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Ruthenium indenylidene complexes bearing *bis*(*N*-Alkyl/*N'*-Mesityl)-sided heterocyclic carbene ligands[1]

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Abstract. *We report on the synthesis and characterization of new ruthenium indenylidene complexes bearing two unsymmetrical N-heterocyclic carbene (NHC) ligands denoted as RuCl2(3-phenyl-1-indenylidene)bis(1-mesityl-3-R-4,5-dihydroimidazole-2-ylidene) in which R is methyl* ***7a*** *and cyclohexyl* ***7b****. Complexes* ***7a*** *and* ***7b*** *were analyzed using single-crystal X-ray diffraction analysis, elemental analysis, IR, NMR spectroscopy, and HRMS. The catalytic activities of complexes* ***7a*** *and* ***7b*** *were evaluated in olefin metathesis reactions: ring-opening metathesis polymerization (ROMP) of cis,cis-1,5-cyclooctadiene (COD) and ring-closing metathesis (RCM) of diethyl diallyl malonate (DEDAM) as well as in the isomerization of allylic alcohols. Complexes* ***7a*** *and* ***7b*** *failed to initiate the reactions at room temperature in all tested reactions, which might be due to the high thermal stability and low degree of lability of the Ru-CNHC bonds. At 80 °C, the complex* ***7a*** *showed the best performance due to an increased initiation and a decreased steric obstruction towards the incoming substrates.*

Keywords: *homogeneous catalysis, indenylidene, olefin metathesis, ruthenium catalysts*

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[1]Supplementary material (Appendix A) related to this article can be found, in the online version at doi: https://doi.org/10.21285/2227-2925-2022-12-2-180-191
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ХИМИЧЕСКИЕ НАУКИ

Научная статья
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Инденилиденовые комплексы рутения, содержащие бис(*N*-алкил/*N'*-мезитил) гетероциклические карбеновые лиганды[1]

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Аннотация. *В работе сообщается о синтезе и исследовании характеристик новых инденилиденовых комплексов рутения с двумя несимметричными N-гетероциклическими карбеновыми лигандами (NHC), обозначаемыми как $RuCl_2$(3-фенил-1-инденилиден)бис(1-мезитил-3-R-4,5-дигидроимидазол-2-илиден), в котором R представляет собой метил **7а** и циклогексил **7b**. Комплексы **7а** и **7b** анализировали методами рентгеноструктурного анализа монокристаллов, элементного анализа, ИК-, ЯМР-спектроскопии и HRMS. Каталитическую активность комплексов **7а** и **7b** оценивали в реакциях метатезиса олефинов: метатезисной полимеризации с раскрытием цикла (ROMP) цис,цис-1,5-циклооктадиена (COD) и метатезиса с замыканием цикла (RCM) диэтилдиаллилмалоната (DEDAM), а также при изомеризации аллиловых спиртов. Комплексы **7а** и **7б** не инициировали реакции при комнатной температуре во всех исследованных реакциях, что может быть связано с высокой термической стабильностью и низкой степенью лабильности связей Ru–C_{NHC}. При 80 °C комплекс **7а** показал наилучшие характеристики благодаря усилению инициирования и уменьшению стерической непроходимости по отношению к поступающим субстратам.*

Ключевые слова: *гомогенный катализ, инденилиден, метатезис олефинов, рутениевые катализаторы*

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INTRODUCTION

Ruthenium-catalyzed olefin metathesis is among the essential methods for carbon-carbon double bond formation/redistribution, utilized widely in both organic and polymer synthesis [1–10]. Contributions made by R. H. Grubbs in olefin metathesis are highly acknowledged due to the invention of a 16-electrons ruthenium benzylidene complex (*e.g.*, **1a**, Fig. 1) [11, 12]. Complex **1a** bearing a mono-*N*-heterocyclic carbene (NHC) ligand named “Grubbs’ second-generation catalyst” shows better catalytic performance in terms of both efficiency and stability relative to its *bis*-PCy_3 analogs [1–10]. The strong *δ*-donating and *π*-back donating properties enabled NHC ligands to be firmly bonded to the metal center and stabilizing the formed complexes, leading to wide utilization of NHC ligands in organometallic complexes [13–16].

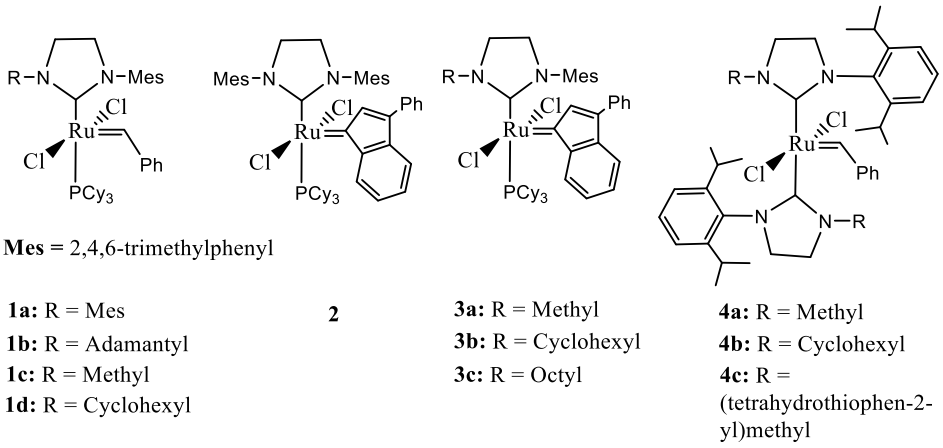


Fig. 1. Selected ruthenium metathesis catalysts

Рис. 1. Выбранные рутениевые катализаторы метатезисной полимеризации

The catalysts' reactivity performance can be significantly affected by electronic and steric modification of the NHC ligands [13–16]. The unsymmetrical transformation is worth noticing since it provides a dual-site configuration in the vicinity of the ruthenium core due to the two different steric environments [17–19]. The dual-site configuration can lead to catalysts with improved selectivity in various metathesis reactions such as *E:Z* selectivity in cross-metathesis (CM), selectivity in diastereo ring-closing metathesis (RCM), and *cis*-selectivity in ring-opening metathesis (ROMP).

The better-donating properties of aliphatic groups have attracted much attention. Mol's group [20] reported an *N*-adamantyl/*N'*-mesityl sided NHC containing ruthenium complex **1b** (Fig. 1). However, the anticipated increase in catalytic efficiency and stability due to the increased donation was not found as complex **1b** showed poor catalytic activity in olefin metathesis reactions. The low catalytic ability of complex **1b** was due to the greater-sized adamantyl group caused a steric repulsion towards the incoming substrate during metatheses progress. To gain more insight into the structure-activity relationship, catalysts **1c-d** bearing *N*-alkyl/*N'*-mesityl heterocyclic carbenes with decreased steric bulkiness (Fig. 1) were synthesized and evaluated in metathesis reactions [21, 22]. Complex **1c**, coordinated with the smallest alkyl (methyl) group, exhibited activity comparable to the parent catalyst **1a**.

In some cases, the isomerization reaction is favored over CM or RCM, applying Grubbs' type complexes. For example, complex **1a** efficiently mediated isomerization of a range of allyl and homoallyl ethers to the corresponding enol ethers and subsequent to alcohols upon acid treatment [23]. The isomerization of allylamine and *N*-allyllactam [24] was instead afforded than CM and RCM reactions, respectively, using complex **1a**. Rutjes *et al.* [25] encountered remarkable isomerization of allenamides to dienamides catalyzed by complex **1a** in the RCM of enamides.

Ruthenium indenylidene complexes are considered another unique class of olefin metathesis catalysts, which combine an easy way of preparation, comparative catalytic activities in the metathesis reactions, and relatively greater stability [1–10]. The reports on the strength of *N*-alkyl/*N'*-aryl heterocyclic carbenes in influencing the catalytic efficiency of ruthenium indenylidene pre-catalysts are also available [26–30]. The ruthenium indenylidene complexes (**3a-c**) reported [29], showed faster catalytic initiation than the reference complex **2**. The less sterically hindered complex **3a** performed better than others in terms of both catalytic initiation and efficiency. While the improved initiation was attributed to stronger donating properties, the better catalytic efficiency was associated with steric properties. In other strategy [31], the mixed ligands coordinated complexes bearing NHC and NHC_{ewg} were developed, and the precatalysts usually needed higher temperature to initiate the activity. During the catalytic process, the electron deficient NHC functioned as the leaving group to generate the active species.

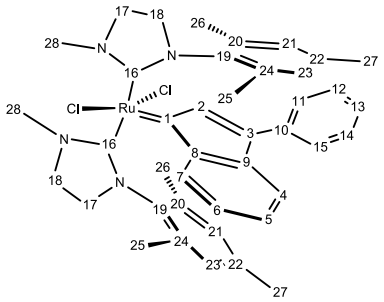
Some of the alkyl-based unsymmetrical heterocyclic carbene ligands have shown an exceptional tendency to form *bis*-NHCs coordinated complexes. Complexes (**4a-c**), for example, were obtained preferentially and exhibited substantial olefin metathesis activity at higher temperatures [22, 32]. Ruthenium indenylidene complexes coordinated with *bis*-(*N*-cyloalkyl/*N'*-mesityl) heterocyclic carbenes where cycloalkyl is cyclopentyl or cyclododecyl were also noted to be formed competitively [26]. Based on the previous report, we explored the utility of ruthenium indenylidene catalysts bearing *bis*(*N*-alkyl/*N*-mesityl)-heterocyclic carbene ligands.

EXPERIMENTAL SECTION

*General procedure for the preparation of complexes **7a-b**.* In an oven-dried Schlenk vessel, KHMDS (4 eq., 6.4 mL, 3.2 mmol) (0.5 M toluene solution) was added to a suspension of imidazolium salt (3 eq., 2.4 mmol) in dry toluene (24 mL) at r.t.

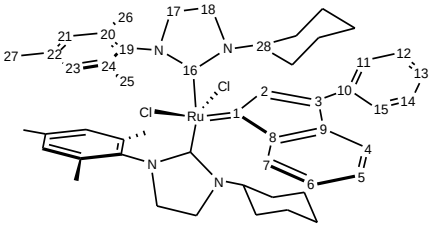
and the resulting solution was vigorously stirred for 30 minutes. The solution was then added to the reactor containing a solution of $RuCl_2$(3-phenyl-1-indenylidene)$(PCy_3)_2$ (**6**) (1eq., 0.74 g, 0.8 mmol) in toluene (16 mL) and further stirred overnight. Purification using silica gel chromatography (EtOAc for **7a** and hexane:EtOAc = 60:1 for **7b**) afforded a brown solid. After that, the solid was rinsed three times with pentane and three times with methanol.

$RuCl_2$bis(1-mesityl-3-methylimidazolidin-2-ylidene) (3-phenyl-1-indenylidene) (7a):



Brown powder (0.45 g, Yield: 74%). The X-ray structure of complex **7a** was measured using the crystals, which were grown up by evaporation of a complex solution in CH_2Cl_2/EtOAc/hexane. Anal. Calcd. (%) for $C_{41}H_{46}Cl_2N_4Ru$: C, 64.22; H, 6.05; N, 7.31. found (%): C, 64.53; H, 6.00; N, 7.15; ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): *δ* 7.98 (d, 1 H, $^3J_{H,H}$ = 7.0 Hz, H-7), 7.67 (d, 2 H ,$^3J_{H,H}$ = 7.3 Hz, H-11, H-15), 7.50 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-13), 7.40 (t, 2 H, $^3J_{H,H}$ = 7.6 Hz, H-12, H-14), 7.08 (t, 1 H, $^3J_{H,H}$ = 7.0 Hz, H-5), 7.03 (t, 1 H, $^3J_{H,H}$ = 7.0 Hz, H-6), 6.79 (d, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-4), 6.77 (s, 1 H, H-2), 6.21 (s, 1 H, H-21), 5.78 (s, 1 H, H-23), 4.16 (s, 6 H, H-28), 3.87–3.91 (m, 2 H, H-17), 3.51–3.67 (m, 2 H, H-18), 1.98 (s, 6 H, H-26), 1.77 (s, 6 H, H-25), 1.73 (s, 6 H, H-27); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$, 20 °C): *δ* 299.2 (C-1), 219.6 (C-16), 142.7 (C-8), 139.6 (C-9), 136.9 (C-10), 136.7 (C-22), 136.6 (C-20), 136.43 (C-24), 136.38 (C-3), 136.3 (C-19), 135.4 (C-2), 128.64 (C-12, C-14), 128.61 (C-21), 128.2 (C-23), 127.3 (C-7), 127.2 (C-13), 127.7 (C-6), 126.6 (C-11, C-15), 126.2 (C-5), 115.0 (C-4), 52.5 (C-17), 52.0 (C-18), 38.2 (C-28), 20.8 (C-27), 18.4 (C-25), 18.2 (C-26); IR (Neat): *ν* = 2946, 2915, 2880, 1503, 1490, 1451, 1376, 1357, 1334, 1292, 1259, 1236, 1175, 1161, 1073, 1037, 1029, 1010, 991, 888, 850, 837, 778, 700, 756, 701, 654; ESI-MS: $[M]^+$ calcd for $C_{41}H_{46}Cl_2N_4Ru$, 766.2143; found: 766.2122; $[M\text{-}Cl]^+$ calcd for $C_{41}H_{46}ClN_4Ru$, 731.2454; found: 731.2458.

$RuCl_2$bis(1-cyclohexyl-3-mesitylimidazolidin-2-ylidene)(3-phenylinden-1-ylidene) (7b):



Brown powder (0.59 g, Yield: 82%). The X-ray structure of complex **7b** was measured using the crystals, which were grown up by evaporation of a complex solution in CH_2Cl_2/EtOAc/hexane. The assignments and identification of resonances for C19, C20, C22, C24 could not be achieved because of the low intensity of the carbons signals in the NHC group on the ^{13}C{^{1}H}NMR spectrum. Anal. Calcd. (%) for $C_{51}H_{62}Cl_2N_4Ru$: C, 67.83; H, 6.92; N, 6.20. found (%): C, 67.66; H, 6.85; N, 6.13; ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 20 °C): *δ* 8.47 (d, 1 H, $^3J_{H,H}$ = 7.0 Hz, H-7), 7.87 (d, 2 H, $^3J_{H,H}$ = 7.6 Hz, H-11, H-15), 7.54 (d, 2 H, $^3J_{H,H}$ = 7.0 Hz, H-13), 7.47 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-5), 7.42 (t, 2 H, $^3J_{H,H}$ = 7.3 Hz, H-12, H-14), 7.36 (t, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-6), 7.20 (d, 1 H, $^3J_{H,H}$ = 7.3 Hz, H-4), 7.05 (s, 1 H, H-2), 7.01 (s, 2 H, H-21/H-23), 6.97 (s, 2 H, H-21/H-23), 3.31–3.83 (m, 8 H, H-17/H-18), 2.43 (s, 6 H, H-27), 2.83 (s, 3 H, H-25/H-26), 2.74 (s, 3 H, H-25/H-26), 2.68 (t, 2 H, $^3J_{H,H}$ = 11.0 Hz,H-28),1.67 (s, 2 H, H-Cy),1.52 (s, 6 H, H-25/26),1.13–1.38 (m, 8 H, H-Cy), 1.00–1.11 (m, 2 H, H-Cy), 0.88 (s, 2 H, H-Cy), 0.55–0.77 (m, 6 H, H-Cy); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$, 20 °C): *δ*300.4 (C-1), 206.6 (C-16), 204.3 (C-16), 144.2 (C-3), 141.2 (C-9), 140.7 (C-8), 137.7 (C-2), 137.0 (C-10), 129.9 (C-21/C23), 129.7 (C-21/C23), 129.3 (C-5), 129.2 (C-6), 129.1 (C-12/C-14), 129.0 (C-21/C23), 128.9 (C-21/C-23), 128.3 (C-7), 128.1(C-13), 126.2 (C-11, C-15), 117.4 (C-4), 56.1 (C-28), 55.8 (C-21), 51.8,51.4, 44.1, 43.6 (C-17/C18), 34.1, 33.7, 32.0, 31.7, 30.0, 29.7, 25.6, 25.2 (C-Cy), 21.3 (C-27), 20.3, 20.2, 19.1, 19.0 (C-25/C-26); IR (Neat): *ν* = 3052, 3002, 2976, 2922, 2853, 1485, 1470, 1446, 1433, 1402, 1385, 1366, 1352, 1329, 1298, 1282, 1250, 1235, 1177, 1030, 994, 896, 852, 846, 775, 750, 697, 651; ESI-MS: $[M\text{-}Cl]^+$ calcd for $C_{51}H_{62}Cl_1N_4Ru$, 867.3706; found: 867.3704.

Single-crystal X-ray diffraction analysis. Crystal data for compound **7a**. CCDC 1830901, $C_{41}H_{46}N_4Cl_2Ru$, M = 766.79, triclinic, space group P-1 (No. 2), a = 9.8123(6) Å, b = 11.1346(8) Å, c = 18.2094(9) Å, α = 88.320(5)°, β = 85.219(5)°, γ = 65.454(7)°, V = 1803.4(2) Å^3, Z = 2, T = 100 K, ρ_{calc} = 1.412 g cm^{-3}, μ(Cu-Kα) = 5.149 mm^{-1}, F(000) = 796, 20129 reflections measured, 6339 unique (R_{int} = 0.1159) which were used in all calculations. The final R1 was 0.0587 (I >2σ (I)) and wR2 was 0.1433 (all data).

Crystal data for compound **7b**. CCDC 1049432, $C_{51}H_{62}N_4Cl_2Ru$, M = 903.02, monoclinic, space group $P2_1/c$ (No. 14), a = 22.6954(6) Å, b = 15.7051(5) Å, c = 12.8872(3) Å, β = 92.902(2)°, V = 4587.5(2) Å^3, Z = 4, T = 100 K, ρ_{calc} = 1.307 g cm^{-3}, μ(Cu-Kα) = = 4.124 mm^{-1}, F(000) = 1896, 37921 reflections measured, 9508 unique (R_{int} = 0.0876) which were used in all calculations. The final R1 was 0.0472 (I >2σ (I)) and wR2 was 0.1241 (all data).

Catalysts screening. Applied procedure for the ROMP of cis,cis-cycloocta-1,5-diene. For example, 0.05 mol% catalyst loading: 4.07 μmol of the complex was dissolved in 1 mL toluene-d_8. An NMR-

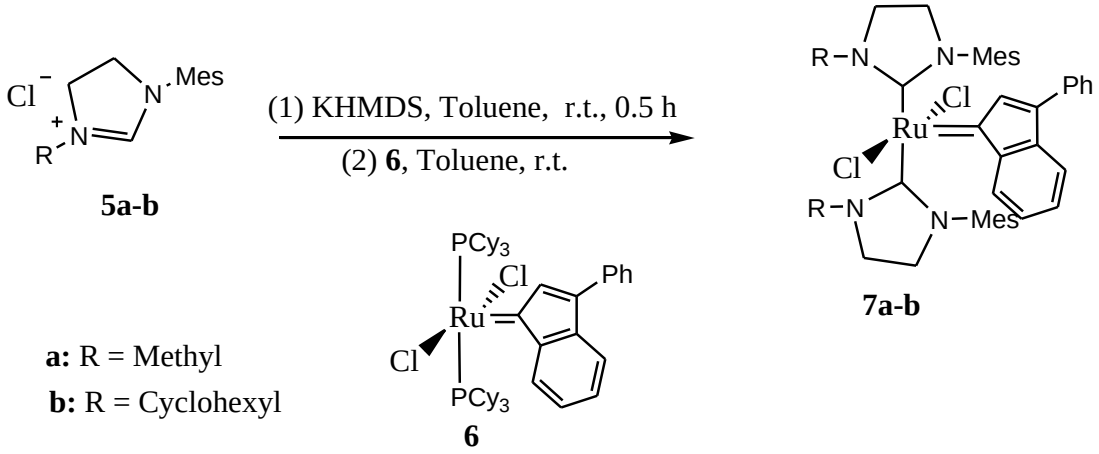
tube was charged with *cis,cis*-cycloocta-1,5-diene (0.1 mL, 0.81 mmol), toluene-d_8 (0.5 mL) and complex solution (0.1 mL). The NMR tube was then closed and the temperature was then raised to 80 °C. By evaluation of integration of the olefinic ^{1}H-NMR signals of the formed polymer and the consumed monomer, the substrate conversion was plotted.

Applied procedure for the RCM of diethyl diallyl malonate. For example, 0.5 mol% catalyst loading: 2.7 μmol of the complex in NMR tube was dissolved in 0.3 ml of toluene-d_8 and left for 2 minutes before addition of 0.13 mL (0.54 mmol) of diethyl diallyl malonate. The NMR tube was then closed and the temperature was raised to 80 °C. Finally, Integration of the allylic methylene peaks in the ^{1}H-NMR spectrum of the diethyl diallyl malonate and the product was used to count the substrate conversion.

Applied procedure for isomerization of allylic alcohols. An NMR-tube was charged with 2.5 μmol (5 mol%) of catalyst and dissolved in 0.5 mL $CDCl_3$. After that, to the tube, 0.05 mmol of the substrate and 2.5 μmol (5 mol%) of KO*t*Bu were added. Afterward, the NMR-tube was sealed and kept at r.t. or at a temperature of 80 °C. The conversion of the substrate was evaluated by integration of the ^{1}H-NMR signals of the starting alcohol (5.68 ppm) and the formed carbonyl compound (1.86 ppm).

RESULTS AND DISCUSSION

Synthesis of the catalysts. Unsymmetrical NHC ligands: 1-mesityl-3-methyl-4,5-dihydroimidazolium chloride (**5a**) and 1-mesityl-3-cyclohexyl-4,5-dihydroimidazolium chloride (**5b**) (1) were prepared according to previously reported procedures [21, 22]. The free / *N*-heterocyclic carbenes were generated by the deprotonation of NHC precursors using potassium hexamethyldisilazide (KHMDS) in toluene at r.t. A replacement of one of the PCy_3 ligands from the first-generation ruthenium indenylidene complex (**6**) using the generated free carbenes [33–36], complexes **7a-b** were obtained. The reaction processes were monitored by TLC. The products were purified by silica gel chromatography and subsequently washed with methanol and pentane to afford air-stable reddish-brown solids (**7a** and **7b**) in moderate yields 74 and 82%, respectively.



General applied strategy for the synthesis of catalysts **7a-b** (1)

The complexes (**7a-b**) were analyzed by ^{1}H and ^{13}C{^{1}H}NMR spectroscopy after isolation. The obtained signals were further assigned using of heteronuclear ^{1}H{^{13}C}HSQC, HMBC, and homo-nuclear ^{1}H{^{1}H}COSY, TOCSY, NOESY NMR spectroscopy [37].

The ^{1}H-NMR spectrum of each complex (Fig. S1, S2) shows peaks characteristic of the indenylidene unit: **7a**, doublet (δ = 7.98 ppm) and singlet (δ = 6.77 ppm); **7b**, doublet (δ = 8.47 ppm) and singlet (δ = 7.05 ppm) [38]. Besides, the imidazolium ligand peaks are also observed as a multiplet at 3.51–3.91 ppm and 3.31–3.83 ppm for complexes **7a** and **7b**, respectively. The ^{1}H-NMR spectrum of each complex strongly suggests the isolation of only one conformer. A single conformer was also detected for ruthenium benzylidene complexes coordinated with *N*-alkyl/*N*-mesityl heterocyclic carbenes [20, 21, 39]; however, for ruthenium indenylidene complexes **3a-c**, two rotamers were observed [29]. The carbene-*C* (Ru=*C*) as the new complexes' characteristic exhibits doublet peaks at about 300 ppm in the ^{13}C-NMR spectra.

The NOESY spectrum of complex **7a** (Fig. 2, a) shows several correlations between the indenylidene moiety and the mesityl's methyl groups from both NHCs. The spectrum reveals no Noe correlation between the *N*-methyl group and indenylidene moiety, suggesting that both NHC ligands have the mesityl groups oriented toward the indenylidene side of the ruthenium center. This observation is in agreement with the single-crystal X-ray diffraction analysis (see next section). The indenylidene ligands in the complexes **3a-c** were also found to be closer to the mesityl group than to the *N*-alkyl group [29]. In contrast, the NOESY spectrum of complex **7b** (Fig. 2, b) shows several correlations between the indenylidene moiety and the *N*-cyclohexyl groups from both NHCs, indicating their relative position.

For the new complexes (**7a-b**), the orientations of the NHC ligands are different from those of the previously reported ruthenium metathesis catalysts featuring two *N*-alkyl/*N*-aryl-heterocyclic carbenes. For example, the aromatic groups of the NHCs in complexes **4a**-**b** have been reported as oriented in different directions relative to the indenylidene fragments [22]. In addition, elemental analysis, mass spectra, and single-crystal X-ray analysis were evaluated to confirm the complexes' purities and configurations.

Single-Crystal X-ray Diffraction Analysis. The crystals of complexes **7a**-**b** are obtained from slow evaporation of their solution (CH_2Cl_2/EtOAc/hexane solution). Thereafter, the crystals were used in X-ray diffraction analysis. The solid-state structures of complexes **7a-b** are depicted in Fig. 3, and some selected bond lengths and angles are listed in Tab. 1. Complex **7a-b** crystallized in the triclinic centrosymmetric space group *P*-1 and $P2_1/c$, respectively. The asymmetric units of **7a-b** accommodate only one ruthenium complex.

In general, complexes **7a** and **7b** exhibit a similar arrangement of the surrounding ligands around the ruthenium core, while an opposite orientation of the *N*-mesityl side of the NHC ligand is observed for **7b**. In complex **7a**, the two mesityl groups lay in a parallel fashion on the five-membered ring of the indenylidene moiety, and *π*-*π* interactions were found (3.408(4) and 3.467(4) Å between the respective ring centroids). In general, the ligands around the ruthenium core in complex **7a** exhibit a similar arrangement to complex **3a** [27].

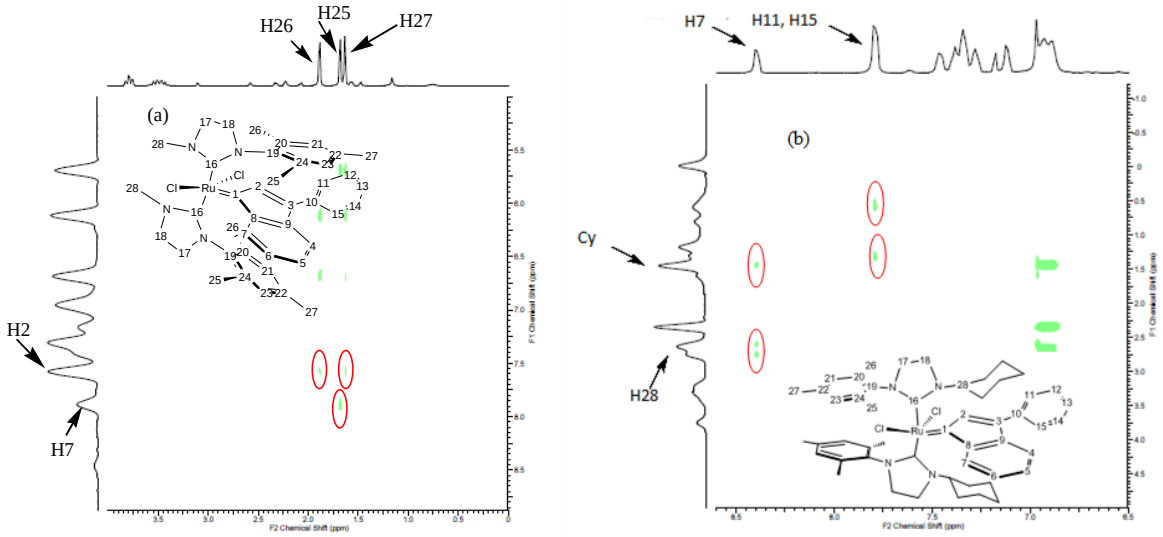


Fig. 2. NOESY spectra (a) complex **7a**, chemical shift of ^{1}H-NMR range from 0.0 to 4.0 ppm (horizontal) and ^{1}H-NMR range from 5.0 to 9.0 ppm (vertical); (b) complex **7b**, chemical shift of ^{1}H-NMR range from 6.5 to 8.6 ppm (horizontal) and ^{1}H-NMR range from -1.5 to 5.0 ppm (vertical)

Рис. 2. Спектры NOESY (a) комплекса **7a**, химический сдвиг ^{1}H-ЯМР в диапазоне от 0,0 до 4,0 м.д. (по горизонтали) и ^{1}H-ЯМР в диапазоне от 5,0 до 9,0 м.д. (по вертикали); (b) комплекс **7b**, химический сдвиг в диапазоне ^{1}H-ЯМР от 6,5 до 8,6 м.д. (по горизонтали) и в диапазоне ^{1}H-ЯМР от -1,5 до 5,0 м.д. (по вертикали)

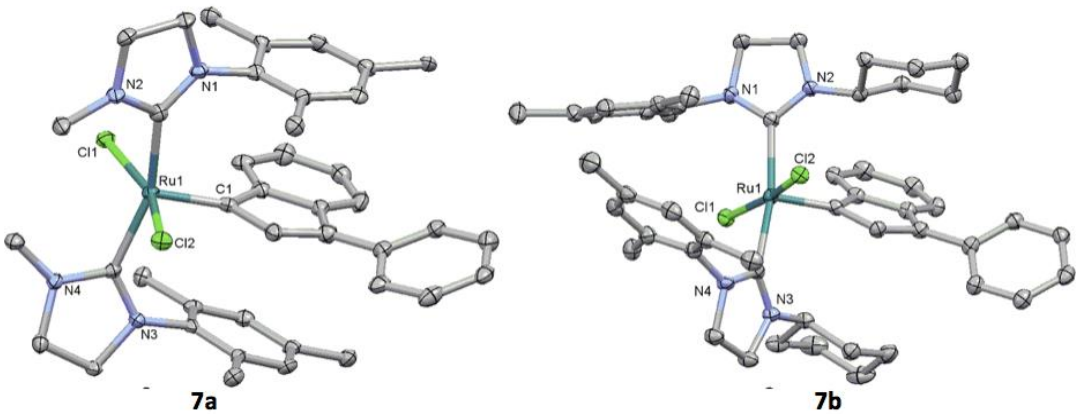


Fig. 3. Solid-state structures of complexes **7a** and **7b** (thermal displacement ellipsoids are shown at the level of 30% probability). The atom-labeling scheme of the heteroatoms is displayed, and Hydrogen atoms are omitted for clarity

Рис. 3. Твердотельные структуры комплексов **7a** и **7б** (показаны эллипсоиды тепловых смещений на уровне 30% вероятности). Отображается схема маркировки гетероатомов, атомы водорода опущены для ясности

Table 1. Selected bond lengths (Å) and bond angles (°) for complexes **7a** and **7b**

Таблица 1. Выбранные длины связей (Å) и валентные углы (°) для комплексов **7a** и **7b**

	7a	**7b**
C_{NHC}-Ru-C_{NHC}	158.4(2)	170.2(2)
C_{NHC}-Ru=C_{Ind}	101.2(3)/99.9(3)	93.4(2)/96.0 (2)
Cl-Ru-Cl	159.84(6)	168.67(4)
Ru=C_{Ind}	1.862(7)	1.864(4)
Ru-C_{NHC}	2.101(8)/2.086(7)	2.131(4)/2.134(4)
Ru-Cl	2.414(1)/2.403(1)	2.368(1)/2.380(1)

For **7a**, the dihedral angles between the least-squares plane of the mesityl groups and the five-membered ring are 5.2(4)° and 11.0(4)°, respectively. In complex **7b**, the two cyclohexyl groups in the NHC ligands orient to the indenylidene moiety, leaving the two mesityl groups at the opposite side of the indenylidene ligand. The dihedral angle between the two least-squares planes of the mesityl groups is 34.8 (2)°.

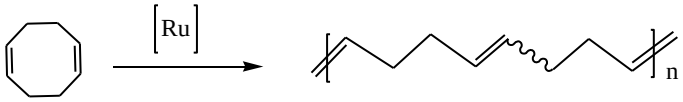
The least-squares plane angles between the respective two imidazole rings of **7a** and **7b** differ significantly from each other. The imidazole rings in **7b** show a larger dihedral angle (63.6(2)°), which is incomparable with that of imidazole rings in **7a** (18.3(4)°).

The Ru-Cl bond lengths for **7a** and **7b** are in values between 2.368(1) Å and 2.414(1) Å, and the Ru-C_{NHC} bond lengths are within the range of 2.086(7)Å to 2.134(4)Å. The Ru=C_{Ind} bond length is 1.862(7) Å for **7a,** and 1.864(4) Å for **7b**. The C_{NHC}-Ru-C_{NHC}, Cl-Ru-Cl and C_{NHC}-Ru=C_{Ind} angles for **7a** are 158.4(2)°, 159.84(6)° and 101.2(3)°/99.9(3)°, respectively, while for **7b** these are 170.2(2)°, 168.67(4)° and 93.4(2)°/96.0(2)°, respectively.

*Catalytic activity of complexes **7a-b** in olefin metathesis reactions.* Firstly, the catalytic abilities of complexes **7a** and **7b** on olefin metathesis reactions were evaluated in ring-closing metathesis polymerization (ROMP) of *cis,cis*-1,5-cyclooctadiene (COD) and ring-closing metathesis (RCM) of diethyl diallyl malonate (DEDAM).

ROMP of COD. The complexes **7a-b were** involved in the ROMP of COD (**8**) (2) under varying reaction conditions. At room temperature with a catalyst loading of 1 mol% in $CDCl_3$, initiators **7a-b** showed negligible conversion after 24 hours. Similar results were found by using complex **4a-b** [22] in which no detectable conversion of COD was found after 24 hours. The poor performance of *bis*-NHC ruthenium complexes at room temperature might be due to the stronger Ru-C_{NHC} bond relative to Ru-P bond, and thus high thermal stability and low degree of lability [22].

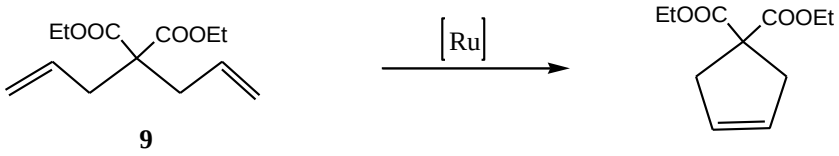
A significant improvement of the catalytic activity was observed when the reaction temperature was controlled at 80 °C. Generally, all catalysts exhibit almost similar kinetic profiles at an elevated temperature. Under a condition of a catalyst loading of 0.33 mol% in toluene at 80 °C, complex **7a** reached full conversion after 90 minutes, while **7b** achieved complete COD consumption after 120 minutes (Fig. 4). The better performance of **7a** might be due to an increased initiation and decreased steric obstruction for the substrates during reaction [29]. Reducing the catalyst loading, a decrease of catalysts initiation rate and the catalytic activity were observed. Complex **7a** needed 3 hours to fully convert the COD with a catalyst loading of 0.1 mol%, and the same time was required for 95% with 0.05 mol% catalyst loading (Fig. 4). Complex **7b**, on the other hand, could not reach full conversion even after 3 hours of reaction with neither 0.1 mol% nor 0.05 mol% catalyst loadings (Fig. 4).



8

The ROMP of COD (8) (2)

RCM of DEDAM. The complexes **7a-b** were further investigated using the RCM of DEDAM (**9**) (3). Since these bis-NHC complexes generally need an elevated temperature to be active, the RCM reaction was performed at 80 °C in toluene at different catalyst loadings. Under these conditions, complex **7a** required 180 minutes to complete the reaction with a catalyst loading of 5 mol%, 240 minutes for 95% conversion of the substrate at 1.25 mol% catalyst loading, and 1170 minutes for 81.75% conversion at 0.5 mol% catalyst loading (Fig. 5). In contrast, complex **7b** needs 240 minutes for full conversion of the substrate (at a catalyst loading of 5 mol%), 1170 minutes for 95% conversion (1.25 mol%), and 1170 minutes for 81.75% conversion of the substrate (catalyst loading of 0.5 mol%) (Fig. 5). The ability of these catalysts to remain in solution at high temperature (80 °C) for such a long time (up to 1170 minutes) during catalytic reactions without noticeable decomposition proves their stability.



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The RCM of diethyl diallylmalonate (3)

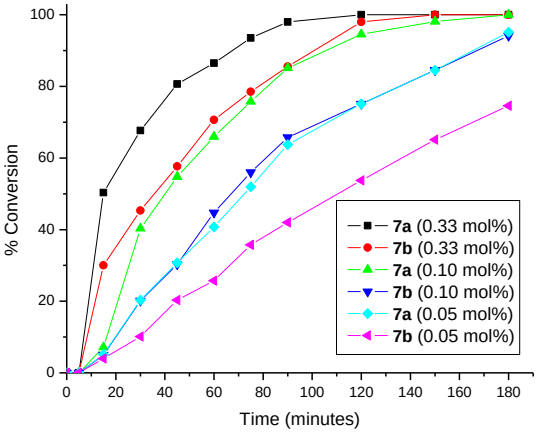


Fig. 4. ROMP of COD with complexes **7a** and **7b** (0.05–0.33 mol%) at 80 °C in toluene

Рис. 4. Метатезисная полимеризация с раскрытием цикла цис,цис-1,5-циклооктадиена с комплексами **7а** и **7б** (0,05–0,33 мол.%) при 80 °С в толуоле

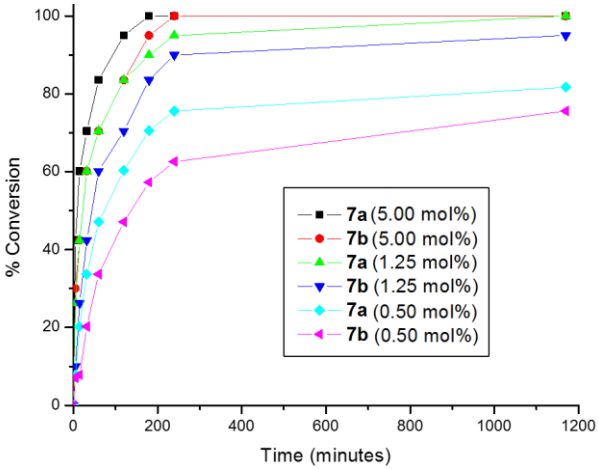
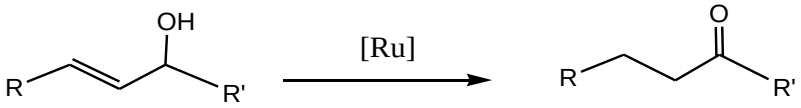


Fig. 5. The RCM of DEDAM with complexes **7a** and **7b** (0.5–5 mol%) at 80 °C in toluene

Рис. 5. Метатезис с замыканием цикла диэтилдиаллилмалоната с комплексами **7а** и **7б** (0,5–5 мол.%) при 80 °С в толуоле

Isomerization of Allylic Alcohols. In addition, the synthesized catalysts were investigated for their performance in the isomerization of allylic alcohols (4).



Isomerization of allylic alcohols (4)

Our initial efforts focused on the isomerization of penten-3-ol, hepten-3-ol, and 2-cyclohexen-1-ol to their corresponding carbonyl compounds at room temperature. However, by applying 5 mol% of either catalyst at room temperature, no noticeable conversion was observed after 72 hours of reaction for all substrates. From a mechanistic perspective, allylic alcohols can coordinate to the ruthenium center either via olefin or alcoholate functionalities. For the isomerization toward the aldehyde to occur, one of the NHC ligands has to disassociate from the complex before consecutive coordination of the olefin moiety to the metal center can be realized [40]. Therefore, the failure to isomerize the substrate using the catalysts at low temperatures is probably due to the difficulty in de-coordination of the NHCs from the ruthenium core. However, upon addition of 5 mol% of KO*t*Bu, 94 and 92% of the isomerization of hepten-3-ol and penten-3-ol, respectively, was observed after 72 hours, applying complex **7a** (Fig. 6). Under these conditions, using catalyst **7b**, the conversion of hepten-3-ol and penten-3-ol reached 95 and 90%, respectively (Fig. 6). In these two reactions, complex **7a** revealed a higher catalyst initiation rate and a similar activity relative to complex **7b**. Nevertheless, even with the addition of 5 mol% of KO*t*Bu at room temperature, the isomerization of 2-cyclohexen-1-ol was not possible applying these catalysts.

By raising the temperature to 80 °C, a significant increase in reaction rate was observed. For the isomerization of hept-3-ol, 98 and 90% conversion were revealed, with complexes **7a** and **7b**, respectively, after 180 minutes (Fig. 7). In the case of the isomerization of penten-3-ol, the reaction reached 95 and 90% conversion, with catalysts **7a** and **7b,** respectively, after 240 minutes (Fig. 7).

Using 5 mol% of catalyst without base, no conversions were observed with all substrates after 24 hours of reactions, even at 80 °C. However, by increasing the catalyst loading to 10 mol%, all catalysts isomerized the substrates without adding a base (Tab. 2). The catalysts' performance under these conditions resembles those when 5 mol% of the base was used in addition to 5 mol% of catalyst (Fig. 6). It is worth noting that 5 mol% of the cata-

lysts can be replaced by 5 mol% of the base in this reaction; however, the catalyst cost is not comparable to that of the base.

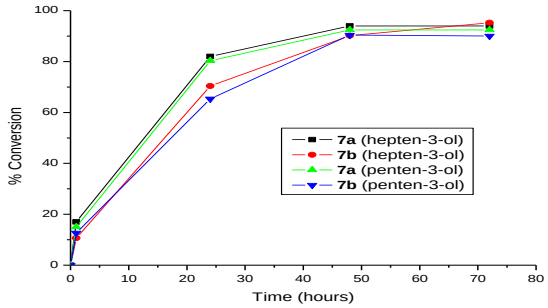


Fig. 6. Isomerization of hepten-3-ol and penten-3-ol using 5 mol% of complexes **7a** and **7b** with 5 mol% of KO*t*Bu at room temperature

Рис. 6. Изомеризация гептен-3-ола и пентен-3-ола с использованием 5 мол.% комплексов **7а** и **7б** при 5 мол.% KOtBu при комнатной температуре

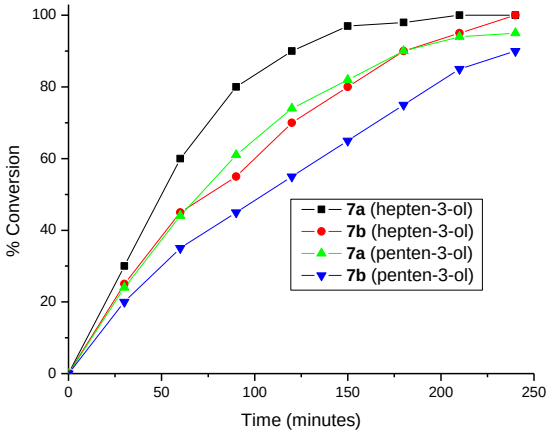


Fig. 7. Isomerization of hepten-3-ol and penten-3-ol using 5 mol% of catalysts**7a** and **7b** with 5 mol% of KO*t*Bu at 80 °C. The lines are intended as a visual aid

Рис. 7. Изомеризация гептен-3-ола и пентен-3-ола с использованием 5 мол.% катализаторов **7а** и **7б** с 5 мол.% KOtBu при 80 °C. Линии представлены в качестве наглядного пособия

Table 2. Isomerization of allylic alcohols using 10 mol% catalysts at 80 °C

Таблица 2. Изомеризация аллиловых спиртов с использованием 10 мол.% катализаторов при 80 °C

Substrate	Catalyst	Time (h)	%Conversion
hepten-3-ol	**7a**	2.5	100
hepten-3-ol	**7b**	4	98
penten-3-ol	**7a**	4	95
penten-3-ol	**7b**	5	90

CONCLUSION

We have successfully synthesized two ruthenium indenylidene initiators bearing *bis*(*N*-alkyl/*N'*-mesityl)-heterocyclic carbene ligands (**7a-b**), which were fully characterized by NMR spectroscopy, elemental analysis, IR, HRMS, and single-crystal X-ray diffraction analysis. It is interesting to observe that the mesityl groups of **7a** and **7b** orient in the opposite direction toward the indenylidene moiety. For complexes **7a** and **7b**, a similar ligand arrangement around the ruthenium center is exhibited, while an opposite direction of the NHC ligands toward the indenylidene moiety was found. For the olefin metathesis reactions, complexes **7a-b** produced activities comparable with complexes **4a-b**, respectively. For the non-metathesis reaction, the new initiators were evaluated on the isomerization of allylic alcohols. The optimum and cost-effective conditions occurred when the KO*t*Bu base was added as co-initiator. The catalyst's failure to initiate reactions at room temperature was associated with the difficulty in de-coordination of the NHCs from the metal center due to the stronger Ru-C_{NHC} bond relative to Ru-P bond, and thus high thermal stability and low degree of lability. In all tested reactions, complex **7a** performed better. The better performance of **7a** was associated with increased initiation and decreased steric obstruction for the substrates during the reaction. The results imply that fine-tuning of the ligands environment can substantially impact both the structure and activity pattern of the resulting catalytic system.

REFERENCES

1. Fürstner A. Olefin metathesis and beyond. *Angewandte Chemie International Edition.* 2000;39 (17):3013-3043. https://doi.org/10.1002/1521-3773(20000901)39:17<3012::AID-ANIE3012>3.0.CO;2-G.

2. Trnka T. M., Grubbs R. H. The development of L_2X_2RuCHR Olefin Metathesis Catalysts: an organometallic success story. *Accounts of Chemical Research*. 2001;34(1):18-29. https://doi.org/10.1021/ar000114f.

3. Grubbs R. H., Wenzel A. G., O'Leary D. J., Khosravi E. *Handbook of metathesis.* Weinheim: Wiley-VCH; 2015. 1608 p.

4. Astruc D. The metathesis reactions: from a historical perspective to recent developments. *New Journal of Chemistry.* 2005;29(1):42-56. https://doi.org/10.1039/B412198H.

5. Deshmukh P. H., Blechert S. Alkene metathesis: the search for better catalysts. *Dalton Transactions.* 2007;(24):2479-2491. https://doi.org/10.1039/B703164P.

6. Samojłowicz C., Bieniek M., Grela K. Ruthenium-based olefin metathesis catalysts bearing

N-heterocyclic carbene ligands. *Chemical Reviews.* 2009;109(8):3708-3742. https://doi.org/10.1021/cr800524f.

7. Dragutan I., Dragutan V., Delaude L., Demonceau A. Exploring new achievements in olefin metathesis catalysts. Part 2. Compelling innovations in ruthenium complexes. *Chimica Oggi-chemistry Today.* 2009;27:13-16.

8. Díez-González S., Marion N., Nolan S. P. N-heterocyclic carbenes in late transition metal catalysis. *Chemical Reviews*. 2009;109(8):3612-3676. https://doi.org/10.1021/cr900074m.

9. Vougioukalakis G. C., Grubbs R. H. Ruthenium-based heterocyclic carbene-coordinated olefin metathesis catalysts. *Chemical Reviews*. 2010;110 (3):1746-1787. https://doi.org/10.1021/cr9002424.

10. Lozano-Vila A. M., Monsaert S., Bajek A., Verpoort F. Ruthenium-based olefin metathesis catalysts derived from alkynes. *Chemical Reviews*. 2010;110(8):4865-4909. https://doi.org/10.1021/cr900346r.

11. Scholl M., Trnka T. M., Morgan J. P., Grubbs R. H. Total synthesis of (−)- and (±)-frontalin *via* ring-closing metathesis. *Tetrahedron Letters*. 1999;40(8): 2247-2250. https://doi.org/10.1016/S0040-4039(98)02677-X.

12. Scholl M., Ding S., Lee C. W., Grubbs R. H. Synthesis and activity of a new generation of ruthenium-based olefin metathesis catalysts coordinated with 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligands. *Organic Letters.* 1999;1(6):953-956. https://doi.org/10.1021/ol990909q.

13. Hu X., Castro-Rodriguez I., Olsen K., Meyer K. Group 11 metal complexes of N-heterocyclic carbene ligands: nature of the metal–carbene bond. *Organometallics.* 2004;23(4);755-764. https://doi.org/10.1021/om0341855.

14. Cavallo L., Correa A., Costabile C., Jacobsen H. Steric and electronic effects in the bonding of *N*-heterocyclic ligands to transition metals. *Journal of Organometallic Chemistry.* 2005;690(24-25): 5407-5413. https://doi.org/10.1016/j.jorganchem.2005.07.012.

15. Jacobsen H., Correa A., Costabile C., Cavallo L. π-Acidity and π-basicity of N-heterocyclic carbene ligands. A computational assessment. *Journal of Organometallic Chemistry.* 2006;691(21): 4350-4358. https://doi.org/10.1016/j.jorganchem.2006.01.026.

16. Jacobsen H., Correa A., Poater A., Costabile C., Cavallo L. Understanding the M–(NHC) (NHC = = N-heterocyclic carbene) bond. *Coordination Chemistry Reviews.* 2009;253(5-6):687-703. https://doi.org/10.1016/j.ccr.2008.06.006.

17. Hamad F. B., Sun T., Xiao S., Verpoort F. Olefin metathesis ruthenium catalysts bearing unsymmetrical heterocylic carbenes. *Coordination Chemistry Reviews.* 2013;257(15-16):2274-2292. https://doi.org/10.1016/j.ccr.2013.04.015.

18. Montgomery T. P., Johns A. M., Grubbs R. H. Recent advancements in stereoselective olefin metathesis using ruthenium catalysts. *Catalysts.* 2017; 7(3):87-125. https://doi.org/10.3390/catal7030087.

19. Paradiso V., Bertolasi V., Costabile C., Grisi F. Ruthenium olefin metathesis catalysts featuring unsymmetrical N-heterocyclic carbenes. *Dalton Transactions.* 2016;45:561-571. https://doi.org/10.1039/C5DT03758A.

20. Dinger M. B., Nieczypor P., Mol J. C. Adamantyl-substituted *N*-heterocyclic carbene ligands in second-generation grubbs-type metathesis catalysts. *Organometallics.* 2003;22(25):5291-5296. https://doi.org/10.1021/om034062k.

21. Ledoux N., Allaert B., Pattyn S., Mierde H. V., Vercaemst C., Verpoort F. *N,N'*-dialkyl- and *N*-alkyl-*N*-mesityl-substituted *N*-heterocyclic carbenes as ligands in grubbs catalysts. *Chemistry – A European Journal*. 2006;12(17):4654-4661. https://doi.org/10.1002/chem.200600064.

22. Ledoux N., Allaert B., Linden A., Van Der Voort P., Verpoort F. Bis-coordination of *N*-(alkyl)-*N*'-(2,6-diisopropylphenyl) heterocyclic carbenes to Grubbs catalysts. *Organometallics.* 2007;26(4): 1052-1056. https://doi.org/10.1021/om060937u.

23. Cadot C., Dalko P. I., Cossy J. Olefin isomerization by a ruthenium carbenoid complex. Cleavage of allyl and homoallyl groups. *Tetrahedron Letters.* 2002;43(10):1839-1841. https://doi.org/10.1016/S0040-4039(02)00141-7.

24. Alcaide B., Almendros P., Alonso J. M., Aly M. F. A novel use of Grubbs' carbene. Application to the catalytic deprotection of tertiary allylamines. *Organic Letters.* 2001;3(23):3781-3784. https://doi.org/10.1021/ol0167412.

25. Kinderman S. S., van Maarseveen J. H., Schoemaker H. E., Hiemstra H., Rutjes F. P. J. T. Enamide-olefin ring-closing metathesis. *Organic Letters*. 2001;(3):2045-2048. https://doi.org/10.1021/ol016013e.

26. Malinowska M., Hryniewicka A. Ruthenium indenylidene metathesis catalysts. *Current Organic Synthesis.* 2017;(14):1022-1035.

27. Rouen M., Borré E., Falivene L., Toupet L., Berthod M., Cavallo L., et al. Cycloalkyl-based unsymmetrical unsaturated (U_2)-NHC ligands: flexibility and dissymmetry in ruthenium-catalysed olefin metathesis. *Dalton Transactions.* 2014;43(19): 7044-7049. https://doi.org/10.1039/C4DT00142G.

28. Ablialimov O., Kedziorek M., Torborg C., Malinska M., Wozniak K., Grela K. New ruthenium(II) indenylidene complexes bearing unsymmetrical N-heterocyclic carbenes. *Organometallics.* 2012;31:7316-7319. https://doi.org/10.1021/om300783g.

29. Ablialimov O., Kedziorek M., Malinska M., Wozniak K., Grela K. Synthesis, structure, and catalytic activity of new ruthenium(II) indenylidene complexes bearing unsymmetrical N-heterocyclic carbenes. *Organometallics.* 2014;33:2160-2171. https://doi.org/10.1021/om4009197.

30. Yu B., Hamad F. B., Sels B., Van Hecke K.,

Verpoort F. Ruthenium indenylidene complexes bearing N-alkyl/N-mesityl-substituted N-heterocyclic carbene ligands. *Dalton Transactions*. 2015;44(26): 11835-11842. https://doi.org/10.1039/c5dt00967g.

31. Peeck L. H., Plenio H. Synthesis and RCM activity of [(NHC)(NHC_{ewg})$RuCl_2$(3-phenylindenylid-1-ene)] complexes. *Organometallics.* 2010;29(12): 2761-2766. https://doi.org/10.1021/om1002717.

32. Smolen M., Kosnik W., Gajda R., Wozniak K., Skoczen A., Kajetanowicz A., et al. Ruthenium complexes bearing thiophene-based unsymmetrical *N*-heterocyclic carbene ligands as selective catalysts for olefin metathesis in toluene and environmentally friendly 2-methyltetrahydrofuran. *Chemistry – A European Journal.* 2018;24(57):15372-15379. https://doi.org/10.1002/chem.201803460.

33. Harlow K., Hill A., Wilton-Ely J. E. The first co-ordinatively unsaturated Group 8 allenylidene complexes: insights into Grubbs' *vs.* Dixneuf–Fürstner olefin metathesis catalysts. *Journal of the Chemical Society, Dalton Transactions.* 1999;(3):285-292. https://doi.org/10.1039/A808817I.

34. Fürstner A., Guth O., Düffels A., Seidel G., Liebl M., Gabor B., et al. Indenylidene complexes of ruthenium: optimized synthesis, structure elucidation, and performance as catalysts for olefin metathesis–application to the synthesis of the ADE-ring system of nakadomarin A. *Chemistry – A European Journal.* 2001;7(22):4811-4820. https://doi.org/10.1002/1521-3765(20011119)7:22<4811::aid-chem4811>3.0.co;2-p.

35. Fürstner A., Grabowski J., Lehmann C. W. Total synthesis and structural refinement of the cyclic tripyrrole pigment nonylprodigiosin. *Journal of Organic Chemistry.* 1999;64(22):8275-8280. https://doi.org/10.1021/jo991021i.

36. Schanz H.-J., Jafarpour L., Stevens E. D., Nolan S. P. Coordinatively unsaturated 16-electron ruthenium allenylidene complexes: synthetic, structural, and catalytic studies. *Organometallics.* 1999;18(24): 5187-5190. https://doi.org/10.1021/om9906316.

37. Monsaert S., De Canck E., Drozdzak R., Van Der Voort P., Verpoort F., Martins J. C., et al. Indenylidene complexes of ruthenium bearing NHC ligands – structure elucidation and performance as catalysts for olefin metathesis. *European Journal of Organic Chemistry*. 2009;(5):655-665. https://doi.org/10.1002/ejoc.200800973.

38. Opstal T., Verpoort F. Synthesis of highly active ruthenium indenylidene complexes for atom-transfer radical polymerization and ring-opening-metathesis polymerization. *Angewandte Chemie International Edition.* 2003;42(25):2876-2879. https://doi.org/10.1002/anie.200250840.

39. Vehlow K., Maechling S., Blechert S. Ruthenium metathesis catalysts with saturated unsymmetrical N-heterocyclic carbene ligands. *Organometallics.* 2006;25(1):25-28. https://doi.org/10.1021/om0508233.

40. van der Drift R. C., Bouwman E., Drent E. J. Homogeneously catalysed isomerisation of allylic alcohols to carbonyl compounds. *Journal of Organometallic Chemistry.* 2002;650(1-2):1-24.

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