regioselectivity of the cyclopolymerization of dipropargyl substrates.[146] Complex **120** demonstrated high catalytic activity in the cyclopolymerization of DEDPM, but was found to be inactive in RCM of DEDMM.[147] Complexes **121a**–**c** and **116g** showed high efficiency in the copolymerization of cyclopentene and norbornene.[148]

The hexafluoroglutaric group can be used as a linkage unit for the immobilization of ruthenium catalysts on a support. The first attempt to immobilize a Grubbs catalyst through a fluorine-containing ligand was reported by Mol and co-workers.[149] For this purpose, hydroxyethyl-functionalized styrene–divinylbenzene copolymer was treated with hexafluoroglutaric anhydride followed by the preparation of the corresponding silver salt and the subsequent addition of Grubbs catalyst **G-I** (Scheme 76). Catalytic system **122** was highly active in RCM of DEDAM (the catalyst retained the activity after five cycles of reuse) and in self-metathesis of methyl oleate and *trans*-4-decene.

Buchmaiser and co-workers[140, 150, 151] and Braddock *et al.*[152] immobilized **HG-II**-type catalysts on polymeric supports using methods similar to that described above. Catalysts **123a** and **123b** immobilized on amphiphilic oligomeric poly(2-oxazoline) allowed the cyclopolymerization of DEDPM in aqueous medium.[141]

The hexafluoroglutaric linkage was utilized to graft Hoveyda-Grubbs-type catalysts on a monolith poly(ether ether ketone) column[150, 151, 153] or silica gel[154–156] for flow reactors. Besides, the hexafluoroglutaric moiety was used to

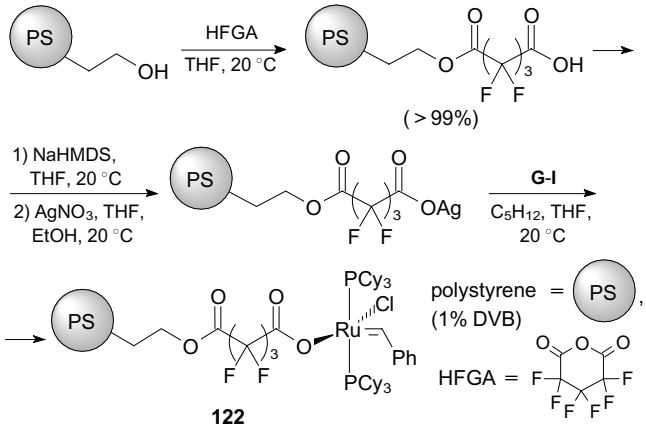
Structures 123



123a,**b**

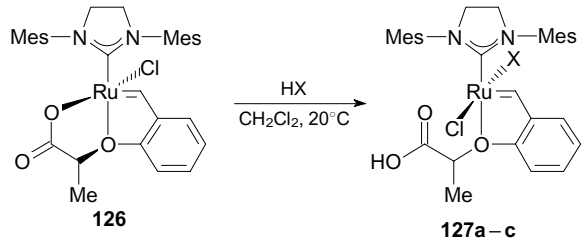
R^1 = Pr^i, R^2 = H (**a**);
R^1 = Me, R^2 = OMe (**b**)

Scheme 76



122

Scheme 77



126

127a–c

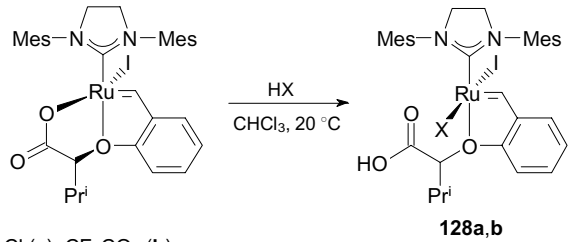
X = Cl (**a**), TfO (**b**), $CF_3(CF_2)_7CO_2$ (**c**)

produce catalysts bearing amphiphilic (**124**) and charged (**125**) ligands.[157, 158]

Grela and co-workers[159] synthesized catalyst **126** bearing a chelating carboxylate group. This catalyst showed latent behaviour, being inactive in RCM at room temperature but highly efficient in the presence of an acid or at elevated temperatures.[159] For instance, complexes **127a–c** were synthesized *in situ*; however, fluorine-containing compounds **127b**,**c** were found to be less active than chlorinated compound **127a** (Scheme 77). The addition of aqueous hydrofluoric acid or the hydrofluoric acid pyridine complex (HF·Py) to a solution of **126** affords unstable complex **127d** with a Ru–F bond.[160]

Subsequently, Gawin and Grela[160] reported the synthesis of isopropyl-containing complexes **128a**,**b** (Scheme 78). Catalyst **128b** bearing the trifluoroacetate ligand proved to be much more active in RCM of DEDAM compared to its chlorinated analogue **128a**. Besides, catalyst **128b** was highly stable and demonstrated excellent conversion at elevated temperatures or at longer reaction times.

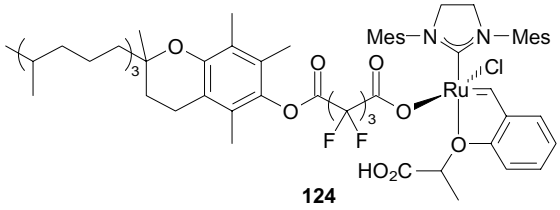
Scheme 78



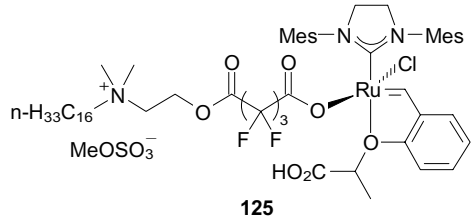
128a,**b**

X = Cl (**a**), CF_3CO_2 (**b**)

Structures 124, 125



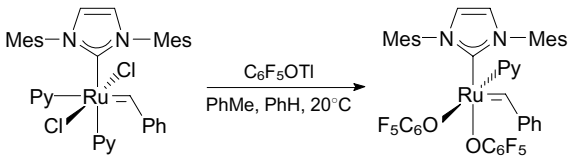
124



125

Fogg and co-workers[161] described the reaction of thallium perfluorophenoxide with an unsaturated analogue of catalyst **G-III** (Scheme 79). The resulting complex **129** exhibited high activity in RCM of DEDAM even at low catalyst loading (0.05 mol.%) and in RCM giving medium-sized rings.[162]

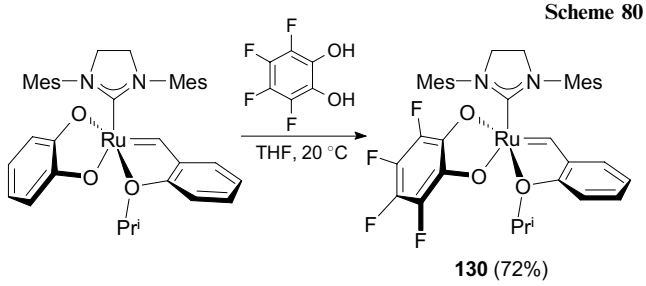
Scheme 79



129 (92%)

In 2014, Hoveyda and co-workers[163] developed a method for the synthesis of complex **130** based on the fast exchange of the catecholate ligand for its tetrafluorine-substituted analogue (Scheme 80). Complex **130** was found to be highly stable in dichloromethane and chloroform however, its catalytic activity was not evaluated.

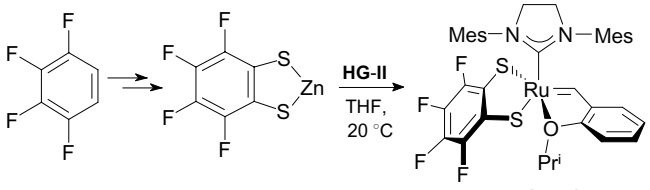
Scheme 80



130 (72%)

A similar complex **131** containing the tetrafluorodithiobenzene ligand (Scheme 81)[41] exhibited high activity in CM of allylbenzene with *Z*-2-butene-1,4-diol, which occurs with the retention of the *Z* configuration. The catalyst was synthesized starting from 1,2,3,4-tetrafluorobenzene *via* the transmetalation with zinc tetrafluorobenzene-1,2-thiolate.

Scheme 81

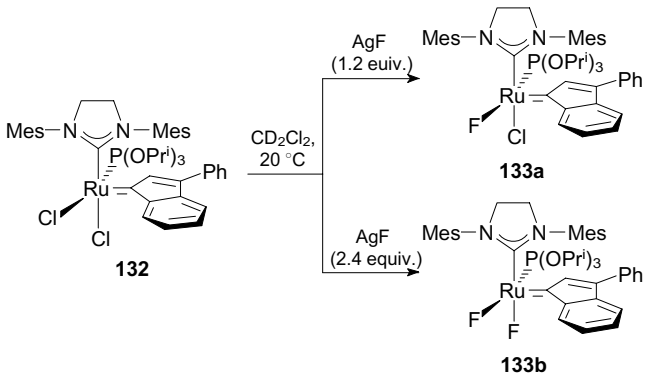


131 (82%)

In 2015, Cazin and co-workers[164] reported the first synthesis of alkene metathesis catalysts **133a**,**b** containing a fluorine atom as the X ligand (Scheme 82). These complexes were prepared by the treatment of compound **132** with silver fluoride. Monofluorinated derivative **133a** was more active than difluorine-substituted analogue **133b** and was tested in CM, RCM and RCEYM reactions, in which it proved to be efficient.

A series of ruthenium catalysts bearing perfluoro(polyoxa)alkanoate ligands **134** – **136** were synthesized by Kvíčala and co-workers[165] in 2014. The fluorous partition

Scheme 82

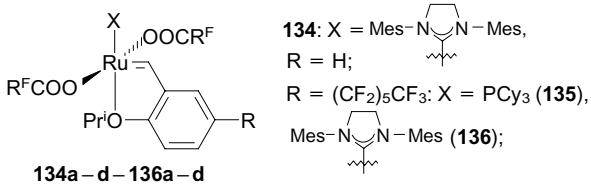


132

133a

133b

Structures 134 – 136



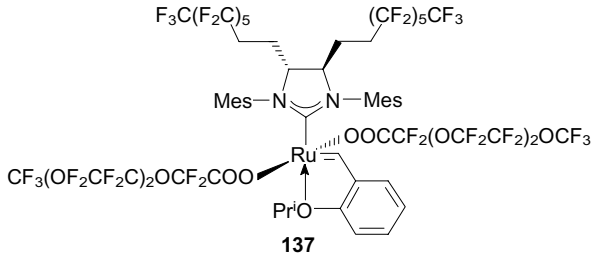
134a – d – 136a – d

R^F = $(CF_2)_5CF_3$ (**a**), $[CF_2OCF(CF_3)]_2CF_2CF_3$ (**b**), $CF_2O(CF_2)_2OCF_3$ (**c**), $CF_2(OCF_2CF_2)_2OCF_3$ (**d**)

coefficients P_i(FBS) were determined for all complexes, the values of which vary from 0.03 (**134a**) to 2.9 (**135d**). In the series of the synthesized catalysts, only compounds **135a – d** and **136b – d** behave as heavy fluorous catalysts [P_i(FBS) > 1]. Complexes of the series **134** and **136** showed the highest activity in RCM reactions. Complex **136d** used in RCM of DEAMM and DEDMM can be recovered with PFMC and reused.

A year later, the same research group[33] synthesized complex **137** having very high fluorophilicity [P_i(FBS) = 27]; however, the data on its activity in metathesis reactions were not reported.[33]

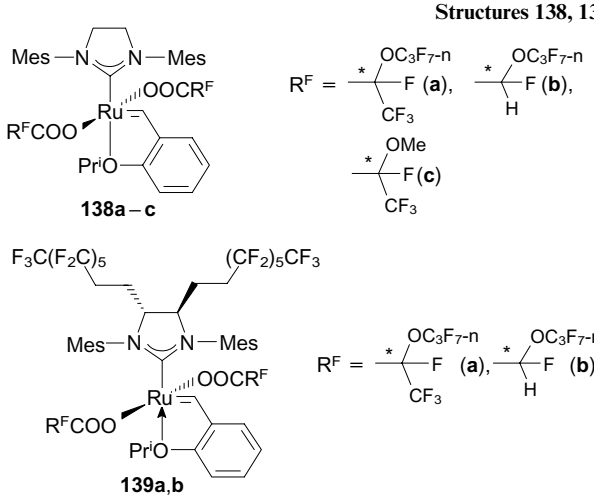
Structure 137



137

A series of fluorous catalysts **138a – c** and **139a**,**b** with polyfluorooxaalkanoate ligands containing an asymmetric carbon centre (chiral carbon) were synthesized in 2016.[166] These complexes were tested in RCM reactions with benchmark substrates. Catalysts **138b** and **139b** were found to be the most active due to low steric hindrance and high electrophilicity of 2-fluoro-2-(perfluoropropoxy)acetate ligands.

Structures 138, 139

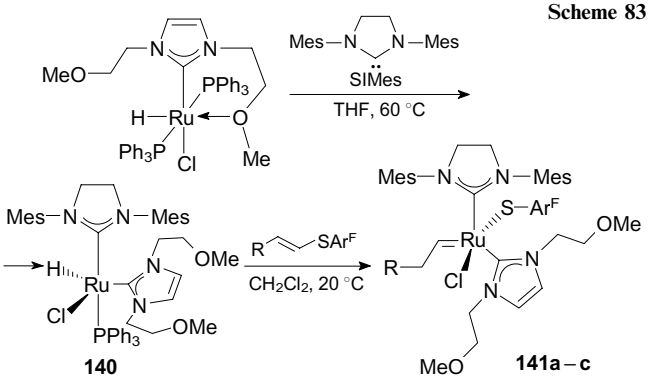


138a – c

139a,**b**

Stephan and co-workers [167] reported the synthesis of a series of ruthenium alkylidene complexes with two different NHC ligands and evaluated their catalytic activity. Among the characterized complexes were those with fluorinated thiophenolate ligands **141a – c**. These catalysts were synthesized by the reaction of hydride complex **140** with fluorinated aryl vinyl sulfides under mild conditions (Scheme 83). The resulting complexes showed moderate activity in ROMP of cyclooctadiene and in RCM of DEDAM, the activity being significantly higher in the presence of Lewis acid (BCl_3).[168]

Scheme 83



Ar^F = C_6H_4F-4, R = H (**a**); Ar^F = C_6F_6: R = Pr^n (**b**), Bu^n (**c**)

Due to the electron-withdrawing properties, fluorine-containing X-type ligands are most often utilized in ruthenium metathesis catalyst to increase the catalytic activity of the latter. Besides, fluorine-containing X-type ligands, most often hexafluoroglutarate, are employed for catalyst immobilization on solid or polymeric supports. Such supported catalytic systems are mentioned in dedicated reviews.[169 – 172]

7. Conclusion

The alkene metathesis is one of the most efficient tools applied by synthetic chemists to construct various unsaturated systems, from simple olefins to complex biologically active compounds and polymers. Ruthenium alkylidene complexes, particularly those bearing NHC ligands, which are characterized by high air- and moisture-stability combined with tolerance to a wide range of functional groups, are most commonly used for these purposes. Since the design of an ideal catalyst for all types of metathesis reactions is unlikely, the important strategy for the development of the most efficient and selective catalytic systems to solve a particular synthetic or engineering problem is based on the alteration of the structure of ligands and substituents at the ruthenium centre. Significant advances in organofluorine chemistry achieved in the past two decades provide additional opportunities for performing targeted modifications of alkene metathesis catalysts taking into account the unique physicochemical properties of the fluorine atom and fluoroalkyl groups, *e.g.*, the small atomic radius, high electronegativity, lipophilicity and the ability to form hydrogen and coordination bonds. This review summarizes literature data on the methods for the introduction of fluorine atoms and fluoralkyl groups into different ligands to construct metathesis-active ruthenium carbene complexes. It also analyzes the influence of fluorine-containing ligands on the catalytic activity of the complexes.

In most cases, the choice of fluorinated substituents and their attachment sites in NHC ligands are dictated by the desire to increase the electrophilicity of the ruthenium atom due to the electron-withdrawing effect of fluorine atoms and fluoroalkyl groups. These modifications facilitate the interaction of an alkylidene complex with an olefin substrate in the key step of the catalytic cycle, thereby increasing its activity. Besides, in some cases, catalysts bearing unsymmetrical fluorinated NHC ligands were found to have additional Ru – F coordination, which significantly stabilizes the complex. The presence of fluorine atoms in chelating alkylidene ligands provides an increase in the catalyst initiation rate due to a weakening of the ruthenium – heteroatom bond. A decrease in the electron density on L- and X-type ligands also often leads to an increase in the catalytic activity of the complexes in metathesis reactions. The introduction of polyfluoroalkyl groups into ligands allows for the solution of the problem of catalyst recovery with fluorous biphasic systems for reuse.

Despite considerable progress in the field of fluorous modifications of ruthenium alkylidene complexes aimed at increasing their selectivity and efficiency in metathesis reactions, developing tools for catalyst immobilization on solid supports, improving recyclability and recoverability of catalysts and increasing their solubility in industrially important hydrocarbon solvents, these issues are still challenging.

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8. List of abbreviations and designations

ADMET — acyclic diene metathesis polymerization,
AIBN — azobis(isobutyronitrile),
Am^t — *tert*-amyl,
ARCM — asymmetric ring-closing metathesis,
AROCM — asymmetric ring-opening cross-metathesis,
CM — cross-metathesis,
COE — cyclooctene,
Cy — cyclohexyl,
DCE — 1,2-dichloroethane,
DEAMM — diethyl allylmethallylmalonate,
DEDAM — diethyl diallylmalonate,
DEDMM — diethyl dimethallylmalonate,
DEDPM — diethyl dipropargylmalonate,
DIPEA — diisopropylethylamine,
DIPP — 2,6-diisopropylphenyl,
DMAP — 4-dimethylaminopyridine,
FBS — fluorous biphasic system,
F-SPE — fluorous solid-phase extraction,
KHMDS — potassium hexamethyldisilazide,
Mes — mesityl,
Naph — naphthyl,
Nf — perfluorobutyl (nonaflyl),
NHC — *N*-heterocyclic carbene,
PFMC — perfluoro(methylcyclohexane),
Piv — pivaloyl (*tert*-butylcarbonyl),
polyCOE — poly(cyclooctene),
Py — pyridine,

RCEYM — ring-closing enyne metathesis,
RCM — ring-closing metathesis,
RGO — reduced graphene oxide,
ROMP — ring-opening metathesis polymerization,
RRM —ring-rearrangement metathesis,
SM — self-metathesis,
Tf — trifluoromethanesulfonyl (triflyl),
TON — turnover number.

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