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Towards Long-Living Metathesis Catalysts by Tuning the N-Heterocyclic Carbene (NHC) Ligand on Trifluoroacetamide-Activated Boomerang Ru Complexes

Hervé Clavier,[a,b] Fréderic Caijo,[c] Etienne Borré,[d] Diane Rix,[d] Fabien Boeda,[a] Steven P. Nolan,*[a,b] and Marc Mauduit*[d]

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The synthesis and characterization of three novel trifluoromethylamido-containing "boomerang" precatalysts bearing various N-heterocyclic carbene (NHC) ligands are reported. Comparative kinetic and stability studies show the significant effect of the NHC on the catalyst reaction profile. An investigation of the reaction scope for diverse metathesis transformations has allowed us to establish the influence of the NHC on catalyst activity, especially as a function of substrate steric bulk. The excellent stability of one of the novel precatalysts is disclosed, and allowed for its recovery at the end of catalytic reactions. Large-scale ring-closing metathesis, enyne-metathesis and cross-metathesis experiments have revealed the recoverability of the catalyst. ICP-MS analyses of the synthesized products reveal Ru contamination levels of less than 2.5 ppm.

Introduction

Over the past decade, ruthenium-mediated olefin metathesis has emerged as an indispensable tool in organic synthesis for the formation carbon–carbon double bonds.[1] This ubiquitous use of metathesis is clearly illustrated by the large number of applications in natural product synthesis.[2] The rapid development of this area has been punctuated by ground-breaking developments involving well-defined ruthenium–carbene complexes. Of these, the benzylidene[3] and boomerang-type catalysts[4] are most widely used. Further improvements to the reactivity and stability of these complexes have been achieved by the introduction of a N-heterocyclic carbene (NHC) ligand.[5] Thus, the now well-known 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (SIMes) and 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) were introduced into the coordination sphere of the ruthenium metal center of both benzylidene and boomerang catalysts leading to complexes **1a**,[6] **1b**,[7] and **2a**[8] (Figure 1). Synthetic manipulations were carried out to tune the NHC, for example, by using 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (complexes **1c**,[9] **1d**,[10] and **2c**[11]), and other NHC ligands.[12,13]

Catalysts of type **2** suffer from somewhat slow activation kinetics. Some activated versions of the boomerang catalyst have been developed based on either steric (complex **3a**[14]) or electronic modulation of the coordination environment (complexes **4a**[15] and **5a**[16]). We recently disclosed a series of analogues of the Hoveyda complex **2a** bearing an aminocarbonyl group, for example, **6a**, which have allowed significant catalytic improvements.[17] Surprisingly, of these activated boomerang catalysts, only the SIMes NHC has been employed so far.[18]

By appropriately substituting the styrenyl ether ligand, which influences the catalyst activation step, and by varying the NHC ligand, which can enhance the competence of the active species, a simultaneous variation could very well allow the development of ever more efficient catalysts. Moreover, because styrenyl ether and NHC ligands control the stability of the precatalyst and active species, respectively, appropriate ligand selection could lead to longer-living catalysts. Such a variation should allow for a decrease in the often high catalyst loading required in most olefin metathe-

[a] Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain
[b] School of Chemistry, Purdie Building, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, United Kingdom
Fax: +44-1334-463808
E-mail: sn17@st-andrews.ac.uk
[c] Ω^{cat} SYSTEM®, Ecole Nationale Supérieure de Chimie de Rennes,
Av. du Général Leclerc, 35700 Rennes, France
Fax: +33-2-23238108
E-mail: frederic.caijo@ensc-rennes.fr
[d] Sciences Chimiques de Rennes, UMR 6226 CNRS, Equipe Chimie Organique et Supramoléculaire, Ecole Nationale Supérieure de Chimie de Rennes,
Av. du Général Leclerc, 35700 Rennes, France
Fax: +33-2-23238108
E-mail: marc.mauduit@ensc-rennes.fr
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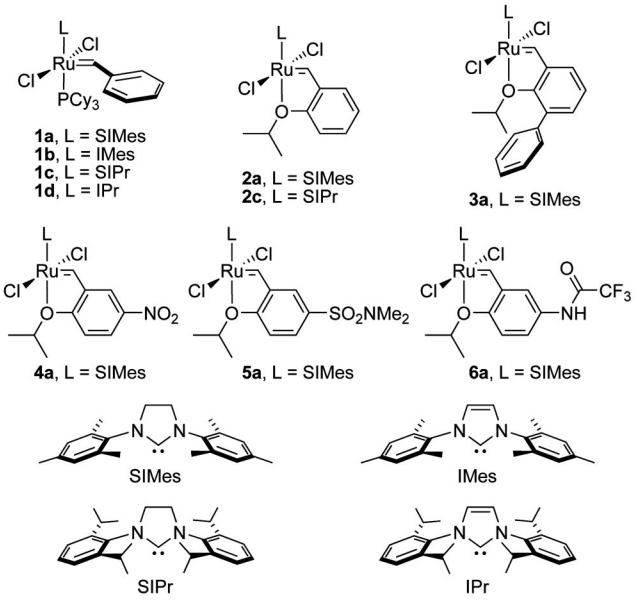


Figure 1. Representative NHC-containing Ru-based complexes for olefin metathesis.

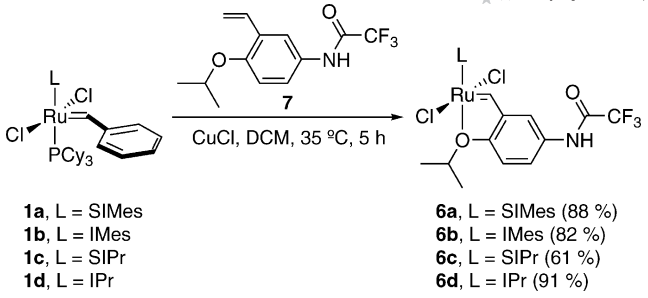
sis transformations.[19] It is clear that this high catalyst loading requirement and associated elevated levels of ruthenium contamination in the final organic products have with no doubt delayed the industrial-scale use of olefin metathesis.

We report herein the synthesis and full characterization of new NHC-containing boomerang-type complexes. A beneficial pairing of a NHC ligand with the trifluoromethylamide group has been achieved and excellent stability was observed for one of the novel complexes. This enhanced stability permits the recovery of the catalyst after catalytic reactions. The catalytic activity of these new well-defined, air-stable metathesis catalysts was evaluated and compared in ring-closing-metathesis (RCM), enyne-metathesis, and cross-metathesis (CM) reactions.

Results and Discussion

Synthesis and Characterization of the Catalysts

A metathesis reaction involving the previously described trifluoromethylamide-containing ligand **7**[17] with a second-generation benzylidene complex **1a**–**d** in the presence of CuCl afforded in good-to-excellent isolated yields complexes **6a**–**d** as microcrystalline green solids (Scheme 1). Note, **6a** could also be synthesized from the ruthenium–indenylidene complex bearing SIMes[20] in a similar isolated yield (90%).[17] In the case of the SIPr-containing catalyst **6c**, we believe that the lower yield (61%) is due to the poorer stability in solution of its precursor **1c**. As a testimony to their excellent stability, complexes **6a**–**d** bearing SIMes, IMes, SIPr, and IPr, respectively, were purified by silica gel chromatography using technical-grade pentane and acetone and could be handled in air.



Scheme 1. Synthesis of the Ru-based boomerang precatalysts **6**.

The ^{1}H NMR spectra of complexes **6a** and **6c** with saturated NHC ligands have resonances at 4 ppm arising from the imidazole protons, whereas the ^{1}H NMR spectra of complexes **6b** and **6d** with unsaturated NHC backbones display a single low-field resonance at around 7 ppm corresponding to the imidazole ring protons. The proton of the Ru=C carbenic carbon has a resonance at around 16.5 ppm in all complexes, which is the shift expected for a Hoveyda-type catalyst. This same proton is shifted to 19.5–20 ppm in complexes **1a**–**d**. The ^{13}C NMR spectra of the unsaturated complexes have a characteristic resonance arising from the NHC carbenic carbon atom at around 175 ppm, whereas the NHC carbenic carbon resonance for the saturated complex is found at a lower field (around 210 ppm). All Ru=C carbenic carbons resonate in the 282–292 ppm range.

The structures of the Ru-based complexes **6a**–**d** were unambiguously determined by single-crystal X-ray diffraction studies. Ball-and-stick representations are depicted in Figure 2. Note that during the crystallization assays, complex **6c** was found to be extremely stable. As an sample, five different solvent systems were tested without any precaution or apparent catalyst decomposition. All the complexes show the expected distorted square-based pyramidal geometry around the metal center with coordination of the oxygen to the ruthenium center. Selected bond lengths and angles are provided in Table 1. The smaller N(1)–C(22)–N(2) angles in IMes and IPr in comparison with those found in SIMes and SIPr is a general feature observed between unsaturated and saturated NHC ligands.[21] Other bond lengths and angles are similar for complexes **6a**, **6b** and **6d**, whereas **6c** bearing SIPr shows deviations from those of its congeners. For all the catalysts, the NHC (C)–Ru and Ru=C bond lengths were found to be comparable to those previously reported in the literature for NHC-containing "boomerang" complexes and are, respectively, in the range of 1.82–1.84 and 1.96–2.00 Å.[8,13,17,21,22] The Ru–O bond lengths were found to vary: For complexes **6a**, **6b**, and **6d** the oxygen atom appears to coordinate tightly and distances in the range of 2.21–2.24 Å are found; the Ru–O bond length in **6c** is longer at 2.30 Å. The differences in the NHC backbones of SIMes and IMes do not lead to noticeable variations in the bond lengths[21] whereas for SIPr and IPr the Ru–O length varies by almost 0.1 Å. Moreover, the use of SIPr leads to variations in the Cl(1)–Ru(1)–Cl(2), C(1)–Ru(1)–C(22), and especially in the C(22)–Ru(1)–O(1)

angle (171°), which is one of the smallest angles reported in the literature (usual range 174–180°) for this moiety. To the best of our knowledge, no X-ray structure of Hoveyda-type complex bearing the SIPr ligand has been reported to date; disparities observed in the bond lengths and angles of **6c** could be due to the SIPr ligand itself or to the combination of the SIPr and $NHCOCF_3$ functions.

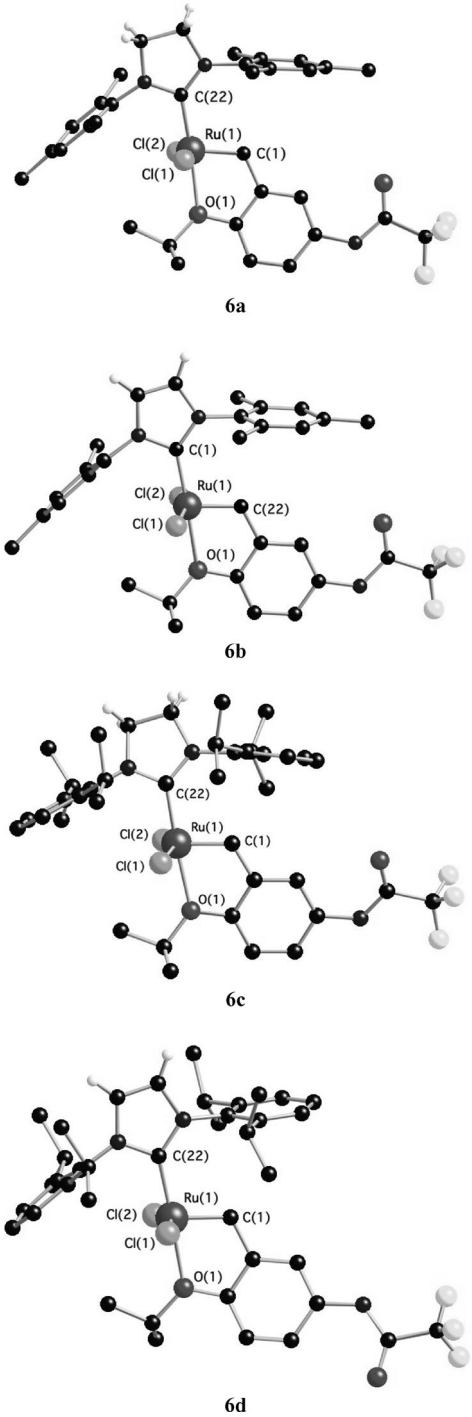


Figure 2. Ball-and-stick representations of complexes **6** (most hydrogen atoms have been omitted for clarity).

Table 1. Selected bond lengths [Å] and angles [°] for the Ru-based complexes **6**.

	6a	6b	6c	6d
Ru(1)–C(1)	1.8338(9)	1.8318(12)	1.8266(14)	1.8301(12)
Ru(1)–C(22)	1.9852(8)	1.9960(12)	1.9911(13)	1.9846(13)
Ru(1)–O(1)	2.2383(7)	2.2374(9)	2.3002(10)	2.2111(10)
Ru(1)–Cl(1)	2.3315(3)	2.3467(3)	2.3293(4)	2.3300(4)
Ru(1)–Cl(2)	2.3537(3)	2.3558(3)	2.3358(4)	2.3412(4)
C(1)–Ru(1)–C(22)	103.42(4)	101.58(5)	99.75(6)	102.05(6)
C(1)–Ru(1)–O(1)	79.98(3)	79.97(4)	78.27(5)	80.36(5)
C(22)–Ru(1)–O(1)	175.27(4)	178.38(4)	171.09(4)	176.16(4)
Cl(1)–Ru(1)–Cl(2)	160.219(10)	162.376(12)	153.478(14)	160.867(14)
N(1)–C(22)–N(2)	107.14(7)	103.58(10)	106.41(11)	103.40(11)

Reaction Profile and Stability Studies[23]

The reactivity profiles of these novel boomerang-type catalysts, monitored by NMR spectroscopy, were then carried out to gauge the influence of the NHC ligand on the initiation and the overall reaction. The 2-allyl-2-methallylmalonate **8** was chosen as a benchmark substrate for ring-closing metathesis carried out at 30 °C in CD_2Cl_2 using 1 mol-% catalyst (Figure 3). Interestingly, whereas after 1 h of reaction no striking differences in the conversions were observed, the reactivity profiles were found to be quite distinct. As expected,[24] complexes **6a** and **6c** bearing the saturated NHCs SIMes and SIPr, respectively, were found to be more active than their unsaturated NHC-containing congeners **6b** and **6d**. In spite of an initial induction period of 5 min, complexes **6c** and **6d** with the more bulky NHCs SIPr and IPr[25] reached full conversion before their SIMes and IMes analogues. After this initial period of low activity for **6c** and **6d**, the reaction rates increase and the conversions surpass those of **6a** and **6b** after 20 (70% conversion) and 45 min (75% conversion), respectively. This particular reaction profile might be an indication of the enhanced stability of precatalysts **6c** and **6d**.

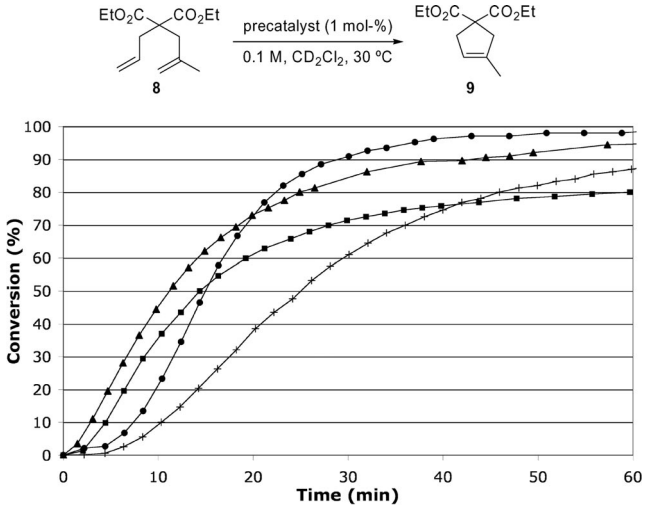


Figure 3. RCM of trisubstituted olefin **8** with precatalysts **6a**–**d** (1 mol-%) in CD_2Cl_2 (0.1 M) at 30 °C: ▲ **6a**; ■ **6b**; ● **6c**; + **6d**. The conversions were monitored by ^1H NMR spectroscopy.

These reactions were repeated under identical conditions but at 45 °C. Toluene, the customary solvent for catalysis at elevated temperatures, was also used; the reaction profiles are presented in Figure 4. The change in temperature was found to have a crucial influence on the reaction outcome. A short induction period was again observed for **6c** and **6d** bearing SIPr and IPr but the reactions reached completion after 30 min whereas **6a** and **6b** did not reach conversions of 50% in the same time interval. The differences in the reactivity can be attributed to either the improved stability/activity of **6c** and **6d** at 45 °C or to the solvent (catalyst solubility). In either case, smaller differences in activity were observed between saturated and unsaturated NHC ligands at elevated temperatures.

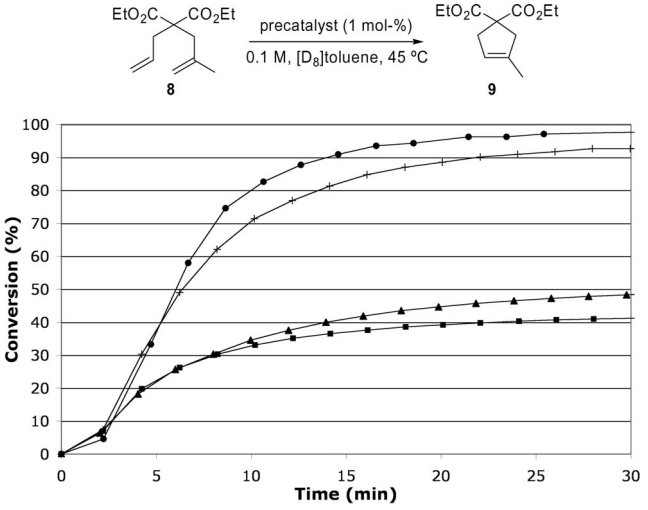


Figure 4. RCM of trisubstitued olefin **8** with precatalysts **6a**–**d** (1 mol-%) in [D_8]toluene (0.1 M) at 45 °C: ▲ **6a**; ■ **6b**; ● **6c**; + **6d**. The conversions were monitored by ^{1}H NMR spectroscopy.

To examine the effect of the trifluoroacetamide group, the reactivity profiles of catalysts **2c** and **6c** were monitored at various temperatures (Figure 5).[26] Unexpectedly, catalyst **2c** showed an extremely poor activity at 30 °C (less than 10% of **9** was obtained after 1 h) whereas the reaction reached completion after 40 min when using **6c**. At 45 °C, **2c** exhibited an improved activity (50% conversion after 1 h), but its analogue **6c**, bearing the trifluoroacetamide group, was far superior. At 60 °C, even smaller activity differences between **2c** and **6c** were observed, which highlights the fact that increasing the temperature moderates the effect of the aryl-activating group. Intriguingly, the ability of the aminocarbonyl group to enhance the activity of the boomerang catalysts was found to be modest when SIMes was used as the ligand,[17] whereas the use of complexes bearing SIPr led to enhanced catalytic behavior.

The reaction with boomerang catalyst **6c** was also compared with its benzylidene counterpart **1c** at 30 and 45 °C (Figure 6).[26] The poor stability of **1c** in solution is evident. Complex **1c** showed an excellent initial activity but regrettably, after roughly 5 min, it decomposed and the reaction ceased. An 80% yield of **9** could be achieved at 30 °C but heating the reaction to 45 °C led to increased decomposition of **1c** to give 25% conversion.

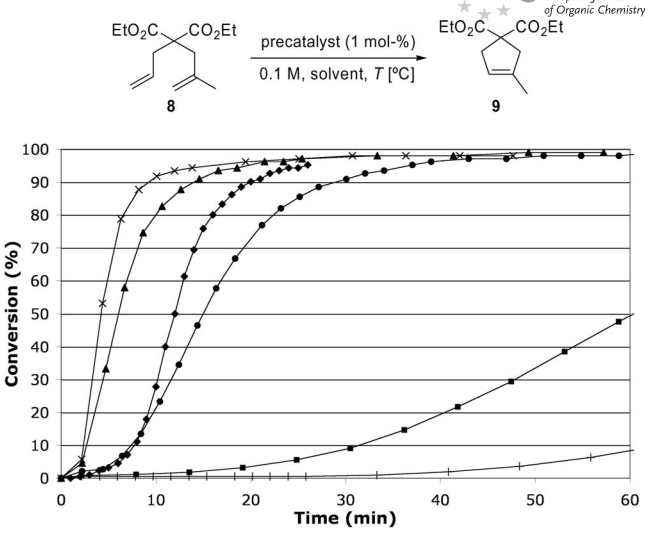


Figure 5. Reaction profiles of the RCM of **8** with precatalysts **2c** and **6c** (1 mol-%) as a function of temperature: + **2c**, 30 °C, CD_2Cl_2, 0.1 M; ■ **2c**, 45 °C, [D_8]toluene, 0.1 M; ♦ **2c**, 60 °C, [D_8]-toluene 0.1 M; ● **6c**, 30 °C, CD_2Cl_2, 0.1 M; ▲ **6c**, 45 °C, [D_8]toluene, 0.1 M; χ **6c**, 60 °C, [D_8]toluene, 0.1 M. The conversions were monitored by ^{1}H NMR spectroscopy.

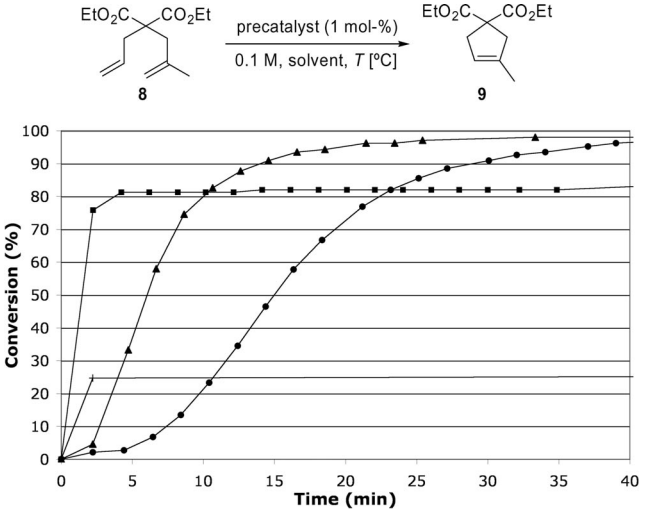


Figure 6. Reaction profiles of the RCM of **8** with precatalysts **1c** and **6c** (1 mol-%) as a function of temperature: ■ **1c**, 30 °C, CD_2Cl_2, 0.1 M; + **1c**, 45 °C, [D_8]toluene, 0.1 M; ● **6c**, 30 °C, CD_2Cl_2, 0.1 M; ▲ **6c**, 45 °C, [D_8]toluene, 0.1 M. The conversions were monitored by ^{1}H NMR spectroscopy.

Finally we compared boomerang catalysts **6a** and **6c** to the commercially available second-generation Grubbs and Hoveyda complexes **1a** and **2a** for the RCM reaction involving diallyltosylamine (**10**) at 0 °C (Figure 7).[26] Under these conditions, the reaction profiles of **6a** and **6c** were similar to those obtained for the RCM of **8** at 45 °C, that is, in spite of a longer initial activation period **6c** reached full

conversion before its SIMes analogue. Both **6a** and **6c** were found to display significantly higher activity than **2a** and even more compared with **1a**.

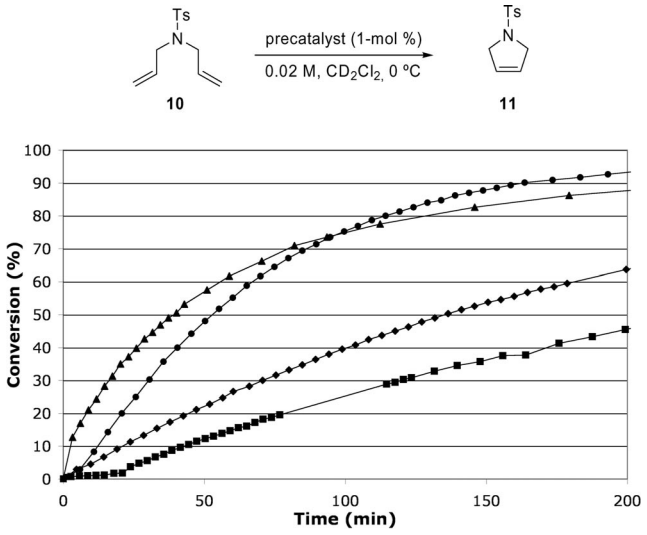
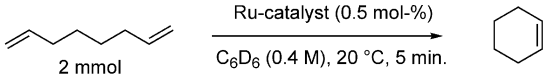


Figure 7. Reaction profiles of the RCM of **10** with precatalysts **1a**, **2a**, **6a**, and **6c** (1 mol-%) in CD_2Cl_2 (0.02 M) at 0 °C: ■ **1a**; ♦ **2a**; ▲ **6a**; ● **6c**. The conversions were monitored by ^{1}H NMR spectroscopy.

From the gathered data, the use of SIPr appears to be beneficial and leads to a longer-living precatalyst **6c** (see the above synthesis, X-ray determination, and reaction profile studies). The stability of **6c** in solution was examined in the absence of substrate and at several temperatures. As anticipated, the benzylidene complex **1c** exhibited rapid and complete decomposition after only 5 min in [D_4]dichloroethane solution at room temperature. This was supported by ^{1}H NMR spectroscopy, which showed the loss of the characteristic signal of the benzylidene proton at δ = 20 ppm, and also by a change in the color of the solution from purple to black. On the other hand, **6c** was found to be highly stable in solution because a single sample could be heated at 60 °C for 20 min, then at 80 °C, and finally stored at room temperature for a week without any sign of decomposition. Some catalyst degradation was observed by NMR spectroscopy after one month in solution, but complex **6c** could still be identified as the major component in solution.

Table 2. Stability of complexes **1c**, **2c**, **6a**, and **6c** under metathesis conditions.



Entry	Catalyst	cycle / conv. (%)[a]								
		1	2	3	4	5	6	7	8	9
1	**1c**	> 99	–	–	–	–	–	–	–	–
2	**6a**	> 99	96	89	74	–	–	–	–	–
3	**2c**	> 99	> 99	> 99	> 99	> 99	99	98	97	97
4	**6c**	> 99	> 99	> 99	> 99	> 99	98	99	97	95

[a] Determined by NMR spectroscopy.

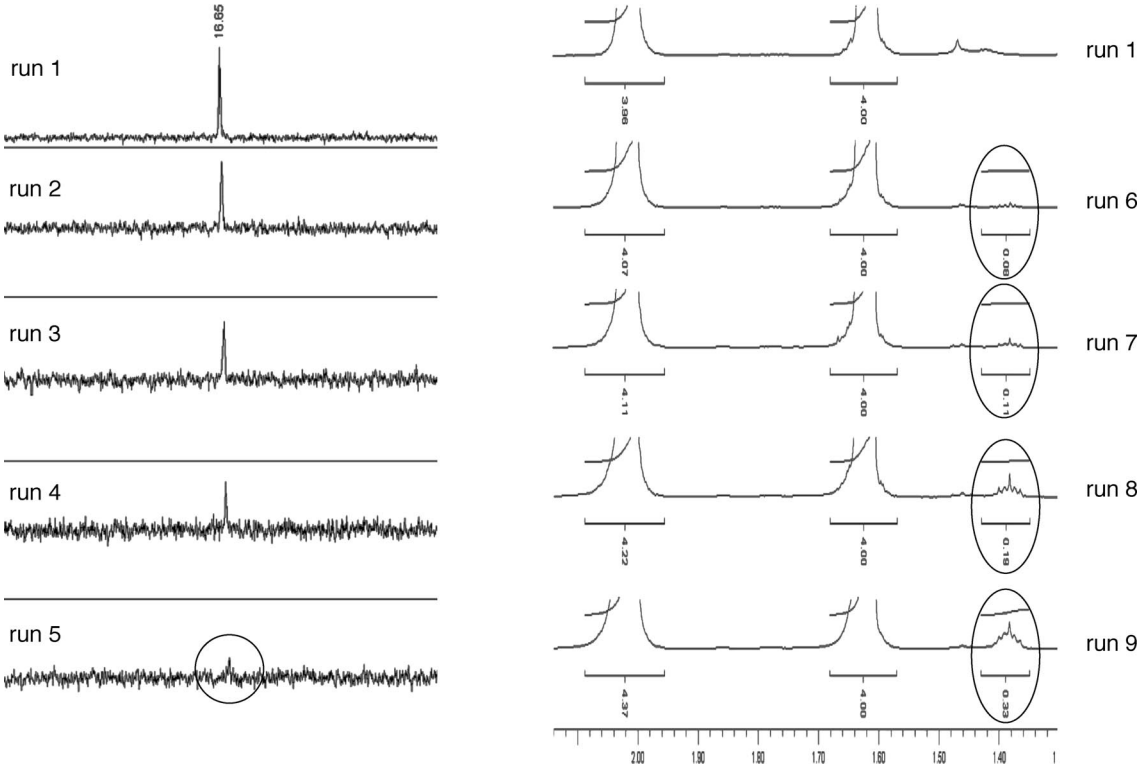


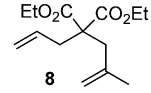
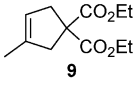
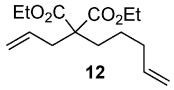
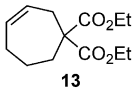
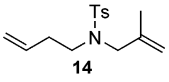
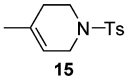
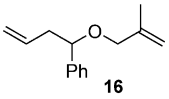
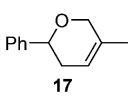
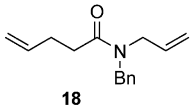
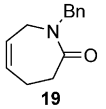
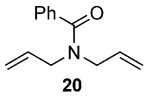
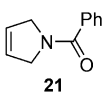
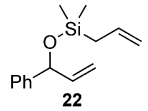
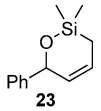
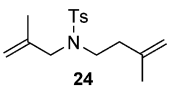
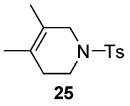
Figure 8. ^{1}H NMR spectra of the metathesis reaction of 1,7-octadiene using **6c** (C_6D_6, 400 MHz).

To further examine their stability, complexes **1c** and **6c** were treated with an alkene substrate. The RCM reaction of 1,7-octadiene was examined (Table 2) to test the stability of the precatalyst and the catalytic species. Indeed, the degradation of metathesis-active species is well known to occur rapidly when all the substrate has been consumed. Thus, we investigated the possibility of carrying out consecutive metathesis runs by adding substrate after it has been consumed. This should provide information on the stability of metathesis species under true reaction conditions. The starting material was added every 5 min in aliquots of 2 mmol to a 5 mL C_6D_6 solution containing 0.5 mol-% of precatalyst. RCM conversions were monitored by NMR spectroscopy.[27] The benzylidene-SIPr catalyst **1c** showed rapid degradation after the first cycle of substrate addition (Table 2, entry 1), whereas the activated boomerang SIMes complex **6a** was able to perform two full metathesis reactions. After the second cycle, the conversions decreased rapidly to reach only 74% by the fourth cycle (entry 2). Remarkably, both SIPr complexes **2c** and **6c** were found to be efficient in promoting metathesis reactions in six consecutive cycles with quantitative conversions (entries 3 and 4). Moreover, the characteristic signal of the benzylidene proton at $\delta = 16.6$ ppm was still detected in the NMR spectrum of the fifth run (Figure 8). This evidences the long lifetime of both boomerang SIPr catalysts. Despite the increasing concentration of olefin in the reaction mixture reaching up to 2.8 M by the seventh run (corresponding to a total of 14 mmol of consumed substrate for only 0.5 mol-% of catalyst), **2c** and **6c** remained active and stable; no polymerization products were detected. By the sixth cycle, some unreacted 1,7-octadiene was noticeable and this we take to indicate the beginning of catalyst decomposition (see the NMR spectra in Figure 8).

Reaction Scope

Next the scope of the metathesis transformations catalyzed by the trifluoromethylamide-containing complexes **6a**–**d** was investigated. The RCM reactions involving dienes bearing various functional groups, the effect on the ring size formed, and the influence of double bond substitution (Table 3) were examined. Only slight differences in activity were observed for reactions involving substrates requiring short reaction times (less than 1 h; entries 1 and 3–6). However, in general, the trends observed in the reaction profile studies were confirmed, that is, catalysts **6c** and **6d** bearing SIPr and IPr ligands, respectively, are more active than **6a** and **6b**. Moreover, the saturated NHC-containing complexes (**6a** and **6c**) are more active than the unsaturated NHC analogues. The contrast is more significant for "difficult" substrates such as **12**, which gives the seven-membered ring **13**. For this RCM, a slight thermal activation was necessary with catalysts **6a** and **6b**, whereas **6c** and **6d** performed well at room temperature within 15 min (entry 2). The formation of five- to seven-membered rings with di- or trisubstituted dienes was easily achieved and a tolerance to ester, amide, and ether groups was observed. However, the RCM of silyl ether **22** was not so straightforward (entry 7). In the presence of this substrate, catalyst degradation occurred rapidly and consequently only the very stable and active **6c** gave a good isolated yield (88% in 1 h). Interestingly, for the tetrasubstituted diene **24**, the activity trends were reversed; catalysts **6a** and **6b** bearing the smaller NHC exhibited a better performance, but the saturated NHC complexes were still better than their unsaturated counterparts. This confirms the close relationship between the steric hindrance of the NHC ligand and the steric hindrance of the substrate.[13c,13d,24a]

Table 3. Comparison of the catalyst activities in the RCM of various dienes.[a]

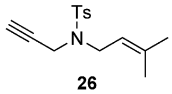
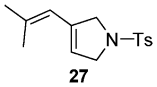
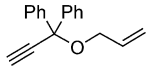
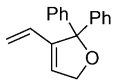
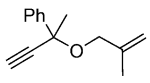
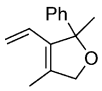
Entry	Substrate	Product	Catalyst	Time (h)	Yield (%)
1	 **8**	 **9**	**6a**	0.75	> 98
			6b	1.5	96
			6c	0.5	> 98
			6d	0.5	> 98
2	 **12**	 **13**	**6a**[b]	0.5	96
			6b[b]	0.75	91
			6c	0.25	> 98
			6d	0.5	> 98
3	 **14**	 **15**	**6a**	0.5	> 98
			6b	1.25	> 98
			6c	0.25	> 98
			6d	0.25	> 98
4	 **16**	 **17**	**6a**	0.25	> 98
			6b	0.5	> 98
			6c	0.25	> 98
			6d	0.25	> 98
5	 **18**	 **19**	**6a**	1.5	> 98
			6b	5	> 98
			6c	0.75	> 98
			6d	0.75	> 98
6	 **20**	 **21**	**6a**	0.25	> 98
			6b	0.5	> 98
			6c	0.25	> 98
			6d	0.25	> 98
7	 **22**	 **23**	**6a**	10	39
			6b	10	15
			6c	1	88
			6d	2	59
8	 **24**	 **25**	**6a**[b,c]	24	80
			6b[b,c]	24	64
			6c[b,c]	24	47
			6d[b,c]	24	31

[a] Reaction conditions: 1 mol-% catalyst loading, CH_2Cl_2, 0.1 M, 25 °C. [b] Reactions performed at 40 °C. [c] 2 mol-% of catalyst were used.

The scope of the RCM was extended to several enynes using only 1 mol-% catalyst (Table 4). The reactivity with the selected substrates parallels the information obtained on the precatalyst activity previously obtained in the RCM of dienes. For a substrate such as **28** (entry 2), almost no difference in reactivity was observed when using **6a**–**d** as the catalyst. However, with the sterically demanding enyne **30** catalysts **6a** and **6b**, with the smaller SIMes and IMes, provided significantly better isolated yields of **31** (entry 3). However, **6c** and **6d** were found to be extremely competent because a reaction time of only 1 h at room temperature was required to complete the RCM of **26** (entry 1). On the other hand, **6a** and **6b** provided 67 and 92% yields, respectively, of the diene **27** after 24 h at 25 °C. Note, this represents an uncommon example of the superior activity of IMes- over SIMes-bearing catalysts.

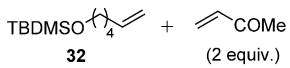
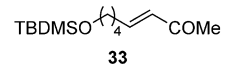
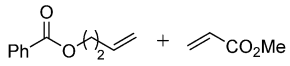
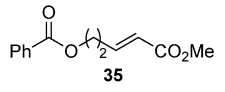
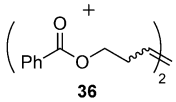
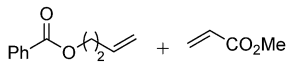
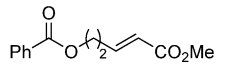
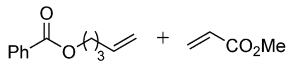
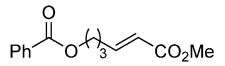
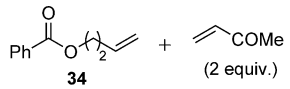
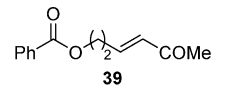
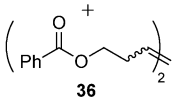
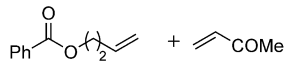
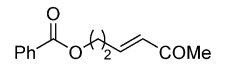
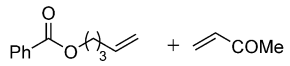
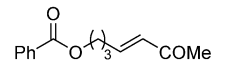
As shown in Table 5, the activities of catalysts **6a**–**d** were also compared in the cross-metathesis reactions of terminal alkenes and α,β-unsaturated olefins. Entry 1 corroborated the superior catalytic performances of complexes bearing SIPr and IPr over their SIMes and IMes analogues **6a** and **6b** as reactions were completed in 0.5 h with only 1 mol-% catalyst loading. With alkene **34**, cross metathesis with 2 equiv. of methyl acrylate and methyl vinyl ketone (en-

Table 4. Comparison of the catalyst activities in the RCM of enynes.[a]

Entry	Substrate	Product	Catalyst	Time (h)	Yield (%)
1	 **26**	 **27**	**6a**	24	67
			6b	24	92
			6c	1	> 98
			6d	1	> 98
2	 **28**	 **29**	**6a**	0.3	> 98
			6b	0.4	> 98
			6c	0.2	> 98
			6d	0.2	> 98
3	 **30**	 **31**	**6a**[b]	24	> 98
			6b[b]	24	84
			6c[b]	24	61
			6d[b]	24	78

[a] Reaction conditions: 1 mol-% catalyst loading, CH_2Cl_2, 0.1 M, 25 °C. [b] Reactions performed at 40 °C.

Table 5. Comparison of the catalyst activities in the cross-metathesis reactions.[a]

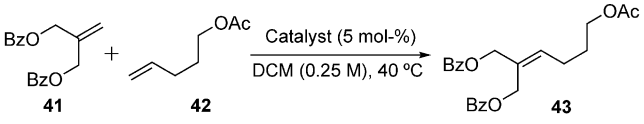
Entry	Substrates	Products	Catalyst	Time (h)	Yield (%)
1	 **32** (2 equiv.)	 **33**	**6a**	0.5	**33**: 86 (*E*/*Z* > 20:1)
			6b	0.5	**33**: 48 (*E*/*Z* > 20:1)
			6c	0.5	**33**: > 98 (*E*/*Z* > 20:1)
			6d	0.5	**33**: > 98 (*E*/*Z* > 20:1)
2	 **34** (2 equiv.)	 **35** +  **36**	**6a**	0.5	**35**: 76 (*E*/*Z* > 20:1)
			6b	0.5	**35**: 74 (*E*/*Z* > 20:1)
			6c	0.5	**35**: 64 (*E*/*Z* > 20:1) **36**: 34 (*E*/*Z* = 4:1)
			6d	0.5	**35**: 62 (*E*/*Z* > 20:1) **36**: 31 (*E*/*Z* = 4:1)
3	 **34** (5 equiv.)	 **35**	**6c**	1	**35**: 92 (*E*/*Z* > 20:1)
4	 **37** (2 equiv.)	 **38**	**6c**	1	**38**: 91 (*E*/*Z* > 20:1)
5	 **34** (2 equiv.)	 **39** +  **36**	**6a**	0.5	**39**: 78 (*E*/*Z* > 20:1)
			6b	0.5	**39**: 76 (*E*/*Z* > 20:1)
			6c	0.5	**39**: 68 (*E*/*Z* > 20:1) **36**: 30 (*E*/*Z* = 4:1)
			6d	0.5	**39**: 71 (*E*/*Z* > 20:1) **36**: 26 (*E*/*Z* = 4:1)
6	 **34** (5 equiv.)	 **39**	**6c**	1	**39**: > 98 (*E*/*Z* > 20:1)
7	 **37** (2 equiv.)	 **40**	**6c**	1	**40**: 95 (*E*/*Z* > 20:1)

[a] Reaction conditions: 1 mol-% catalyst loading, CH_2Cl_2, 0.1 M, 25 °C.

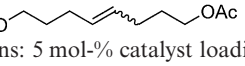
tries 2 and 5) using **6a** and **6b** gave good isolated yields (74–78%) of **35** and **39**, respectively, as the single product with the starting material **34** as the only other organic product observed. Unexpectedly, the same CM transformations carried out with catalysts **6c** and **6d** led to the formation of a significant amount of the self-metathesis dimer **36** (ca. 30% with *E*/*Z* = 4:1, entries 2 and 5). This seems to be a result of the improved activity of the (S)IPr-containing catalysts. We attempted to circumvent the formation of this dimer by either using a larger excess of the deactivated olefin (entries 3 and 6) or by employing a more active CM partner (entries 4 and 7). With catalyst **6c**, both approaches lead to successful outcomes as only traces of the corresponding dimers were observed by thin-layer chromatography. At this stage, the difference in reactivity between alkenes **34** and **37** is due perhaps to the distance between the deactivating ester function and the C–C double bond.

Having obtained encouraging results in the cross-metathesis reactions, we proceeded to evaluate the performance of catalysts in the challenging and scarcely studied formation of trisubstituted double bonds by CM.[28] The CM between 1,1-disubstituted olefin **41** and activated partner **42** was selected as a benchmark reaction (Table 6). Because it had been reported that **2c** (5 mol-%) performed this reaction quantitatively in 24 h at 40 °C,[28c] we hoped to shorten the reaction time with our activated analogue **6c**. Unfortunately, only traces of **43** were isolated (3%, entry 3) and even after a reaction time of 24 h, significant product yields could not be obtained (10%, entry 2).[29] Nonetheless, we noticed again for sterically demanding substrates that the SIMes-containing complex **6a** (entry 1) performed better than its SIPr counterpart **6c** (entry 2). We then attempted to enhance the formation of **43** by varying the reaction conditions. Inverting the olefin ratio led to an improved CM outcome (entry 4).

Table 6. The formation of trisubstituted olefins by cross metathesis.[a]



Entry	Ratio **41**/**42**	Catalyst	Time (h)	Isolated yield of **43** (%)
1	1/3	**6a**	24	32
2	1/3	**6c**	24	10
3	1/3	**6c**	10	3
4	3/1	**6c**	10	43[b]
5	3/1 (**44**)[c]	**6c**	10	54
6	1/0.5 (**44**)[c]	**6a**	24	32
7	1/0.5 (**44**)[c]	**6c**	24	33

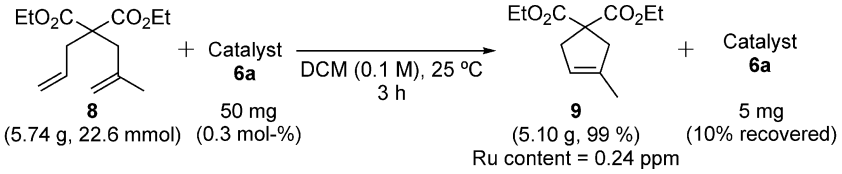
44 =  *E*/*Z* = 3:1

[a] Reaction conditions: 5 mol-% catalyst loading, CH_2Cl_2, 0.25 M, 40 °C. [b] 58% of dimer **44** was also isolated. [c] Dimer **44** was used as the reaction partner instead of **42**.

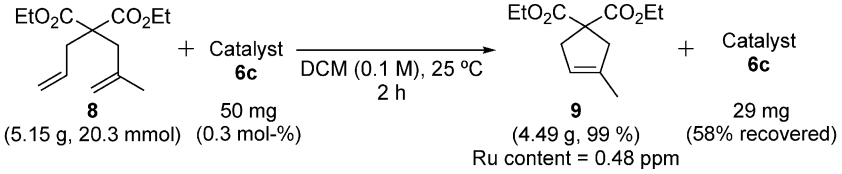
In this instance, **42** was the limiting reagent and so the formation of self-metathesis product **44** (58%), which was observed in all these reactions, becomes significant. As we were wondering if **44** could act as a potential partner of this CM, we employed **44** instead of **42** (entry 5). The reaction was found to proceed and a larger amount of **43** was obtained (54%). Note, the unreacted **44** recovered at the end of the reaction with a decreased *E*/*Z* ratio lets us believe that the *E* isomer might react faster than the *Z* isomer. An alternative explanation might be that the variation in the *E*/*Z* ratio could result from a nonproductive metathesis. Because the 1,1-disubtituted partner is generally the most expensive one and in order to make the reaction more atom economic, a **41**/**44** ratio of 1:0.5 was employed and the catalyst activity was reinvestigated (entries 6 and 7). Under these conditions, the contrast between SIMes and SIPr catalysts was found to be minute.

Catalyst Recovery Studies

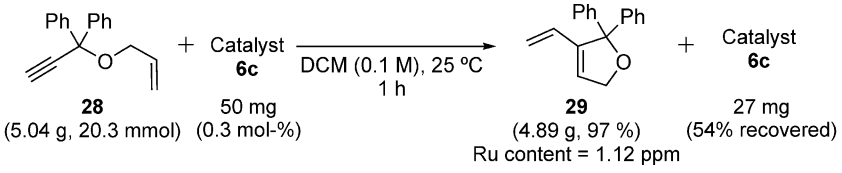
As part of our research program directed towards catalyst recyclability and low ruthenium contamination of metathesis products,[21,30] the possibility of recovering the trifluoroacetamide "boomerang" catalysts at the end of the transformation was investigated. Hoveyda and co-workers have shown that "boomerang" catalysts such as **2a** could be isolated at the end of RCM in good-to-excellent yields and could be reused thereafter.[4,8a] However, these experiments were carried out using a relatively high catalyst loading (up to 5 mol-%) and consequently it appears possible that the amount of catalyst recovered could represent the amount of precatalyst not activated. Moreover, these recovery tests were performed on quantities usually used for substrate scope investigation (ca. 10 mg of catalyst used), which does not allow for an accurate measure of the amount of complex recovered. Bearing these facts in mind, catalyst recovery experiments were performed by using 50 mg catalyst loading, which corresponds to a 0.3 mol-% loading relative to the substrate. Because ruthenium residue levels must be less than 10 ppm for drug product synthesis,[31] the Ru content in metathesis transformation products was quantified by ICP-MS analyses. As depicted in Equation (1), 50 mg (0.3 mol-%) of the catalyst **6a** bearing the SIMes ligand was used in the RCM of 5.74 g of **8** in only 3 h at room temperature. After silica gel chromatography product **9** was isolated in quantitative yield and contained a very low level of Ru waste (δ = 0.24 ppm). Unfortunately, only 5 mg of **6a** was recovered (10% of the initial loading). The same experiment was repeated with the SIPr-containing catalyst **6c** with 20.3 mmol of **8** and an identical catalyst loading. In this instance, the reaction reached completion in 2 h with a Ru content in the product **9** of approximately 0.5 ppm [Equation (2)]. Silica gel purification and subsequent crystallization (octane/DCM) allowed 29 mg of **6c** (58%) to be recovered in a pure form, as judged by its ^{1}H NMR spectrum.[32] This residue was reused in catalysis and led to identical catalytic behavior in a subsequent reaction.



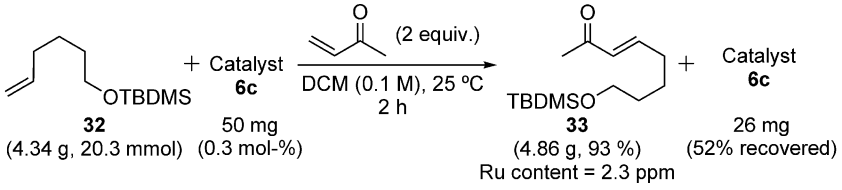
(1)



(2)



(3)



(4)

The scope of catalyst **6c** recovery was then extended to enyne RCM and cross-metathesis reactions; see Equation (3)] and (4). In both cases, 0.3 mol-% of **6c** was found to be suitable for rapidly catalyzing the reaction and excellent isolated yields were obtained with only a few ppm of residual ruthenium in the organic products. In addition, catalyst **6c** was recovered in similar quantities as in the RCM of **8**.

Conclusions

We have described the synthesis of "boomerang"-type catalysts activated by a trifluoromethylamide function and bearing various sterically demanding NHCs (SIMes, IMes, SIPr, and IPr).[33] The complexes were obtained in a straightforward manner and fully characterized by NMR spectroscopy and X-ray diffraction studies. Activity profiles of these catalysts were determined and compared with other analogous complexes to clarify the role of both NHC and $NHCOCF_3$ groups. It appears that the trifluoromethylamide-activating effect is more important for the catalyst bearing SIPr than for the one bearing the SIMes ligand. Surprisingly, a matching effect was observed between the activating function and SIPr or IPr that allows for improved catalyst activity and stability. The investigation of the reaction scope highlights the effect of the NHC because catalysts **6c** and **6d** exhibited better catalytic performances in metathesis transformations involving less congested substrates. On the other hand, catalysts **6a** and **6b** bearing SIMes and IMes, respectively, were found to be more efficient for sterically hindered olefins. Attempts to form trisubstituted C–C double bonds by CM afforded moderate yields, but showed again the beneficial effect of the $NHCOCF_3$ group. The possibility of recovering the catalyst at the end of metathesis transformations was examined by performing large-scale reactions with low catalyst loadings. Catalyst **6c** displayed a good reaction profile and an ability to be recycled (52–58% of recovered catalyst for several reaction types). Furthermore, Ru contamination in the final organic products was found to be extremely low (less than 2.5 ppm). In the light of this study, the development of complexes bearing novel NHC ligands, immobilized versions of catalyst **6c**, and continuous flow processes involving **6c** appear promising and related ongoing investigations will be reported in due course.

Experimental Section

General: All reagents were used as received. Dichloromethane (DCM) and toluene were dispensed from a solvent purification system from Innovative Technology. The catalysts were synthesized in an MBraun glove-box containing dry argon and less than 1 ppm oxygen or on a Schlenk line according to previously described procedures. Complexes **1b**,[7a] **1c**,[9b] and **1d**[10] were synthesized according to previously described procedures. Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Bruker Avance 400 Ultrashield NMR spectrometer. HRMS analyses were performed at the ICIQ with a Waters LCT Premier or GCT mass spectrometer. Elemental analyses were performed at the Universidad Complutense de Madrid. The ICP-MS measurements were performed by the UT2A Company, France. Substrates and products **8**–**21**,[24b] **23**–**31**,[24b] **32**,[34] **33**,[15b] **34**,[35] **35**,[17] **36**,[21] **37**,[36] **40**,[14a] **41**,[37] **43**,[28c] and **44**[38] have been described previously; for the others see the Supporting Information.

General Procedure for the Synthesis of the Catalysts: The styrenyl ether ligand **7** (1 equiv.) in DCM solution (1 mL per 0.05 mmol of ligand) was added to a solution of the Ru-based catalyst and copper chloride (1.1 equiv.) in dry DCM (1 mL per 0.02 mmol of Ru complex). The resulting mixture was stirred at 35 °C for 5 h. Volatiles were removed under reduced pressure, acetone was added to the residue, and the solution was filtered through a plug of Celite®. The filtrate was concentrated and purified by chromatography on silica gel (pentane/acetone, 75:25) to yield catalysts **6a**–**d** as green microcrystalline solids.

[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene][2-isopropoxy-5-(2,2,2-trifluoroacetamido)benzylidene]ruthenium(II) Dichloride (6a): Following the general procedure for complex **1a** afforded the title product (237 mg, 88% yield). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 16.44 (s, 1 H, CH=Ru), 7.79 [dd, ^3J(H,H) = 8.8, ^4J(H,H) = 2.5 Hz, 1 H, CH^{Ar}], 7.61 [d, ^4J(H,H) = 2.6 Hz, 1 H, CH^{Ar}], 7.08–7.06 (m, 5 H, CH^{Ar}), 4.97 [sept., ^3J(H,H) = 6.1 Hz, 1 H, CH(CH$_3$)$_2$], 4.28 (s, 4 H, CH$_2$-CH$_2$), 2.47 (s, 12 H, CH$_3^{ortho}$), 2.43 (s, 6 H, CH$_3^{para}$), 1.26 [d, ^3J(H,H) = 6.1 Hz, 6 H, CH(CH$_3$)$_2$] ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 291.3 [d, J(C,Ru) = 12.3 Hz, CH, CH=Ru], 209.9 (NCN), 149.5 (C=O), 145.0 (C^{Ar}), 138.7 (C^{Ar}), 131.3 (C^{Ar}), 129.1 (CH^{Ar}), 121.1 (CH^{Ar}), 121.0 (CH^{Ar}), 116.0 [q, J(C,F) = 286.7 Hz, CF$_3$], 114.2 (CH^{Ar}), 114.1 (CH^{Ar}), 113.2 (CH^{Ar}), 75.3 [*C*H(CH$_3$)$_2$], 51.4 (CH$_2$), 20.6 (CH$_3$), 20.3 (CH$_3$) ppm. ^{19}F NMR (376 MHz, [D$_6$]-acetone, 25 °C, TMS): δ = –76.2 (s, CF$_3$) ppm. HRMS (ESI): calcd. for C$_{35}$H$_{41}$ClF$_3$N$_4$O$_2$Ru 743.1914 [M$^+$ – Cl+CH$_3$CN]; found 743.1926. C$_{33}$H$_{38}$Cl$_2$F$_3$N$_3$O$_2$Ru (737.65): calcd. C 53.73, H 5.19, N 5.67; found C 53.81, H 5.30, N 5.64.

[1,3-Dimesityl-1*H*-imidazol-2(3*H*)-ylidene][2-isopropoxy-5-(2,2,2-trifluoroacetamido)benzylidene]ruthenium(II) Chloride (6b): Following the general procedure for complex **1b** afforded the title product (110 mg, 82% yield). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 16.57 (s, 1 H, CH=Ru), 7.80 [dd, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 2.5 Hz, 1 H, CH^{Ar}], 7.72 [d, ^4J(H,H) = 2.5 Hz, 1 H, CH^{Ar}], 7.49 (s, 2 H, CH^{Ar}), 7.17 (s, 4 H, CH^{Ar}), 7.11–7.09 (m, 2 H, CH^{Ar}), 5.01 [sept., ^3J(H,H) = 6.1 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.50 (s, 12 H, CH$_3^{ortho}$), 2.26 (s, 6 H, CH$_3^{para}$), 1.34 [d, ^3J(H,H) = 6.1 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 287.2 [d, J(C,Ru) = 12.4 Hz, CH=Ru], 174.2 (NCN), 149.6 (C=O), 145.2 (C^{Ar}), 139.5 (C^{Ar}), 139.2 (C^{Ar}), 137.9 (C^{Ar}), 136.2 (C^{Ar}), 131.5 (C^{Ar}), 129.2 (CH^{Ar}), 128.9 (CH^{Ar}), 125.3 (CH^{Ar}), 116.1 [q, J(C,F) = 286.7 Hz, CF$_3$], 113.7 (CH^{Ar}), 113.3 (CH^{Ar}), 75.4 [*C*H(CH$_3$)$_2$], 20.7 (CH$_3$), 20.3 (CH$_3$), 18.4 (CH$_3$) ppm. ^{19}F NMR (376 MHz, [D$_6$]acetone, 25 °C, TMS): δ = –76.2 (s, CF$_3$) ppm. HRMS (ESI): calcd. for C$_{35}$H$_{39}$ClF$_3$N$_4$O$_2$Ru 741.1757 [M – Cl + CH$_3$CN]$^+$; found 741.1735. C$_{33}$H$_{36}$Cl$_2$F$_3$N$_3$O$_2$Ru (735.64): calcd. C 53.73, H 5.19, N 5.67; found C 53.05, H 5.17, N 5.40.

[1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene][2-isopropoxy-5-(2,2,2-trifluoroacetamido)benzylidene]ruthenium(II) Chloride (6c): Following the general procedure for complex **1c** afforded the title product (125 mg, 61% yield). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 16.37 (s, 1 H, CH=Ru), 10.24 (s, 1 H, NH-CO), 7.92 [dd, ^3J(H,H) = 8.9, ^4J(H,H) = 2.5 Hz, 1 H, CH^{Ar}], 7.57 [t, ^3J(H,H) = 7.7 Hz, 2 H, CH^{Ar}], 7.43 [d, ^3J(H,H) = 7.7 Hz, 4 H, CH^{Ar}], 7.31 [t, ^4J(H,H) = 2.6 Hz, 1 H, CH^{Ar}], 7.11 [d, ^3J(H,H) = 8.9 Hz, 1 H, CH^{Ar}], 5.03 [sept., ^3J(H,H) = 6.1 Hz, 1 H, OCH-(CH$_3$)$_2$], 4.32 (s, 4 H, CH$_2$-CH$_2$), 3.69 [sept., ^3J(H,H) = 6.7 Hz, 1 H, CH(CH$_3$)$_2^{NHC}$], 1.37 [d, ^3J(H,H) = 6.1 Hz, 6 H, OCH-(CH$_3$)$_2$], 1.28–1.22 (m, 24 H, CH$_3^{NHC}$) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 285.2 [d, J(C,Ru) = 12.3 Hz, CH=Ru], 212.3 (NCN), 154.9 (C^{Ar}), 154.6 (C^{Ar}), 149.9 (NH-C=O), 149.1 (C^{Ar}), 144.0 (C^{Ar}), 137.0 (C^{Ar}), 131.2 (C^{Ar}), 131.1 (C^{Ar}), 129.6 (CH^{Ar}), 124.2 (CH^{Ar}), 121.3 (CH^{Ar}), 121.2 (CH^{Ar}), 116.1 [q, J(C,F) = 285.6 Hz, CF$_3$], 114.0 (CH^{Ar}), 113.9 (C^{Ar}), 113.2 (CH^{Ar}), 75.3 [O*C*H(CH$_3$)$_2$], 54.8 (CH$_2$-CH$_2$) 28.6 [*C*H(CH$_3$)$_2^{NHC}$], 25.9 (CH$_3$), 22.9 (CH$_3$), 21.1 (CH$_3$) ppm. ^{19}F NMR (376 MHz, [D$_6$]acetone, 25 °C, TMS): δ = –76.2 (s, CF$_3$) ppm. HRMS (ESI): calcd. for C$_{39}$H$_{49}$F$_3$N$_3$O$_2$Ru 750.2820 [M – Cl – HCl]$^+$; found 750.2858. C$_{39}$H$_{50}$Cl$_2$F$_3$N$_3$O$_2$Ru (821.81): calcd. C 57.00, H 6.13, N 5.11; found C 56.67, H 6.09, N 5.03.

[1,3-Bis(2,6-diisopropylphenyl)-1*H*-imidazol-2(3*H*)-ylidene][2-isopropoxy-5-(2,2,2-trifluoroacetamido)benzylidene]ruthenium(II) Chloride (6d): Following the general procedure for complex **1d** afforded the title product (192 mg, 91% yield). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 16.47 (s, 1 H, CH=Ru), 7.94 [dt, ^3J(H,H) = 8.9 Hz, ^4J(H,H) = 2.6 Hz, 1 H, CH^{Ar}], 7.66 [t, ^3J(H,H) = 7.8 Hz, 2 H, CH^{Ar}], 7.63 (s, 2 H, CH^{NHC}), 7.49 [d, ^3J(H,H) = 8.9 Hz, 4 H, CH^{Ar}], 7.66 [t, ^4J(H,H) = 2.6 Hz, 1 H, CH^{Ar}], 7.12 [d, ^3J(H,H) = 8.9 Hz, 1 H, CH^{Ar}], 5.03 [sept., ^3J(H,H) = 6.1 Hz, 1 H, O*C*H(CH$_3$)$_2$], 3.17 [sept, ^3J(H,H) = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2^{NHC}$], 1.40 [d, ^3J(H,H) = 6.1 Hz, 6 H, OCH(C*H*$_3$)$_2$], 1.22 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH$_3^{NHC}$], 1.17 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH$_3^{NHC}$] ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 282.5 [d, J(C,Ru) = 12.6 Hz, CH=Ru], 175.9 (NCN), 149.9 (C=O), 148.1 (CH^{Ar}), 144.6 (C^{Ar}), 136.3 (C^{Ar}), 131.4 (C^{Ar}), 130.4 (CH^{Ar}), 126.9 (CH^{Ar}), 123.8 (CH^{Ar}), 120.7 (CH^{Ar}), 123.8 (CH^{Ar}), 116.1 [q, J(C,F) = 286.5 Hz, CF$_3$], 113.5 (CH^{Ar}), 113.2 (CH^{Ar}), 75.5 [O*C*H(CH$_3$)$_2$], 28.6 [*C*H(CH$_3$)$_2^{NHC}$], 25.6 (CH$_3$), 22.3 (CH$_3$), 21.0 (CH$_3$) ppm. ^{19}F NMR (376 MHz, [D$_6$]acetone, 25 °C, TMS): δ = –76.1 (s, CF$_3$) ppm. HRMS (ESI): calcd. for C$_{39}$H$_{48}$ClF$_3$N$_3$O$_2$Ru 784.2431 [M – Cl]$^+$; found 784.2497. C$_{39}$H$_{48}$Cl$_2$F$_3$N$_3$O$_2$Ru (819.80): calcd. C 57.14, H 5.90, N 5.13; found C 56.81, H 5.86, N 5.07.

General Procedure for the Reaction Profiling Studies: A NMR tube equipped with a septum was charged with diethyl allyl(methallyl)-malonate **8** (25 mg, 0.1 mmol) and CD_2Cl_2 or $C_2D_4Cl_2$ (0.9 mL) under argon. The sample was equilibrated at the required temperature in the NMR probe. The sample was locked and shimmed before the addition of the catalyst (100 μL, 1 μmol, 0.1 M solution of catalyst). The reaction progress was monitored by the periodic acquisition of data over 1 h and integration of the characteristic signals for the allylic proton resonances.

Procedure for the Stability Studies: A Schlenk apparatus was filled with the precatalyst (0.01 mmol) and the C_6D_6 solvent (5 mL) under argon and then 1,7-octadiene (2 mmol, 300 μL) was added. Af-

ter 5 min of reaction, a small amount (50 μL) of the reaction media was taken for NMR monitoring followed by another loading of 1,7-octadiene (2 mmol). This procedure was repeated every 5 min. until a significant amount of unconsumed starting material was detected. All the aliquots were diluted in C_6D_6 (400 μL) and the conversion of the cyclohexene product was measured by NMR spectroscopy (see the NMR spectra in Figure 7).

General Procedure for the Metathesis Reactions: A Schlenk apparatus was filled with the substrate (0.5 mmol) [unactivated partner for the cross-metathesis reactions (1–2.5 mmol)] and the solvent (5 mL) (DCM for the reactions at room temp. and 40 °C, toluene for the reactions at 80 °C) under argon and then the precatalyst (0.005–0.01 mmol) was added. The progress of the reaction was monitored by TLC. The solvent was removed under vacuum and the crude residue was purified by flash column chromatography to yield the pure product. For the synthesis of trisubstituted alkenes by CM, the reported procedure was used.[28c]

General Procedure for the Large-Scale Metathesis Reactions: A 500 mL round-bottomed flask was filled with the substrate (22.6 mmol for **6a**, 20.3 mmol for **6c**), [methyl vinyl ketone for the cross-metathesis reactions (40.6 mmol)] and DCM (200 mL) under argon and then the catalyst (50 mg) was added. The progress of the reaction was monitored by TLC. The solvent was removed under vacuum and the crude residue was purified by flash column chromatography (pentane/Et_2O, 9:1) to yield the pure product and then the column was eluted with pentane/acetone (75:25) to yield the catalyst, which was subsequently recrystallized from DCM/octane (1:2).

Supporting Information (see also the footnote on the first page of this article): Synthetic procedures and characterization of the new compounds **22**, **23**, **36**, and **39**, and all kinetic data.

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[26] Catalysts **1c** and **2c** are not commercially available, for the kinetic studies we used homemade complexes synthesized according to the procedures reported in refs.[9b,11]; the purities were found to be above 99% (see NMR spectra in the Supporting Information). Catalysts **1a** and **2a** were purchased from Aldrich.

[27] Of note, the resulting cyclohexene product could not be removed from the reaction medium during this experiment due to cross-metathesis side-reactions occurring between the substrate and the styrenyl ligand **7** during the solvent evaporation.

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[29] Surprisingly and unintelligibly, these results are in sharp contrast to those previously reported for complexes **2a** and **2c**, see ref.[28c]

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