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Metathesis Catalysts with Fluorinated Unsymmetrical NHC Ligands

Salekh M. Masoud,[†,∥] Artur K. Mailyan,[†,‡] Vincent Dorcet,[§] Thierry Roisnel,[§] Pierre H. Dixneuf,[∥] Christian Bruneau,*[,∥] and Sergey N. Osipov*[,†]

[†]A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, 119991, Moscow, Russia

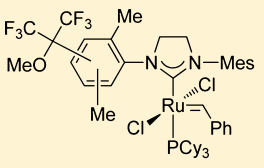
[‡]Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, United States

[§]UMR 6226 CNRS-Université de Rennes 1, Institut des Sciences Chimiques de Rennes, Centre de Diffractométrie X, Campus de Beaulieu, 35042 Rennes, France

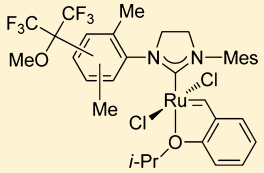
[∥]UMR 6226 CNRS-Université de Rennes 1, Institut des Sciences Chimiques de Rennes, Organométalliques: Matériaux et Catalyse, Centre for Catalysis and Green Chemistry, Campus de Beaulieu, 35042 Rennes, France

Supporting Information

ABSTRACT: The synthesis of new fluorinated ruthenium(II) carbene second-generation precatalysts with unsymmetrical N-heterocyclic carbene ligands has been developed. The reaction profiles of these complexes have been studied in RCM with model substrates such as diethyl diallyl- and allylmethallyl-malonate, and CM model reaction of allylbenzene with 1,4-diacetoxybut-2-ene. In olefin metathesis reactions, the new fluorinated second-generation Grubbs complexes exhibit comparable activity with respect to commercially available Grubbs catalysts. On the other hand, in RCM reactions, the Hoveyda-type catalysts present a latent character, which is not present in the classical second-generation Hoveyda catalyst.



Grubbs-type catalysts



Hoveyda-type catalysts

INTRODUCTION

Transition-metal-catalyzed olefin metathesis is a powerful tool for the synthesis of carbon−carbon double bonds in a wide variety of applications.[1] In particular, the development of well-defined ruthenium alkylidene complexes has broadened the scope and utility of the olefin metathesis reaction in the synthesis of small molecules, preparation of complex bioactive compounds, natural products[2] as well as construction of various functionalized materials and polymers.[3]

Despite remarkable progress in the area, the design of new more effective catalysts that are readily available, easy to handle, and highly selective continues to be crucial. Indeed, still many metathesis applications such as asymmetric,[4] sterically demanding,[5] or aqueous[6] transformations can be essentially improved by discovering more active catalytic systems. Recent progress in developing new Ru-based olefin metathesis catalysts is evidently related to the modification of the *N*-heterocyclic carbene (NHC) ligand architecture of the commercially available second-generation Grubbs and Hoveyda complexes, which has directly influenced the catalysts performance. For instance, the fine-tuning of the electronic and steric properties of the substituents on the nitrogen atoms located in the vicinity of the carbenic center has had a significant impact on catalyst activity, stability, and selectivity in many metathesis applications.[7]

In this context, the importance of unsymmetrical N-heterocyclic carbenes (uNHCs) as ligands in metathesis initiators is incontestable. While uNHCs show similar properties as compared with symmetrical NHCs, desymmetrization allows for further fine-tuning. The introduction of chelation, bifunctionality, shielding effects, and chirality transfer influences the catalyst stability, reactivity, and selectivity, thus stimulating the search for new tailor-made systems including mono- and multidentate uNHC ligands.[8]

On the other hand, fluorinated compounds have found widespread applications in key industrial fields such as the pharmaceutical[9] and medicinal chemistry[10] or crops[11] and material sciences,[12] due to the unique physicochemical features of fluorine atoms introduced in organic molecules. This modification can dramatically alter the key chemical characteristics such as acidity/basicity of neighboring groups, H-bonding ability, electron density distribution, or conformations to result in more desired properties, e.g., such as increased lipophilicity or chemical stability.[13]

In the field of ruthenium−alkylidene complexes, the steric and electronic impact of fluorine and fluoroalkyl groups on their catalytic properties has been mainly studied by usage of properly modified phosphine,[14] styrene[15] ligands, as well as by the replacement of one or two chlorine atoms at ruthenium, for example, with perfluoroalkoxylates and fluorocatecholates.[16] Therefore, it is somewhat surprising that the number of publications on metathesis catalysts decorated with fluorinated NHC ligands is extremely limited,[17] with the first report appearing in early 2000. For example, Fürstner et al. described an unsymmetrical complex with a $C_6F_{13}(CH_2)_2$ group at one of the imidazolyl nitrogen to increase the solubility of the catalyst

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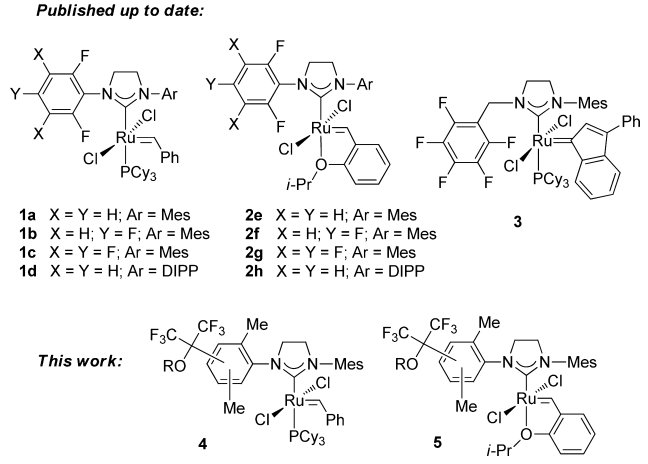
in supercritical CO_2.[18] In 2006, Grubbs reported rate acceleration in RCM of diethyl diallylmalonate arising from a Ru···F interaction between one ring of a *N*,*N*′-bis(2,6-difluorophenyl)imidazol-2-ylidene and the metal center in the Grubbs II catalyst analogue.[19] This work has been further extended with studies of synthesis and catalytic activities of closely related nonsymmetrical analogues[20] (**1** and **2**, Chart 1).

Chart 1. Fluorinated Metathesis Catalysts with Unsymmetrical Imidazolinylidene Ligands



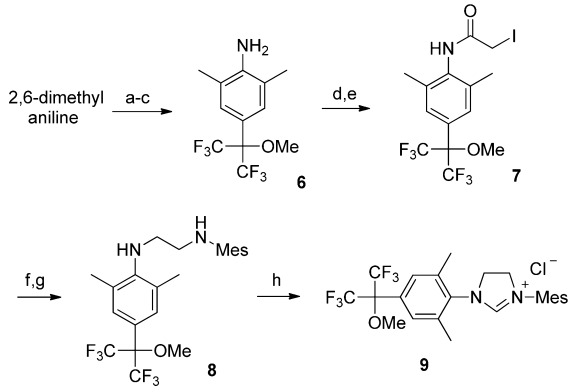
Very recently, Grela and co-workers have published the first indenylidene-type precatalyst with a $C_6F_5CH_2$-containing uNHC ligand[21] (**3**, Chart 1). Therefore, the development of new metathesis catalysts bearing fluorinated unsymmetrical NHC ligands is of current interest.

We have previously described several metathetic transformations of various unsaturated fluorine-containing molecules using commercially available Grubbs and Hoveyda complexes and ruthenium−allenylidene catalysts developed by us[22] to afford a new family of CF_3-containing heterocyclic compounds.[23] Now, we wish to disclose an efficient route to a novel type of metathesis catalysts comprising an unsymmetrical imidazolinylidene ligand with a hexafluoroisopropylalkoxy [$(CF_3)_2(OR)C-$] group in one of the N-aryl substituents (**4** and **5**, Chart 1) as well as our initial results of their catalytic activity.

RESULTS AND DISCUSSION

First, we directed our efforts toward the synthesis of the unsymmetrical 1,3-bis(aryl)-4,5-dihydroimidazolium salt **9** (Scheme 1) as a precursor of the corresponding NHC ligand bearing the hexafluoroisopropylmethoxy group in the *para*-position of the *N*-aryl moiety. For this purpose, the fluorinated aniline **6** was synthesized via a simple procedure including (a) the alkylation of 2,6-dimethylaniline with commercially available hexafluoroacetone hydrate,[24] (b) protection of the amino function with benzaldehyde to form the corresponding Schiff base, and (c) selective *O*-methylation/*N*-deprotection to afford **6** in good yield. To construct the imidazoline ring, the fluorinated amine **6** was further acetylated by chloroacetyl chloride with subsequent halogen exchange with NaI to give the iodide **7**. Then, a slightly modified literature route involved condensation of **7** with mesitylamine, reduction of the amide function, and conventional treatment with HCl and an *ortho*-formate ester led to the formation of the desired imidazolinium salt **9**.

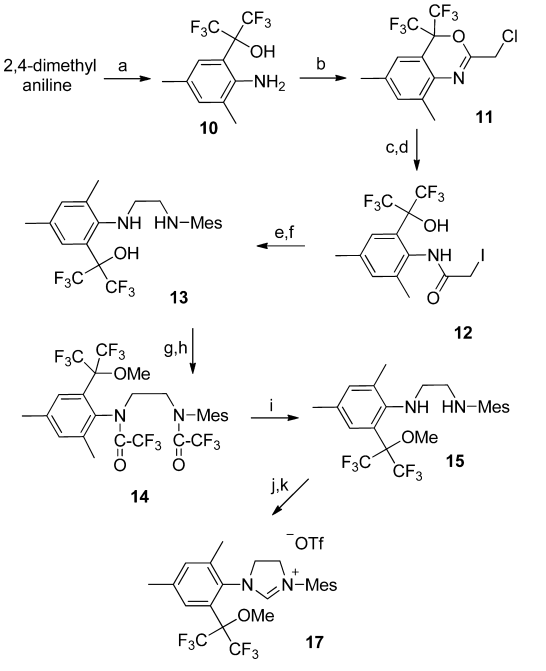
Scheme 1. Synthesis of *p*-Fluoroalkylaryl-Substituted uNHC[a]



[a](a) HFA·1.5 H_2O, *p*-TSA (1 mol %), 100 °C, 95%; (b) PhCHO, toluene, 110 °C; (c) MeI, K_2CO_3, MeCN; 70 °C then HCl/H_2O, rt; 72% for 3 steps; (d) $ClCH_2C(O)Cl$, DMAP, CH_2Cl_2, rt; (e) NaI, acetone, rt; 74% for 2 steps; (f) $MesNH_2$ (15-fold excess), rt; 94%; (g) $BH_3{\cdot}SMe_2$, THF, 85%; (h) MeOH/HCl, rt then $HC(OEt)_3$, 100 °C, 60%. HFA = hexafluoroacetone; *p*-TSA = *p*-tolylsulfonic acid, DMAP = dimethylaminopyridine.

For the preparation of the analogous *ortho*-substituted salt **17** (Scheme 2), the amine **10** formed upon alkylation of 2,4-

Scheme 2. Synthesis of *o*-Fluoroalkylaryl-Substituted uNHC[a]



[a](a) HFA·1.5 H_2O, *p*-TSA (1 mol %), 100 °C, 92%; (b) $ClCH_2C(O)Cl$, DMAP, CH_2Cl_2, rt; (c) HCl/MeOH, rt; (d) NaI, acetone, rt; 79% for 3 steps; (e) $MesNH_2$ (15-fold excess), rt; 94%; (f) $BH_3{\cdot}SMe_2$, THF, 75% for 2 steps; (g) TFAA/Py, CH_2Cl_2, rt; (h) MeI, K_2CO_3, DMF; **14** 93% for 2 steps; (i) KOH, 18-crown-6, DMSO/H_2O, 130 °C, **15** 75%; (j) CH_3CO_2CHO, CH_2Cl_2, rt, **16** 71%, (k) TfOH, rt, 1 h then Tf_2O, 60 °C, 1 h, then DIPEA, 80 °C, 2 h; **17** 95%. DIPEA = diisopropylethylamine.

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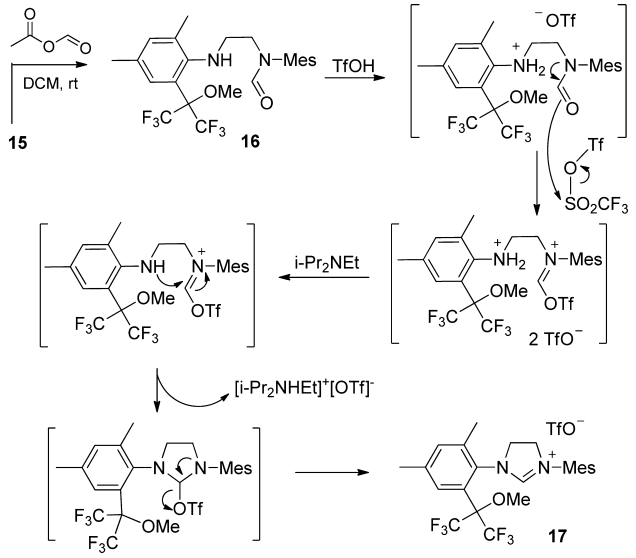
dimethylaniline with HFA hydrate was directly treated with chloroacetyl chloride to give the corresponding benzoxazine **11** quantitatively. After ring opening of **11** under mild acidic conditions, the same procedure as for compound **8** (Scheme 1) was used to afford the hydroxylated diamine **13**. In order to introduce an alkyl substituent selectively on the OH function, we successively protected the diamino moiety of **13** with two trifluoroacetyl groups, performed *O*-alkylation, and then removed the protecting groups treating **14** with KOH, yielding the diaminoether **15**. Since all our attempts to get the imidazoline ring from **15** using conventional methods failed, we slightly modified the protocol recently developed by Organ and co-workers[25] for sterically demanding imidazolinium salts. Thus, we found that **15** can be selectively formylated at the more sterically accessible amino group using acetic–formic mixed anhydride to give **16** (Scheme 3) in good yield.

Scheme 3. Plausible Mechanism for the Formation of 17

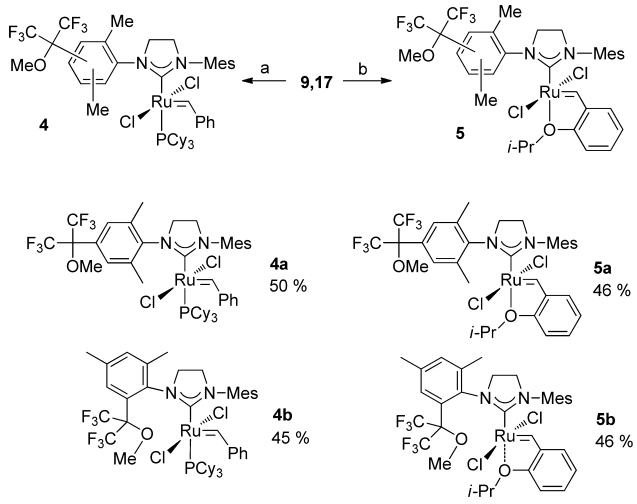


Successive addition of stoichiometric amounts of triflic acid (TfOH) and triflic anhydride (Tf_2O) to the formylated compound **16** provided conditions for Vilsmeyer–Haack reaction. The use of Hünig's base (DIPEA) has proved to be optimal for the final cyclization step to produce the desired imidazolinium triflate salt **17** (Scheme 3). Fortunately, in contrast to Organ's salts,[25] the final fluorinated imidazolinium triflates **17** can be easily purified by single recrystallization from hexanes.

With these new fluorinated uNHC salts in hand, we prepared the ruthenium complexes **4** and **5**. Following the conventional route by the reaction of *in situ* generated carbene with commercially available $RuCl_2(PCy_3)_2(=CHPh)$ **G-I**[26] and $RuCl_2(PCy_3)(=CH(o\text{-}^iPrO\text{-}C_6H_4))$ **H-I**,[27] these complexes were obtained in moderate yields. Purification by silica gel chromatography and further recrystallization from a DCM/*n*-pentane mixture afforded dark-brown (**4**) and dark-green (**5**), air stable solids (Scheme 4).

Complexes **4a**,**b** and **5a**,**b** were completely characterized by NMR spectroscopy and elemental analysis (see the Supporting Information). The NHC ligands of complexes **5a**,**b** rotate fast on the NMR timescale, and therefore, only one absorption is observed in the benzylidene region of the ^1H NMR spectra (around 16.5 ppm) for these phosphine-free complexes. In the

Scheme 4. Synthesis of Fluorinated Metathesis Catalysts 4 and 5[a]



[a](a) KHMDS, **G-I** catalyst, toluene, room temperature, 2 h; (b) KHMDS, **H-I** catalyst, toluene, 80 °C, 40 min.

case of phosphine-containing complex **4a**, a mixture of two rotational isomers (~2:1) is formed. It can be rationalized by the different location of mesityl and fluorinated aryl rings above the benzylidene group due to possible $\pi-\pi$ stacking interaction.[28] In contrast, the sole carbene proton signal of **4b** (20.2 ppm) is observed as the result of hindered rotation of the NHC ligand due to the anchoring effect of the bulky *ortho*-substituent. 2D NMR (HMBC) experiment unambiguously evidences the location of the fluorinated aryl moiety above the benzylidene ring (cross-peak between styrene *ortho-H* (7.33 ppm) and quaternary carbon (84.35 ppm) of $(CF_3)_2\underline{C}$-OMe group; see the Supporting Information).

Single crystals of good quality for X-ray analysis from complexes **5a**,**b** were obtained (Figures 1 and 2).[29]

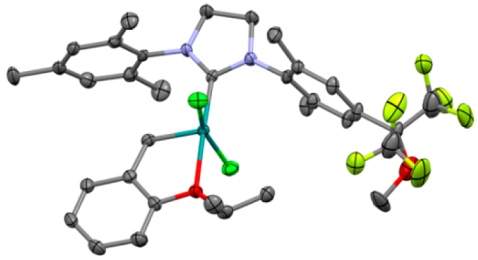


Figure 1. X-ray structure of **5a**.

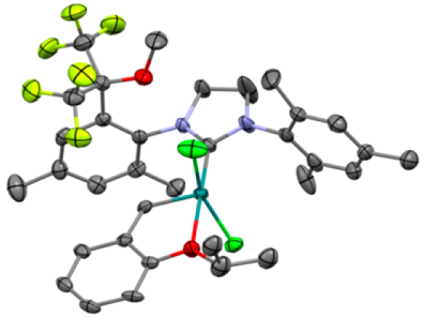


Figure 2. X-ray structure of **5b**.

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The structures of complexes **5a** and **5b** were compared to that of the olefin metathesis catalyst $RuCl_2$(bis(mesityl)imidazolinylidene)(*ortho*-isopropoxybenzylidene) **H-II**.[30] These three complexes crystallize in a monoclinic system. All bond lengths and angles are quite similar, which shows that the substitution does not have a strong effect on the structures of the different complexes, especially around the metal center (Table 1). The chelate (Ru-C(1)-C(3)-O) is almost planar and

Table 1. Selected Structural Data for 5a and 5b

	H-II[30]	5a	5b
bond length (Å)			
Ru−C(1) (benzylidene)	1.828(5)	1.832(4)	1.825(5)
Ru−C(2) (NHC)	1.981(5)	1.987(4)	1.975(5)
Ru−O	2.261(3)	2.257(3)	2.272(3)
Ru−Cl^1	2.3279(12)	2.3492(11)	2.3116(14)
Ru−Cl^2	2.3393(12)	2.3505(11)	2.3393(13)
angle (deg)			
C(1)−Ru−C(2)	101.59(19)	102.64(17)	101.2(2)
C(1)−Ru−O	79.28(17)	79.59(15)	78.91(17)
C(2)−Ru−O	176.22(14)	177.69(14)	177.96(16)
Cl^1−Ru−Cl^2	156.47(5)	159.88(5)	156.80(6)
C(1)−Ru−Cl^1	100.18(15)	98.37 (14)	98.92(15)
C(1)−Ru−Cl^2	100.12(15)	98.54(14)	100.30(15)
C(2)−Ru−Cl^1	96.59(12)	93.46(11)	97.02(13)
C(2)−Ru−Cl^2	90.89(12)	93.40(11)	91.86(14)
torsion angle (deg)			
C(2)−Ru−C(1)−C(3)	171.0(3)	176.2(3)	176.6(4)
Cl^1−Ru−C(1)−C(3)	78.0(3)	80.8(3)	84.1(4)
Cl^2−Ru−C(1)−C(3)	90.1(3)	88.3(3)	82.9(4)
O−Ru−C(1)−C(3)	5.3(3)	3.2(3)	1.4(3)

parallel to the plane of the five-membered NHC ring. The two chloride atoms are in a *trans*-position with a Cl^1−Ru−Cl^2 angle of 156−159°, in a plane which is perpendicular to the bidentate isopropoxybenzylidene and NHC ligands.

It can be noted that, in the solid state, the fluorinated group in the Hoveyda-type complex **5a** is located at the opposite side of the benzylidene ligand, whereas, for complex **5b**, this group sits above the benzylidene ligand, bringing more steric hindrance on the carbene side.

Catalytic activities of the prepared precatalysts **4a,b** and **5a,b** were investigated in RCM reactions with diethyl diallylmalonate (DEDAM), diethyl allylmethallylmalonate as well as in CM reaction of allylbenzene with 1,4-diacetoxybut-2-ene following standard protocols for evaluation of olefin metathesis catalysts.[31] The commercially available $RuCl_2(PCy_3)(H_2IMes)$(=CHPh) (**G-II**)[32] and $RuCl_2(PCy_3)(H_2IMes)$(=CH-(*o*-^{i}PrO-C_6H_4)) (**H-II**)[30] catalysts were used as reference catalysts (H_2IMes = bis(mesityl)imidazolinylidene).

The **G-II** and **H-II** catalysts are efficient for the RCM of diethyl diallylmalonate at 30 °C, and full conversion is obtained within 30 min.[31] The Grubbs-type catalysts **4a** and **4b** behaved similarly with very close kinetic profiles (Figure 3). On the other hand, the Hoveyda-type catalysts **5a** and **5b** presented a very different reactivity from the **H-II** catalyst. A pronounced initiation period (about 30 min) was necessary before they could achieve full conversion with lower reaction rates and thus in longer reaction times (2−4 h). The significant negative effect of an electron-withdrawing substituent such as a chloride directly connected to the *ortho*-position of an aryl substituent of

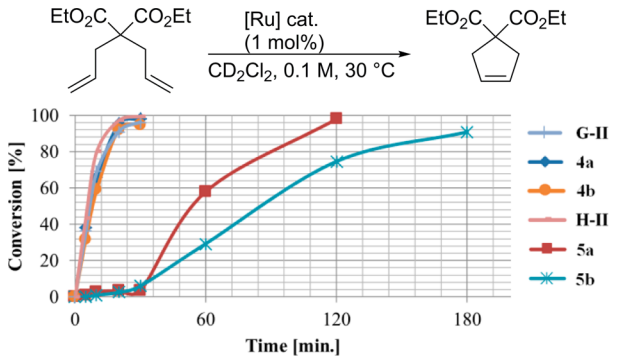

Figure 3. RCM of DEDAM with catalysts **4a**, **4b**, **5a**, and **5b** as compared to **G-II** and **H-II**.

the NHC in a Grubbs-type second-generation catalyst is not observed when a hexafluoroisopropyl group is located at the same position (**4a**).[33]

The ring-closing metathesis of the more sterically hindered diethyl allylmethallylmalonate was also achieved with the new catalysts **4a,b** and **5a,b** (Figure 4). A similar reactivity profile as starting from diallyl malonate was observed, but the reaction rates were lower in all cases, as previously reported for **G-II** and **H-II**.[31]

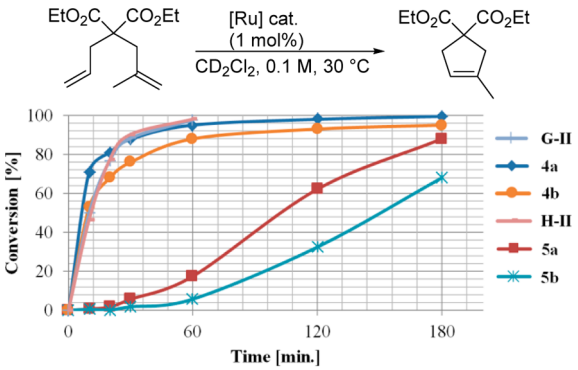

Figure 4. RCM of diethyl allylmethallylmalonate with catalysts **4a**, **4b**, **5a**, and **5b** as compared to **G-II** and **H-II**.

In these RCM reactions, the reactivity of the Grubbs-type catalysts **4a** and **4b** was not strongly affected by the presence of the fluorinated substituents of the NHC ligands as compared to **G-II**. On the contrary, a strong influence was observed in the Hoveyda-type catalysts **5a** and **5b**. The presence of the hexafluoroisopropoxy group induced a long induction period and a latent behavior before the catalytic systems operate efficiently.[34] The reaction rates were lower, but the robustness of these catalysts allowed reaching high conversion of the substrates after long reaction times. It is noteworthy that this initiation period is more pronounced with complex **5b** featuring the fluorinated *ortho*-substituted NHC ligand.

In the cross-metathesis of allylbenzene with an excess of 1,3-diacetoxybut-2-ene, these differences in reactivity did not exist and all complexes allowed reaching an equilibrium at 70−80% conversion within 30 min with closely related kinetic profiles (Figure 5).

■ CONCLUSION

Two new fluorinated imidazolidinium salts, precursors of *N*-heterocyclic carbene ligands, have been prepared. They contain

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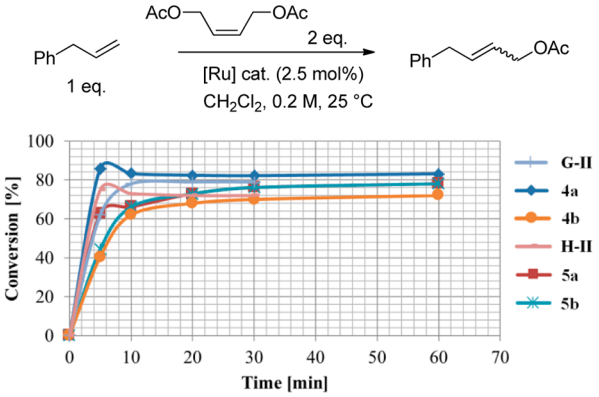

Figure 5. CM of allylbenzene with 1,3-diacetoxybut-2-ene with catalysts **4a**, **4b**, **5a**, and **5b** as compared to **G-II** and **H-II**.

a hexafluoroisopropylmethoxy group connected in the *ortho*- or *para*-position of one *N*-aryl-substituted imidazolidine derivative, whereas the other nitrogen atom is connected to a mesityl group, leading to unsymmetrical NHC ligands. Ruthenium complexes featuring such an unsymmetrical NHC ligand and a benzylidene ligand, in the families of second-generation Grubbs and Hoveyda olefin metathesis catalysts, have been prepared. These ligands do not bring significant structural modifications with respect to the symmetrical $RuCl_2(H_2IMes)$ Hoveyda catalyst. The performance of the Grubbs catalysts in olefin metathesis is similar to the classical Grubbs second-generation catalyst. On the other hand, the new Hoveyda-type catalysts behave differently from the symmetrical Hoveyda-II catalyst equipped with the H_2IMes carbene ligand in ring-closing metathesis of malonate derivatives and show a latent character characterized by an induction period, followed by a lower reaction rate. Profit could be taken of this property for applications in ROMP of strained olefins including fluorinated ones. The latency might be increased by introduction of additional electron-withdrawing trifluoromethylated groups on the NHC ligand.

EXPERIMENTAL SECTION

General Remarks. All solvents were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. Syntheses of ruthenium complexes were performed under an argon atmosphere using a standard Schlenk technique. Analytical TLC was performed with Merck silica gel 60 F254 plates. Visualization was accomplished by UV light (254 and 366 nm), spraying by $Ce(SO_4)_2$ solution in 5% H_2SO_4 or $KMnO_4$ solution in water. Column chromatography was carried out using Merck silica gel 60 (230−400 mesh ASTM) and ethyl acetate/petroleum ether or ethyl acetate/CH_2Cl_2 as eluent. NMR spectra were recorded at room temperature on Bruker AV-300, AV-400, AV-600 spectrometers operating at 300, 400, and 600 MHz for ^1H; 101 and 151 MHz for ^{13}C; 282 and 376 MHz for ^{19}F (CF_3CO_2H as reference), and 121 MHz for ^{31}P (85% H_3PO_4 as reference). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks.

Synthesis of 4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylaniline (6). A mixture of 2,6-dimethylaniline (10.0 g, 82.6 mmol), hexafluoroacetone sesquihydrate (30 g, 153.8 mmol), and PTSA (200 mg, 1.1 mmol) was heated at 100 °C for 20 h. After cooling to r.t., water (50 mL) was added and a resulting mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O and brine and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting solid was recrystallized from petroleum ether to give 23.7 g of the corresponding hexafluoroisopropoxyl aniline. This compound was further treated with benzaldehyde (12.5 g, 118 mmol) in toluene (160 mL) in the presence of PTSA (0.7 g, 4 mmol) under refluxing in a Dean−Stark apparatus for 3 h. After cooling to r.t. and toluene removal, the residue was redissolved in acetonitrile (150 mL). Iodomethane (2.8 g, 102 mmol) and potassium carbonate (21.7 g, 157 mmol) were added to the solution, and the mixture was stirred at 70 °C for 5 h. Then, the cooled (r.t.) reaction mixture was treated with H_2O (100 mL) and extracted with EtOAc (3 × 100 mL). Organic layers were concentrated to the dryness under reduced pressure. 6 N HCl (300 mL) was added to the residue, and the mixture was stirred at r.t. for 3 h. The formed precipitate was separated by filtration, washed with petroleum ether, and treated with saturated solution of $NaHCO_3$ (200 mL) under stirring at r.t. for 1 h. The resulting solid was filtered off and dried to the constant weight to yield 17.0 g (68%) of **6** as a white solid. mp 84−85 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (s, 2H, Ar*H*), 3.79 (s, 2H, NH_2), 3.47 (s, 3H, OCH_3), 2.22 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.6, 128.2, 122.9 (q, $^1J_{C,F}$ = 288 Hz), 121.5, 115.8, 83.1 (quint, $^2J_{C,F}$ = 28 Hz), 54.0, 18.0; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ 6.58 (s). Anal. Calcd for $C_{12}H_{13}F_6NO$ (%): C, 47.85; H, 4.35; N, 4.65. Found: C, 47.79; H, 4.43; N, 4.58.

Synthesis of *N*-(4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl)-2-iodoacetamide (7). Chloroacetyl chloride (3.5 g, 31.0 mmol) was added dropwise to the solution of **6** (8.5 g, 28.2 mmol) and DMAP (4.48 g, 36.7 mmol) in 120 mL of anhydrous CH_2Cl_2 at 0 °C. The reaction mixture was stirred overnight at r.t. Then, the mixture was concentrated to 30 mL under reduced pressure, treated with 5% HCl (100 mL), and extracted with CH_2Cl_2 (3 × 50 mL). Combined organic layers were washed with saturated solution of $NaHCO_3$ (50 mL) and of water (50 mL) and dried over $MgSO_4$. After solvent removal under vacuum, the crude acetylated intermediate was purified by column chromatography in a gradient manner using EtOAc/petroleum ether (1:4−1:2−1:1−1:0) as the eluent to yield 8.2 g (77%) of the corresponding chloromethylamide as a white solid. This compound was further dissolved in acetone (190 mL), and then sodium iodide (8.2 g, 54.5 mmol) was added. The reaction mixture was stirred at r.t. for 24 h. After filtration, the mother liquor was concentrated, and the residue was dissolved in EtOAc (50 mL) and washed with a 5% solution of $Na_2S_2O_3$ (50 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). Combined organic layers were dried using $CaCl_2$, filtered, and concentrated. The crude product was recrystallized from petroleum ether to give 9.8 g (20.9 mmol, 74% for 2 steps) of **7** as a white solid. ^1H NMR (400 MHz, Acetone-d_6): δ 9.08 (s, 1H, N*H*), 7.33 (s, 2H, Ar*H*), 3.98 (s, 2H, CH_2), 3.51 (s, 3H, OCH_3), 2.34 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 167.1, 137.6, 128.4, 126.4, 123.5 (q, $^1J_{C,F}$ = 290 Hz), 83.6 (q, $^2J_{C,F}$ = 28 Hz), 54.9, 18.7, −0.8; $^{19}F\{^1H\}$ NMR (376 MHz, Acetone-d_6): δ 6.26 (s). Anal. Calcd for $C_{14}H_{14}F_6INO_2$ (%): C, 35.84; H, 3.01; N, 2.99. Found: C, 35.76; H, 3.13; N, 2.89.

Synthesis of N^1-(4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl)-N^2-mesitylethane-1,2-diamine (8). A mixture of **7** (9.8 g, 20.9 mmol) and mesitylamine (42.3 g, 313.3 mmol) was stirred at r.t. for 4 days. After reaction completion, the mixture was treated with a 10% solution of $NaHCO_3$ (100 mL) and extracted with EtOAc (3 × 60 mL). Combined organic layers were washed with brine and water and then dried over $MgSO_4$ and concentrated under reduced pressure. The excess of $MesNH_2$ was removed at 70 °C/0.05 mm Hg. The residual solid was recrystallized from petroleum ether to give 9.4 g (19.6 mmol, 94%) of the corresponding adduct as a white solid. This compound was further dissolved in anhydrous toluene (100 mL), and $BH_3{\cdot}SMe_2$ (44.1 mL of 2 M solution in THF, 88.2 mmol) was added dropwise under an argon atmosphere at r.t. The resulting mixture was stirred at 90 °C for 3 h. After cooling to r.t., MeOH was slowly added until ceasing of gas evolution. Then, a 5% solution (300 mL) of HCl was added and resulting mixture was extracted with EtOAc (2 × 120 mL). The aqueous layer was separated, treated with $NaHCO_3$, and extracted with EtOAc (2 × 120 mL). Combined organic layers were washed with a saturated solution of $NaHCO_3$, dried over $MgSO_4$, and concentrated

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under reduced pressure. The crude product was purified by column chromatography using EtOAc/petroleum (1:6) ether as eluent to yield 7.7 g (16.7 mmol, 80% for 2 steps) of **8** as a colorless oil. ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.18 (s, 2H, Ar*H*), 6.77 (s, 2H, Ar*H*), 4.30 (bs, 1H, N*H*), 3.52 (bs, 1H, N*H*), 3.47 (s, 3H, OCH_3), 3.37 (t, $^3J_{H,H}$ = 5.9 Hz, 2H, CH_2), 3.12 (t, $^3J_{H,H}$ = 6.0 Hz, 2H, CH_2), 2.36 (s, 6H, *o*-CH_3), 2.21 (s, 6H, *o*-CH_3), 2.17 (s, 3H, *p*-CH_3); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ 149.6, 144.47, 131.8, 131.0, 130.1, 129.3, 129.2, 123.8 (q, $^1J_{C,F}$ = 290 Hz), 119.0, 83.7 (q, $^2J_{C,F}$ = 28 Hz), 54.5, 49.4, 48.8, 20.7, 19.5, 18.5; ^{19}F{^{1}H} NMR (376 MHz, Acetone-d_6): δ 6.11 (s). Anal. Calcd for $C_{23}H_{28}F_6N_2O$ (%): C, 59.73; H, 6.10; N, 6.06. Found: C, 59.71; H, 6.12; N, 5.99.

Synthesis of 1-(4-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl)-3-mesityl-4,5-dihydroimidazolium Chloride (9). Concentrated HCl (10 mL, 120 mmol) was added to the solution of **8** (6 g, 13.0 mmol) in MeOH (100 mL) and stirred for 10 min. The solution was evaporated under reduced pressure. To the residual solid CH(OEt)$_3$ (26.7 g, 180 mmol) was added, and the mixture was heated at 100 °C for 4 h. Then, the excess of CH(OEt)$_3$ was removed under vacuum and the resulting solid was washed with 100 mL of Et$_2$O. The recrystallization from EtOAc gave pure **9** (3.98 g, 60%) as a white solid. mp 190−194 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ 10.41 (s, 1H, H$_2$I C*H*), 7.48 (s, 2H, Ar*H*), 7.00 (s, 2H, Ar*H*), 4.86−4.69 (m, 4H, H$_2$I CH_2CH_2), 3.53 (s, 3H, OCH_3), 2.64 (s, 6H, *o*-CH_3), 2.47 (s, 6H, *o*-CH_3), 2.28 (s, 3H, Mes *p*-CH_3); ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ 162.0, 140.6, 138.6, 137.0, 136.7, 132.2, 130.4, 129.6, 129.4, 123.3 (q, $^1J_{C,F}$ = 290 Hz), 83.6 (t, $^2J_{C,F}$ = 28 Hz), 55.2, 52.6, 52.3, 21.0, 18.8, 18.2; ^{19}F{^{1}H} NMR (376 MHz, Acetone-d_6): δ 6.44 (s). Anal. Calcd for $C_{24}H_{27}ClF_6N_2O$ (%): C, 56.64; H, 5.35; N, 5.50. Found: C, 56.54; H, 5.42; N, 5.48.

Synthesis of 2-(2-Amino-3,5-dimethylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (10). A mixture of 2,4-dimethylaniline (10.0 g, 82.6 mmol), hexafluoroacetone sesquihydrate (30 g, 153.8 mmol), and PTSA (200 mg, 1.1 mmol) was heated at 100 °C for 20 h. After cooling to r.t., water (50 mL) was added and the resulting mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H$_2$O and brine and then dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude product was recrystallized from petroleum ether to give 21.9 g (92%) of **10** as a brown solid. mp 110−112 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26 (s, 1H, Ar*H*), 7.12 (s, 1H, Ar*H*), 5.58 (bs, 3H, NH_2, O*H*), 2.32 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 137.2, 135.0, 134.3, 132.8, 127.1−127.0 (m), 123.6, 123.6 (q, $^1J_{C,F}$ = 289 Hz), 80.3 (quint, $^2J_{C,F}$ = 30 Hz), 21.2, 18.2; ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$): δ 2.59 (s). Anal. Calcd for $C_{11}H_{11}F_6NO$ (%): C, 46.00; H, 3.86; N, 4.88. Found: C, 46.05; H, 3.91; N, 4.76.

Synthesis of 2-(Chloromethyl)-6,8-dimethyl-4,4-bis(trifluoromethyl)-4*H*-benzo[*d*][1,3]oxazine (11). (isolated as intermediate in synthesis of **12**). Chloroacetyl chloride (0.21 g, 1.9 mmol) was added dropwise to the solution of **10** (0.5 g, 1.7 mmol) and DMAP (0.21 g, 1.7 mmol) in 20 mL of anhydrous CH$_2$Cl$_2$ at 0 °C and stirred overnight at r.t. The reaction mixture was treated with 5% HCl (30 mL) and extracted with CH$_2$Cl$_2$ (2 × 20 mL). Combined organic layers were washed with a solution of NaHCO$_3$ and water and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography using EtOAc/petroleum ether (1:6) as the eluent to yield 250 mg (0.7 mmol, 43%) of **11** as a colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.18 (s, 1H, Ar*H*), 7.10 (s, 1H, Ar*H*), 4.23 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.35 (s, 3H, CH_3); ^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$): δ 1.80 (s). Anal. Calcd for $C_{13}H_{10}ClF_6NO$ (%): C, 45.17; H, 2.92; N, 4.05. Found: C, 45.09; H, 2.99; N, 4.01.

Synthesis of *N*-(2-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropan-2-yl)-4,6-dimethylphenyl)-2-iodoacetamide (12). Chloroacetyl chloride (7.0 g, 62.6 mmol) was added dropwise to the solution of **10** (15 g, 52.2 mmol) and DMAP (6.4 g, 52.2 mmol) in 20 mL of anhydrous CH$_2$Cl$_2$ at 0 °C and stirred overnight at r.t. The reaction mixture was treated with 5% HCl (150 mL) and extracted with CH$_2$Cl$_2$ (3 × 60 mL). Combined organic layers were washed with 60 mL of water and dried over MgSO$_4$. Then, solvents were evaporated under reduced pressure, the residue was dissolved in MeOH (300 mL), and concentrated HCl (15 mL) was added to the solution. The mixture was stirred overnight. Then, solvents were removed under reduced pressure and the residue was treated with a saturated solution of NaHCO$_3$ (500 mL) and extracted with EtOAc (2 × 200 mL). Combined organic layers were washed with 200 mL of water, dried using MgSO$_4$, filtered, and concentrated under low pressure. The residual dark brown solid was recrystallized from petroleum ether to afford 17.7 g (93%) of the corresponding chloromethylamide as a light brown solid. This compound was further dissolved in acetone (300 mL), and then sodium iodide (12.1 g, 80.7 mmol) was added. The reaction mixture was stirred at r.t. for 24 h. After filtration, the mother liquor was concentrated, and the residue was dissolved in EtOAc (50 mL) and washed with a 5% solution of Na$_2$S$_2$O$_3$ (50 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). Combined organic layers were dried over MgSO$_4$, filtered, and concentrated. The crude product was recrystallized from petroleum ether to give 12.5 g, 79% (for 3 steps) of **12** as a brown solid, mp 143−145 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.13 (s, 1H, N*H*), 7.26 (s, 1H, Ar*H*), 7.20 (s, 1H, Ar*H*), 5.04 (s, 1H, O*H*), 3.74 (s, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 166.5, 138.7, 137.3, 134.6, 134.2, 131.9, 127.0−126.8 (m), 124.6, 121.5, 80.7−79.2 (m), 21.3, 18.8, −1.5; ^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$): δ 3.86 (s). Anal. Calcd for $C_{13}H_{12}F_6INO_2$ (%): C, 34.31; H, 2.66; N, 3.08. Found: C, 34.26; H, 2.73; N, 2.98.

Synthesis of 1,1,1,3,3,3-Hexafluoro-2-(2-((2-(mesitylamino)-ethyl)amino)-3,5-dimethylphenyl)propan-2-ol (13). A mixture of **12** (12.5 g, 27.5 mmol) and mesitylamine (55.7 g, 412.0 mmol) was stirred at r.t. for 4 days. After reaction completion, the mixture was treated with a 10% solution of NaHCO$_3$ (100 mL) and extracted with EtOAc (3 × 60 mL). Combined organic layers were washed with brine and water and then dried over MgSO$_4$ and concentrated under reduced pressure. The excess of MesNH$_2$ was removed at 70 °C/0.05 mmHg. The residual solid was recrystallized from petroleum ether to give 12.0 g (25.9 mmol, 94%) of the corresponding adduct as a white solid. This compound was further dissolved in anhydrous toluene (150 mL), and BH$_3$·SMe$_2$ (58.3 mL of 2 M solution in THF, 116.6 mmol) was added dropwise under an argon atmosphere at r.t. The resulting mixture was stirred at 90 °C for 3 h. After cooling to r.t., MeOH was slowly added until ceasing of gas evolution. Then, a 10% solution (300 mL) of HCl was added and resulting mixture was extracted with EtOAc (2 × 120 mL). The aqueous layer was separated, treated with NaHCO$_3$, and extracted with EtOAc (2 × 120 mL). Combined organic layers were washed with a saturated solution of NaHCO$_3$, dried over MgSO$_4$, and concentrated under reduced pressure. The crude product was recrystallized from petroleum ether to give 9.3 g (20.7 mmol, 75% for 2 steps) of **13** as a beige solid. mp 148−150 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 13.78 (s, 1H, N*H*), 7.34 (s, 1H, Ar*H*), 7.16 (s, 1H, Ar*H*), 6.87 (s, 2H, Mes Ar*H*), 4.01 (s, 1H, N*H*), 3.26−3.22 (m, 2H, CH_2), 3.08−3.03 (m, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.31 (s, 6H, Mes *o*-CH_3), 2.25 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ 142.3, 141.6, 136.4, 135.6, 133.7, 132.7, 130.6, 129.8, 127.5, 124.2, 123.5 (q, $^1J_{C,F}$ = 288 Hz), 80.5 (quint, $^2J_{C,F}$ = 29 Hz), 51.0, 47.8, 21.3, 20.7, 18.5, 17.2; ^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$): δ 2.11 (s). Anal. Calcd for $C_{22}H_{26}F_6N_2O$ (%): C, 58.92; H, 5.84; N, 6.25. Found: C, 58.85; H, 5.93; N, 6.20.

Synthesis of 2,2,2-Trifluoro-*N*-(2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4,6-dimethylphenyl)-*N*-(2-(2,2,2-trifluoro-*N*-mesitylacetamido)ethyl)acetamide (14). TFAA (1.5 g, 13.4 mmol) and pyridine (1.1 g, 13.4 mmol) were added sequentially to the solution of **13** (3 g, 6.7 mmol) in CH$_2$Cl$_2$ (30 mL) at 0 °C. The reaction mixture was stirred at r.t. for 1 h, and then water (30 mL) was added to the mixture. The organic layer was separated; the aqueous layer was extracted with CH$_2$Cl$_2$ (2 × 20 mL). Combined organic layers were dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The crude product was recrystallized from petroleum ether to yield 4.0 g (6.3 mmol, 94%) of the corresponding protected diamine as a white solid. This compound (2.0 g, 3.2 mmol) was solved in dry DMF (25 mL). MeI (1.3 g, 9.5 mmol) and

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anhydrous K_2CO_3 (1.74 g, 12.6 mmol) were added, and the resulting solution was heated overnight at 80 °C. Then, after cooling to r.t., 20 mL of water was added to the mixture. The crude product was extracted with EtOAc (3 × 15 mL). Combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 2.1 g (99%) of **14** as a white solid. mp 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 1H, Ar*H*), 7.27 (s, 1H, Ar*H*), 6.93 (s, 2H, Mes Ar*H*), 4.23 (td, $J_{H,H}$ = 11.6, 3.7 Hz, 1H, CH_2CH_2), 4.13 (td, $J_{H,H}$ = 11.8, 4.8 Hz, 1H, CH_2CH_2), 3.91 (td, $J_{H,H}$ = 11.6, 4.8 Hz, 1H, CH_2CH_2), 3.75 (s, 3H, OCH_3), 3.32 (td, $J_{H,H}$ = 11.9, 3.5 Hz, 1H, CH_2CH_2), 2.42 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.17 (s, 6H, Mes *o*-CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.7 (q, $^2J_{C,F}$ = 36 Hz), 158.3 (q, $^2J_{C,F}$ = 36 Hz), 139.3, 139.0, 138.7, 136.6, 136.2, 135.8, 134.8, 134.5, 130.0, 129.7, 128.6, 126.4, 123.3 (q, $^1J_{C,F}$ = 293 Hz), 116.1 (q, $^1J_{C,F}$ = 288 Hz), 84.6−83.0 (m), 57.7, 51.1, 49.0, 21.4, 21.1, 19.6, 18.3, 18.1; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ 10.24−10.09 (m), 9.62 (br.s), 7.94−7.78 (m), 6.91 (s). Anal. Calcd for $C_{27}H_{26}F_{12}N_2O_3$ (%): C, 49.55; H, 4.00; N, 4.28. Found: C, 49.49; H, 4.13; N, 4.19.

Synthesis of *N*^{1}-(2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4,6-dimethylphenyl)-*N*^{2}-mesitylethane-1,2-diamine (15). A mixture of **14** (2.1 g, 3.2 mmol), 18-crown-6 (5 mg, 0.02 mmol), and a solution of KOH (15.1 g, 0.270 mmol) in water (8 mL) was heated in DMSO (15 mL) at 130 °C for 1.5 h; then the reaction mixture was allowed to stir overnight at r.t. Water (30 mL) was added, and the crude product was extracted with EtOAc (3 × 20 mL). Combined organic layers were washed with 20 mL of water, dried over $MgSO_4$, and concentrated. The product was purified by column chromatography using EtOAc/petroleum ether (1:20) as eluent to yield 1.05 g (71%) of **15** as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07 (s, 1H, Ar*H*), 7.00 (s, 1H, Ar*H*), 6.84 (s, 2H, Mes Ar*H*), 5.21 (br.s, 1H, N*H*), 3.51 (s, 3H, OCH_3), 3.17 (s, 4H, CH_2CH_2), 2.32 (s, 3H, CH_3), 2.31 (s, 6H, Mes *o*-CH_3), 2.26 (s, 3H, CH_3), 2.24 (s, 3H, CH_3); ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ 8.31 (s). Anal. Calcd for $C_{23}H_{28}F_6N_2O$ (%): C, 59.73; H, 6.10; N, 6.06. Found: C, 59.71; H, 6.19; N, 6.01.

Synthesis of *N*-(2-((2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4,6-dimethylphenyl)amino)ethyl)-*N*-mesitylformamide (16). Acetic formic anhydride (0.4 g, 4.54 mmol) was added dropwise to the solution of **15** (1.05 g, 2.27 mmol) in CH_2Cl_2 (20 mL). After homogenization, the reaction mixture was allowed to stir for 30 min at r.t. Then, 40 mL of water was added and the mixture was extracted with CH_2Cl_2 (2 × 30 mL). Combined organic layers were washed with a saturated solution of $NaHCO_3$ and water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc/petroleum ether (1:4) as eluent to yield 0.67 g (60%) of **16** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (s, 1H, C*H*O), 7.03 (s, 1H, Ar*H*), 6.95 (s, 3H, Ar*H*), 5.06 (s, 1H, N*H*), 3.80 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, CH_2), 3.43 (s, 3H, OCH_3), 3.13 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.22 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 163.9, 147.0, 138.3, 136.4, 135.8, 135.3, 135.2, 130.9, 129.7, 127.7, 123.9, 121.0, 85.6, 54.5, 46.7, 45.6, 29.7, 20.9, 20.6, 20.5, 18.3; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ 8.26 (s). Anal. Calcd for $C_{24}H_{28}F_6N_2O_2$ (%): C, 58.77; H, 5.75; N, 5.71. Found: C, 58.72; H, 5.81; N, 5.67.

Synthesis of 1-(2-(1,1,1,3,3,3-Hexafluoro-2-methoxypropan-2-yl)-4,6-dimethylphenyl)-3-mesityl-4,5-dihydroimidazolium Triflate (17). Triflic acid (0.2 g, 1.37 mmol) was added to the solution of **16** (0.67 g, 1.37 mmol) in toluene (30 mL), and the mixture was stirred at r.t. for 15 min. Then, triflic anhydride (0.29 g, 1.37 mmol) was added, and the reaction mixture was heated at 65 °C for 1.5 h. DIPEA (0.53 g, 4.11 mmol) was added, and the reaction mixture was heated at 80 °C for another 1.5 h. After cooling to r.t., 30 mL of water was added and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried using $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was recrystallized from petroleum ether to give 0.82 g (1.33 mmol, 95%) of **17** as a beige solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H, H_2I C*H*), 7.42 (s, 1H, Ar*H*), 7.31 (s, 1H, Ar*H*), 6.94 (s, 2H, Mes Ar*H*), 4.54−4.24 (m, 4H, H_2I CH_2CH_2), 3.57 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.26 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.3, 141.4, 140.9, 139.0, 135.8, 135.2, 134.7, 130.5, 130.4−130.0 (m), 129.9, 124.2, 123.5, 122.1, 121.3, 120.6, 119.0, 83.5 (t, $^2J_{C,F}$ = 30 Hz), 55.7, 53.0, 51.7, 21.5, 21.1, 18.7, 17.9, 17.4; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ 10.44 (s), 6.69 (br.s), −1.21 (s). Anal. Calcd for $C_{25}H_{27}F_9N_2O_4S$ (%): C, 46.00; H, 3.86; N, 4.88. Found: C, 45.97; H, 3.88; N, 4.86.

General Procedure for the Synthesis of Grubbs-Type Catalysts 4a and 4b. In a flame-dried Schlenk flask, imidazolinium salt (1.00 mmol) was mixed with 20 mL of anhydrous toluene. The resulting mixture was cooled to 0 °C and degassed three times, and then KHMDS (1.04 mL of 1 M solution in THF, 1.04 mmol) was added to the mixture under an argon atmosphere. The reaction mixture was stirred for 30 min at r.t.; then Grubbs' catalyst G-I (0.63 g, 0.82 mmol) was added and mixture was stirred for 2 h. During this time, the reaction mixture changed color from violet to red-brown. Once complete (TLC-control), solvents were removed from the reaction mixture under reduced pressure, and the resulting substance was purified by column chromatography in a gradient manner using EtOAc/petroleum ether (1:8−1:3) as eluent under an argon atmosphere. The resulting solid was recrystallized from MeOH to yield **4** as a brown solid.

*Catalyst $RuCl_2$\{1-(4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl)-3-mesityl-4,5-dihydroimidazol-2-ylidene\}-(=CH-Ph)(PCy_3) (**4a**).* ^{1}H NMR (400 MHz, C_6D_6): δ 19.79, 19.53 (s, 1H, C*H*Ph), 8.35 (s, 1H, Ar*H*), 7.61 (s, 1H, Ar*H*), 7.05−6.71 (m, 6H, Ar*H*), 6.23 (s, 1H), 3.33−1.04 (m, 54H); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 296.7 (d, $^2J_{C,P}$ = 122 Hz), 295.8 (d, $^2J_{C,P}$ = 134 Hz) 221.5 (d, $^2J_{C,P}$ = 76 Hz), 220.3 (d, $^2J_{C,P}$ = 79 Hz), 153.2, 152.0, 142.5, 141.2, 140.2, 139.2, 138.9, 138.5, 137.7, 137.5, 137.1, 135.6, 130.4, 129.5, 128.8, 128.7, 128.6, 128.4, 127.5, 123.4 (q, $^1J_{C,F}$ = 290 Hz), 123.0 (q, $^1J_{C,F}$ = 290 Hz), 84.0−82.8 (m), 54.5, 54.3, 52.1, 51.6, 51.3, 33.0, 32.9, 32.1, 31.9, 29.6, 29.3, 28.3, 28.2, 27.9, 27.8, 26.7, 26.5, 21.2, 21.0, 20.8, 20.5, 19.4, 19.0; ^{19}F{^{1}H} NMR (376 MHz, C_6D_6): δ 7.42 (s); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 28.00 (s), 23.07 (s). Anal. Calcd for $C_{49}H_{65}Cl_2F_6N_2OPRu$ (%): C, 57.98; H, 6.45; N, 2.76. Found: C, 57.93; H, 6.49; N, 2.74.

*Catalyst $RuCl_2$\{1-(2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-4,6-dimethylphenyl)-3-mesityl-4,5-dihydroimidazol-2-ylidene\}-(=CH-Ph)(PCy_3) (**4b**).* ^{1}H NMR (600 MHz, C_6D_6): δ 20.19 (s, 1H, C*H*Ph), 9.36 (s, 1H, Ar*H*), 7.32 (s, 1H, Ar*H*), 7.25 (s, 1H, Ar*H*), 7.11 (t, $J_{H,H}$ = 7.2 Hz, 1H, Ar*H*), 7.06 (s, 1H, Ar*H*), 6.97 (s, 1H, Ar*H*), 6.94 (s, 1H, Ar*H*), 6.82 (s, 1H, Ar*H*), 5.94 (s, 1H, Ar*H*), 4.04 (s, 3H, OCH_3), 3.91 (m, 1H, H_2I CH_2CH_2), 3.55 (dd, $J_{H,H}$ = 22.0, 10.3 Hz, 1H, H_2I CH_2CH_2), 3.28 (m, 1H, H_2I CH_2CH_2), 3.15 (dd, $J_{H,H}$ = 22.0, 10.3 Hz, 1H, H_2I CH_2CH_2), 2.95 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 2.52 (q, $J_{H,P}$ = 11.7 Hz, 3H, PCy_3), 2.28 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.59 (m, 16H, PCy_3), 1.15 (m, 13H, PCy_3), 0.90 (q, $J_{H,P}$ = 12.4 Hz, 3H, PCy_3); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 294.4 (d, $^2J_{C,P}$ = 117 Hz), 220.3 (d, $^2J_{C,P}$ = 79 Hz), 152.5, 152.5, 141.8, 140.5, 138.6, 138.5, 138.4, 137.1, 135.9, 134.5, 132.2, 130.5, 130.4, 129.5, 128.8, 128.4, 128.1, 127.3, 125.2, 125.0, 123.2, 123.1, 84.4 (quint, $^2J_{C,F}$ = 26 Hz), 57.3, 53.0, 52.05, 50.02, 31.8, 31.7, 29.8, 29.4, 28.3, 28.22, 28.15, 26.6, 21.2, 21.0, 20.9, 20.7, 20.4; ^{19}F{^{1}H} NMR (376 MHz, C_6D_6): δ 14.1 (s), 8.7 (s); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 27.2 (s). Anal. Calcd for $C_{49}H_{65}Cl_2F_6N_2OPRu$ (%): C, 57.98; H, 6.45; N, 2.76. Found: C, 58.04; H, 6.51; N, 2.67.

General Procedure for Synthesis of Hoveyda-Type Catalysts 5a and 5b. In a flame-dried Schlenk flask, imidazolinium salt (0.98 mmol) was mixed with 35 mL of anhydrous toluene. The resulting mixture was cooled to 0 °C and degassed three times; then KHMDS (1.25 mL of 1 M solution in THF, 1.25 mmol) was added to the mixture under an argon atmosphere. The reaction mixture was stirred for 30 min at r.t.; then Hoveyda catalyst **H-I** (0.49 g, 0.82 mmol) was added and mixture was stirred for 40 min at 80 °C. During this time, the reaction mixture changed color from brown to green. Once complete, solvents were removed from the reaction mixture under reduced pressure, and the resulting substance was purified by column

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chromatography using EtOAc/petroleum ether (1:3) as eluent to yield Hoveyda-type catalyst as a green solid. Suitable for X-ray crystals of **5a** and **5b** were grown by slow diffusion of hexane vapors in CH_2Cl_2 solution.

*Catalyst $RuCl_2$\{1-(4-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl)-3-mesityl-4,5-dihydroimidazol-2-ylidene\}(=CH-o-iPrO-Ph) (**5a**).* ^{1}H NMR (600 MHz, C_6D_6): δ 16.61 (s, 1H, CHAr), 7.64 (s, 2H, ArH), 7.11 (d, $J_{H,H}$ = 7.4 Hz, 1H, ArH), 7.08 (m, 1H, ArH), 6.87 (s, 2H, ArH), 6.64 (t, $J_{H,H}$ = 7.4 Hz, 1H, ArH), 6.30 (d, $J_{H,H}$ = 8.3 Hz, 1H, ArH), 4.46 (sept, $^3J_{H,H}$ = 6.0 Hz, 1H, O^{i}Pr CH), 3.35 (m, 2H, H_2I CH_2CH_2), 3.28 (m, 5H, H_2I CH_2CH_2, OCH_3), 2.60 (s, 6H, CH_3), 2.43 (s, 6H, CH_3), 2.22 (s, 3H, Mes *p*-CH_3), 1.28 (d, $^3J_{H,H}$ = 6.1 Hz, 6H, O^{i}Pr CH_3); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 291.4, 213.2, 152.7, 145.7, 141.4, 138.8, 129.8, 129.3, 128.7, 128.4, 123.4 (q, $^1J_{C,F}$ = 290 Hz), 122.34, 122.27, 113.3, 83.5 (quint, $^2J_{C,F}$ = 28 Hz), 75.2, 54.2, 21.4, 21.1; ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): δ 7.57 (s). Anal. Calcd for $C_{34}H_{38}Cl_2F_6N_2O_2Ru$ (%): C, 51.52; H, 4.83; N, 3.53. Found: C, 51.49; H, 4.86; N, 3.53.

*Catalyst $RuCl_2$\{1-(2-(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)-2,6-dimethylphenyl)-3-mesityl-4,5-dihydroimidazol-2-ylidene\}(=CH-o-iPrO-Ph) (**5b**).* ^{1}H NMR (400 MHz, C_6D_6): δ 16.68 (s, 1H, CHAr), 7.72 (s, 1H, ArH), 7.09 (m, 2H, ArH), 6.98 (d, $J_{H,H}$ = 7.6 Hz, 2H, ArH), 6.74 (s, 1H, ArH), 6.66 (t, $J_{H,H}$ = 7.3 Hz, 1H, ArH), 6.32 (d, $J_{H,H}$ = 8.1 Hz, 1H, ArH), 4.46 (sept, $^3J_{H,H}$ = 5.7 Hz, 1H, O^{i}Pr CH), 4.17 (m, 1H, H_2I CH_2CH_2), 3.78 (s, 3H, OCH_3), 3.46 (m, 3H, H_2I CH_2CH_2), 2.72 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.29 (dd, $J_{H,H}$ = 12.8, 5.9 Hz, 6H, O^{i}Pr CH_3); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 289.4, 215.3, 153.2, 145.4, 142.9, 140.8, 140.4, 139.7, 138.8, 138.4, 135.7, 134.8, 129.7, 129.6, 129.3, 123.8 (q, $^1J_{C,F}$ = 294 Hz), 123.5 (q, $^1J_{C,F}$ = 290 Hz), 122.2, 122.1, 113.5, 85.0 (quint, $^2J_{C,F}$ = 28 Hz), 75.3, 58.2, 53.5, 51.1, 21.4, 21.31, 21.29, 21.25, 21.1, 21.0, 20.8; ^{19}F{^{1}H} NMR (376 MHz, C_6D_6): δ 12.29 (s), 6.70 (s). Anal. Calcd for $C_{34}H_{38}Cl_2F_6N_2O_2Ru$ (%): C, 51.52; H, 4.83; N, 3.53. Found: C, 51.48; H, 4.85; N, 3.49.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra for all new compounds, 2D NMR (HMBC) spectra for **4b**, and crystallography data for **5a** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: christian.bruneau@univ-rennes1.fr (C.B.).
*E-mail: osipov@ineos.ac.ru. Fax: +74991355085 (S.N.O.).

Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to the memory of Prof. Michael F. Lappert for his outstanding contribution to organometallic chemistry.

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