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Homogeneous Catalysis

Ruthenium Complexes Bearing Thiophene-Based Unsymmetrical *N*-Heterocyclic Carbene Ligands as Selective Catalysts for Olefin Metathesis in Toluene and Environmentally Friendly 2-Methyltetrahydrofuran

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Abstract: Three mono-*N*-heterocyclic carbene (NHC) ruthenium 2-isopropoxybenzylidene (**10a**–**c**) and one bis(NHC) indenylidene complex (**8**) bearing an unsymmetrical *N*-heterocyclic carbene ligand were synthesized and structurally characterized by single-crystal X-ray diffraction. The catalytic activity of the newly obtained complexes were evaluated in ring-closing metathesis (RCM) and ene–yne (RCEYM) reactions in toluene and environmentally friendly 2-MeTHF under air. The results confirmed that although all tested reactions can be successfully mediated by catalysts **10a**–**c**, their general reactivity is lower than the benchmark all-purpose Ru catalysts with symmetrical NHC ligands. However, the latter cannot compete with specialized ruthenium complex **10a** in industrially relevant self-CM of terminal olefins in neat conditions.

Introduction

To change the production of chemicals into a truly environmentally friendly and sustainable technology, cleaner and more intensified catalytic processes have to be developed.[1] Catalysis represents a key technology for the so-called Circular Economy,[2] as it opens new innovative routes to sustainable green processes and products. This will require, however, conceptually new types of catalysts which are able to control selectively the reaction pathways, even in the presence of varying levels of impurities, which are characteristic for biomass-derived starting materials or solvents.[3] Catalytic olefin metathesis is a powerful transformation in organic synthesis that allows the formation of new carbon–carbon double bonds in a truly atom-economical and effective way.[4] After decades of development, olefin metathesis has started to be used in production of, inter alia, fine chemicals, pharmaceuticals, and polymeric composite materials. The rapid expansion of metathesis methodology is largely attributed to the discovery of the stable, well-defined, transition-metal alkylidene catalysts.[5] A crucial development in this area was the introduction of *N*-heterocyclic carbene (NHC) ligands in 1999, proposed simultaneously by the groups of Nolan,[6] Grubbs,[7] and Fürstner and Herrmann.[8] NHC ligands, such as IMes, SIMes, and SIPr (Figure 1 a), have strong σ-donor and poor π-acceptor properties, which helps to stabilize the 14-electron ruthenium intermediates during metathesis, resulting in a large improvement in activity and stability over other metathesis catalysts.[9] Therefore, the so-called "second-generation catalysts" have gained high popularity.[10] Despite the supremacy offered by the general purpose catalysts **1**–**4** (Figure 1 a), they share some disadvantages, such as limited selectivity in some challenging reactions, poor control over the *E*/*Z* geometry of the newly formed C=C double bond, and susceptibility to decomposition and then isomerization of alkene double bonds.

By contrast, unsymmetrical heterocyclic carbene ligands (uNHC; Figure 1 b) proved to be highly amenable for modifications, yielding a number of new Ru catalysts tailored for challenging metathesis transformations such as ethenolysis, self-metathesis of α-olefins, or macrocyclization reactions.[11,12] Independently, uNHC ligands have allowed the development of *Z*-selective[13] and enantioselective Ru catalysts.[12e,13d,14] In our previous studies on benzyl-substituted uNHC (e.g., **L2**), we found that an increase of the steric bulk of the *N*-aromatic substituent, by replacing Mes with DIPP, brought promising enhanced selectivity to the catalysts derived from such altered ligands, however at the cost of slightly diminished activity.[11d,g] In the present work, we decided to focus on the not yet fully explored class of uNHC ligands that bear a heterocyclic *N*-substituent in their structure.[11c,e,h] We opted to check if modification of the thiophene-based uNHC ligand can lead to a catalyst of higher selectivity, which is at the same time easy to handle, tolerant to diverse functional groups, and sufficiently active to

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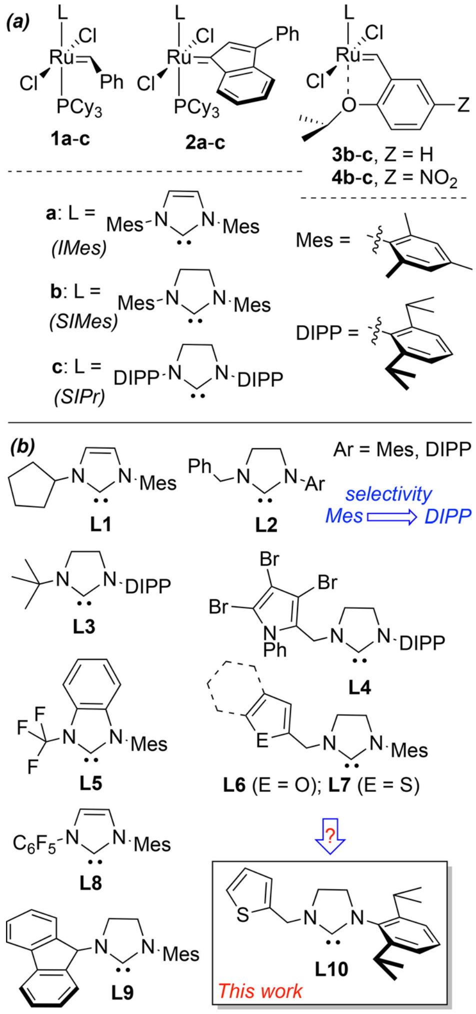


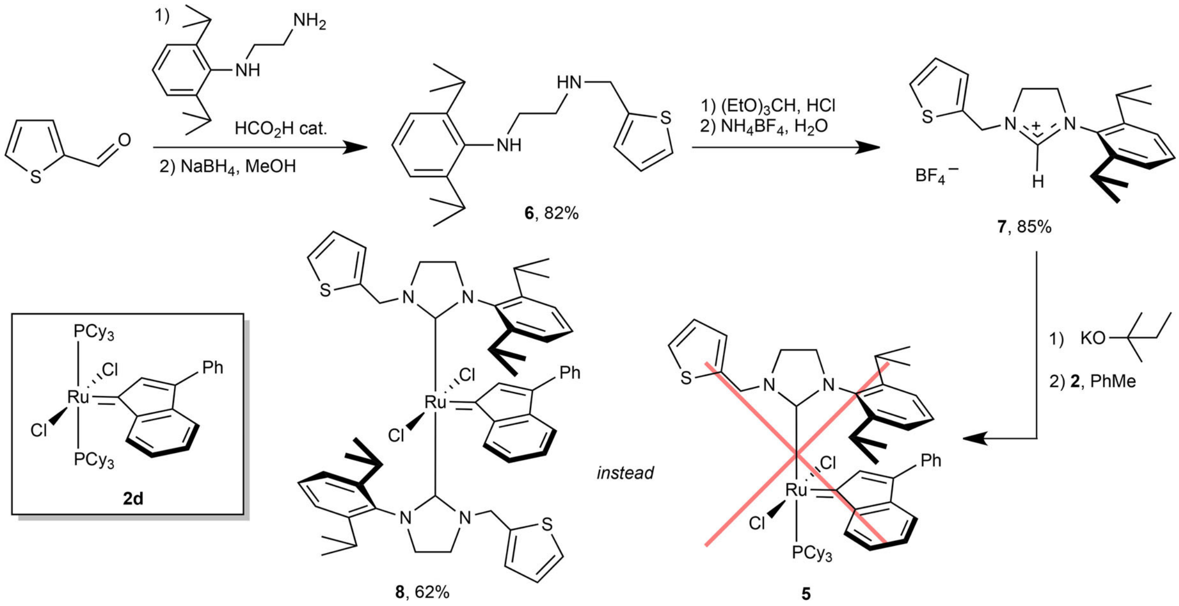
Figure 1. a) Selected general-purpose IMes, SIMes, and SIPr-bearing catalysts, and b) selected uNHC ligands tested with Ru metathesis catalysts.

be applied in more polar (green) solvents. As a platform to test the new *N*-CH$_2$-thiophene-*N'*-DIPP ligand, **L10**, we have chosen ruthenium indenylidene type precatalysts (**2**), as they are known to offer high stability and robustness.[15] The class of ruthenium indenylidene precatalysts with *symmetrical* NHC carbenes (**2a**–**c**) has been extensively studied.[16] In contrast, ruthenium indenylidene complexes bearing *unsymmetrical* NHC carbene subunits are largely unexplored.[11a–c,h, 12b,d,h]

Results and Discussion

We attempted to synthesize the catalyst of interest (**5**) in the following short synthetic sequence (Scheme 1). Commercially available thiophene-2-carbaldehyde was reacted with *N'*-(2,6-diisopropylphenyl)ethane-1,2-diamine[11h] and the resulting Schiff base was then reduced with NaBH$_4$ to furnish the corresponding diamine **6** in 82% isolated yield. Condensation of **6** with triethyl orthoformate and then the exchange of the chloride anion with NH$_4$BF$_4$ afforded corresponding tetrafluoroborate salt **7** in 85% yield. The approach to the synthesis of catalyst **5** was based on the conventional metalation route, where the free carbene **L10**, generated in situ from imidazolinium salt **7** and potassium *tert*-pentoxide in toluene, reacts with **2d** (Umicore Grubbs Catalyst™ M1). However, as we, and others[17] learned, in the specific case of unsymmetrical carbenes containing one smaller and one sufficiently bulkier substituent, both phosphines of complex **2d** undergo the ligand exchange reaction. Thus, instead of the expected **5**, the corresponding bis(uNHC) complex **8** was obtained as a red crystalline solid (62% yield). Unfortunately, all attempts (changing conditions and reactant stoichiometry) to obtain the mono-uNHC catalyst **5** proved to be unsuccessful.

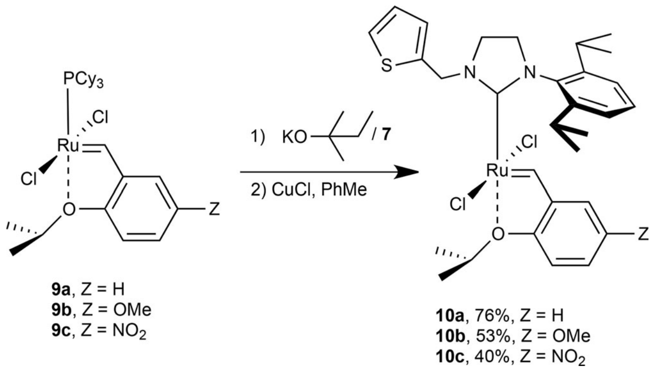
As the new bis(uNHC) complex exhibited very low activity in metathesis (see below), we started to look for other Ru alkylidene platforms to mount ligand **L10** on it.



Scheme 1. Attempted synthesis of uNHC indenylidene complex **5**.

Consequently, we decided to switch to the reliable 2-isopropoxybenzylidene architecture. In addition to the classical Hoveyda–Grubbs variant (**10a**),[18] we attempted to synthesize the electron-donating group (EDG) substituted analog (**10b**) and the electronically activated catalyst (Apeiron Nitro-catalyst type,[19] **10c**) in a hope to introduce differences in the resulting catalysts' initiation rates.

To turn this plan into reality, according to the literature procedure, we prepared the substrate first-generation ruthenium complexes **9a**–**c**.[20] Catalysts **10a**–**c** were then synthesized by deprotonation of imidazolinium salt **7** in toluene by using potassium *tert*-pentoxide and subsequent reaction of the resulting free **L10** with first-generation complexes **9a**–**c** in the presence of CuCl as a PCy_3 scavenger (Scheme 2). Products were isolated as air-stable green microcrystalline solids.



Scheme 2. Synthesis of complexes **10a**–**c**.

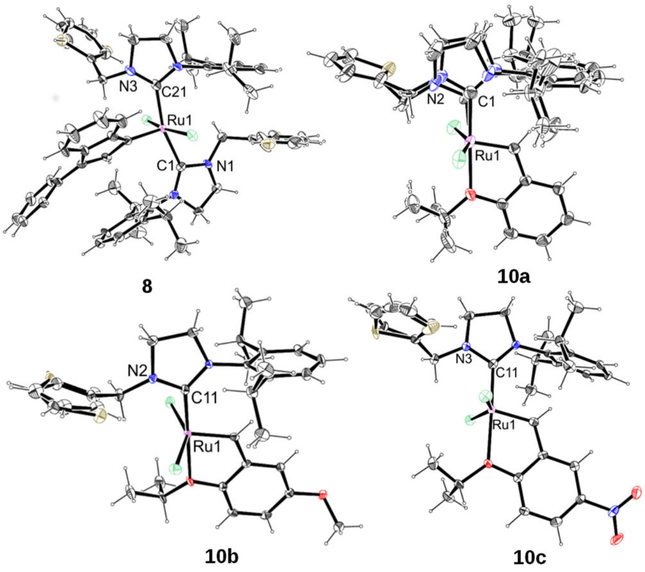


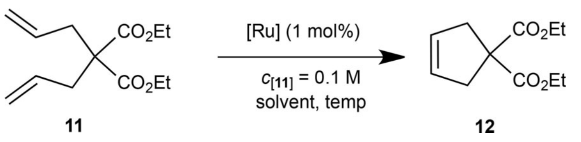
Figure 2. ORTEP drawing showing thermal ellipsoids drawn at the 50% probability level (for heavy atoms) of complexes **8** and **10a**–**c**. Hydrogen atoms are shown as open circles. Color code: oxygen, red; nitrogen, blue; chlorine, green; sulfur, bronze; ruthenium, orchid. Labeled are only these atoms for which bond lengths and angles are discussed in the text.

X-ray crystallographic studies

Bis(uNHC) complex **8** crystallizes in the *Cc* space group of the monoclinic crystal system with four molecules in the unit cell, which does not contain any solvent molecules. All the atoms are placed at general positions. Both thiophene rings are disordered in such a way that each of them takes two positions. This type of disorder is typical in the case of such heterocyclic rings and is also found in some other structures.[21] The structure of **8** was refined as an inversion twin with the ratio between the two forms equal to 0.40:0.60. The bond lengths between the ruthenium atom and carbon atoms of the carbene ligand (Ru1–C1 and Ru1–C21) are comparable: 2.100(6) Å and 2.104(7) Å. The Ru-C(carbene)-N valence angles (Ru1-C1-N1, Ru1-C21-N3) are 114.8(4)° and 128.5(5)° (Figure 2). Two of the new 2-isopropoxybenzylidene-type precatalysts (**10a** and **10b**) crystallize in the $P2_1/c$ space group of the monoclinic crystal system. However, even between these two structures some differences are noticed. The compound **10a** contains four molecules in the unit cell, whereas **10b** has eight molecules in the unit cell. Moreover, in both structures positional disorder is observed. However, different moieties are affected. In the molecule of **10a**, disorder is not only restricted to the diisopropylphenyl (DIPP) and isopropyl group bonded to the oxygen atom but also the whole imidazolidine. In the molecule of **10b**, only the thiophene ring is disordered in the same manner as described in the case of **10a**. The ratio between disordered positions of thiophene ring is 0.90:0.10. Neither structures of **10a** nor **10b** contain any solvent molecules and all atoms are located at general positions. Compound **2c** crystallizes in the $Pca2_1$ space group of the orthorhombic crystal system with four molecules in the unit cell. Again, the thiophene ring is disordered and has two positions. The ratio between disordered positions of thiophene ring is 0.86:0.14. Similar to the structure of **10a** described above, **10c** has been refined as an inversion twin with a ratio between the two forms of 0.16:0.84. The bond lengths between the Ru and C atoms of the carbene ligand in this group of precatalysts are consistent but slightly shorter than the values obtained for **8**. In the case of **10a**, there are two values because of disorder of the imidazolidine group, that is, 1.917(10) Å and 2.070(14) Å. In the case of **10b**, the Ru–C(carbene) bond length is 1.963(3) Å (the same for both molecules in the asymmetric part of the unit cell), and for **10c** it is 1.970(3) Å. The Ru-C(carbene)-N(thiophene) valence angles are equal: 118.5(7)° and 117.5(9)° for **10a** (two values because of disordered imidazolidine group); 118.76(18)° and 119.34(18)° for **10b** (two values because of two molecules in the asymmetric unit), and 118.9(2)° for **10c**. These values closely resemble those obtained for **8**. All relevant experimental details regarding catalysts **8** (Table S1) and **10a**, **10b**, and **10c** (Table S2) as well as all geometric parameters describing these molecules (Tables S3–S6) are presented in the Supporting Information. The ORTEP drawings of these molecules are presented in Figure 2. CCDC 1486691–1486696 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre or from the authors.

Catalytic activity studies

Next, we compared the catalytic activity of the newly obtained complexes with the activity of known structurally related general-purpose catalysts bearing the symmetrical NHC ligand (**3 c**, **4 c**, Figure 1). As a model transformation, the standard ring-closing metathesis (RCM) of diethyl diallylmalonate (**11**) was selected (Scheme 3).



Scheme 3. Model RCM reaction of diethyl diallylmalonate **11**.

In preliminary tests, we found quickly that, unfortunately, bis(uNHC) complex **8** is of low activity. This is probably due to hindered dissociation of one of the neutral NHC ligands, an activation step required for $(Cl)_2(L)_2Ru{=}CR_2$ type complexes to enter the catalytic cycle.[22] As we checked, the bis(uNHC)-ruthenium indenylidene complex was practically inactive at ambient temperature and needed at least 70 °C to initiate. At this temperature, **8** was found to achieve almost full conversion in toluene after 3 h (Figure 3).

Compare with that, the 2-isopropoxy analogs **10 a–c** bearing the same uNHC ligand **L10**, were much more reactive, and high to complete conversion of **11** was reached at 50 °C. This activity is still much lower than standard, SIPr-bearing **3 c** and **4 c**, a phenomenon already noted for complexes bearing other uNHC ligands, and used as "latent" catalysts in some applications.[23] The relative activity of differently substituted catalysts **10 a–c** was distinguishable and only the EWG-activated **10 c** resulted in full conversion of **11**, whereas **10 a–b** were slightly less reactive (Figure 3).

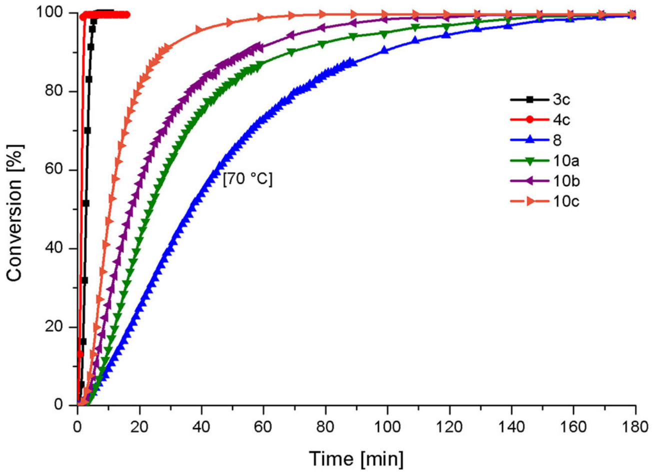


Figure 3. Time–conversion profiles for RCM of diethyl diallylmalonate **11** (0.1 M) with 1 mol% of precatalysts **8** (at 70 °C) and **3 c**, **4 c**, **10 a–c** (at 50 °C), in dry and degassed toluene at 50 °C under argon. Lines are visual aids only.

We decided to repeat the same activity tests in 2-methyltetrahydrofuran (2-MeTHF), a green solvent derived from renewable resources like corn cobs and oat hulls.

Taking into account its low toxicity and high biodegradability, 2-MeTHF is considered as an environmentally friendly solvent.[24] This solvent has already a broad application in organic chemistry, including in the pharmaceutical industry.[25] It was tested also in olefin metathesis, utilizing a general-purpose Hoveyda–Grubbs catalyst, **3 b**, and three rather exotically substituted variants (**14 a–c**).[26] In parallel, Skowerski et al. tested a wide set of commercially available catalysts, reporting lower activities in this solvent (Figure 4).[27] To the best of our knowledge, except this individual example, there are no other reports on the use of 2-MeTHF as a medium for olefin metathesis reactions. In the present work, standard catalysts **3 c** and **4 c** bearing the symmetrical SIPr carbene were tested and possessed very high activity in 2-MeTHF, as the full conversion of **11** was easily reached after 10 min (Figure 5).

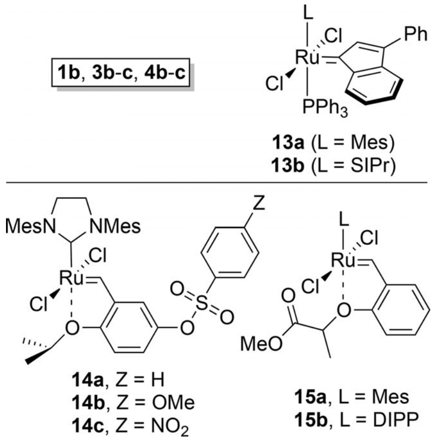


Figure 4. Catalysts previously tested in 2-MeTHF.[26]

Analogously to toluene, the activity of catalysts **10 a–c** bearing unsymmetrical NHC ligands proved to be lower and only catalyst **10 c** bearing a nitro-substituent in the benzylidene ligand allowed full conversion. Bis(uNHC) complex of **8** showed some reactivity, but again only at increased temperature (Figure 5). Encouraged by the results from the initial catalytic tests, we decided to investigate the activity of the catalysts bearing unsymmetrical NHC ligand **L10** with selected model compounds in non-degassed 2-MeTHF under air (Table 1). We used model compounds **11**, **14**, and **16** for RCM reaction and **18** for ene–yne metathesis (RCEYM). To put the results in context, we applied general-purpose catalysts **3 c** and **4 c** for the same trial.

Despite the tests being performed under air in commercially available non-degassed 2-methyltetrahydrofuran (as received from Sigma–Aldrich), we found that reactions catalyzed by SIPr-bearing catalysts **3 c** and **4 c** easily reached high conversions in all studied cases. Under these conditions, commercially available Apeiron's Nitro-SIPr catalyst **4 c** turned out to be slightly more active than **3 c**, completing all metathesis trans-

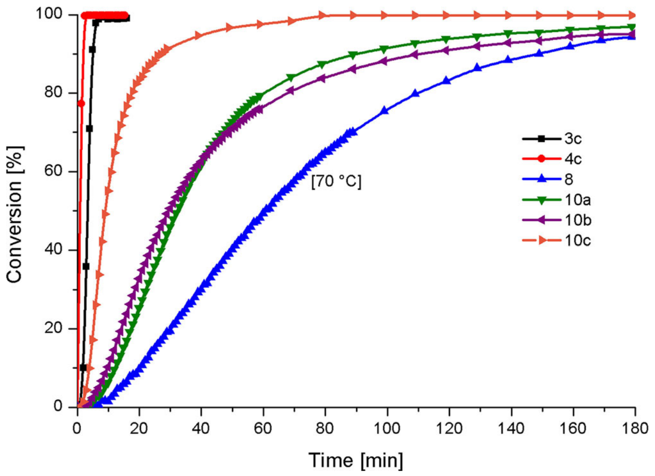


Figure 5. Time–conversion profiles for RCM of diethyl diallylmalonate **11** (0.1 м) with 1 mol% of precatalyst **8** (at 70 °C) and **3 c**, **4 c**, **10 a–c**, in dry and degassed 2-methyltetrahydrofuran at 50 °C under argon. Lines are visual aids only.

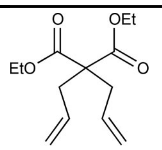
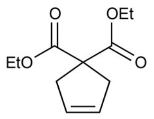
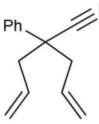
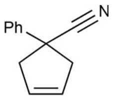
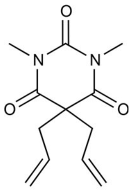
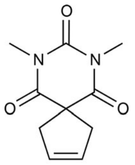
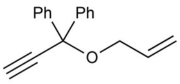
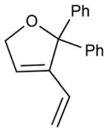
formations in less than 30 min. As expected, catalysts **10 a–c** bearing unsymmetrical NHC ligands required longer reaction times and higher temperatures to provide comparative results, and the EWG-activated **10 c** was again the most active in its class (Table 1).

Having established a general comparison between complexes **10 a–c** and standard all-purpose catalysts **3 c**, **4 c**, we turned our attention to more specialized applications, where the new unsymmetrical NHC complexes could hypothetically show their superiority.

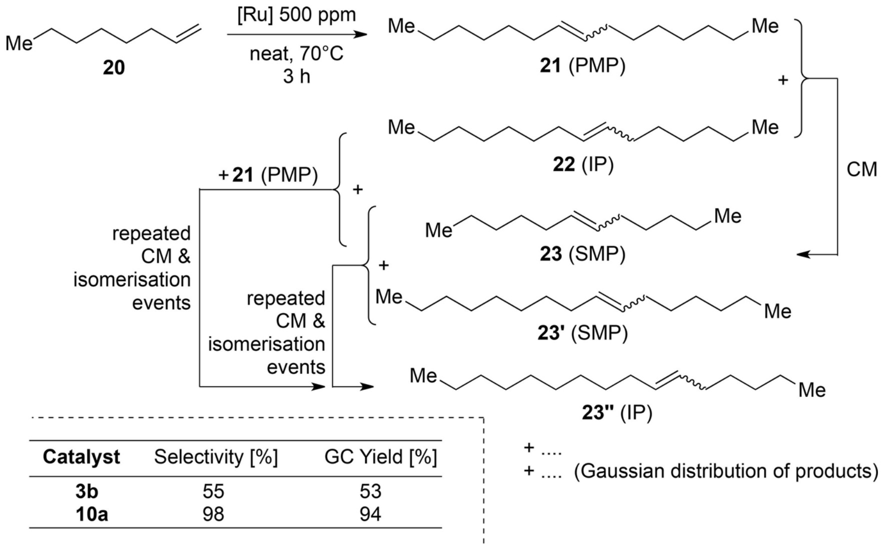
One such challenging transformation is the industrially relevant self-metathesis reaction (self-CM) of α-olefins.[28] These types of substrates are known to be prone to migration of the double bond along the carbon chain, especially when the second-generation Ru catalysts are used. This undesired side process is induced by catalyst decomposition products, mainly ruthenium hydrides[29] and dimers,[30] and even Ru nanoparticles.[31] The most common solution for this difficulty is the application of various additives, including: metallic mercury,[31] quinones,[32] chlorocatecholborane,[33] or phenylphosphoric acids,[34] however, none of them are universal. Recent developments in this field have shown that the application of specialized Ru-complexes with either unsymmetrical NHC ligands[12d] or quinones built into the catalyst structure[35] can significantly reduce the double bond migration during the metathesis reaction, providing selectivity levels ≥90%. The suppressed isomerization of the C–C double bond may be related to the increased stability of uNHC complexes under the reaction conditions, and thus their lower susceptibility to the degradation to undesired ruthenium compounds.

In the self-CM reaction of 1-octene (**20**), we decided to test Umicore Hoveyda–Grubbs Catalyst (**3 b**) as the representative regular metathesis catalyst and **10 a** as the specialized one. All tests were carried out in the presence of 500 ppm of catalyst

Table 1. Application of precatalysts **3 c**, **4 c**, and **10 a–c** in RCM and ene–yne reactions in 2-MeTHF under air.[a]

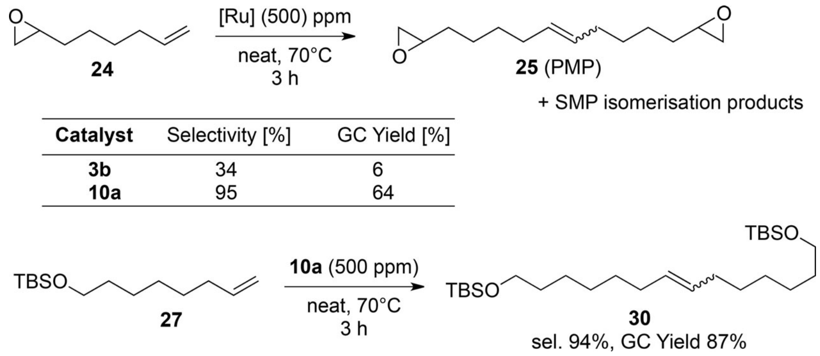
Entry[a]	Substrate	Product[b]	Catalyst [mol%]	*T* [°C]	*t* [h]	Conversion [%][b]
1	 **11**	 **12**	**3 c** (1)	30	3	95
			4 c (1)	30	0.5	98
			10 a (1)	50	4	72
			10 b (1)	50	4	75
			10 c (1)	50	4	93
2	 **14**	 **15**	**3 c** (1)	30	0.5	99
			4 c (1)	30	0.5	99
			10 a (1)	50	4	94
			10 b (1)	50	4	92
			10 c (1)	50	4	97
3	 **16**	 **17**	**3 c** (2)	30	2	99
			4 c (2)	30	0.16 (10 min)	99
			10 a (2)	50	4	80
			10 b (2)	50	4	69
			10 c (2)	50	4	82
4	 **18**	 **19**	**3 c** (2)	30	3	98
			4 c (2)	30	0.5	98
			10 a (2)	50	24	94
			10 b (2)	50	24	96
			10 c (2)	50	24	98

[a] All reactions were performed in non-degassed 2-methyltetrahydrofuran (Sigma–Aldrich) at 30 or 50 °C under air. [b] Conversion was determined by gas chromatography by using durene as an internal standard.



Catalyst	Selectivity [%]	GC Yield [%]
3b	55	53
10a	98	94

Scheme 4. Possible pathways in self-CM reaction of 1-octene. PMP = primary metathesis product; IP = isomerization product; SMP = secondary metathesis product. The progress of the reaction was monitored by gas chromatography (GC). Selectivity = (expected products/sum of all products). Determined by GC.



Catalyst	Selectivity [%]	GC Yield [%]
3b	34	6
10a	95	64

Scheme 5. Self-CM of **24** and **27**. Selectivity = (expected products/sum of all products). Determined by GC.

at 70 °C in neat conditions. The GC traces of the crude products presented in Scheme 4 shows that the standard Hoveyda–Grubbs catalyst **3b** and catalyst containing uNHC ligand **10a** differ significantly in terms of selectivity, and only the latter was able to deliver the expected product **21** in pure form.

Two other challenging substrates bearing a terminal C–C double bond sensitive to isomerization were tested (Scheme 5). In the case of self-CM of epoxide **24** catalyzed by unspecialized **3b**, the desired product **25** was contaminated with its homologs of shorter and longer carbon chains, and possibly with other products as well, forming a complicated mixture. The same reaction was conducted by using **10a** in ten times higher yield and with an impressive 95 % selectivity. Apparently, the impurities present in substrate **24** were less nocuous to catalyst **10a** compared with symmetrical SIMes-bearing **3b**. Similarly, alkene **27** underwent metathesis with **10a** without formation of unwanted byproducts, demonstrating the high selectivity of this complex in self-CM of fragile substrates.[12d]

Conclusions

Failed attempts to obtain indenylidene complex **5** led to preparation of low reactive bis(NHC) complex **8** and three 2-isopropoxybenzylidene catalysts **10a–c** bearing unsymmetrical NHC ligands with one DIPP and one thiophenylmethylene *N*-substituent. Although a number of model RCM and RCEYM reactions can be successfully performed with the new complexes in toluene or in environmentally friendly 2-methyltetrahydrofuran under air, their general efficiency is lower than standard all-purpose complexes **3c**, **4c** bearing symmetrical SIPr ligands. We were, however, pleased to see that specialized catalyst **10a** in the self-CM of olefins offers results unreachable for commercially available general-purpose Grubbs–Hoveyda catalyst **3b**.[36]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: green solvents · metathesis · *N*-heterocyclic carbenes · Ru catalysts · selectivity

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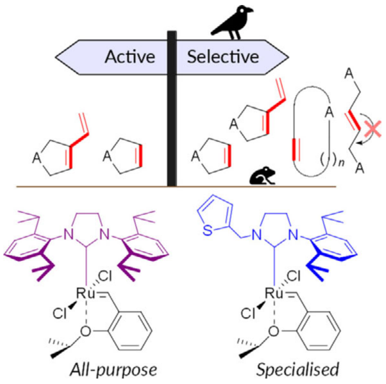
Joining the elite: New “special tasks” catalysts have been developed. They exhibited much better reactivity than the commercially available complexes in self-metathesis reactions of α-olefins, enabling high yields and selectivities to be reached.



Homogeneous Catalysis

*M. Smoleń, W. Kośnik, R. Gajda, K. Woźniak, A. Skoczeń, A. Kajetanowicz, K. Grela**

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Ruthenium Complexes Bearing Thiophene-Based Unsymmetrical *N*-Heterocyclic Carbene Ligands as Selective Catalysts for Olefin Metathesis in Toluene and Environmentally Friendly 2-Methyltetrahydrofuran