Olefin Metathesis

Bis(Cyclic Alkyl Amino Carbene) Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis

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Abstract: The state-of-the-art in olefin metathesis is application of N-heterocyclic carbene (NHC)-containing ruthenium alkylidenes for the formation of internal C=C bonds and of cyclic alkyl amino carbene (CAAC)-containing ruthenium benzylidenes in the production of terminal olefins. A straightforward synthesis of bis(CAAC)Ru indenylidene complexes, which are highly effective in the formation of both terminal and internal C=C bonds at loadings as low as 1 ppm, is now reported.

Significant efforts have been made in the last two decades to develop efficient olefin metathesis (OM) processes.[1] Those efforts focused on the proper selection of the substrate structure,[2] purification of the starting material,[3] and most importantly, on the modification of (pre)catalysts.[4] The efficiency of OM catalysts still remains too low for many transformations, prohibiting wider implementation of this technology in the industry. This is particularly true for the processes in which commodity and specialty chemicals are formed, for which the turnover numbers (TONs) of at least 50 000 and 35 000, respectively, should be obtained.[5] Notably, however, since the development of N-heterocyclic carbene (NHC)-ligated Grubbs (**1**),[6] Hoveyda–Grubbs (**2**),[7] and indenylidene (**3**)[8] catalysts, the vast majority of new ruthe-
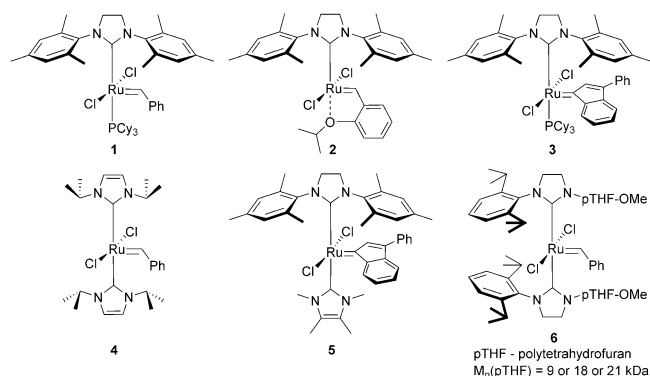

Figure 1. NHC- and bis(NHC)-ligated complexes.

nium-based complexes for OM have been synthesized by modifications of these parent structures (Figure 1).[4]

Ligation of two identical [bis(NHC)Ru][9] or different [(NHC)(NHC′)Ru][10] NHCs to the ruthenium center has been significantly less explored. Some of those complexes revealed interesting features such as good efficiency in ring-opening metathesis polymerization (ROMP) (**4**),[11] effectiveness in the formation of tetrasubstituted double bonds (**5**),[12] or mechanochemical activation (**6**).[13] In general, the complexes containing two identical NHCs exhibit low activity, as exemplified by catalyst **6**, whereas the ligation of two different NHCs is somewhat tedious.

The presence of NHC ligand is a common feature for basically all modern ruthenium catalysts designed for general applications. Those complexes show, in the majority of cases, a low level of degenerate (unproductive) metathesis and low stability of ruthenium methylidenes. This characteristic makes them practically useless in the industrially important cross-metathesis of unsaturated fatty acid derivatives such as methyl oleate (MO, **7**) with ethylene, commonly referred to as ethenolysis.[14] Linear α-olefins (LAOs, for example **8** and **9**, Scheme 1), obtained as a result of ethenolysis, can be easily transformed to higher added-value products.[15] Benzylidene ruthenium complexes containing the CAAC ligand[16] (for example, **12**) are the only catalysts that can reach the required level of TON in the ethenolysis of MO.[17] Of note, even at a catalyst loading as low as 3 ppm, the ethenolysis of 1 million metric tons of oils would require a few metric tons of catalyst.

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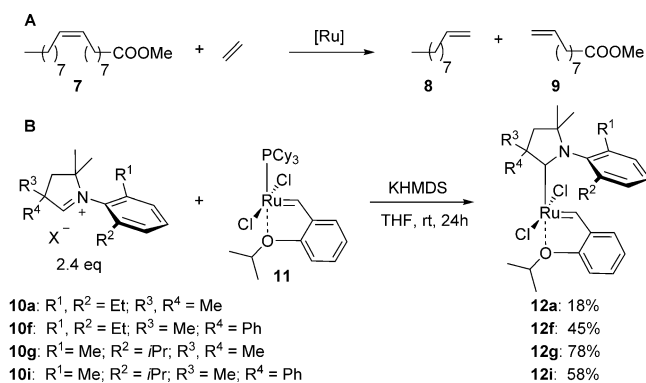E-mail: krzysztof.skowerski@apeiron-synthesis.com

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Scheme 1. A) Ethenolysis of methyl oleate; B) state-of-the-art method for the synthesis of (CAAC)Ru benzylidenes.

Scheme 2. Synthesis of bis(CAAC)Ru indenylidene complex.

Therefore, a safe and economically viable method of catalyst synthesis is crucial for industrialization.

It is important to note that until now, the (CAAC)Ru benzylidene complexes have only been obtained from Hoveyda first-generation catalyst **11**,[18] the preparation of which is burdened with significant safety and/or processing issues. The reported methods of synthesis of **11** require 1) application of diazocompound at −78°C,[19] 2) conducting the Wittig or Stille coupling reaction to synthesize 2-isopropoxystyrene,[20] or 3) using as much as 9 equiv of 2-isopropoxypropenyl benzene (**13**).[21]

No reports on the practical use of (CAAC)Ru benzylidenes in the formation of internal C=C bonds can be found.[22] This might be due to the difficult synthesis of these catalysts and lack of their commercial availability. The second fact that can discourage chemists from their general use is a relatively high degree of degenerate metathesis exhibited by the CAAC complexes which can potentially reduce productive TON.[23] We hypothesize, however, that the high stability of the CAAC-ruthenium methylidenes can prevail over degenerate metathesis and result in a very effective formation of internal C=C.

Thus, we aimed to develop one of the most versatile ruthenium based catalysts for OM, which could deliver both internal and terminal olefins at very low loadings and with high selectivity. For the above-mentioned reasons we decided to examine the possibility of synthesizing the CAAC catalysts directly from the readily accessible and patent free first-generation complexes bearing two phosphine ligands.

To start with, indenylidene complex **14a**[24] was reacted with CAAC generated in situ from 2 equivalents of salt **10a**[22a] with the use of lithium hexamethyldisilazane (LiHMDS) (Scheme 2).

A short time for the deprotonation step and application of LiHMDS proved to be critical for a good yield. Commonly utilized KHMDS or longer times of deprotonation in some cases completely prohibited the formation of products.[25] The product was isolated as a red solid in 70% yield. Surprisingly, the signal from the phosphorus atom was not present in ^{31}P NMR spectra, which suggests substitution of both phosphines by CAACs. The ^{1}H NMR spectra of product was complicated owing to the presence of rotational isomers,[26]
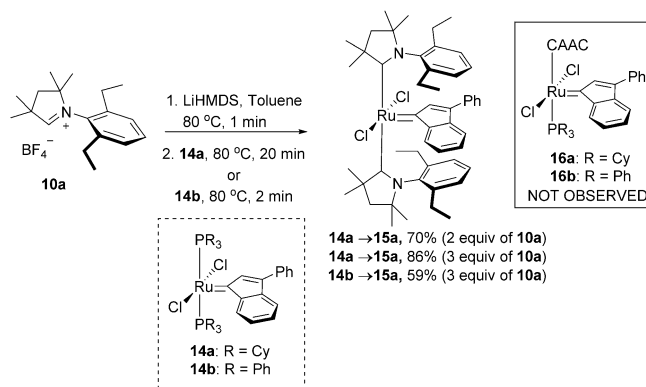
and could not provide reliable information about its structure. Nevertheless, the mass spectra, elemental analysis, and single-crystal X-ray diffraction analysis confirmed the formation of bis(CAAC)Ru complex **15a**. The yield of **15a** was improved to 86% by increasing the excess of **10a** to 3 equivalents. Interestingly, even with 1.25 equiv of **10a**, complex **16a** was not observed on a TLC plate even though complex **14a** was not fully consumed. This fact suggests a strong steric repulsion between CAAC and tricyclohexylphosphine in **16a**, which facilitates dissociation of the latter and complexation of the second CAAC.[27] From practical and economical point of view, complex **14b** is the most preferred Ru source.[24] Conveniently, **15a** was obtained from **14b** as a sole product with 59% yield. Analogously, the treatment of CAACs, generated by deprotonation of 3 equiv of salts **10b–h** with **14b**, provided exclusively bis(CAAC) complexes **15b–h** (Table 1). In the case of complex **15h**, the two isomers were separated by crystallization.

Table 1: Synthesis of bis(CAAC)Ru indenylidene complexes.

R	Ar	CAAC precursor	15 (yield [%])
Me		**10b**	**15b** (37)
Ph		**10c**	**15c** (37)
Me		**10d**	**15d** (35)
Ph		**10e**	**15e** (28)
Ph		**10f**	**15f** (60)
Me		**10g**	**15g** (41)
Me		**10h**	**15h** (39)
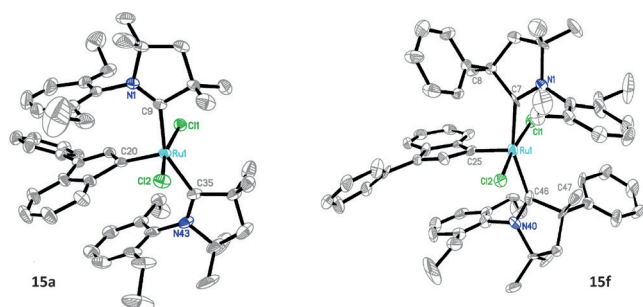
Figure 2. X-ray crystal structures of **15a** and **15f**. Ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity.[37]

Crystals suitable for single-crystal X-ray diffraction were obtained for complexes **15a–c**, **15e**, and **15f** (selected bond lengths and angles within coordination sphere are given in the Supporting Information, Table S2). These complexes show a distorted square pyramidal geometry with the carbon atom of the indenylidene ligand in the apical position (Figure 2). A similar geometry of the coordination sphere can be found in CAAC-benzylidenes (for example, **12a**)[22a,17a] and (NHC)-(NHC′)indenylidene complexes (**5**).[12] The CAACs exhibit stronger σ-donation abilities than the NHCs. Consequently, the Ru−C$_{carbene}$ bond in **12a** (1.9482(14) Å) is noticeably shorter than Ru−C$_{carbene}$ in complex **2** (1.981(5) Å). Surprisingly, the Ru−C$_{carbene}$ bonds in complexes **15** were found to be significantly longer than Ru−C$_{carbene}$ in **12a** and very similar to the Ru−C$_{carbene}$ distances in **5** (2.105(4) and 2.091(4) Å). For example, the distances in **15f** are Ru−C7$_{carbene}$ 2.093(11) and Ru−C46$_{carbene}$ 2.103(11) Å.

To examine the possible initiation pathway of **15**, we reacted **15a** and **15f** with doubly chelating olefin **13**. Clean conversion of **15f** to complex **12f** was observed within 1 h in the presence of 1.2 equiv of **13** (toluene, 60°C), and the product was isolated in 86% yield. Under the same conditions no conversion of **15a** was observed within two days. However, in the presence of 2 equiv of CuCl, complex **12a** was formed within 30 minutes.[28] This results strongly support the classical mechanism in which active, 14-electron species are formed via neutral ligand release and also prove that for **15a** dissociation of CAAC is the rate-limiting step. NMR kinetic studies were undertaken to gain more information about the possible mechanism of initiation of **15f**. The rate of the reaction between **15f** and olefin **13** ([D$_8$]toluene, 60°C) proved to be independent of the concentration of **13** (see the Supporting Information) and was in good agreement with the stability of **15f** in solution (which appears to be limited by the high
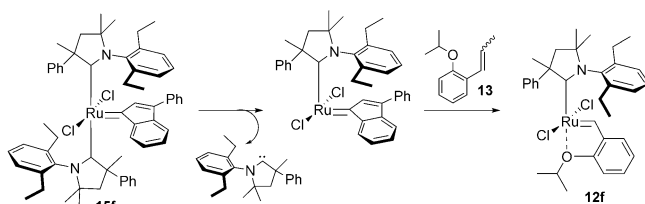
lability and low stability of CAAC).[25] Experimental results suggest that a dissociative mechanism operates for **15f** (Scheme 3). This, however, cannot be extrapolated to all complexes **15**, and further theoretical and kinetic studies are needed to shed more light on the initiation mechanism of these (pre)catalysts.[29]

Complexes **15a–h** and highly efficient in ethenolysis reaction complex **12g** were tested in the benchmark ring closing metathesis (RCM) of diethyl diallylmalonate (DEDAM, **17**, Figure 3), to compare their activity.
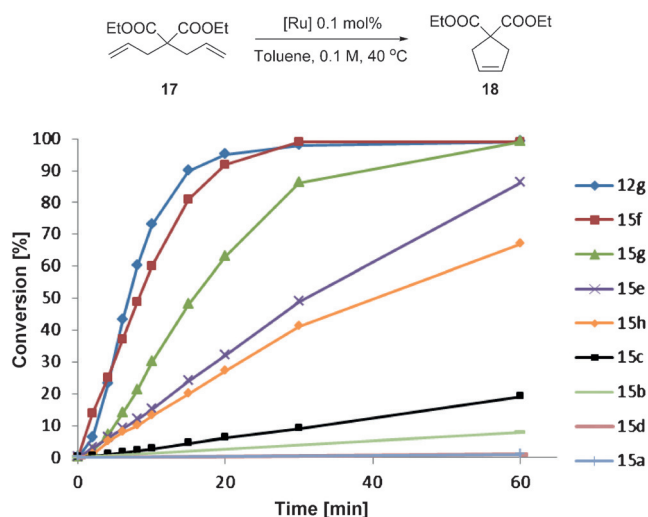
Figure 3. Reaction profiles for RCM of DEDAM with catalysts **12g**, **15a–h**.

The structure of the CAAC ligand proved to have a dramatic influence on the initiation rate. Complexes **15a–d** exhibited a very low (or lack of) activity, which could be expected in the case of (pre)catalysts bearing two strongly binding CAACs. These complexes can be activated by CuCl (Supporting Information). Unexpectedly, complexes **15e–h** showed a promising, moderate-to-high activity under these mild conditions.

For the complexes with a symmetric substitution of the *N*-aryl ring (**15a–c**, **15f**), the ratio of isomers in the solution can be conveniently determined by ^{1}H NMR based on the chemical shift of the characteristic proton of the indenylidene ligand (see the Supporting Information for details).[30] Crystal structures and ^{1}H NMR spectra of **15f** and **15c** suggest that introduction of a phenyl ring into the quaternary carbon atom favors the formation of a rotamer having *N*-aryl groups on the opposite side with respect to the coordination pyramid base. These complexes are more active than their close analogues which contain methyl instead of a phenyl substituent (**15a**, **15b**) and which exist mainly in the rotamer having *N*-aryl groups on the same side with respect to the coordination pyramid base. However, specific rotamer does not ensure high activity, as exemplified by the poor conversion of **17** obtained with **15c**. The electronic properties of CAACs in **15a** and **15g** must be similar since these ligands differ only in the position of one methyl group in the *N*-aryl substituent. At

Scheme 3. Proposed mechanism for initiation of **15f**.

the same time, a striking difference in activity of **15a** and **15g** was observed. Therefore, the most plausible explanation for the very broad range of activities covered by catalysts **15** is that the degree of steric repulsion between two CAACs determines the initiation rate.[31]
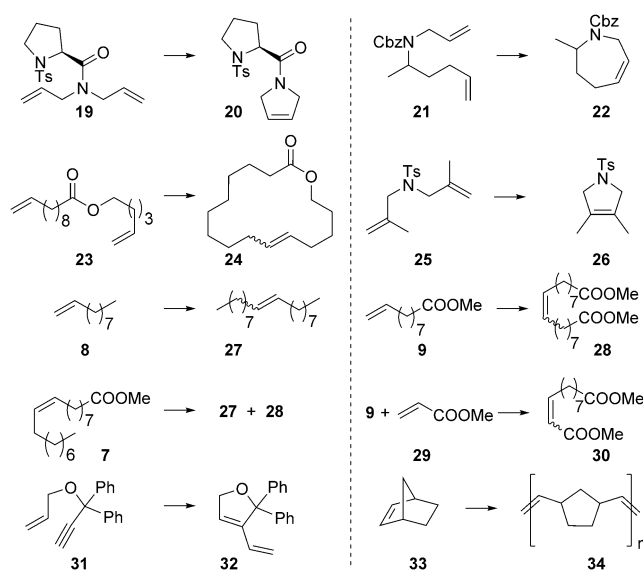
Next, ethenolysis of methyl oleate **7** was performed. Also in this case, **12g** was used for the comparative reasons.

Initially, reactions were run using 10 ppm catalyst loading in neat MO at 150 psi of ethylene (99.99% purity).[32] The catalysts were compared at the conditions at which they were most efficient. Catalyst **12g** provided maximum TON at 40°C in just 2 h. The bis(CAAC)Ru indenylidene complexes **15** required a temperature between 50 and 60°C and 4 h to reach maximum TON. Even at this increased temperature, the slow initiators, namely **15a,b**, and **15d**, did not provide significant amounts of ethenolysis products. On the other hand, the highly active complexes **15e–g** delivered products with over 50 000 TON. Under these conditions, catalyst **15g** was the most efficient (TON 60 000), slightly outperforming **12g** (TON 56 000). The most efficient initiators, **12g** and **15f,g**, were tested at 5 ppm loading (Table 2, entry 2, 9, and 11). Upon reduction of catalyst loading **12g** performed the best (TON 94 000) followed by **15g** (TON 86 000) and **15f** (TON 74 000). It was not possible to further effectively reduce the catalyst loading (drop of TON was observed for each catalyst at 3 ppm), which is most probably due to the insufficient purity of MO or lack of a glovebox.[33] Because of the easy synthesis, **15g** and especially **15f** are (from an economic point of view) an interesting alternative to **12g**. For tests in the formation of internal alkenes (Scheme 4), catalyst **15f** was selected owing to 1) its good activity at low temperatures, 2) high efficiency, and 3) the inexpensive starting material (2,6-diethylaniline) used in the synthesis of the CAAC precursor **10f**. First, the efficiencies of **15f** and state-of-the-art complex **1** in RCM of highly polar proline derivative **19** (Table 3) were compared. The reaction was run in toluene at 0.25 M concentration, with the use of 60 ppm of initiators. We were pleased to see that **15f** (92% isolated yield) significantly outperformed **1** (50% GC yield). It was reported that productivity of active species generated from **1** is reduced by PCy₃ reuptake and additionally by attack of the free PCy₃

Scheme 4. Metathetic transformations accomplished with catalyst **15f**.

Table 3: Results of OM reactions.[a]

Substr.	Prod.	[Ru], ppm	T [°C]	C [M]	Conv. (select.) [%]	GC Yield [%][b]	TON
19	20	15f, 60	60	0.25	96 (98)	(92)	15300
19	20	1, 60	60	0.25	51 (98)	50	8300
21	22	15f, 50	55	0.25	>99 (>99)	>99 (91)	20000
23	24	15f, 250[c]	70	0.005	95 (96)	91[d]	3640
25	26	15f, 1000[e]	70	0.25	90 (>99)	(79)	790
8	27	15f, 1	60	neat	64 (98)	63 (55)	315000
8	27	1, 2	60	neat	33 (95)	31	77500
8	27	2, 2	60	neat	16 (88)	14	35000
9	28	15f, 2	60	neat	69 (98)	68 (62)	170000
7	27+28	15f, 5[c]	55	neat	45 (>99)	45	90000
9+29	30	15f, 200[f]	60	0.5	99 (98)	97[g] (95)	4850
31	32	15f, 250	60	0.25	94 (>99)	(79)	3160
33[h]	34	15f, 1000	27	0.1	–	(87)	870

[a] In toluene, reaction time 2 h. [b] Isolated yield provided in brackets. [c] Catalyst added in 5 portions. [d] E/Z = 65:35. [e] Catalyst added in 10 portions. [f] Catalyst added in 4 portions. [g] E/Z = 87:13. [h] reaction in DCM with 1.5 mol% of CuCl, reaction time 10 min, PDI 1.81.

on methylidene carbon.[34] In respect to that, the low stability of CAAC liberated from **15f** can potentially contribute to high efficiency of this complex. The RCM of **21** promoted by 50 ppm of **15f** delivered an azepine derivative **22**, a useful building block in the synthesis of Cathepsin K inhibitors, with over 99% yield.[35] Excellent result was achieved for a highly challenging macrocyclization of **23** run at 5 mM concentration (91% yield of **24**, 250 ppm of **15f**). Compatibility of **15f** (1000 ppm catalyst loading) with sterically crowded substrates

Table 2: Ethenolysis of methyl oleate with catalysts **12g**, **15a–h**.[a]

Entry	[Ru], ppm	T [°C]	Conv. (Select)[b] [%]	Yield [%]	TON
1	**12g**, 10	40	61 (91)	56	56000
2	**12g**, 5	40	51 (92)	47	94000
3	**15a**, 10	60	<1	–	
4	**15b**, 10	60	3	–	
5	**15c**, 10	60	21 (92)	19	19000
6	**15d**, 10	60	1	–	
7	**15e**, 10	60	57 (89)	51	51000
8	**15f**, 10	50	60 (88)	53	53000
9	**15f**, 5	50	41 (91)	37	74000
10	**15g**, 10	55	69 (87)	60	60000
11	**15g**, 5	60	48 (90)	43	86000
12	**15h**, 10	60	37 (91)	34	34000

[a] Reactions in neat MO, 150 psi of ethylene; entries 1,2: 2 h, entries 3–12: 4 h. [b] For details regarding calculation of selectivity, yield, and TON, see the Supporting Information.

was proved by RCM of **25** which provided tetra-substituted **26** in 79% isolated yield.

Self-cross-metathesis (SM) of simple, terminal alkenes is an example of a transformation which requires very high TONs to be economically viable. In our hands, SM of 1-decene **8** proceeded up to 63% of GC yield when run with 1 ppm of **15f**, which relates to a TON_{27} of 315000.[36] Moreover, a very high selectivity of 98% was observed without any additive typically applied to inhibit the C=C bond migration. Under the same conditions, 2 ppm of catalyst **1** delivered dimer **27** with only 31% yield and 95% selectivity (TON_{27} 77500), whereas 2 ppm of initiator **2** gave 14% of product with a poor selectivity of 88% (TON_{27} 35000). Similarly, 2 ppm of **15f** delivered diester **28** with excellent TON_{28} of 170000. Self-metathesis of methyl oleate **7** proceeded up to 45% of conversion in the presence of 5 ppm of **15f**. Almost quantitative yield in challenging cross-metathesis of ester **9** with electron-deficient methyl acrylate **29** was achieved with 200 ppm of **15f**. Additionally, alkene–alkyne (ene-yne) RCM of **31** and ROMP of norbornene **33** were successfully accomplished with the use of 250 and 1000 ppm of **15f**, respectively. The obtained polynorbornene **34** was characterized by a number-average molecular weight of 61 kg mol^{-1}, weight-average molecular weight of 110 kg mol^{-1}, and polydispersity (PDI) of 1.81.

In summary, we have synthesized for the first time the bis(CAAC) ruthenium complexes. Activity of complexes **15** depends on the steric repulsion between CAAC ligands. Importantly, synthesis of **15** requires only 6 steps starting from commercially available raw materials and is not burdened with any safety or processing issues. The level of TON required for production of commodities (50000) was significantly exceeded with complexes **15f** and **15g** in ethenolysis of methyl oleate. Testing our hypothesis we confirmed that **15f** can efficiently and selectively promote formation of internal olefins in RCM, CM, SM, ene-yne RCM, and ROMP. A TON exceeding 300000 was achieved in self-metathesis of 1-decene promoted by **15f**.

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