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Cite this: *New J. Chem.*, 2015, 39, 1858

Synthesis and characterization of non-chelating ruthenium–indenylidene olefin metathesis catalysts derived from substituted 1,1-diphenyl-2-propyn-1-ols†

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Received (in Porto Alegre, Brazil) 14th November 2014,
Accepted 16th December 2014

DOI: 10.1039/c4nj02034k

www.rsc.org/njc

We report on the synthesis and characterization of the first generation of modified non-chelating indenylidene ruthenium catalysts denoted as $RuCl_2$(4-methyl-3-(*o*-tolyl)-1-indenylidene)(PCy_3)$_2$ **5a**, $RuCl_2$(3-(*p*-fluorophenyl)-1-indenylidene)(PCy_3)$_2$ **5b**, $RuCl_2$(3-(2,6-xylyl)-1-indenylidene)(PCy_3)$_2$ **5c** and $RuCl_2$(3-(1-naphthyl)-1-indenylidene)(PCy_3)$_2$ **5d**. The obtained complexes of **5a–d** were characterized by means of NMR spectroscopy and elemental analysis. Moreover the structures of **5a–d** were confirmed by single-crystal X-ray diffraction and compared with the standard ruthenium indenylidene complex **3** and the chelating benzylidene complex **2**. Additionally, the catalytic performances of the obtained complexes **5a–d** were evaluated in various metathesis reactions demonstrating that the ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) reactions revealed a similar catalytic activity in comparison with the reference indenylidene catalyst **3**.

Introduction

The successful development of versatile catalysts enabled olefin metathesis to become a powerful synthetic tool in organic and polymer chemistry.[1] An important contribution in the area of the ruthenium based olefin metathesis catalysts was made by Grubbs group through the introduction of the ruthenium benzylidene catalyst **1a** (Fig. 1).[2] Based on complex **1a**, various catalysts bearing different types of ligands were made to enhance the catalytic performance.[3] The so-called "second generation Grubbs catalyst" **1b** was synthesized by replacing one of the tricyclohexylphosphine (PCy_3) ligands by the N-heterocyclic carbene (NHC) ligand, which resulted in a more stable complex in comparison to the "first generation Grubbs catalyst" **1a**.[4] Further on, various modifications based on NHC ligands have been reported, using symmetric, asymmetric, or highly steric NHCs.[3a–c,5] The introduction of other ligands to replace the second PCy_3 ligand gave rise to several groups of complexes with different catalytic performance. Some of these materials showed a very high initial activity, *e.g.* including pyridine,[6] while others first needed to be activated, *e.g.* with Schiff bases.[7] Modification of the alkylidene part, on the other hand, resulted into different families of ruthenium based catalysts, such as the Grubbs–Hoveyda 2,[8] indenylidene,[9] allenylidene,[10] vinylidene,[11] and thiophenylidene catalysts.[12]

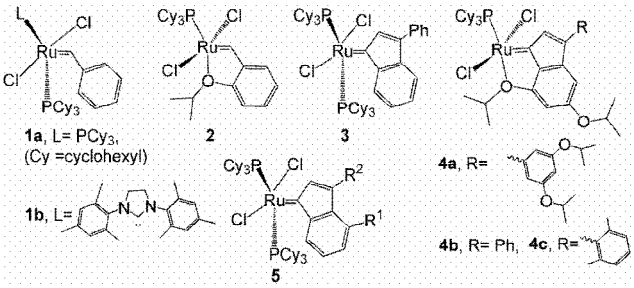


Fig. 1 Ruthenium-based olefin metathesis catalysts.

Complexes **1** and **2** are widely applied because of their stability, functional group compatibility and high catalytic efficiency.[1b,c]

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† Electronic supplementary information (ESI) available: Detailed synthesis procedure of the propargylic alcohols **6a–d**, **8**; X-ray data of **6a** and **2**; Plausible mechanism for ruthenium indenyldene catalysts synthesis process as well as ^{1}H, ^{13}C and ^{31}P NMR spectra of obtained compounds are included here. CCDC 986932–986934 and 1005472–1005476. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4nj02034k

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The systematic exploration of the electronic effects of the alkylidene group on the catalytic performance revealed that electron withdrawing *para*-substituents not only withdraw electron density from the aromatic ring but also from the Ru=C center, which resulted in a fast initiating catalyst.[13]

The direct treatment of propargylic alcohols with $RuCl_2(PPh_3)_3$ gave rise to alkenylidene[14] (vinylidene,[15] allenylidene[10,16] and indenylidene[9a,17]) ruthenium complexes. The latter method is a much more convenient way to obtain the ruthenium catalysts[3d] compared with their benzylidene analogue **1a**.[2] However, these vinylidene and allenylidene catalysts exhibit a much lower catalytic performance[3d] in comparison to the benchmark catalysts **1**[3a,4d] and **2**.[8] On the contrary, ruthenium indenylidene catalysts show an increased stability and comparable, or sometimes a higher, catalytic activity in metathesis reactions in comparison to the ruthenium benzylidene complexes **1a** and **2**.[9c,18] Aiming at improving the properties of the latter catalysts, a number of modifications have been carried out starting from the ruthenium indenylidene complex **3**. These modifications include the introduction of NHCs,[19] and substitution of PCy_3 by other ligands such as phosphines,[20] pyridine[21] and Schiff bases.[22]

In addition, a variety of bidentate catalysts bearing (κ_2O,C)-iso-propoxy-indenylidene moieties (**4a–c**) have been reported to date.[23] For instance, Bruneau *et al.* reported on the chelating complex **4a**, which showed a rather good thermal stability. Nevertheless, it showed a poor initiation for olefin metathesis at low temperature. Ring-closing metathesis (RCM) of diethyl diallylmalonate (DEDAM), using compound **4a**, still reached comparable yields as obtained for the complexes **2** and **3**, although a longer reaction time was needed.[23a] Nearly simultaneous, Schrodi *et al.* reported on an *in situ* generated methoxy-chelating ruthenium indenylidene, which showed a comparable activity as Grubbs–Hoveyda **2** for the RCM of DEDAM.[24] In another paper of the same group, a process was described where **2** was decomposed, induced by ethylene, yielding RCM-inactive species. The decomposed compound could be reactivated by a treatment with 1-(3,5-di-iso-propoxyphenyl)-1-phenyl-2-propyn-1-ol.[25]

The relatively low cost and easy synthesis strategy and the excellent catalytic performance in olefin metathesis of the indenylidene type catalysts[9c] have attracted our attention. However, the chelating modified ruthenium indenylidene catalysts showed a lower initial catalytic activity in comparison with the reference non-chelating complex **3**.[23,24] Therefore, in this paper, we report on the synthesis, characterization and catalytic performance of non-chelating modified ruthenium indenylidene complexes, bearing different substituents on the indenylidene moiety. The general structure of these complexes is represented in **5** (Fig. 1).

Results and discussion

Synthesis and characterization of the catalysts

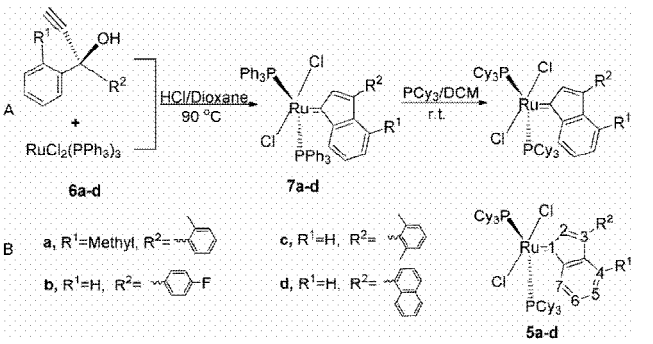
The first ruthenium indenylidene complex **3** was discovered incidentally by Hill's group on their attempt to synthesize the ruthenium allenylidene complex from the reaction of propargylic alcohol with $RuCl_2(PPh_3)_3$.[9a] Afterward, the groups of Nolan and Fürstner reported the proper structure,[9b,10] while later on, Fürstner's group revealed the detailed synthesis procedure and characterization of **3**.[9c] Nevertheless, the synthesis of complex **3** was not always straightforward and in many cases the complex having four doublet peaks [(μ-Cl)$_3$-bridged Ru_2(allenylidene) complex] in the ^{31}P NMR spectrum was obtained. In 2007, the group of Schanz reported on the involved mechanism, which demonstrated that an acid catalyst is required to obtain the complex.[17d]

In this work, series of 1,1-diphenyl-2-propyn-1-ol (**6a**, **6b**,[26] **6c** and **6d**) derivates were prepared for the synthesis of new ruthenium indenylidene catalysts (see ESI† for the detailed synthesis procedure of each ligand and crystal data of **6a**).

The complex **7a** was prepared according to the earlier reported synthesis procedure using an acid catalyzed reaction of propargylic alcohol with $RuCl_2(PPh_3)_3$ (Scheme 1A).[27] Hence, a 1.3 eq. of **6a** was allowed to react with the $RuCl_2(PPh_3)_3$ in dioxane at 90 °C in the presence of HCl. During the reaction, aliquots were taken out and were analyzed by means of ^{31}P NMR spectroscopy. After 10 minutes of reaction, the $RuCl_2(PPh_3)_3$ was completely consumed while a new phosphine signal at 29.3 ppm appeared, which was assigned to the PPh_3 coordinated complex **7a** in addition to that of free PPh_3 (−5.4 ppm). Additional structural information of compound **7a** was obtained by single crystal X-ray diffraction (see the section "single crystal X-ray diffraction analysis").

In a next step, complex **7a** was applied as a precursor for the synthesis of the 1st generation modified ruthenium indenylidene complex **5a** (Scheme 1A) by treatment of **7a** with 3 eq. PCy_3 in CH_2Cl_2 at room temperature. The purification was carried out to obtain compound **5a** in a high yield (>90%) as a red brown compound by simply washing with iso-propanol. The ^{1}H NMR spectrum of **5a** was measured showing a characteristic peak of the indenylidene unit, a typical doublet peak for H7 (Scheme 1B) at δ = 8.54 ppm while the ^{13}C NMR spectrum exhibited a triplet at δ = 296.0 ppm with a $^2J_{P,C}$ of 7.6 Hz for the C1 (see Fig. S11 and S12 in the ESI†).

Complexes **5b–d** were synthesized in a similar manner as **5a**. Nevertheless, a slower conversion of **6b–d** towards complexes **7b–d** was observed in comparison to the formation of complex **7a**.



Scheme 1 (A) General applied synthesis strategy for the synthesis of functionalized non-chelating indenylidene catalysts. (B) Numbering scheme of the indenylidene atoms.

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Table 1 Typical NMR spectra peaks (^{1}H for H7, ^{13}C for C1, ^{31}P) for **3**, **5a–d**

	^{1}H NMR (H7)	^{13}C NMR (C1)	^{31}P NMR	Solvent
3[a]	8.67	293.9	32.6	CD_2Cl_2
5a	8.54	296.0	31.7	$CDCl_3$
5b	8.67	293.3	32.3	$CDCl_3$
5c	8.71	295.6	32.9	$CDCl_3$
5d	8.70	294.9	32.1	$CDCl_3$

[a] Data according to ref. 9*c*.

The ^{31}P NMR spectra of **7b** and **7d** exhibited single signals at 28.3 ppm and 28.8 ppm, respectively, while the ^{31}P NMR signal of **7c** exhibited a peak at 29.7 ppm. Further on, complexes **5b–d** were synthesized and isolated in high purity by using column chromatography with a yield of 60%, 76% and 43%, respectively. All the synthesized complexes **5a–d** were analyzed by ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} (see Fig. S11–S23 in the ESI†), ^{1}H{^{1}H} COSY, ^{1}H{^{13}C} HSQC and HMBC NMR spectra. Proton and carbon signals on the indenylidene moieties were assigned according the obtained spectral data (the exact number labeling for each atom is indicated on the molecular structure in the ^{1}H NMR and ^{13}C NMR spectra figures in the ESI†). The characteristic chemical shifts of compounds **5a–d** were compared with complex **3** and are summarized in Table 1. Additionally, the structural configurations of **5a–d** were confirmed by single-crystal X-ray diffraction (see the section "single crystal X-ray diffraction analysis").

Encouraged by the success in the synthesis of **5a–d**, another ligand, denoted as 1,1-bis(3,5-dichlorophenyl)-2-propyn-1-ol **8** was synthesized, bearing a more electron-withdrawing substituent.

Following the general reaction procedure outlined in Scheme 1 for the synthesis of **7a–d**, the propargylic alcohol **8** was added to react with the $RuCl_2(PPh_3)_3$ and was stirred at 90 °C. The ^{31}P NMR spectrum of the crude reaction mixture in $CDCl_3$ revealed four clear doublet peaks at 49.8 (d, $^2J_{P-P}$ = 37.1 Hz), 46.8 (d, $^2J_{P-P}$ = 37.1 Hz), 41.2 (d, $^2J_{P-P}$ = 25.3 Hz) and 39.1 (d, $^2J_{P-P}$ = 25.3 Hz) ppm besides few low-intensity unidentified peaks. This ^{31}P NMR spectrum signal pattern is similar to the one reported for the well-defined $(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(PPh_3)_2(=C=C=CPh_2)$ complex in which four doublets peaks at 51.4 (d, $^2J_{P-P}$ = 37.8 Hz), 48.9 (d, $^2J_{P-P}$ = 37.8 Hz), 40.8 (d, $^2J_{P-P}$ = 26.6 Hz) and 37.0 (d, $^2J_{P-P}$ = 26.6 Hz) ppm were observed.[17d] Furthermore, Schrödi *et al.* obtained an identical pattern by using the ligands 1-(3,5-dimethoxyphenyl)-2-propyn-1-ol and 1-(3,5-dimethoxyphenyl)-1-methyl-2-propyn-1-ol, suggesting the *in situ* formation of $(\mu\text{-}Cl)_3$-bridged Ru_2(allenylidene) complexes.[24b] Based on these previous observation in literature, we assume that the propargylic alcohol **8** only leads to the formation of a $(\mu\text{-}Cl)_3$-bridged Ru_2(allenylidene) complex, and the further reorganization to form an indenylidene is prohibited by the strong electron withdrawing substituents. A plausible reaction mechanism based on current work and earlier literature reports is presented in the supporting information to explain the formation of the indenylidene complexes.

Single crystal X-ray diffraction analysis

Crystals of complexes **5a** and **7a** were obtained by slow diffusion of iso-propanol, layered on a solution of the complex in CH_2Cl_2 in an NMR tube and submitted to single crystal X-ray analysis. The compound **7a** crystallized in the centro-symmetric triclinic space group $P\bar{1}$. The asymmetric unit of the structure consists of one $RuCl_2$(4-methyl-3-(*o*-tolyl)-1-indenylidene)$(PPh_3)_2$ molecule (Fig. 2), two of the six phenyl groups in PPh_3 are disordered over two positions. Complex **7a** features a slightly distorted square-pyramidal geometry around the ruthenium atom, with the indenylidene moiety in the axial position. The basal square plane is defined by the two phosphorus atoms of the PPh_3 ligands and two chlorides, positioned in *trans* configuration. The ruthenium atom is displaced from the square plane towards the indenylidene ligand by 0.3688(4) Å. The Ru–Cl bond lengths are 2.355(2) and 2.374(2) Å, and the Ru–P bond lengths are 2.382(2) and 2.399(1) Å. The Ru=C bond length is 1.852(6) Å, and the Cl–Ru–Cl and P–Ru–P angles are 155.26(5) and 168.35(5)°, respectively. The angle between the RuP_2 and $RuCl_2$ least-squares planes is 89.2(2)°. The indenylidene ligand is torsioned with respect to the *trans* chlorides (Cl1–Ru1–C1–C2 torsion angle of 151.3(4)°). A potential intramolecular hydrogen bond is observed between the indenylidene ligand and one of the chlorides: C7–H7···Cl1 (C···Cl distance of 3.471(6) Å).

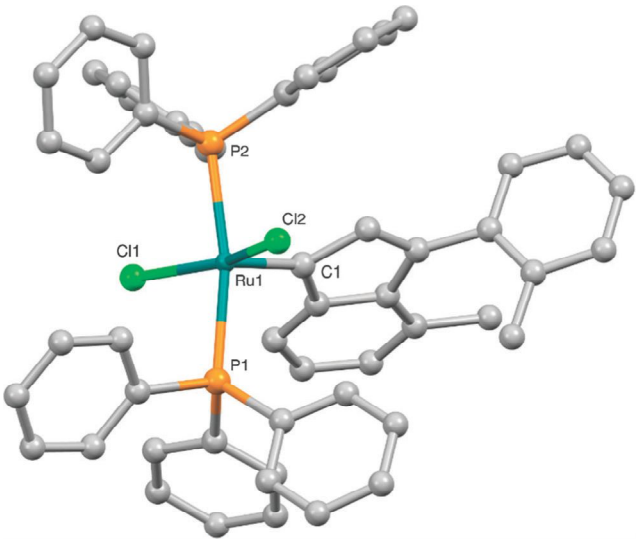


Fig. 2 Molecular structure of compound **7a**, showing the atom labeling scheme of the heteroatoms and carbon atom C1. Hydrogen atoms and the disorder of two of the phenyl groups in PPh_3 are omitted for clarity.

Compound **5a** crystallized in the centro-symmetric monoclinic space group $P2_1/c$. The asymmetric unit of the structure consists of one $RuCl_2$(4-methyl-3-(*o*-tolyl)-1-indenylidene)$(PCy_3)_2$ molecule and one CH_2Cl_2 solvent molecule. The *o*-tolyl moiety is found disordered over two positions, rotated about 162° with respect to each other (Fig. 3). Analogous to **7a**, complex **5a** features a slightly distorted square-pyramidal geometry around the ruthenium atom, with the indenylidene moiety in the axial position. The ruthenium atom is displaced from the basal square plane towards the indenylidene ligand by 0.3699(3) Å. The Ru–Cl bond lengths are 2.379(1) and 2.401(2) Å, and the Ru–P bond lengths are 2.415(1) and 2.429(1) Å. The Ru=C bond for **5a** (1.864(4) Å) is a bit longer than its PPh_3 analogue **7a** (1.852(6) Å). The Cl–Ru–Cl and P–Ru–P angles are 163.33(4) and 161.27(4)°, respectively.

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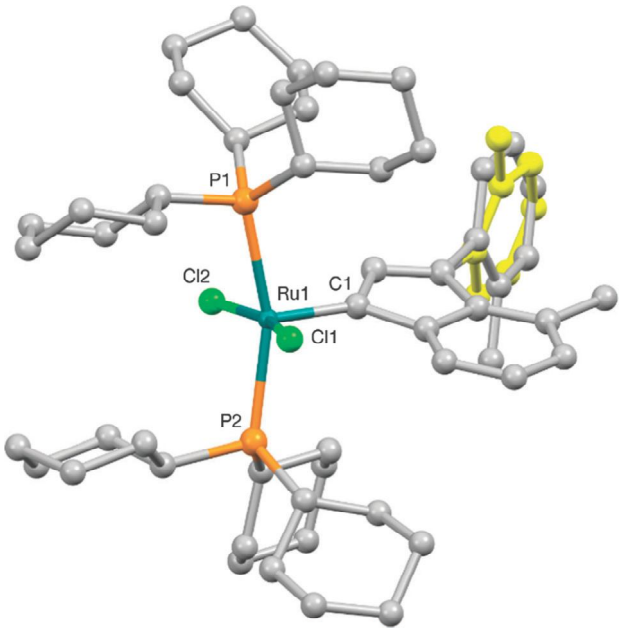


Fig. 3 Molecular structure of compound **5a**, showing the atom labeling scheme of the heteroatoms and carbon atom C1. The disorder of the *o*-tolyl moiety is shown in yellow. Hydrogen atoms and the CH_2Cl_2 solvent molecule are omitted for clarity.

The angle between the RuP_2 and $RuCl_2$ least-squares planes is 87.8(2)°. The indenylidene ligand is torsioned with respect to the *trans* chlorides (Cl1–Ru1–C1–C2 torsion angle of −159.4(4)°). Potential intramolecular hydrogen bonds are observed between the indenylidene ligand and the chlorides: C2–H2···Cl2 (C···Cl distance of 3.200(5) Å) and C7–H7···Cl1 (C···Cl distance of 3.287(5) Å).

Crystals of compounds **3** and **5b–d** were obtained by fast evaporation of a solution of the complex in CH_2Cl_2 on a glass slide and submitted to single crystal X-ray analysis. All compounds **3**, **5b–d** crystallized in the centro-symmetric trigonal space group $R\bar{3}$ with 18 ruthenium based molecules in one unit cell. The indenylidene ligands of **3**, **5c** and **5d** are completely disordered over two positions, torsioned over about 166°, 150° and 163°, respectively, with respect to each other (Fig. 4). Similar to **5a** and **7a**, a square-pyramidal geometry around the ruthenium atom is observed for the complexes. The Ru–Cl bond lengths for **3**, **5b–d** are within the range of 2.379(2) Å to 2.397(2) Å and Ru–P bond lengths are found between 2.410(1) to 2.424(4) Å. Ru=C bond length are 1.83(1) and 1.88(1) Å for **3**, 1.885(8) Å for **5b**, 1.88(1) and 1.93(1) Å for **5c** and 1.90(1) and 1.93(2) Å for **5d**. Cl–Ru–Cl and P–Ru–P angles for these four species are about 164° and 160°, respectively.

The obtained structural information of **5a–d** now allows us to compare and analyze the structural data with the three most famous families of ruthenium metathesis catalysts (the benzylidene **1a**,[28] the benzylidene ether chelating **2** (see ESI†) and the indenylidene **3** (Table 2)).

Catalytic activity of complexes 5a–d

The catalytic performance of the complexes **5a–d** was tested in comparison with the commercial available indenylidene catalyst **3**

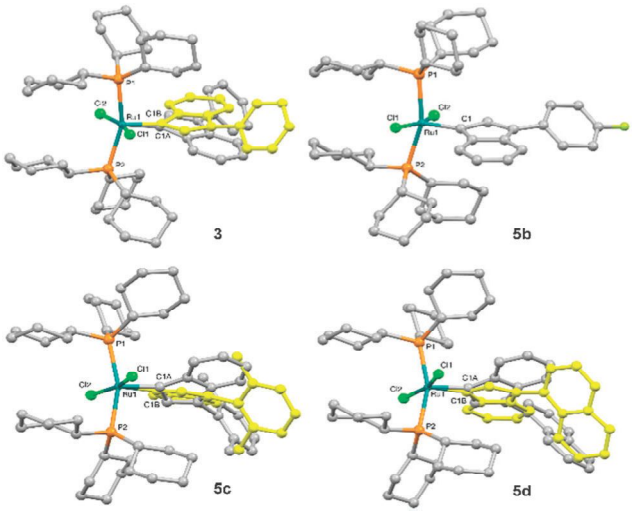
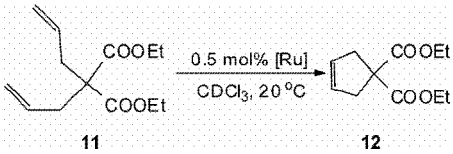


Fig. 4 Molecular structures of compounds **3** and **5b–d**, showing atom labeling scheme of the hetero-atoms and carbon atom C1. Hydrogen atoms are omitted for clarity. For **3**, **5c** and **5d**, the disorder of the 3-phenyl-1-indenylidene, 3-(2,6-xylyl)-1-indenylidene and 3-(1-naphthyl)-1-indenylidene moieties are shown in yellow.

in various benchmark metathesis reactions.[21,30] These include the RCM of diethyl 2,2-diallylmalonate **11**, the RCM of diethyl 2-allyl-2-(2-methylallyl)malonate **13** and the ring-opening metathesis polymerization (ROMP) of *cis*,*cis*-cycloocta-1,5-diene (COD).

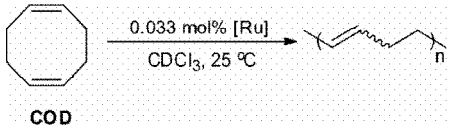


(1)

In Fig. 5, the catalytic performance of the complexes **5a–d** and **3** for the RCM of substrate **11** (eqn (1)) is depicted. The catalytic tests were carried out in $CDCl_3$ at 20 °C using a catalyst loading of 0.5 mol%. As can be seen from this figure, all the synthesized complexes **5a–d** show a similar activity in comparison to the standard complex **3**. A conversion of approximately 90% was observed after a reaction time of 35 minutes.

Besides the RCM reaction, the performance of catalysts **5a–d** in ROMP of COD (eqn (2)) is compared to the catalyst **3** (Fig. 6). Also, for this reaction, no significant differences were observed between the catalysts **5a–d** and **3**. A conversion of approximately 93% was noted after 180 minutes of reaction, which is in accordance to the benchmark complex **3**.

In a last catalytic study, the complexes **5a–d** were examined for the RCM of the partially steric hindered substrate **13** (eqn (3)) at 35 °C using a catalyst loading of 1 mol% (Fig. 7). Nevertheless, despite the more steric hindered substrate was used, all the catalysts exhibited again a similar kinetic profile and efficiency.



(2)

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Table 2 Selected bond lengths (Å) and angles (°) for catalysts **1a**, **2**, **3**, **5a–d**

	1a[a]	**2**[b]	**3**[c]	**3**[d]	**5a**	**5b**	**5c**[d]	**5d**[d]
Ru–Cl	2.3949(6)	2.330(1)/2.332(1)	2.389(2)	2.393(1)	2.379(2)	2.384(3)	2.379(2)	2.388(3)
	2.3957(6)	2.331(1)/2.344(1)	2.408(2)	2.394(2)	2.400(2)	2.391(3)	2.387(2)	2.397(2)
Ru–P	2.4030(7)	2.274(1)/2.277(1)	2.416(2)	2.410(1)	2.415(1)	2.414(3)	2.416(3)	2.415(3)
	2.4066(7)	na	2.427(2)	2.415(1)	2.429(1)	2.416(3)	2.422(2)	2.424(4)
Ru=C1	1.841(2)	1.832(5)/1.841(4)	1.882(6)	1.83(1)/1.88(1)	1.863(4)	1.885(8)	1.88(1)/1.93(1)	1.90(1)/1.93(1)
Cl–Ru–Cl	166.87(2)	148.81(5)/153.95(5)	163.91(7)	163.49(5)	163.33(5)	164.1(1)	163.98(8)	163.7(1)
P–Ru–P	162.22(2)	na	159.03(7)	159.89(5)	161.27(5)	159.6(1)	160.66(7)	159.3(1)

[a] Data according to ref. 28. [b] For compound **2**, the asymmetric unit contains two $RuCl_2$(2-iso-propoxybenzylidene)(PCy_3) molecules (see ESI). [c] Data according to ref. 29. [d] For compound **3**, **5c** and **5d**, the indenylidene ligands are disordered over two parts, the Ru=C distances were not restrained during refinement.

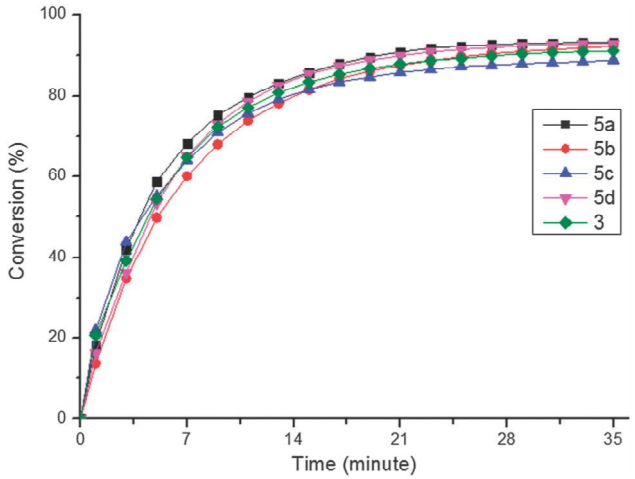


Fig. 5 RCM of substrate **11** with **3**, **5a–d** (0.5 mol%) at 20 °C in $CDCl_3$ (0.6 mL), lines are intended as visual aid.

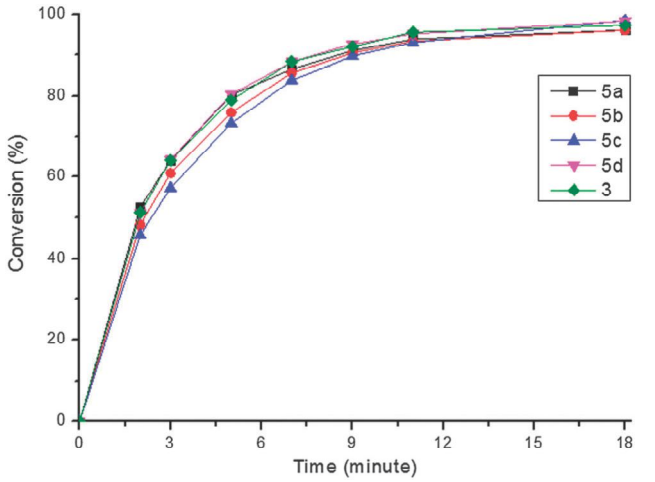


Fig. 7 RCM of substrate **13** with complex **3** and **5a–d** (1 mol%) at 35 °C in CH_2Cl_2 (0.1 M), lines are intended as visual aid.

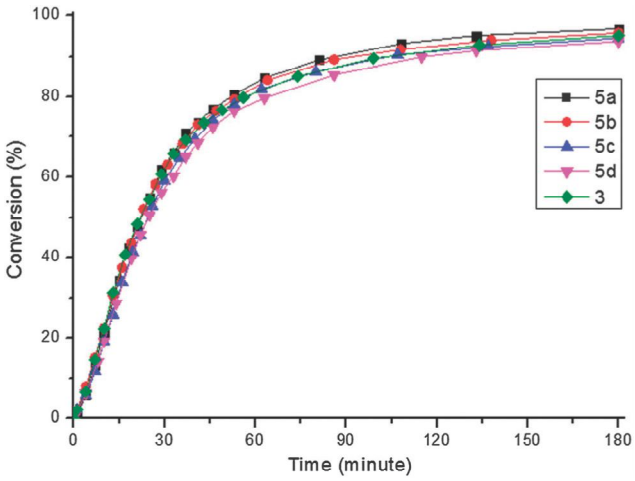
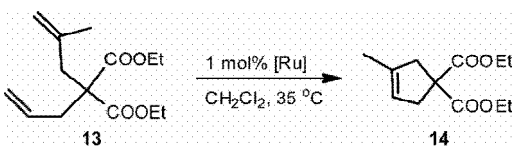


Fig. 6 ROMP of COD with complexes **3**, **5a–d** (0.033 mol%) at 25 °C in $CDCl_3$ (0.6 mL), lines are intended as visual aid.



(3)

In conclusion, no significant differences in the initiation and efficiency of the examined catalysts can be drawn based on the examined substrates and metathesis reactions.

In Table 3, the catalytic performance (expressed as the time used for 50% conversion of **11** in the RCM reaction using similar conditions) and the Cl–Ru–Cl angles of complexes **5a–d** in comparison with other previous reported ruthenium catalysts **2**, **3**, **4a** and **4c** are shown. As can be seen from this table, complexes **5a–d** (entries 6–9) as well as **3** (entries 2, 3) show a much faster initiation in comparison to the chelating ruthenium catalysts **2** and **4a–c**. The time necessary to obtain 50% conversion of the substrate for the non-chelating ruthenium indenylidene species are all around 5 minutes (entries 2, 6–9), while for the chelating complex **2**, a reaction time of 15 minutes is required (entry 1) and for the complexes **4a** and **4c**, about 33 and 69 minutes are needed to obtain 50% of conversion (entries 4, 5). On one hand, these chelating complexes show different performance in catalytic activities, on the other hand, they exhibit significant dissimilarities in the environments around the ruthenium center. For example, the angles of the Cl–Ru–Cl are 148.81(5)/153.95(5) for **2**, 147.86(4) for **4a** and 145.00(2) for **4c**, respectively (see Table 3).[23b] However, for the non-chelating catalysts **3** and **5a–d** (studied in this work), the Cl–Ru–Cl angles of the catalysts are quite similar and are merely in a range from 163.33(5) to 164.1(1)°. Furthermore, no clear differences

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Table 3 Comparative information of RCM of **11**, using complexes **2**, **3**, **4a**, **4c**, **5a–d**, together with a list of the Cl–Ru–Cl angles (°) in their crystal structures

Entry	Complexes	Time for 50% conversion (minutes)	Solvents	Catalysts loading (mol%)	Temperature (°C)	Angles of Cl–Ru–Cl (°)
1[a]	**2**	~12	CD_2Cl_2	1	30	148.81(5)/153.95(5)
2	**3**	~5	$CDCl_3$	0.5	20	163.49(5)/163.91(7)[b]
3[a]	**3**	<5	CD_2Cl_2	1	30	na
4[a]	**4a**	~33	CD_2Cl_2	1	30	147.86(4)
5[a]	**4c**	~69	CD_2Cl_2	1	30	145.00(2)
6	**5a**	~5	$CDCl_3$	0.5	20	163.33(5)
7	**5b**	~5	$CDCl_3$	0.5	20	164.1(1)
8	**5c**	~5	$CDCl_3$	0.5	20	163.98(8)
9	**5d**	~5	$CDCl_3$	0.5	20	163.7(1)

[a] Data according to ref. 23*b*. [b] Data according to ref. 29.

are observed in the bond lengths and other angles (see Table 2) for species **3** and **5a–d** showing once more the geometrical similarity between these complexes. This could be a plausible reason for the fact that no clear differences are observed in the catalytic performance of these complexes.

Conclusions

In this work, four new air stable ruthenium indenylidene complexes were successfully synthesized and isolated from moderate to high yield. Single-crystal diffraction analyses were carried out to fully unravel the structures of **6a**, **7a** and **5a–d**. From these analyses, the structures **5a–d** show a similar geometry, bond lengths as well as bond angles around the ruthenium center. All the complexes exhibited an identical initiation and catalytic efficiency in comparison to complex **3** in all the examined catalytic tests. In ring-closing metathesis reaction, after 35 minutes of reaction more than 90% of the diethyl 2,2-diallylmalonate was converted whereas for diethyl 2-allyl-2-(2-methylallyl)malonate more than 96% is converted after only 18 minutes of reaction. For the ring-opening metathesis polymerization of *cis*,*cis*-cycloocta-1,5-diene, 95% was converted after approximately 180 minutes. Based on the current investigation, the steric modifications on the bis-PCy_3 coordinated ruthenium indenylidene catalysts showed negligible effect on the catalytic activity. The resemblance in the catalytic performance is most probably related to the geometrical similarity between these complexes.

Experimental

General consideration

All the reactions were carried out under an argon atmosphere by using Schlenk techniques. Solvents were dried and freshly distilled prior to use. For drying dichloromethane, CaH_2 was used as drying agent. Whereas for toluene, THF, diethyl ether and dioxane, sodium was employed as drying agent and benzophenone as indicator. $RuCl_2(PPh_3)_3$,[31] 1-(*p*-fluorophenyl)-1-phenyl-2-propyn-1-ol,[26] 1-(2,6-xylyl)-3-(trimethylsilyl)-2-propyn-1-one[23*b*] and diethyl 2-allyl-2-(2-methylallyl)malonate[32] were prepared according to literature procedures. Silica gel 60 (60-nominal pore diameter, 0.04–0.063 mm particle size) supplied by Acros Organics was used for flash chromatography. *n*-Hexane, *n*-pentane, ethyl acetate, methanol, toluene, THF and diethyl ether were purchased from Fiers. Ethynyltrimethylsilane, *t*-butyl lithium, *n*-butyl lithium, bromobenzene, di-*o*-tolylmethanone, potassium carbonate, diethyl 2,2-diallylmalonate, 1-naphthalenyl(phenyl)methanone and *cis*,*cis*-cycloocta-1,5-diene were purchased from Sigma Aldrich. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance 300 MHz and 500 MHz spectrometers. Chemical shifts are listed in ppm from tetramethylsilane with the solvent resonance as an internal standard (^1H, ^{13}C) or external H_3PO_4 (^{31}P). In the supporting information, the exact indicated number of each assigned proton and carbon of the new compounds and the new complexes could be found from the molecular structure on their ^1H and ^{13}C NMR spectra. Elemental analyses were performed on a CHNS-0 Analyzer from Interscience. The gas chromatography experiments were done on a Agilent 7890A instrument equipped with a flame ionization detector and a HP-5 5% phenyl methyl siloxane column (DB-5, column length: 30 m, inside diameter: 0.25 mm, outside diameter: 0.32 mm, film thickness: 0.25 mm). HPLC-MS (ESI) measurements were performed on an Agilent NOD series HPLC with G1946CMSD.

X-ray diffraction. For the structures of compound **5a** and **7a**, X-ray intensity data were collected on a Rigaku RU200 rotating anode equipped with a MAR345 image plate detector using MoKα radiation (λ = 0.71073 Å) and φ scans. For the structures of compounds **2**, **3**, **6a** and **5b–d**, X-ray intensity data were collected on an Agilent Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using CuKα radiation (λ = 1.54178 Å) or MoKα radiation (λ = 0.71073 Å) and ω scans. All images were interpreted and integrated with the program CrysAlisPro (Agilent Technologies).[33] Using Olex2,[34] the structures were solved by direct methods using the ShelXS structure solution program[35] and refined by full-matrix least-squares on F^2 using the ShelXL program.[36] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups).

Synthesis of the ligands

1,1-Di-*o*-tolyl-2-propyn-1-ol (6a). *n*-BuLi (2.5 M in hexane) (1.5 eq., 5.7 mL, 14.28 mmol) was added drop wise to a stirred solution of trimethylsilylacetylene (1.5 eq., 2 mL, 14.28 mmol) in anhydrous THF (17 mL) at −90 °C under an argon atmosphere. After addition, the resulting solution was stirred for another

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5 minutes followed by stirring for 30 minutes at room temperature. Hereafter, di-*o*-tolylmethanone (1.0 eq., 2.0 g, 9.52 mmol) in dry THF (17 mL) was added slowly to the solution at −90 °C and the resulting mixture was allowed to heat up and was refluxed for 30 minutes. The crude reaction mixture was quenched using 1 N HCl (15 mL) and was diluted with diethyl ether. The organic phase was washed with water and the aqueous phases were combined and extracted twice with diethyl ether, thereafter the ether fractions were combined and dried with anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, and evaporation of the solvent, a yellow liquid was obtained. The obtained material was further mixed with K_2CO_3 (1.0 eq., 1.3 g, 9.52 mmol) in dry methanol (10 mL) and was stirred at room temperature for 3 hours. The crude reaction mixture was quenched using 1 N HCl (20 mL) and was diluted with diethyl ether. The organic phase was washed with water and the aqueous phase was extracted twice with diethyl ether, thereafter, the ether fractions were combined and dried on anhydrous $MgSO_4$. Removal of $MgSO_4$ by filtration followed by purification using flash column chromatography (silica gel, hexane/EtOAc = 30/1) and evaporation of the solvent, a white solid (2.06 g, 92%) was obtained. m.p. 57 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 7.92–7.97 (m, 2H, H-9), 7.20–7.26 (m, 4H, H-7, H-8), 7.07–7.11 (m, 2H, H-6) 2.88 (s, 1H, H-1), 2.66 (s, 1H, O*H*), 2.02 (s, 6H, H-10). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): δ 140.6 (C-4), 136.3 (C-5), 132.3 (C-6), 128.2 (C-7), 127.2 (C-9), 125.6 (C-8), 85.5 (C-2), 76.1 (C-1), 74.8 (C-3), 21.2 (C-10). Anal. calcd for $C_{17}H_{16}O$ (236.12): C, 86.40, H, 6.82; found: C, 86.45, H, 6.86. ESI-MS: $[M + H]^+$ called for $C_{17}H_{17}O$, 237.1280; found: 237.1274; $[M - OH]^+$ calcd for $C_{17}H_{15}$, 219.1174; found: 219.1166.

1-(2,6-Xylyl)-1-phenyl-2-propyn-1-ol (6c). *t*-BuLi (1.9 M in hexane) (2 eq., 7.9 mL, 15 mmol) was added drop wise to a solution of bromobenzene (1.0 eq., 1.2 g, 7.5 mmol) in dry diethyl ether (50 mL) at −90 °C under argon atmosphere. The resulting solution was stirred for another 30 minutes at room temperature before slowly adding 1-(2,6-xylyl)-3-(trimethylsilyl)-2-propyn-1-one (1.1 eq., 1.9 g, 8.25 mmol) dissolved in dry diethyl ether. The resulting mixture was stirred overnight at room temperature and then quenched using a saturated NH_4Cl (10 mL) and diluted with diethyl ether. The organic phase was washed with water and the aqueous phase were combined and extracted twice with ether, thereafter the ether fractions were combined and dried on anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, and evaporation of the solvent an oily liquid was obtained. The obtained oil was mixed with K_2CO_3 (1.0 eq., 1 g, 7.5 mmol) in dry methanol (8 mL) and was stirred at room temperature for 3 hours. Subsequently, methanol was removed by vacuum and followed by an addition of diethyl ether (20 mL) and washed with 1 N HCl (15 mL). The organic layer was separated and the aqueous layer was extracted twice with diethyl ether. Next, the organic fractions were combined and dried on $MgSO_4$. Removal of $MgSO_4$ by filtration, column chromatography (silica gel, hexane/EtOAc = 30/1) and solvent evaporation afforded 1-(2,6-xylyl)-1-phenyl-2-propyn-1-ol as a colorless oil (1.42 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 7.50–7.53 (m, 2H, H-5), 7.28–7.35 (m, 3H, H-6, H-7), 7.09 (t, $^3J_{H,H}$ = 10.0 Hz, 1H, H-11), 7.00 (d, $^3J_{H,H}$ = 4.5 Hz, 2H, H-10), 2.85 (s, 1H, H-1), 2.52–2.53 (m, 1H, O*H*), 2.36 (s, 6H, H-12). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): δ 144.9 (C-4), 139.1 (C-8), 137.0 (C-9), 130.8 (C-10), 128.6 (C-6), 128.1 (C-7), 127.3 (C-11), 126.3 (C-5), 86.1 (C-2), 76.7 (C-3), 75.7 (C-1), 24.1 (C-12). Anal. calcd for $C_{17}H_{16}O$ (236.12): C, 86.40, H, 6.82; found: C, 86.38, H, 6.67. ESI-MS: $[M + H]^+$ calcd for $C_{17}H_{17}O$, 237.1280; found: 237.1275; $[M - OH]^+$ calcd for $C_{17}H_{15}$, 219.1174; found: 219.1166.

1-(1-Naphthyl)-1-phenyl-2-propyn-1-ol (6d). *n*-BuLi (2.5 M in hexane) (1.3 eq., 1.90 mL, 4.76 mmol) was added drop wise to a cold solution (−90 °C) of trimethylsilylacetylene (1.3 eq., 0.68 mL, 4.76 mmol) in anhydrous THF (7 mL) under an argon atmosphere. After addition, the resulting solution was stirred for another 5 minutes in a cold bath and 30 minutes at room temperature. Thereafter, (1-naphthyl)(phenyl)methanone (1.0 eq. 0.85 g, 3.66 mmol) in dry THF (7 mL) was added slowly to the trimethylsilylacetylene solution at −90 °C and the resulting mixture was allowed to worm up to room temperature and vigorously stirred for 3 hours. The crude reaction mixture was quenched by using 1 N HCl (5 mL) and was diluted with diethyl ether. The organic phase was washed with water and the aqueous phase was extracted twice with diethyl ether, thereafter the ether fractions were combined and dried on anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, and evaporation of the solvent an oily liquid was obtained. The latter oily liquid was added to K_2CO_3 (1.0 eq., 0.5 g, 3.58 mmol) in dry methanol (4 mL) and was stirred at room temperature for 3 hours. Subsequently, methanol was removed followed by the addition of diethyl ether (40 mL) and water (10 mL). The organic phase was separated and washed with water; the aqueous phases were combined and extracted three times with diethyl ether (20 mL). Next, the organic fractions were combined and dried on $MgSO_4$. Removal of $MgSO_4$ by filtration, column chromatography (silica gel, hexane/EtOAc = 30/1) and solvent evaporation yielding a colorless sticky material (0.8 g, 84.7%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 8.16 (dd, $^3J_{H,H}$ = 7.4 Hz, 1H, H-9), 8.10 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H-15), 7.82–7.90 (m, 2H, H-11, H-12), 7.59–7.62 (m, 2H, H-5), 7.53 (t, $^3J_{H,H}$ = 8.1 Hz, 1H, H-10), 7.42 (td, $^3J_{H,H}$ = 7.5, 1.1 Hz, 1H, H-13), 7.29–7.38 (m, 4H, H-6, H-7, H-14), 2.99 (s, 1H, O*H*), 2.97 (s, 1H, H-1). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): δ 144.1 (C-4), 138.1 (C-8), 134.7 (C-17), 129.9 (C-16), 129.7 (C-11), 128.7 (C-12), 128.6 (C-6), 128.2 (C-7), 126.8 (C-15), 126.3 (C-5), 125.5 (C-14), 125.4 (C-13), 124.8 (C-9), 124.7 (C-10), 86.2 (C-2), 76.7(C-1), 74.5 (C-3). Anal. calcd for $C_{19}H_{14}O$ (258.10): C, 88.34, H, 5.46; found: C, 88.39, H, 5.67. ESI-MS: $[M + H]^+$ calcd for $C_{19}H_{15}O$, 259.1123; found: 259.1115; $[M - OH]^+$ calcd for $C_{19}H_{13}$, 241.1017; found: 241.1011.

1,1-Bis(3,5-dichlorophenyl)-2-propyn-1-ol (8). Ethynylmagnesium bromide (1.2 eq., 16.8 mL, 8.4 mmol) (0.5 M in THF) was added to bis(3,5-dichlorophenyl)methanone (1.0 eq., 2.24 g, 7 mmol) in dry THF (5 mL) at room temperature. The resulting solution was monitored by TLC. After the completion, the crude mixture was quenched by addition of 1 N HCl (8.4 mL) and diluted with diethyl ether. The organic layer was separated; the aqueous layer was extracted twice with diethyl ether. The organic layers

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were combined, dried on anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The solid was further purified by column chromatography (silica gel, hexane/EtOAc = 30/1). After the solvent evaporation a white solid (2.1 g, 86%) was obtained. m.p. 145 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 7.47 (d, $^4J_{H,H}$ = 1.9 Hz, 4H, H-5), 7.30 (t, $^4J_{H,H}$ = 1.9 Hz, 2H, H-7), 2.99 (s, 1H, H-1), 2.94 (s, 1H, O*H*); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): δ 146.5 (C-4), 135.3 (C-6), 128.6 (C-7), 124.5 (C-5), 83.8 (C-2), 77.6 (C-1), 72.7 (C-3). Anal. calcd for $C_{15}H_8Cl_4O$ (343.93): C 52.06, H 2.33; found: C 52.43, H 2.03. ESI-MS: $[M - H]^-$ calcd for $C_{15}H_7Cl_4O$, 344.9222; found: 344.9216. $[M–C_2H_2–H]^-$ calcd for $C_{13}H_5Cl_4O$, 318.9065; found: 318.9062.

Synthesis of the catalysts

$RuCl_2(PPh_3)_3$ (1.0 eq., 0.50 mmol) and propargylic alcohols (1.3 eq., 0.65 mmol) were added into a 5 mL HCl–dioxane solution (0.1 mol L^{-1}) at 90 °C. The reaction solution was monitored by pilot sampling checking with ^{31}P NMR spectrum. After the completion, the solvent was removed under vacuum. Hexane (20 mL) was added to the flask and the solid was ultrasonically removed from the wall. The resulting suspension was filtered and washed two times using hexane (5 mL). The remaining solvent was evaporated affording a red-brown powder, the products were analyzed with ^{31}P NMR to confirm the structures.

The obtained ruthenium complex was dissolved in dry dichloromethane (10 mL) and PCy_3 (3.0 eq., 1.5 mmol) at argon atmosphere and vigorously stirred at room temperature. After completion of the reaction, the resulting slurry was dried under vacuum and iso-propanol (20 mL) was added. Filtration yielded a red-brown powder, which after washing with iso-propanol (2 × 5 mL) and drying under vacuum afforded reddish brown powder.

$RuCl_2$(4-methyl-3-(*o*-tolyl)-1-indenylidene)(PPh_3)$_2$ (7a). Brown crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of iso-propanol into a saturated dichloromethane solution at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 7.54–7.56 (m, 11H), 7.32–7.40 (m, 6H), 7.21–7.30 (m, 13H), 7.05–7.13 (m, 3H), 6.93–6.97 (m, 3H), 6.47 (t, $^3J_{H,H}$ = 7.5 Hz, 1H), 6.14 (s, 1H), 2.20 (s, 3H, C*H*$_3$), 1.66 (s, 3H, C*H*$_3$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): δ 29.3 (s).

$RuCl_2$(4-methyl-3-(*o*-tolyl)-1-indenylidene)(PCy_3)$_2$ (5a). (0.43 g, 90%). Brown crystals, suitable for X-ray diffraction analysis, were obtained by slow diffusion of iso-propanol into a saturated dichloromethane solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 8.54 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, H-7), 7.24–7.28 (m, 1H, H-15), 7.14–7.17 (m, 3H, H-12, H-13, H-14), 7.12 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, H-6), 7.07 (s, 1H, H-2), 7.02 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, H-5), cyclohexyl and methyl signals: 2.58–2.64, 2.22 (s, H-17), 1.94, 1.74–1.78, 1.68 (s, H-16), 1.45–1.52, 1.54–1.58, 1.18–1.20. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 20 °C): δ = 296.0 (t, $^2J_{C,P}$ = 7.6 Hz, C-1), 143.8 (C-8), 141.9 (C-3), 140.3 (C-2), 139.7 (C-9), 139.1 (C-11), 133.7 (C-10), 132.3 (C-5), 129.6 (C-12), 129.0 (C-6), 127.8 (C-4), 127.5 (C-15), 127.3 (C-7), 125.3 (C-14), 125.1 (C-13), cyclohexyl and methyl signals: 32.6, 29.8, 27.8, 25.6, 19.7 (C-17), 18.3 (C-16). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 20 °C): δ 31.7 (q). Anal. calcd for $C_{53}H_{80}Cl_2P_2Ru$ (950.42): C 66.93, H 8.48; found: C 66.80, H 8.50.

$RuCl_2$(3-(*p*-fluorophenyl)-1-indenylidene)(PPh_3)$_2$ (7b). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): δ 28.3 (s).

$RuCl_2$(3-(*p*-florophenyl)-1-indenylidene)(PCy_3)$_2$ (5b). The obtained powder was further purified using column chromatography (silica gel, hexane/EtOAc = 60/1) and was washed with 5 mL cold pentane leaving a yellowish red powder (0.28 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 8.67 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, H-7), 7.71–7.74 (m, 2H, H-11), 7.38 (s, 1H, H-2), 7.29–7.36 (m, 2H, H-5, H-6), 7.20 (d, $^3J_{H,H}$ = 7.0 Hz, 1H, H-4), 7.05–7.11 (m, 2H, H-12), cyclohexyl signals: 2.61, 1.89–1.91, 1.72–1.78, 1.65–1.66, 1.42–1.54, 1.18; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 20 °C): δ 293.3 (t, $^2J_{C,P}$ = 7.6 Hz, C-1), 162.4 (d, $^1J_{C,F}$ = 247.2 Hz, C-13), 144.6 (C-8), 140.8 (C-9), 138.61 (C-2), 138.58 (C-3), 132.4 (d, $^4J_{C,F}$ = 3.1 Hz, C-10), 129.2 (C-7), 129.1 (C-6), 128.3 (C-5), 128.1 (d, $^3J_{C,F}$ = 7.6 Hz, C-11), 117.1 (C-4), 116.1 (d, $^2J_{C,F}$ = 21.4 Hz, C-12), cyclohexyl signals: 32.7, 29.87, 27.82, 26.5. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 20 °C): δ 32.3 (s). Anal. calcd for $C_{51}H_{75}Cl_2FP_2Ru$ (940.37): C 65.09, H 8.03; found: C 65.32, H 7.87.

$RuCl_2$(3-(2,6-xylyl)-1-indenylidene)(PPh_3)$_2$ (7c). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): δ 29.7 (s).

$RuCl_2$(3-(2,6-xylyl)-1-indenylidene)(PCy_3)$_2$ (5c). The obtained powder was further purified using column chromatography (silica gel, hexane/EtOAc = 60/1) and was washed with 5 mL cold pentane leaving a yellowish red powder (0.36 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 8.70–8.71 (m, 1H, H-7), 7.23–7.24 (m, 2H, H-5, H-6), 7.19 (s, 1H, H-2), 7.17 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, H-13), 7.03 (d, $^3J_{H,H}$ = 7.3 Hz, 2H, H-12), 6.50–6.51 (m, 1H, H-4), cyclohexyl and methyl signals: 2.60, 2.16 (s, 6H, H-14), 1.93–1.95, 1.73–1.79, 1.66, 1.44–1.55, 1.18–1.19. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 20 °C): δ 295.6 (t, $^2J_{C,P}$ = 7.6 Hz, C-1), 143.4 (C-8), 142.7 (C-9), 141.3 (C-3), 139.8 (C-2), 135.2 (C-10), 134.2 (C-11), 129.1 (C-7), 128.9 (C-6), 128.8 (C-5), 127.4 (C-13), 127.1 (C-12), 116.6 (C-4), cyclohexyl and methyl signals: 32.6, 29.8, 26.8, 26.5, 20.3 (C-14). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 20 °C): δ 32.9 (s). Anal. calcd for $C_{53}H_{80}Cl_2P_2Ru$ (950.42): C 66.93, H 8.48; found: C 66.83, H 8.67.

$RuCl_2$(3-(1-naphthyl)-1-indenylidene)(PPh_3)$_2$ (7d). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): δ 28.8 (s).

$RuCl_2$(3-(1-naphthyl)-1-indenylidene)(PCy_3)$_2$ (5d). The obtained powder was further purified using column chromatography (silica gel, hexane/EtOAc = 60/1) and was washed with cold pentane (5 mL) leaving a yellowish red powder (0.21 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 8.70 (d, $^3J_{H,H}$ = 7.3 Hz, 1H, H-7), 7.89–7.93 (m, 3H, H-13, H-14, H-17), 7.56 (d, $^3J_{H,H}$ = 7.0 Hz, 1H, H-11), 7.45–7.50 (m, 3H, H-2, H-12, H-15), 7.41 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, H-16), 7.22–7.27 (m, 2H, H-5, H-6), 6.69 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, H-4), cyclohexyl signals: 2.64, 1.96–1.99, 1.81–1.84, 1.74, 1.47–1.60, 1.19–1.25 ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 20 °C): δ 294.9 (t, $^2J_{C,P}$ = 7.6 Hz, C-1), 143.7 (C-8), 143.1 (C-9), 140.4 (C-2), 140.1 (C-3), 134.5 (C-10), 133.9 (C-19), 130.0 (C-18), 129.0 (C-6), 128.9 (C-7), 128.6 (C-5), 128.3 (C-13), 128.2 (C-14), 126.5 (C-17), 126.0 (C-15), 125.8 (C-16), 125.4 (C-12), 123.5 (C-11), 117.7 (C-4), cyclohexyl signals: 32.8, 29.9, 27.8, 26.6. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 20 °C): δ 32.1 (s). Anal. calcd for $C_{55}H_{78}Cl_2P_2Ru$ (972.40): C 67.88, H 8.08; found: C 67.80, H 8.06.

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Monitoring the catalytic process of the ruthenium complexes 3 and **5a–d**.

Standard benchmark screening procedures, ROMP of COD and the RCM catalytic tests were performed as in literature.[21,30,37,38] Experimental details are given below.

Applied procedure for the RCM of diethyl diallylmalonate (11). A 0.1 M stock solution was prepared by dissolving diethyl diallylmalonate (120 mg, 0.5 mmol) in $CDCl_3$ (5 mL). For each ruthenium complex, 0.00125 mmol of the precursor was added and dissolved in $CDCl_3$ (0.5 mL). The NMR tube was filled with the substrate solution (0.5 mL) and the complex solution (0.1 mL). The catalytic activity was monitored by ^1H NMR spectroscopy during the examined time interval. The catalytic tests were done at 20 °C.

Applied procedure for the ROMP of COD. The ruthenium complex (0.00163 mmol) was weighted and dissolved in $CDCl_3$ (0.6 mL). Then, An NMR tube is charged with COD (0.1 mL) and $CDCl_3$ (0.5 mL). After adding the ruthenium solution (0.1 mL), the NMR tube was closed and subjected in to measurement. The catalytic tests were done at 25 °C. The conversion was determined by integration of the olefinic ^1H NMR signals of the formed polymer and the consumed monomer.

Applied procedure for the RCM of diethyl 2-allyl-2-(2-methylallyl)malonate (13). The substrate, diethyl 2-allyl-2-(2-methylallyl)malonate (0.25 g, 1 mmol) and dodecane (0.17 g, 1 mmol), was employed as an internal standard, were added in a Schlenk vessel and flushed with argon. CH_2Cl_2 (9 mL) was added and the solution was heat up to 35 °C. Then, 1 mol% of the catalyst in CH_2Cl_2 (1 mL) was added. During the reaction aliquots were taken out from the reaction mixture and were diluted with CH_2Cl_2 and ethoxyethene before GC analysis.

Acknowledgements

K. V. H. thanks the Hercules Foundation (project AUGE/11/029 "3D-SPACE: 3D Structural Platform Aiming for Chemical Excellence") for funding. Y. X. and F. V. would like to express their deep appreciation to the State Key Lab of Advanced Technology for Materials Synthesis and Processing for financial support (Wuhan University of Technology). F. V. acknowledges the Chinese Central Government for an Expert of the State position in the program of Thousand Talents and the support of the Natural Science Foundation of China (No. 21172027). B. Y. and F. V. appreciate the Research Fund – Flanders (FWO) (project No. 3G022912) for funding. K. L. acknowledges the Special Research Fund of Ghent University for a postdoctoral grant (No. 01P06813T).

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