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Synthesis and catalytic olefin metathesis activity of amberlyst-15 supported cyclic and bicyclic alkyl amino carbene ruthenium complexes

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Abstract

Amberlyst-15 supported cyclic alkyl amino carbene and bicyclic alkyl amino carbene ruthenium olefin metathesis catalysts for sustainable catalytic applications have been synthesized by the well-known wet impregnation method utilizing ionic complex/support interaction. Surface coverages are as high as 4 and 7 wt% were achieved in the case of the significantly higher pore volume Amberlyst-15, compared to Amberlyst-36. These phase separable catalysts show high activity in cross metathesis, ring closing metathesis and ethenolysis reactions compared to the reported heterogenized olefin metathesis catalysts. Leeching tests revealed no more than 1.5 ppm ruthenium content for the investigated metathesis reactions, which is well below the accepted 10 ppm limit in case of consumer products.

Keywords Ruthenium · CAAC · BICAAC · Metathesis · Amberlyst support

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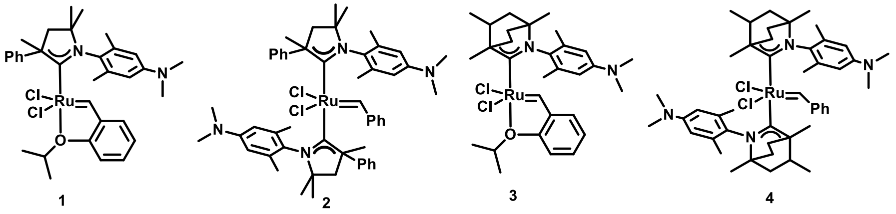
Introduction

The industrial application of sustainable catalysis is crucial from the point of contemporary chemical technologies view. It is estimated, that 90% of the commercial chemicals are manufactured via some catalytic process [1]. Recent trends in the widespread use of catalysis in sustainable and green chemical applications have created further challenges requiring robust solutions [2]. Olefin metathesis is one of the novel organometallics-catalyzed reactions discovered in the last fifty years, that initiated new industrial technology avenues [3]. Its application on the field of green chemistry—especially in oleo chemistry—is growing [4, 5]. Although in general, the homogeneous olefin metathesis catalysts render higher activity and functional group tolerance than heterogeneous systems [6], their separation from the reaction mixture is often cumbersome limiting their industrial application [7–9]. This is especially important in the pharmaceutical industry, where the acceptable remaining ruthenium content cannot be exceed 10 ppm [10–12], causing a sudden interest in the purification of metathesis products [13, 14]. One method to overcome this recurring problem is to combine the advantages of homogeneous and heterogeneous catalysis, by the heterogenization of homogeneous catalysts [15, 16]. Since the first solid-supported well-defined metathesis catalyst [17], numerous reviews summarized this growing area of metathesis chemistry [18–23], while their commercial availability is readily growing [24]. As of today, both primary and secondary interactions are used to deposit catalyst to different supports. Examples for the covalent bond based immobilizations include silica [25–27] and SBA-15 supported species [28], substituted polystyrenes [29] and polynorbornenes [30, 31] among others [32]. An interesting primary ionic bond-based solution is the application of *tertiary* amine-tagged ruthenium species together with acidic ion-exchange resin precipitated on glass Raschig rings [33]. Although many olefin metathesis reactions using solid-supported ruthenium based catalyst have been demonstrated, their application in ethenolysis reactions are rare: besides heterogeneous systems are proven to be effective catalysts for ethenolysis [34, 35], solid- (MOF) [36] or phase-supported (biphasic/SLIP) [37] complexes have been reported as effective catalysts. Turnover number of supported systems in olefin metathesis exceeds the order of one hundred thousand using Schrock systems [38], but only a few thousand at most when applying Grubbs-systems [37, 39, 40].

An emerging, new class of olefin metathesis catalyst bearing cyclic and bicyclic alkyl amino carbene (CAAC and BICAAC) family ligands appeared recently showing superior catalyst activity and stability. In our laboratories new CAAC (1 and 2) and latent BICAAC (3 and 4) ruthenium alkylidene complexes bearing dimethyl amino group have been synthesized recently [41, 42], showing exceptional stability and catalytic activity even in protic solvents or at elevated temperature (Scheme 1).

In this paper, the preparation and application of first Amberlyst-15 supported CAAC-Ru and BICAAC-Ru complexes in olefin metathesis including ethenolysis reactions will be demonstrated.



Scheme 1 CAAC and BICAAC ruthenium complexes bearing dimethyl amino functionalities

Experimental methods and materials

Materials

Ruthenium CAAC [33] and BICAAC [34] complexes (1 and 3) were synthesized according to literature procedure. Amberlyst-15 (hydrogen form, dry, total pore volume: 0.2 mL/g, average pore size: 24 nm, ACROS) and Amberlyst-36 (hydrogen form, 55% water content, total pore volume: 0.06 mL/g, average pore size: 27 nm, Sigma Aldrich) were dried in vacuum at 75 °C overnight before use.

1-Octene (9), diethyl diallylmalonate (5) and cyclopentene (7) were purchased from Sigma Aldrich and used as received.

Methyl oleate (11) was received from Sigma Aldrich and passed through a plug of dried alumina in a glove box prior to use.

7-Tetradecene (10) was prepared according to literature procedure [43].

Amberlyst supported catalyst preparation

Amberlyst supported CAAC and BiCAAC catalysts were prepared via wet impregnation method. First, the ion-exchange resin (Amberlyst-15 or Amberlyst-36) was dried in vacuo at 75 °C and transferred to a glove-box. In the glovebox, the ruthenium alkylidene complex (1 or 3) was dissolved in dichloromethane (DCM, 5 mM) and added in excess to the resin. After 15 h of continuous stirring at room temperature, the resin was filtered and washed with DCM, followed by drying in vacuo. The combined DCM phase was evaporated and the mass of the residual ruthenium complex in the liquid phase was measured, indicating the amount of impregnated ruthenium alkylidene. This gravimetric ruthenium content was in good agreement with the following ICP-OES measurement, namely: **1-AL-15**: 3.4 m%, **1-AL-36**: 0.03 m%, **3-AL-15**: 6.1 m% and **3-AL-36**: 0.05 m% ruthenium complex content.

Characterization methods

Inductively coupled plasma—optical emission spectrometry (ICP-OES)

For the ruthenium content analysis, sample solutions were measured with a simultaneous ICP-OES spectrometer with axial plasma viewing (Spectro Genesis, Germany). For the calibration of the instrument, the following standard solutions were applied: CPAChem Ltd. multi-element standard solution (33 elements, M8A96.K1.5 N.L5) and Inorganic Ventures multi-element standard solution (8 elements including Ru, 31-ICPMS-71C).

Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDS)

SEM measurements of the gold- (carbon- in case of EDS analysis) coated support resins and the impregnated catalyst beads were carried out with a ZEISS EVO 40 scanning electron microscope operated at 5 keV, coupled with an Oxford Instruments, INCAx-sight x-ray detector.

Electrospray time-of-flight mass spectrometry (ESI-TOF MS)

ESI-TOF MS measurements were carried out using a Bruker MicroTOF Q instrument (Bruker Daltonik, Bremen, Germany) equipped with an ESI source operated in the positive ion mode. The voltage on the spray was 3.5 kV, nitrogen was used as nebulizer and drying gas (180 °C, 4 L/min). The mass spectra were recorded using a digitalizer at a sampling rate of 2 GHz. The calibration was performed using the exact masses of clusters formed from the electrosprayed solution of sodium trifluoroacetate (NaTFA). The mass spectra were assessed with the DataAnalysis 3.4 software from Bruker.

Sample preparation for ESI-TOF MS

2.1 mg (CAAC) and 2.3 mg (BICAAC) were added to 200 μL methanol and placed in an ultrasound bath, where they were stirred for 20 min. After filtration, the samples were injected directly into the ion-source of ESI-TOF MS instrument and the MS spectra were recorded (Figs. S1–S4).

Table 1 Different metathesis reaction types, catalyzed by Amberlyst-15 supported catalysts 1-AL-15 and 3-AL-15

Entry	Reaction	Substrate	Product	Catalyst	T (°C)	Reaction time [h]	Substrate V% [a]	Catalyst [mol%]	Yield [%]	$n_{product}/n_{Ru\text{-}cat}$
1	RCM	5	6	1	25	0.5	20%	0.1	95	950
2	RCM	5	6	1-AL-15	25	3	20%	0.1	65	650
3	RCM	5	6	1-AL-15	25	6.5	20%	0.1	82	820
4	RCM	5	6	1-AL-15	25	24	20%	0.1	94	940
5	RCM	5	6	1-AL-15	25	24	20%	0.01	28	2850
6	RCM	5	6	1-AL-15	25	24	Neat	0.01	23	2280
7	RCM	5	6	1-AL-36	25	24	20%	0.1	13	130
8	RCM	5	6	3-AL-15	75	24	20%	0.1	2	20
9	RCM	5	6	3-AL-15	75	24	Neat	0.1	5	50
10	CM	9	10	1-AL-15	25	24	20%	0.01	39	3900
11	CM	9	10	1-AL-15	25	24	Neat	0.01	44	4440
12	CM	9	10	3-AL-15	75	24	20%	0.01	47	4650
13	CM [a]	9	10	3-AL-15	75	24	Neat	0.01	31 [b]	3170 [b]
14	ET	10	9	1-AL-15	25	24	20%	0.1	72	720
15	ET	10	9	1-AL-15	25	24	Neat	0.01	22	2170
16	ET	10	9	3-AL-15	75	24	20%	0.1	18	180 [c]
17	ET	10	9	3-AL-15	75	24	Neat	0.01	6	600 [c]
18	ET	11	12, 13	1-AL-15	25	24	20%	0.1	18	180
19	ET	11	12, 13	1-AL-15	40	24	20%	0.1	27	270
20	ET	11	12, 13	1-AL-15	40	24	20%	0.1	36	360
21	ROMP	7	8	1-AL-15	25	24	Neat	0.1	24	240

[a] Hexane solvent

[b] Isomerization-metathesis also occured along the cross-metathesis

[c] Yield of tetradecene isomers were determined based on GC–MS integral area

[d] Trace amounts of isomerization product were detected

Model reactions

Representative example of solid-supported ring-closing metathesis (RCM) reaction (Table 1 Entry 6)

In a glove box, diethyl diallylmalonate (**5,** 1000 mg, 4.2 mmol) and solid-supported catalyst (**1-AL-15**, 0.01% Ru, 6.8 mg) was measured in a small vial. The reaction mixture was stirred at RT for 24 h in the box. Portion of the crude material was dissolved in $CDCl_3$ and measured via ^{1}H-NMR spectroscopy. Yields were calculated from the internal and terminal alkene proton signals. To determine the ruthenium content of the reaction mixture, part of the crude product was evaporated and stirred with aqua regia at 65 °C overnigth. After diluting with water, this sample was analyzed by ICP-OES.

Representative example of solid-supported cross-metathesis (CM) reaction (Table 1 Entry 11)

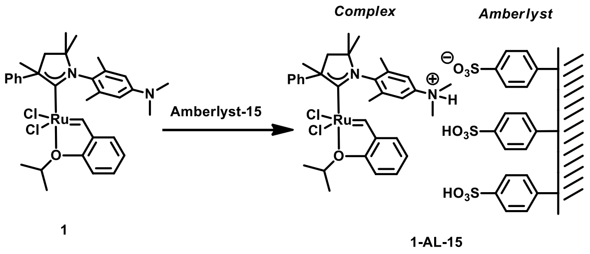
In a glove-box, 1-octene (**9**, 2000 mg, 17.8 mmol) and solid-supported catalyst (**1-AL-15**, 0.01% Ru, 26 mg) were measured in a small vial and stirred at RT for 24 h. Portion of the crude material was dissolved in $CDCl_3$ and measured via ^{1}H-NMR spectroscopy. Yields were calculated from the internal and terminal alkene proton signals. To determine the ruthenium content of the reaction mixture, part of the crude product was evaporated and stirred with aqua regia at 65 °C overnight. After diluting with water, this sample was analyzed by ICP-OES.

Representative example of solid-supported ethenolysis reaction (Table 1 Entry 15)

In a glove-box, 7-tetradecene (**10**, 2000 mg, 10.2 mmol) and solid-supported catalyst (**1-AL-15**, 0.01% Ru, 15 mg) was measured in a 150 mL Fischer-Porter bottle. The vessel was sealed and connected to a high pressure system outside the box. The bottle was flushed with ethylene gas (purity: 4.5) five times and filled to 10 bar. The reaction mixture was stirred at RT for 24 h. Portion of the crude material was dissolved in $CDCl_3$ and measured by ^{1}H-NMR spectroscopy. Yields were calculated from the internal and terminal alkene proton signals. To determine the ruthenium content of the reaction mixture, part of the crude product was evaporated and stirred with aqua regia at 65 °C overnight. After diluting with water, this sample was analyzed by ICP-OES.

Results and discussion

As catalyst 1 and 3 have shown exceptional activity comparing to their bis-carbene anologues (2 and 4) their impregnation to Amberlyst ionexchange resin have been investigated. Catalyst 1 and 3 have been synthesized according to the literature



	Complex 1	Complex 3
Amberlyst-15	1-AL-15	3-AL-15
Amberlyst-36	1-AL-36	3-AL-36

Scheme 2 Preparation of **1-AL-15**, Amberlyst-15 supported CAAC ruthenium catalyst

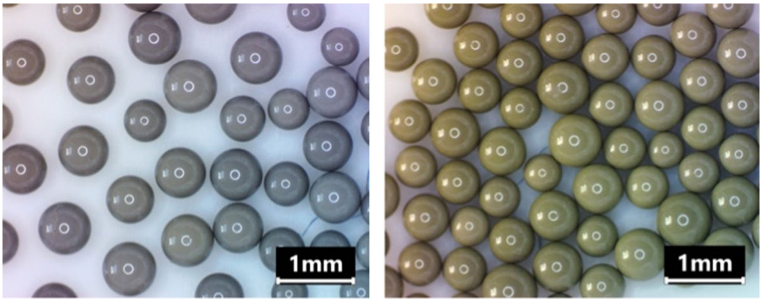


Fig. 1 Light microscope images of Amberlyst-15 (left) and immobilized catalysts **3-AL-15** (right). The white circle in the middle of the beads is the reflection of the light source

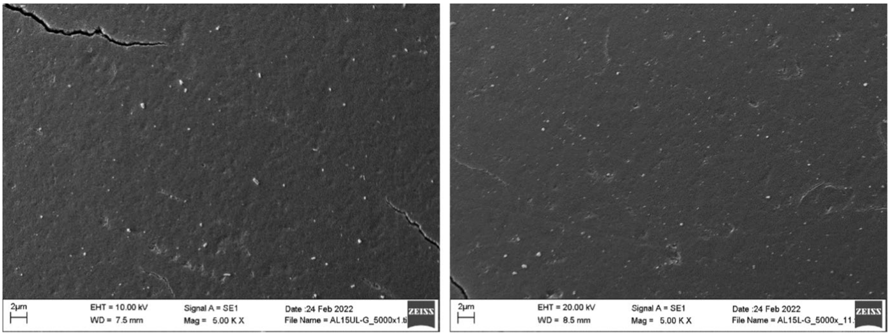
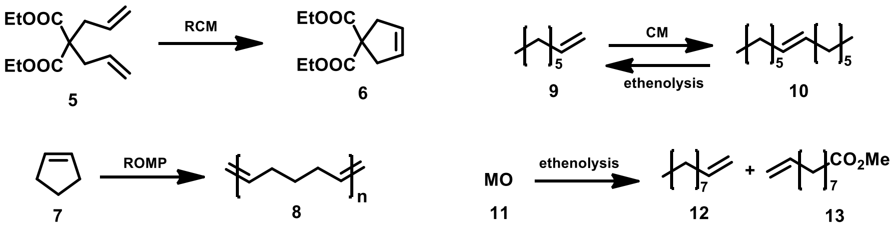


Fig. 2 SEM images of Amberlyst-15 support (left) and the impregnated 3-AL-15 (right) using a magnification of 5000× and a scalebar of 2 μm. SEM images show no indication of aggregated complex precipitated on the surface of the support

procedure [41, 42] and impregnated onto pre-treated Amberlyst resins (Amberlyst 15 yielding **1-AL-15** and **3-AL-15** and Amberlyst-36 resulting in **1-AL-36** and **3-AL-36**) via the well-known wet-impregnation method (Scheme 2). Upon impregnation of the complexes to the Amberlyst solid support followed by multiple washing greenish pearls could be obtained (Fig. 1). Solid-supported catalyst



Scheme 3 Olefin metathesis model reactions using **1-AL-15** and **3-AL-15** solid-supported catalyst (MO: methyl oleate)

characterization has been carried out using Scanning Electron Microscopy coupled with energy dispersive X-ray (SEM/EDX) spectroscopy (Fig. 2). The EDX spectra revealed that there is no ruthenium (K_α 19.233, L_α 2.558) on the outer surface of the solid support, meanwhile the ruthenium complexes were clearly detectable by ESI-TOF MS (Figs. S1–S4) upon treatment of the catalyst with MeOH in ultrasonic bath for 20 min. ICP-MS also clearly indicated the presence of ruthenium. Based on these investigations, it can be assumed that the catalyst species are located primarily in the pores of the solid support. It should be noted that the main differences between the applied supports is their acidity (or the number of the acidic species on the surface) and overall pore volume. It was found that the catalyst coverage—determined by ICP—strongly depends on the Amberlyst type. The highest coverage could be achieved using Amberlyst-15 support and catalyst 3 (6.1% for **3-AL-15**). Impregnation of catalyst 1 gave a solid-supported catalyst having lower catalyst coverage, 3.4% for **1-AL-15**. Using Amberlyst-36, significantly lower coverage was observed for both complexes, 0.03% for **1-AL-36** and 0.05% for **3-AL-36**. This can be explained by the almost one order of magnitude higher pore volume of Amberlyst-15 (0.2 mL/g) compared to Amberlyst-36 (0.06 mL/g) and also supports that the catalytically active ruthenium-alkylidene species are located mainly in the resin pores.

The catalytic activity of **1-AL** and **3-AL** has been investigated on representative olefin metathesis model reactions including cross-metathesis, ethenolysis, ring-closing metathesis and ring-opening metathesis polymerization (**ROMP**) depicted in Scheme 3. It was found that all the reactions can be carried out at as low as 0.01 mol% catalyst loading. High product yields could be achieved using catalyst **1-AL-15** at ambient condition, meanwhile latent catalyst **3-AL-15** showed limited activity even at elevated temperature (Table 1). While preliminary reactions indicated some catalyst leaching in methanol or DCM solvents, changing the solvent to hexane or carrying out the reactions in neat resulted in less than 1.5 ppm ruthenium content in all cases based on ICP-OES.

The RCM of diethyl diallylmalonate (5) is a well-known, simple model reaction used for the comparison of catalyst activities. The reactivity of both homogenous 1 and the supported **1-AL-15** catalysts in the RCM reaction of 5 was examined under similar conditions to investigate the effect of heterogenization of homogeneous catalysts. (Table 1 Entry 1–4). While homogeneous catalyst 1 completed the reaction within a few minutes (95%, Table 1 Entry 1), it took 24 h for the solid-supported

1-AL-15 catalyst to achieve similar yield (94%, Table 1 Entry 4) under the same conditions. Heterogenized ruthenium metathesis catalysts often render a slower reaction and a reduced reactivity compared to their homogeneous analogues. Based on this, all model reactions have been carried out for 24 h. Lowering the ruthenium catalyst loading to 0.01% revealed yields up to 28% for the CAAC based **1-AL-15** catalyst; however, the BiCAAC containing **3-AL-15** showed only traces of the expected product, even at elevated temperatures (Table 1 Entry 5 and 8). Amberlyst-36 supported CAAC species (**1-AL-36**) showed significantly lower yields of RCM of 5 and generally less reactivity than **1-AL-15** even at 0.1% load.

Self-metathesis of 1-octene (9) was carried out in hexane solution and in neat, as well (Table 1 Entry 10 and 11), showing as high yields as 44% at low, 0.01% **1-AL-15** catalyst loading. Since homogenous catalyst 3 catalyzes olefin metathesis reaction only over 75 °C [41], the CM reaction of 9 using catalyst **3-AL-15** was carried out at the same temperature. When hexane was used as solvent (Table 1 Entry 12), only the formation of the expected 7-tetradecene (10) was observed as the sole product. Interestingly, neat reaction conditions (Table 1 Entry 13) lead to a product mixture, containing not only 7-tetradecene (10), but homologues of terminal and internal alkenes, ranging from C7 to C14 (Fig. 3) indicating that not only metathesis, but also double bond isomerization were taking place at the same time. This finding can be explained by the partial intrinsic decomposition of the ruthenium complexes giving Ru–H species showing double bond isomerization activity [44], i.e., isomerization-metathesis (ISOMET) reaction was observed. For these reactions (Table 1 Entry 13) yields were calculated for tetradecene isomers based on the components' GC–MS peak area.

Ethenolysis, which is usually more challenging than CM reaction because of the increased concentration of the less stable $Ru=CH_2$ methylidene species also showed similar results when 7-tetradecene (10) was used as starting material (Table 1 Entry 15), comparable to the CM of 1-octene at RT with **1-AL-15**. Performing the reaction using **3-AL-15** at 75 °C yielded only minor amount of terminal alkenes and only trace amounts of ISOMET products (Table 1 Entry 16 and 17). Unexpectedly, the ethenolysis of methyl oleate (11) yielded only 3% of the expected terminal alkenes when carried out under similar condition as the ethenolysis of 10. This reduced reactivity to the esters is also reflected in the CM reaction of 10 and cis-1,4-diacetoxy-2-butene, which was carried out under the same conditions as above and gives only traces (< 3%) of the expected product. even at a catalyst load of 0.1%.

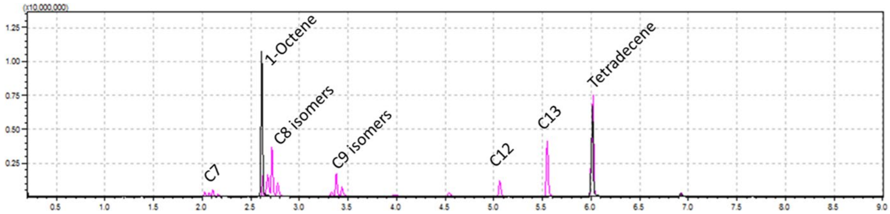


Fig. 3 Superimposed GC–MS chromatograms of the reaction mixture of 1-octene CM, catalyzed by **1-AL-15** at RT (black) and **3-AL-15** at 75 °C (pink)

The equilibrium metathesis polymerization of cyclopentene (7) showed 17% polymer formation, corresponding to 30% yield since the equilibrium polymer/monomer rate is 1.2 on RT [45].

Summary

Styrene–divinylbenzene ion exchange resins with strongly acidic sulfonic groups were wet-impregnated by CAAC and BICAAC ruthenium alkylidene complexes having dimethylamino funcionalities to obtain solid-supported metathesis catalysts. It was found that the active complex is mostly adsorbed in the pores of the solid support. The pore volume was shown to have significant impact on the adsorption capacity of the resin. Resin Amberlyst-36, having low pore volume, bound almost an order of magnitude less complex than the higher porosity resin Amberlyst-15. Model metathesis reactions, such as RCM, CM, ethenolysis and ROMP, showed high yields at low catalyst loadings for the investigated systems. It was found that solvent can play crucial role in the cross metathesis (CM) reactivity of 1-octene. In solvent hexane at 75 °C, the expected 7-tetradecene was formed. However, in neat and at elevated temperature isomerization-metathesis reaction was observed, producing a mixture of internal and terminal alkenes. Tests revealed no more than 1.5 ppm ruthenium leaching in the investigated metathesis reactions.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11144-022-02261-3.

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