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New Indenylidene-Schiff Base-Ruthenium Complexes for Cross-Metathesis and Ring-Closing Metathesis

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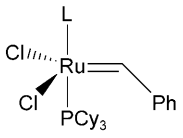
Abstract: We here report on the stability and catalytic activity of new indenylidene-Schiff base-ruthenium complexes **3a–f** through representative cross-metathesis (CM) and ring-closing metathesis (RCM) reactions. Excellent activity of the new complexes was found for the two selected RCM reactions; prominent conversion was obtained compared to the commercial Hoveyda–Grubbs catalyst **2**. Moreover, excellent results were obtained for a standard CM reaction. Higher conversions were achieved with one of the indenylidene catalysts compared with Hoveyda–Grubbs catalyst. Unexpectedly, an isomerization reaction was observed during the CM reaction of allylbenzene. To the best of our knowledge, isomerization reactions in this model CM reaction in closed systems have never been described using first generation catalysts, including the Hoveyda–Grubbs catalyst. The first model CM reactions as well as the RCM reactions have been monitored using ^{1}H NMR. The course of the CM reaction of 3-phenylprop-1-ene (**8**) and *cis*-1,4-diacetoxybut-2-ene (**9**) was monitored by GC. The isomerization reaction was studied by means of GC-mass spectrometry and *in situ* IR spectroscopy. All catalysts were structurally characterized by means of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Keywords: carbene ligands; cross-metathesis; indenylidenes; ring-closing metathesis; ruthenium; Schiff bases

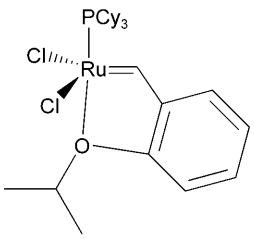
Introduction

Olefin metathesis has evolved into a routine and competent method for the construction of carbon-carbon double bonds, causing a stir with its promise of cleaner, cheaper and more efficient processes. This has been possible by the significant progress in catalyst development and applications that has been made especially during the past 15 years.[1–8] Especially ruthenium-based compounds have shown a versatile and increasing potential for organic synthesis and polymer chemistry, such as the Grubbs first generation catalyst **1a** and the Grubbs second generation catalyst **1b**.[9] An important advance in the design of ruthenium-alkylidene precatalysts was the incorporation of a bidentate chelating carbene ligand in the Grubbs 1st generation complex leading to the family commonly known today as the Hoveyda–Grubbs catalysts. Hoveyda et al. were the first to disclose the preparation of **2** by reaction of (2-isopropoxyphenyl)-diazomethane, PCy_3 and $Cl_2Ru(PPh)_3$.[10] This catalyst showed excellent stability towards air and moisture and could be recycled several times. Various other efforts have been directed towards the modification of the Grubbs catalysts, such as the introduction of bidentate Schiff base ligands,[11,12] substituted acetic acid groups,[13–16] different alkoxides,[17,18] halides,[19] pyridines,[18,20,21] phenoxides,[22,23] less electron-donating phosphines,[24] several pyridinecarboxylates[25] and indenylidene ligand substituting benzylidene.[26,27] Recently, our group has reported new robust ruthenium-indenylidene complexes bearing a saturated N-heterocyclic carbene ligand, showing both high activity and increased stability with an excellent application profile.[28] In addition, the Ru-indenylidene compounds bearing salicylaldimine ligands reveal an impressive stability towards air, moisture and heat. They tolerate storage for months as solids in ambient conditions, including contact with air, without suffering from any degradation or change in isomer ratio. In solution, no decomposition was observed and the isomer ratio was preserved over a period of months.[29] O,N-chelating

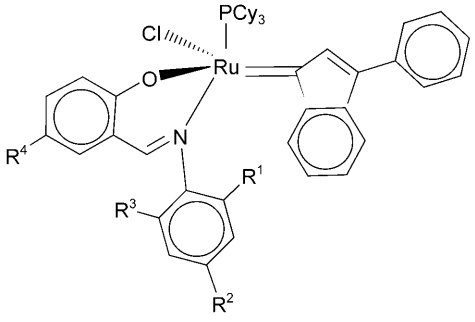
Schiff base ligands have proven to be very useful due to different characteristics they provide to Ru-based catalysts. Thus, the catalytic activity and stability of the ruthenium complexes can be easily tuned by varying the steric and electronic configuration of the Schiff base. Besides, the N and O donor atoms display different electronic effects: the phenolate oxygen (hard donor atom) stabilizes the higher oxidation state of the metallic atom, while the imine nitrogen (softer donor atom) does the same with the lower oxidation state of the ruthenium. Moreover, these types of ligands can be synthesized in practically quantitative yields through one-step procedures.[30] Furthermore, some salicylaldiminato-type ruthenium complexes have been water-adapted (catalysts for aqueous metathesis) and are excellent for biological applications and green chemistry.[31] Taking into account the highly desirable attributes of this type of ligands, some new indenylidene Schiff base Ru-based complexes have been conveniently designed and prepared (**3a–f**) exhibiting a good tolerance towards organic functionalities, air and moisture. The new indenylidene complexes have been successfully applied in olefin metathesis reactions such as cross metathesis (CM) and ring-closing metathesis (RCM).



1a L = PCy_3
1b L = H_2IMes

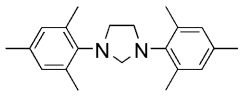


2



3a $R^1 = CH_3$ $R^2 = H$ $R^3 = H$ $R^4 = H$
3b $R^1 = CH_3$ $R^2 = CH_3$ $R^3 = CH_3$ $R^4 = H$
3c $R^1 = CH_3$ $R^2 = H$ $R^3 = CH_3$ $R^4 = NO_2$
3d $R^1 = Cl$ $R^2 = H$ $R^3 = H$ $R^4 = NO_2$
3e $R^1 = CH_3$ $R^2 = CH_3$ $R^3 = CH_3$ $R^4 = NO_2$
3f $R^1 = i\text{-Pr}$ $R^2 = H$ $R^3 = i\text{-Pr}$ $R^4 = NO_2$

H_2IMes =



Results and Discussion

In the present study, we report on the synthesis and structure determination of new indenylidene-Schiff base-ruthenium complexes as well as their kinetics, stability and catalytic activity compared to first generation Hoveyda–Grubbs catalyst **2**. For this benchmark study, a set of carefully chosen olefin metathesis reactions involving model substrates, either commercially available or prepared by synthetic methods reported in the literature, were applied. The main objective throughout this investigation is to bring into light new catalytic systems and their potential towards olefin metathesis reactions.

Structure of Catalysts

The synthesis of catalysts **3a–f** was carried out following the general procedure.[12] To dichloro-(3-phenyl-1*H*-inden-1-ylidene)bis(tricyclohexylphosphine)ruthenium(II) the appropriate amount of the Schiff base Tl salt was added resulting in catalysts **3a–f**. The synthetic ease of preparation of these complexes renders this class of ruthenium catalysts cheap alternatives to expensive commercially available compounds.

Structure Elucidation of 3a and 3d

The assignment of resonances in the ^1H, ^{13}C, and ^{31}P NMR spectra was performed using 1-D and 2-D homonuclear COSY and NOESY and HSQC and HMBC (^1H-^{13}C and ^1H-^{31}P) heteronuclear experiments. The NMR spectra of **3a** and **3d** were recorded at 295 K in dichloromethane-d_2 and $CDCl_3$, respectively.

The most characteristic features of the ^1H NMR spectrum are the presence of a singlet resonance of indenylidene H-16 (**3a**) and H-15 (**3d**) protons at 6.88 ppm (**3a**) and 6.70 ppm (**3d**), respectively, which have been assigned *via* heteronuclear long-range coupling with carbon C-15 (**3a**) and C-14 (**3d**) in HMBC experiments. Interestingly, the proton H-22 of the indenylidene ligand in **3a** (doublet at 8.38 ppm in CD_2Cl_2, 8.29 ppm in $CDCl_3$ and multiplet at 8.97 ppm in benzene-d_6) showed the same coupling with C-15. In the case of **3d**, the most downfield shifted doublet at 8.27 ppm was assigned to H-21 of the indenylidene moiety. This proton showed long-range coupling to the C-14 resonance centered at 299.2 ppm in the HMBC (^1H-^{13}C) spectrum. The H-21 doublet is scalar

coupled with the doublet resonance of H-20 centered at 7.16 ppm. Further scalar coupling with H-19 and H-18 protons was not found. These allowed assigning the ^{1}H and ^{13}C signals of the indenylidene part of the complex through homonuclear COSY/NOESY and heteronuclear HSQC/HMBC couplings.

The ^{1}H NMR spectrum of Schiff base ligand is more complicated due to overlapping of the salicylidene proton as well as aromatic *o*-methylphenyl proton resonances in the 7.20–7.35 ppm region in **3a**. Nevertheless, the doublet resonance of the azomethine proton was found typically at 7.84 ppm (in **3a**), which was confirmed by a heteronuclear ^{1}H-^{31}P HMBC experiment. The H-2 and H-3 resonances of the salicylidene residue of **3a** were found considerably shifted upfield as doublet and doublet of doublets at 7.04 and 6.50 ppm, respectively. Whereas in **3d**, the salicylidene resonances were observed as mutually coupled H-2 and H-3 doublets at 6.97 and 7.96 ppm, respectively; the H-3 doublet was further split into a doublet with H-5. This proton gave the doublet resonance at 8.02 ppm. Moreover, the protons of the indenylidene-attached phenyl substituent of **3d** were observed as a doublet (intensity 2H, H-24 at 7.30 ppm), a triplet (intensity 2H, H-25 at 7.30 ppm) and a triplet (intensity 1H, H-26 at 7.43 ppm), scalar coupled with a common $J = 7.5$ Hz.

The ^{31}P NMR spectrum consists of a broad singlet resonance at 37.12 ppm in $CDCl_3$ for **3a** and one resonance at 39.7 ppm in $CDCl_3$ for **3d**. The HMBC (^{1}H-^{31}P) spectrum showed a series of cross-peaks between the signal at 39.7 ppm and the cyclohexyl protons and additionally, a strong cross-peak with the proton resonance at 7.76 ppm, which was attributed to azomethine H-7 proton.

The ^{13}C NMR spectrum in dichloromethane showed a series of singlet resonances, except for the C-15 and C-16 resonances (in **3a**), which were split into doublets.

The complete ^{1}H and ^{13}C resonance assignments (Figure 1) of the common ligands are collected in Table 4 in the Experimental Section.

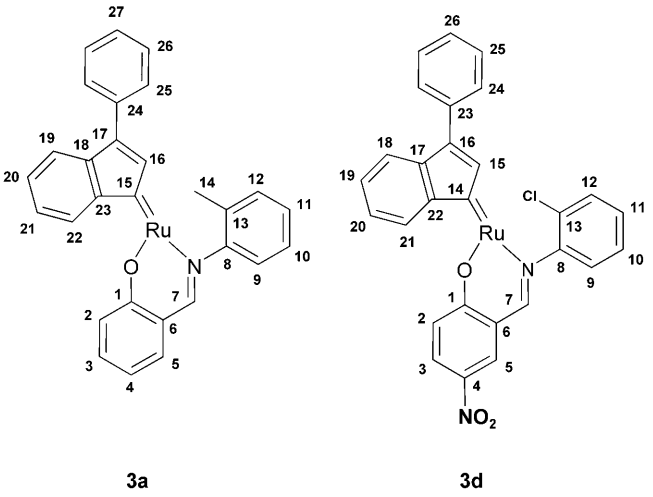


Figure 1. Numbering scheme of ligands in **3a** and **3d** (PCy_3 omitted for clarity).

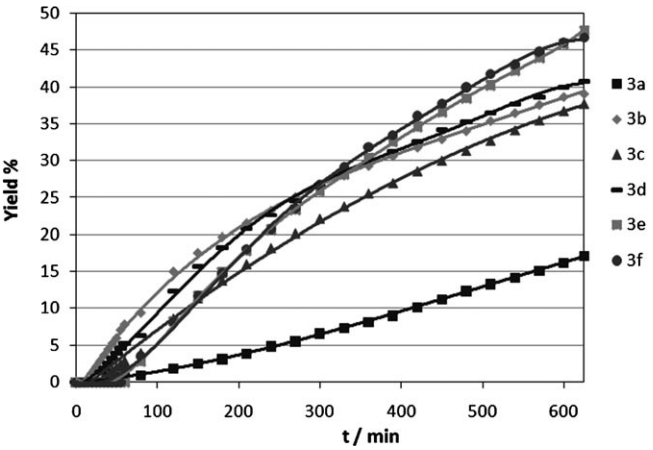
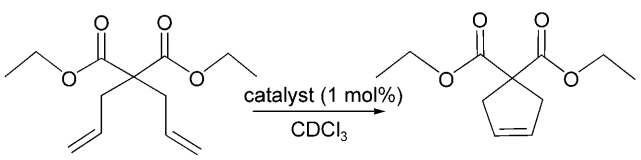


Figure 2. Kinetic plots of ring-closing metathesis (RCM) of DEDAM catalyzed by **3a-f** at room temperature. The lines are only added for better visualization.

Kinetic Study and Stability Test

A kinetic study was conducted based on the activity of the Schiff base catalysts **3** towards the RCM reaction of diethyl diallylmalonate (DEDAM). As can be seen in Figure 2, the two initially catalytic more active catalysts were **3b** and **3d**. The more sterically hindered complex, **3f**, does not show the highest initiation rate but it appears to be the most stable one together with **3e**. Both of them show an induction period that could be related with an increase in steric congestion.



Stability tests of the catalysts were conducted by heating 20 mg of catalyst in benzene-d_6 at 80 °C and taking a ^{31}P NMR spectrum every hour. As can be observed in Figure 3, all catalysts studied were potentially more stable than **2**. For instance, after the first hour, all the indenylidene Schiff base catalysts decompose slightly, whereas decomposition of the Hoveyda–Grubbs complex amounted to 35%. After 3 h of heating, **2** is totally decomposed. In contrast, the Schiff base indenylidene catalysts still have 40–50% of initial catalyst left or even 86% in the case of **3f**. The latter

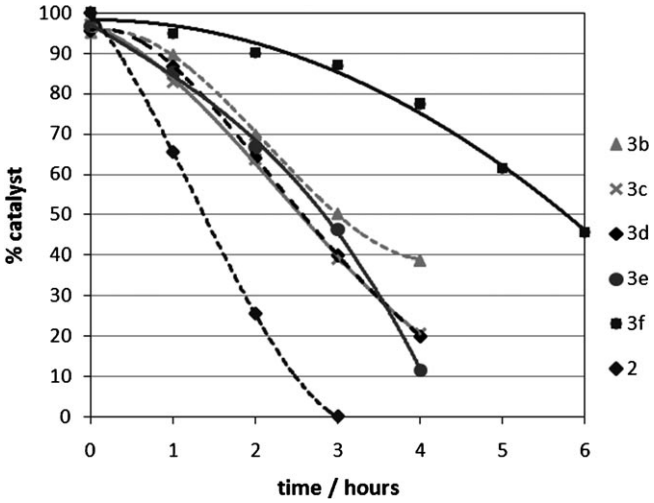


Figure 3. Stability tests of **2** and **3a–f**. The lines are only added for better visualization.

proved to be the most stable one, exhibiting a half-live of 6 h at 80 °C. During this stability test the generation of ruthenium hydride was checked but no peak could be observed in the typical hydride range of the ^{1}H NMR spectra. Nonetheless, the concentration of Ru hydride could be below the detection limit of the NMR spectrometer.

Cross-Metathesis (CM)

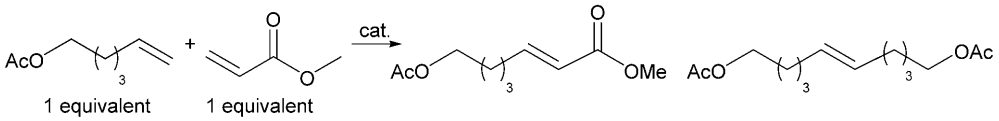
Over the last 10 years, CM has begun to emerge from the shadow of ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) to take its place as a powerful and mild tool for the formation of C–C bonds. This has been made possible with the evolution of new catalysts, and a study of selectivity, efficiency and functional group compatibility of this reaction.[32] Due to this enhancing performance of CM in synthesis of natural and biologically active products, we submitted our catalysts to CM as well.

To compare the activities of the indenylidene-Schiff base-ruthenium-based catalysts and first generation Hoveyda–Grubbs catalyst, we studied two different standard CM reactions. Both of them were conducted under identical conditions: 2.5 mol% of catalyst in different solvents ($CHCl_3$, toluene, CH_2Cl_2 and CH_2ClCH_2Cl) at different temperatures (40 °C, 60 °C and 80 °C) and under air. Important to mention is that all reactions were carried out in closed systems.

The first standard CM reaction, between 5-hexenyl acetate and methyl acrylate (Table 1), is a typical CM reaction between an olefinic partner and an electron-deficient alkene. This type of CM reaction is one of the most attractive transformations since it affords the functionalization of a C=C double bond.[33]

Metathesis reactions involving one substrate with an electron-withdrawing group has started to revolutionize fine chemical synthesis, complementing other methods such as Wittig, Horner–Wadsworth–Emmons or Heck reactions.[32] However, it still needs further investigation in order to establish some rules to permit a good choice of catalysts and conditions for CM of electron-deficient olefins. From a practical point of view, we selected one model CM reaction representing a relatively easy case. Comparing the pre-catalysts, optimized reaction conditions for each initiator are presented in Table 1. Importantly, the cross-product **6** has been obtained with only the *E*-homodimer of 5-hexenyl acetate **7**. This high *E*-*Z* selectivity is principally due to the low dimerization rate of α,β-unsaturated carbonyl compounds. Grubbs and co-workers were the first to prove that CM reactions between terminal alkenes and α,β-unsaturated carbonyl compounds, catalyzed by a Grubbs SIMes-containing complex **1b** (5 mol%) in CH_2Cl_2 at 45 °C,

Table 1. CM reactions catalyzed by **2**, **3a–f** under air. Optimized reaction conditions.



4 **5** **6** **7**

Entry	Catalyst[a]	Solvent	Temperature [°C]	Time [h]	Yield [%][b]
1	**2**	DCE	80	24	62
2	**3a**	toluene	80	1	24
3	**3b**	DCE	40	3	32
4	**3c**	toluene	80	24	53
5	**3d**	toluene	60	24	71
6	**3e**	toluene	60	1	42
7	**3f**	toluene	80	24	26

[a] Catalyst loading: 2.5 mol%.
[b] Conversions of **5** into **6** determined by ^{1}H NMR spectroscopy. Isolated yields (only *E*-isomers).

worked with excellent *E* selectivity and good yields.[34] Because of the total selectivity, the course of the reaction was monitored by NMR spectroscopy, measuring the conversion of the starting material to the product over time, using anthracene as internal standard. The catalyst loading (2.5 mol%) and the concentration of substrates were kept constant throughout the entire screening process.

From a practical point of view, it should be noticed that not only complex **2** can be used for this CM reaction but also some of these indenylidene-Schiff base catalysts like **3c**, **3d** and **3e** yielded good conversions (53%, entry 4; 71%, entry 5, 42%, entry 6; respectively). Interestingly, **3d** showed even a better efficacy as compared to the commercially available **2** (71%, entry 5 *vs.* 62%, entry 1) after a reaction time of 24 h. In order to explain the higher yield of **3d**, we can consider that the electron-withdrawing group in the aldimine fragment (chloride substituent) weakens the N→Ru chelation facilitating the decoordination of the N of the imine and, consequently, faster initiating the catalytic cycle. The "one-arm" dissociation of the Schiff base ligand in **3d**, leading to the formation of the catalytically active 14-electron species, seems to proceed faster than the release of the aryl ether ligand in Hoveyda–Grubbs complex, required for initiation,[35] and as a result **3d** initiates more rapidly than first generation Hoveyda–Grubbs catalyst. Generally, increasing the temperature from 40 °C to 60 °C or even 80 °C, due to the high thermal stability of the ruthenium indenylidene complexes,[36] the conversion of the metathesis product **6** was enhanced. Nevertheless, in some cases a prolonged reaction time was necessary to reach good yields (entries 1, 4, 5 and 7, Table 1).

Figure 4 and Figure 5 illustrate the comparison of the activities of the pre-catalysts in this model CM reaction using four different solvents after 24 h at 80 °C and 60 °C, respectively. As can be seen from these

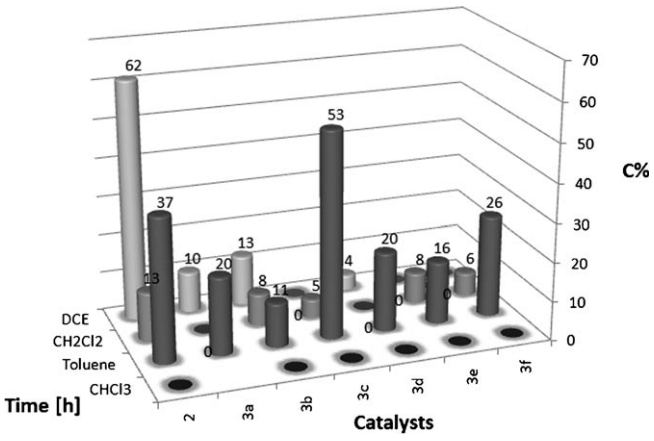


Figure 4. CM of **4** and **5**. *Conditions:* $c_4 = 0.4$ M, 2.5 mol% of catalyst, 80 °C, 24 h, under air.

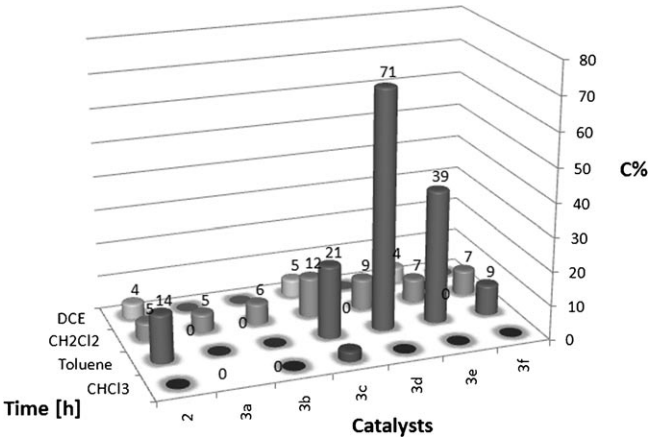


Figure 5. CM of **4** and **5**. *Conditions:* $c_4 = 0.4$ M, 2.5 mol% of catalyst, 60 °C, 24 h, under air.

Figures in combination with the results compiled in Table 1, it is noteworthy to mention that the catalytic activity of the complexes strongly depends on the applied solvent. According to Ledoux, in ROMP of cyclooctadiene, Grubbs second generation catalyst was unambiguously more active in C_6D_6 than in $CDCl_3$, at the same temperature. Two possible explanations for this observation were proposed.[37] In the present study, toluene was found to be the best solvent in almost all cases using Ru-indenylidene complexes. Complex **2** and only one of the Schiff base-indenylidene catalysts (**3b**) preferred dichloroethane (DCE) instead of toluene (entries 1 and 3, Table 1). Related to our observations, it seems that all the catalysts studied do not perform well in CH_2Cl_2 at temperatures higher than 40 °C and the same holds for $CHCl_3$ at all temperatures studied for this model CM reaction.

The progress of the reaction of **4** and **5** conducted in toluene at 60 °C in the presence of the first-generation Schiff base-indenylidene catalysts is shown in Figure 6. Remarkably, catalyst **3d** depicts a high activity enhancement if the reaction is continued up to 24 h. The observable diminishment after 24 h for catalysts **2** and **3c**, although not fully understood, could be explained by assuming a collateral isomerization process. A clear and convincing explanation will be given further on.

Overall, the desired product was isolated in a moderate to good yield with a high stereoselectivity in the first standard CM reaction. Special attention should be given to our very stable (several months at room temperature in air) indenylidene-Schiff base-Ru-based catalyst **3d** as a highly reactive species for the model CM reaction with a pronounced high thermal stability compared to complex **2**.

The second standard reaction of interest is the CM of allylbenzene and *cis*-1,4-diacetoxy-2-butene (Table 2). In this model reaction, the strategy (the use

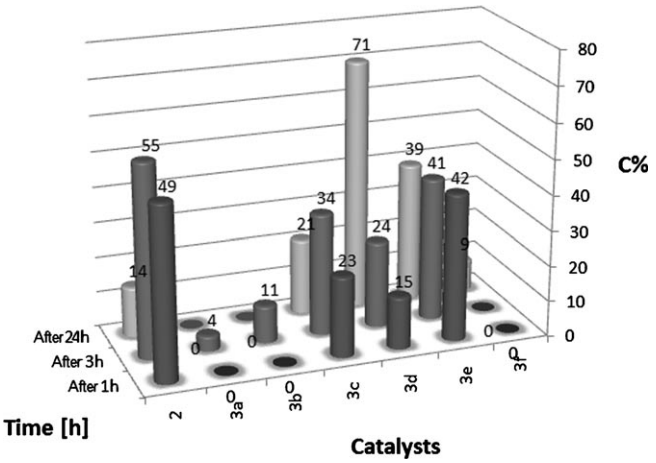


Figure 6. CM of **4** and **5**. *Conditions:* $c_4 = 0.4$ M, 2.5 mol% of catalyst, 60 °C, toluene, under air.

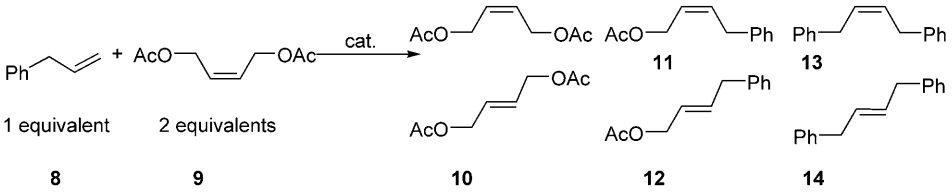
of two equivalents of *cis*-1,4-diacetoxy-2-butene *vs.* one equivalent of allylbenzene) is to obtain the preferable selectivity and to avoid CM coupling of two terminal olefins.

Since both *E* and *Z* dimers of the starting materials and cross-products were found to be reactive, the course of the reaction was now monitored by GC, measuring the conversion of starting material to products over time, using tridecane as internal standard. The catalyst loading (2.5 mol%) and the concentration of substrates were kept constant throughout the entire screening process.

Analysis of the conversions and selectivities yielded some interesting findings. Comparing the pre-catalysts, the best reaction conditions for each initiator are presented in Table 2. Here, the catalyst of preference in CM of allylbenzene and *cis*-1,4-diacetoxy-2-butene was complex **2** in DCE at 40 °C yielding 66% conversion in only 1 h (entry 1, Table 2). Nonetheless, the Schiff base-indenylidene-Ru-containing catalysts gave moderate yields. Again, similar to the first standard CM reaction studied above, complex **3a** showed the lowest efficacy in all screened conditions, owing to an observable decomposition in solution. Surprisingly, as opposed to the highest results obtained for indenylidene catalysts in CM of **4** and **5** (entries 4 and 5, Table 1), these complexes (**3c** and **3d**) failed in this CM reaction since only poor yields (or no conversion) were obtained even after 24 h of reaction (entries 4 and 5, respectively, Table 2). As it can be seen from the data presented in Table 2, DCE was again the preferred solvent for complex **2**, contrary to the results found for the other catalysts. Regarding to *E*-*Z* selectivity, all Schiff base catalysts studied here displayed a good selectivity in all cases (Table 2). Intriguingly, only the reaction conducted with catalyst **3f** could be accelerated under microwave irradiation conditions (1 hour at 80 °C; 16%) but the conversion never exceeded 16% even at elevated temperature (100 °C). In contrast, when we carried out the same microwave-assisted reaction using Hoveyda–Grubbs catalyst, **2**, only a moderate yield (15%) was obtained compared with classical heating conditions (entry 1, Table 2).

Unexpectedly, in the course of this investigation we found a decrease in yield after 24 h that could indicate some type of isomerization reaction. To clearly present this in a graph, we chose the progress of this standard CM reaction performed in CH_2Cl_2 at 80 °C in the presence of the first-generation catalysts **3a–f** as an example, see Figure 7.

Table 2. CM reactions catalyzed by the ruthenium complexes **2** and **3a–f** under air. Optimized reaction conditions.



Entry	Catalyst[a]	Solvent	Temperature [°C]	Time [h]	Yield of **10** [%][b]	Yield of **11** [%][b]	Yield of **12** [%][b]	Yield of **13** [%][b]	Yield of **14** [%][b]
1	**2**	DCE	40	1	4	14	52	0	0
2	**3a**				[c]				
3	**3b**	Toluene	80	1	0	5	14	5	4
4	**3c**	$CHCl_3$	80	24	0	2	5	6	8
5	**3d**								
6	**3e**	$CHCl_3$	40	24	0	6	17	10	14
7	**3f**	CH_2Cl_2	40	1	0	5	13	3	5

[a] Catalyst loading: 2.5 mol%.
[b] Conversions determined by ultrafast GC.
[c] Decomposition of catalyst, no conversion.

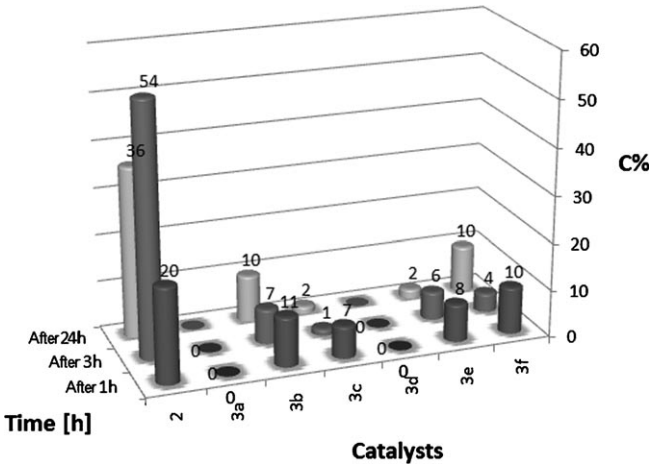


Figure 7. CM of **8** and **9**. *Conditions:* $c_8 = 0.4$ M, 2.5 mol% of catalyst, 80 °C, CH_2Cl_2, under air. Y% = yield (**11**) + yield (**12**).

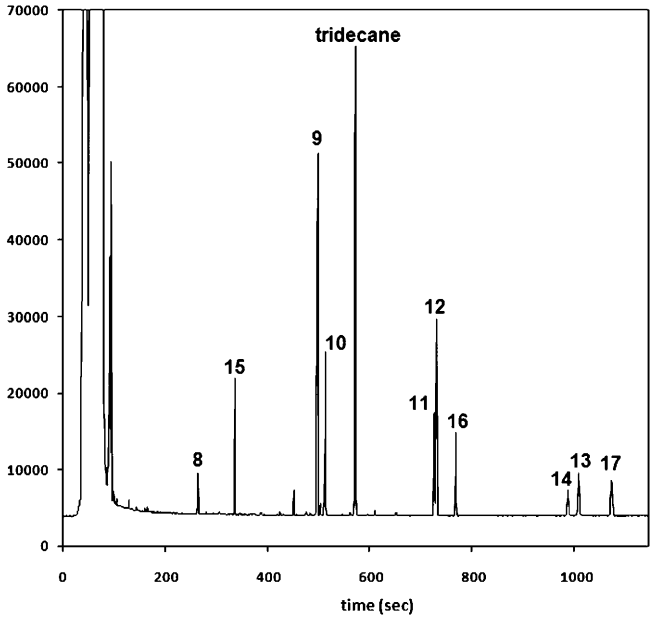


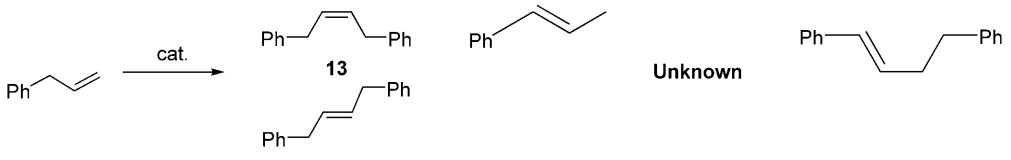
Figure 8. CM of **8** and **9** using complex **2**. *Conditions:* $c_8 =$ 0.4 M, 2.5 mol% of catalyst, 80 °C, $CHCl_3$, 24 h, under air.

Special attention should be given to the performance of complex **2**. Although it reached the highest yield, surprisingly the product conversion decreased from 54% (after 3 h) to 36% (after 24 h). Due to this intriguing fact, we decided to investigate this in more detail and, at this time, we discovered some new peaks in several chromatograms. Above all, these new compounds appeared at 80 °C after 24 h, but they were hardly present in chromatograms where the indenylidene catalysts were used. Moreover, this collateral reaction was found in all of the tested solvents and it seemed to proceed in higher percentage in $CHCl_3$ and CH_2Cl_2. Figure 8 shows the chromatogram of the CM reaction between **8** and **9** using Hoveyda–Grubbs catalyst **2**, in $CHCl_3$ at 80 °C and after 24 h. As can be seen, new peaks, corresponding to new compounds **15**, **16** and **17**, are clearly observable near to **8** (allylbenzene), heterodimers and allylbenzene homodimers, respectively, presumably indicating isomerization side-reactions.

Since *cis*-1,4-diacetoxy-2-butene seemed not to be affected by the isomerization reactions, we focused in the next experiment only on using **8** and the Hoveyda–Grubbs complex **2**. To do so, these reactions were carried out with 1 mol% and 2.5 mol% of catalyst, using $CHCl_3$ as solvent and at 80 °C and 100 °C. Samples were taken after 24 h, 48 h and 72 h and analyzed by ultrafast-GC. Isomer conversions and metathesis percentages attained applying these conditions are presented in Table 3.

From the results presented in Table 3 we can conclude the following: 1) total conversion of allylben-

Table 3. Isomerization percentages (I%) and metathesis percentages (M%) in the reaction of allylbenzene using Hoveyda–Grubbs catalyst in $CHCl_3$.[a]



Entry	Temp. [°C]	Catalyst loading (mol%)	I(**15**)% at 24 h	I(**17**)% at 24 h	I(**15**)% at 48 h	I(**17**)% at 48 h	I(**15**)% at 72 h	I(**17**)% at 72 h	M% at 24 h	M% at 48 h	M% at 72 h
1	80	2.5	36	28	35	30	32	32	34	33	35
2		1	26	7	26	7	15	9	47	47	68
3	100	2.5	45	55	45	55	46	54	0	0	0
4		1	49	51	49	51	50	50	0	0	0

[a] I(**15**)% = isomerization percentage of **15**. I(**17**)% = isomerization percentage of **17**. Metathesis percentages are referred to the homodimerization reactions of **8** into **13** and **14**.

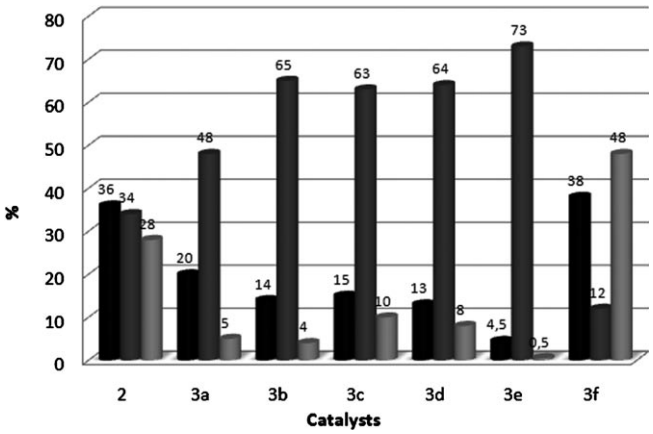


Figure 9. Comparison of catalysts **2** and **3a–f** in the isomerization of allylbenzene. *Conditions:* $c_{5b} = 0.4$ M, 2.5 mol% of catalyst, 80 °C, $CHCl_3$, 24 h, under air, closed vessels. In black colour: isomer of **8** (%); in lighter grey colour: isomer of product (%); in darker grey colour: M%.

zene into its isomer compound is only reached at 100 °C, 2) concerning catalyst loading, a significant difference in isomerization yield was found at 80 °C between 2.5 mol% and 1 mol% (entries 1 and 2, respectively, Table 3). So, the catalyst loading influences the conversion factor. 3) With 2.5 mol% catalyst, the maximum isomerization is obtained after 24 h.

To further extend our investigation, reactions on allylbenzene now using 2.5 mol% of indenylidene-Schiff base catalyst were conducted in $CHCl_3$ at 80 °C for 24 h. Thereafter, the isomerization percentages were calculated and presented for comparison with the commercial Hoveyda–Grubbs catalyst in Figure 9.

We were pleased to see that, except for **3f**, most of the indenylidene-Schiff base catalysts here tested showed low or poor isomers conversions compared to Hoveyda–Grubbs complex. Gratifyingly, the best indenylidene-Ru carbene found in the CM reaction of **8** and **9** (**3e**; entry 6, Table 2) displayed the poorest isomerization percentage (5%) in the above experiment.

In order to further verify the occurrence of the isomerization reaction, it was also confirmed by means of GC-mass spectra analysis and *in situ* IR spectroscopy. Firstly, the CM of **8** and **9** was conducted using 2.5 mol% of Hoveyda–Grubbs catalyst in $CHCl_3$ at 80 °C and for 24 h. At this time, a sample was collected and analyzed by GC-MS. The new products detected (**15** and **17**) were identified by means of the WILEY library linked to the computer as 1-(prop-1-enyl)benzene (rt = 10.271 min; $m/z = 117$) and *cis*-1,4-diphenyl-1-butene (rt = 22.026 min; $mz = 208$), respectively (see Figure 10). Although we did not manage to identify product **16** (rt = 18.416 min; $mz = 130$), all products (**15**, **16** and **17**) were found in a 6:5:4 ratio, respectively, attending to the area proportion. No direct observations regarding the mechanism were recorded. However, it is reasonable to assume that, at least for 1-(prop-1-enyl)benzene and *cis*-1,4-diphenyl-1-butene, the substrate is subjected to a double-bond migration and thereafter enters the catalytic cycle.[38]

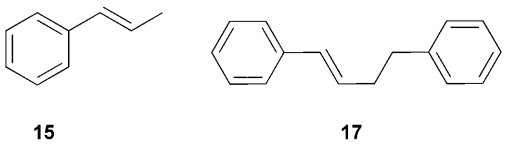


Figure 10. Structural formulae of compounds detected by GC-MS.

Encouraged by these results we also verified the isomerization by using *in situ* IR spectroscopy which monitors reactions in real-time. This technique is very appropriate to characterize components that are difficult to isolate (*in situ* advantage). The CM reaction of **8** and **9** was performed in the same conditions as used before: 2.5 mol% of complex **2** in $CHCl_3$ at 80 °C for 24 h. The course of the reaction was monitored every minute and after 22 h, when the metathesis reaction had finished, a new IR band appeared at about 800 cm^{-1} (Figure 11). In accordance with literature data,[39] this band can be assigned to the wagging vibration of the C–H bond in *para*-substituted benzenes. This means that it is related to the formation of **15**.

To the best of our knowledge, isomerization reactions in this model CM reaction in closed systems using first generation catalysts **3a–f**, including Hoveyda–Grubbs complex **2** are described here for the first time.

Ring-Closing Metathesis (RCM)

Ring-closing metathesis has become an important synthetic method in organic chemistry.[40] For this reason, and due to its high degree of reproducibility

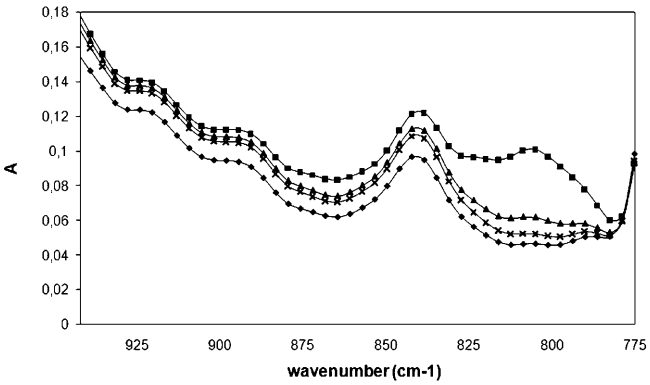


Figure 11. *In situ* IR spectrum of the CM reaction of **5b** and **6b** using catalyst **2**. *Conditions:* $c_{5b} = 0.4$ M, 2.5 mol% of catalyst, 80 °C, $CHCl_3$, 24 h, under air; (◆, after 21 h and 1 min), (×, after 21 h and 6 min), (▲, after 21 h and 16 min), (■, after 22 h).

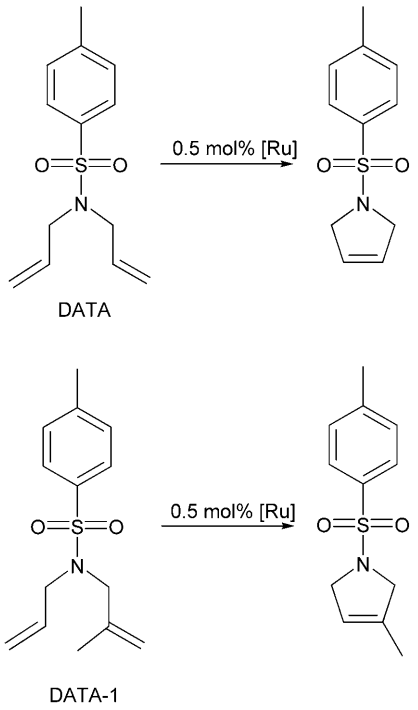


Figure 12. RCM reactions of DATA and DATA-1.

and ease to perform and monitor over time, this reaction class was selected for elaborate study as well. Moreover, it has been used extensively to test numerous catalysts. Having the new catalysts described above in hand, we decided to study their catalytic activity by choosing two model RCM substrates, namely DATA (*N*,*N*-diallyltosylamide) and DATA-1 [*N*-allyl-*N*-(2-methyl-2-propenyl)-*p*-toluenesulfonamide] (Figure 12).

In both cases, the indenylidene catalysts **3a–f** and the commercial catalyst **2** were evaluated at 60 °C in $CHCl_3$. Measurements were performed after 1 h, 3 h and 24 h. The course of the reaction was monitored by NMR spectroscopy by measuring the increase in the amount of product in time. The catalyst loading (0.5 mol%) and the concentrations of substrates were kept constant throughout the entire screening process.

RCM of DATA

Interestingly, all catalysts afforded quantitative yields at 60 °C after only 1 h (Figure 13). The origin of the slight decrease in yield obtained with **3f** after 24 h remains, however, unclear.

RCM of DATA-1

Even more interesting are the results obtained with DATA-1, a more challenging substrate for RCM. As it can be seen in Figure 14, practically all indenylidene-Schiff base catalysts exceeded the yield afforded by the Hoveyda–Grubbs catalyst. It should be emphasized that whereas commercial catalyst **2** only led to 65% conversion after 24 h, four of our catalysts (**3b**, **3d**, **3e** and **3f**) gave overall yields being clearly more efficient. In the case of catalyst **3d**, full conversion was attained after only 3 h, exactly the double compared to Hoveyda–Grubbs catalyst **2** after the same time.

It should be noted that the results of RCM of DATA-1 and the results of the stability tests (see above) are in good agreement. More stable catalysts allow for higher conversions.

In conclusion, the present investigation in RCM reactions has proved that indenylidene-Schiff base-ruthenium catalysts **3a–f** are at least as effective as the Hoveyda–Grubbs complex, while the rigorous

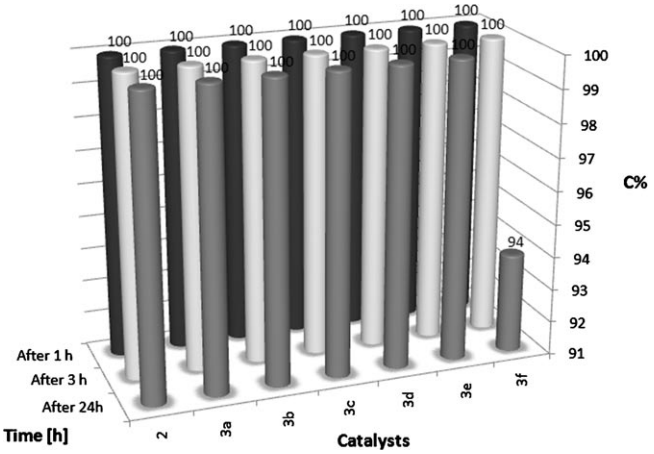


Figure 13. RCM of DATA. Conditions: $c_{\mathbf{DATA}} = 0.1$ M, 0.5 mol% of catalyst, 60 °C, $CHCl_3$, under air.

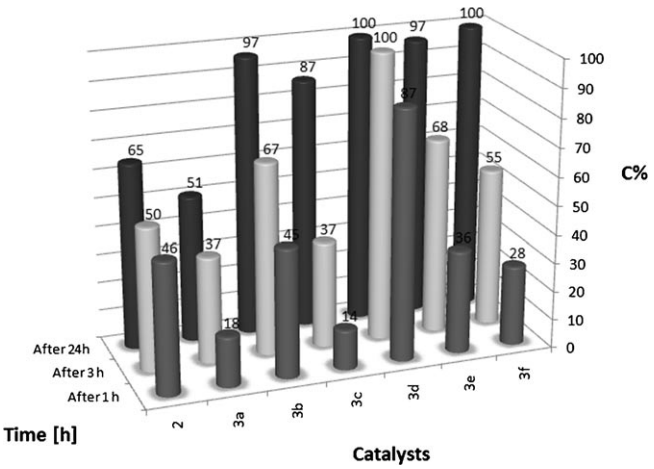


Figure 14. RCM of DATA-1. Conditions: $c_{\mathbf{DATA\text{-}1}} = 0.1$ M, 0.5 mol% of catalyst, 60 °C, $CHCl_3$, under air.

choice of ligand environment enables excellent metathesis activity.

Conclusions

We have prepared a series of indenylidene-ruthenium complexes bearing a salicylaldimine ligand, and their structures were fully confirmed by NMR spectroscopy. These catalysts show no sign of decomposition when stored under ambient conditions. Their robustness also holds at higher temperatures when dissolved in benzene-d_6. With the results presented above, we have demonstrated the great stability and activity of these new complexes. They exhibit a particular electronic and steric configuration and a readily accessible imine ligand that lend them to catalyst tuning.[41] Besides, these catalysts **3a–f** are relatively cheap and easily produced. Another advantage is that all these catalysts show negligible olefin metathesis activity at room temperature. This would be a good choice when commercial polymerization technology requires a latent catalyst.[42–44] Most metathesis catalysts are operative at room temperature and are therefore not well suited for applications where catalyst latency is beneficial.

Overall, the desired product was isolated in moderate to good yields with high stereoselectivities in the first standard CM reaction. It is clear that by changing the electronic configuration of the Schiff base, the catalytic activity and stability of the ruthenium initiators were tuned. In a second standard CM reaction, undesired products due to isomerization and homodimerization of starting materials were formed, thereby resulting in a low selectivity for this process. Regarding RCM reactions, a comparison between the classical Hoveyda–Grubbs complex **2** and complexes **3a–f** demonstrates the excellent conversions obtained with the indenylidene-based initiators, in most cases exceeding the yields achieved using **2**. However, the current difficulty remains the anticipation of the efficacy of pre-catalysts with regard to a specific substrate; no single catalyst outperforms all others in all cases.

Due to the wide possibilities of modifying the structure of the Schiff base ligand, there is still enough room for further investigation and improvement of these catalytic systems. Investigations concerning the activity of other new Schiff base-Ru-indenylidene complexes, bearing NHC ligands, are currently underway in our laboratory and will be reported in due course.

Experimental Section

General Remarks

All synthesis reactions involving organometallic compounds were carried out in oven-dried glassware under an oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried with appropriate drying agents and distilled prior to use. All solvents and reagents, except DATA and DATA-1, were obtained from commercial sources. Substrates DATA and DATA-1 were prepared according to literature procedure.[45] Starting chemicals were used without further purification. ^{1}H, ^{13}C and ^{31}P NMR characterization of **3a–f** and conversion measurements were acquired with a Varian Unity-300 spectrometer and were obtained at room temperature. The detailed assignment of the resonances of **3a** and **3d** in the ^{1}H, ^{13}C, and ^{31}P NMR spectra was performed using a Bruker 500 Mhz. Elemental analysis was performed using a Perkin–Elmer-2400 CHNS/O analyzer.

Flash column chromatography was performed on silica gel 60 (grade 7734, 70–230 mesh, Silicycle). Microwave-assisted reactions were carried out using a MultiSYNTH scientific microwave (Microwave Organic Synthesis System) produced by Milestone. Gas chromatography (GC) was conducted using a Finning Trace GC ultra from Thermo Electron Corporation equipped with a 10 m capillary column and with a flame ionization detector. The temperature program was as follows: 50 °C initial temperature followed by a heating rate of 10 °C/min up to 180 °C and finally an increase up to 190 °C at a heating rate of 2 °C/min. Products **15** and **17** were identified by gas chromatography-mass spectroscopy (Hewlett Packard instrument) equipped with a mass selective detector (HP 5973) and a GC system (HP 6890 series). IR study was possible by using a ReactIR 45 m equipped with a 1.5 m AgX fiber and a 9.5 mm DiComp (Diamond) probe.

Typical Procedure for the CM reaction between 4 and 5 (Catalyst Loading = 2.5 mol%)

A 15-mL, screw-cap, septum tops sealed vial was charged with 100 μL (0.62 mmol; 88 mg) of **4**, 56 μL (0.62 mmol; 54 mg) of **5**, 15–20 mg of anthracene as internal standard and 1.55 mL of solvent ($CHCl_3$, toluene, CH_2Cl_2 or DCE). A first sample was taken and analyzed (initial time), thereafter 0.015 mmol (2.5 mol%) of catalyst was added under air. The solution was heated in a controlled-temperature silicone-oil bath at 40 °C, 60 °C or 80 °C. Progress of the reaction was monitored by NMR spectroscopy. Measurements were performed after 1 h, 3 h and 24 h.

Typical Procedure for the CM Reaction between 8 and 9 (Catalyst Loading = 2.5 mol%)

A 15-mL, screw-cap, septum tops sealed vial was filled with 28.80 μL (0.22 mmol) of **8**, 69.32 μL (0.44 mmol) of **9**, 26.84 μL (0.11 mmol) of tridecane as internal standard and 1 mL of solvent ($CHCl_3$, toluene, CH_2Cl_2 or DCE). A first sample was taken and analyzed (initial time), thereafter 2.5 mol% of catalyst was added under air. The solution was heated in a controlled-temperature silicone-oil bath at 40 °C, 60 °C or 80 °C. The reaction mixture was then analyzed by GC. Measurements were performed after 1 h, 3 h and 24 h.

Typical Procedure for the RCM Reaction of DATA or DATA-1 (Catalyst Loading = 0.5 mol%)

A solution of the substrate (DATA or DATA-1) (0.020 mL; 0.1 M) and 0.5 mol% of catalyst **3a–f** in $CHCl_3$ (0.85 mL) was prepared in a 15-mL, screw-cap, septum tops sealed vial under air and heated at 40 °C or 60 °C. The reaction mixture was analyzed by NMR. Measurements were performed after 1 h, 3 h and 24 h.

General Procedure for Stability Tests

After charging an NMR tube with 20 mg of catalyst dissolved in dry deuterated benzene, the solution was heated at 80 °C in a controlled-temperature silicone-oil bath for 6 h. The catalyst stability was monitored as a function of time by integrating every hour the ^{31}P signal of the decomposing catalyst.

General Procedure for Kinetic Studies

An NMR tube was filled with the precatalyst **3a–f** (0.004 mmol; 1 mol%) and dry $CDCl_3$ (0.4 mL), then DEDAM (diethyl diallylmalonate) was added (0.414 mmol; 0.1 mL). The reaction progress was monitored by ^1H NMR spectroscopy as a function of time at ambient temperature by integrating the olefinic ^1H signals of the formed ring-closed product and the disappearing diene.

Elemental Analysis of 3a–f and ^1H, ^{13}C (Table 4) and ^{31}P NMR Characterization of 3b, 3c, 3e and 3f

3a: Anal. calcd. (%) for $C_{47}H_{55}ClNOPRu$ (817.45): C 69.06, H 6.78, N 1.71; found: C 68.87, H 6.54, N 1.97.

3b: ^1H NMR ($CDCl_3$): δ = 8.31, 7.61, 7.58, 7.49, 7.37, 7.23, 7.08, 7.01, 6.82, 6.74, 6.62, 6.47, 6.21, 5.43, 3.85, 3.14, 2.17, 2.12, 1.63, 1.22, 1.17, 0.85, 0.62, 0.44, 0.12; ^{13}C NMR ($CDCl_3$): δ = 166.9, 144.2, 139.9, 136.7, 134.5, 132.4, 132.3, 132.2, 130.8, 129.5, 129.2, 128.8, 128.7, 128.6, 128.4, 128.3, 127.4, 126.7, 125.9, 123.3, 117.7, 114.6, 36.0, 35.2, 33.4, 33.2, 31.6, 30.1, 29.5, 28.3, 28.2, 28.1, 27.9, 27.3, 27.1, 26.7, 26.6, 26.4, 26.1, 20.7, 18.6; ^{31}P NMR ($CDCl_3$): δ = 48.0, 43.6, 37.1, 32.5; anal. calcd. (%) for $C_{49}H_{59}ClNOPRu$ (845.51): C 69.61, H 7.03, N 1.66; found: C 69.54, H 7.04, N 1.82.

3c: ^1H NMR ($CDCl_3$): δ = 8.37, 7.70, 7.67, 7.51, 7.49, 7.38, 7.19, 7.12, 6.91, 6.86, 6.79, 6.59, 6.33, 5.51, 3.96, 3.27, 2.25, 2.21, 1.76, 1.35, 1.24, 0.95, 0.75, 0.57, 0.25; ^{13}C NMR ($CDCl_3$): δ = 296.2, 295.3, 167.0, 143.6, 139.9, 135.9, 135.8,

Table 4. ^1H and ^{13}C NMR assignments of the compounds **3a** and **3d** at 295 K in dichloromethane-d_2 and $CDCl_3$, respectively.[a]

Atom label	^1H (**3a**)	^{13}C (**3a**)	^1H (**3d**)	^{13}C (**3d**)
1	–	170.5	–	175.0
1	-	170.5	-	175.0
2	7.04	136.0	6.97	123.2
3	6.50	114.4	7.96	127.6
4	7.26-7.21	133.5	–	135.9
5	7.20	122.4	8.02	134.5
6	–	117.5	–	116.5
7	7.84	165.3	7.76	165.4
8	–	154.3	–	150.6; 139.2; 129.0;126.5; 126.0
9	7.26–7.21	128.9; 125.5; 117.3	7.45;7.22; 7.12	150.6; 139.2; 129.0;126.5; 126.0
10	7.26–7.21	128.9; 125.5; 117.3	7.45;7.22; 7.12	150.6; 139.2; 129.0;126.5; 126.0
11	7.26–7.21	128.9; 125.5; 117.3	7.45;7.22; 7.12	150.6; 139.2; 129.0;126.5; 126.0
12	7.30	129.4	7.45;7.22; 7.12	150.6; 139.2; 129.0;126.5; 126.0
13	–	131.2; 130.4	–	150.6; 139.2; 129.0;126.5; 126.0
14	2.42	33.1	–	299.2
15	–	292.8	6.70	136.1
16	6.88	136.6	–	142.0
17	–	139.6	–	142.6
18	–	140.9	6.95	117.8
19	7.40	129.1	–	128.6
20	6.81	124.7	7.16	129.4
21	7.26–7.21	128.9	8.27	128.2
22	8.38	128.2	–	138.8
23	–	131.8	–	135.2
24	–	127.4	7.56	126.2
25	7.71	126.3	7.30	129.2
26	7.36	129.0	7.43	128.5
27	7.51	128.0	–	
PCy_3	2.52	33.1	2.40	33.3
PCy_3	1.95–1.54	29,8; 29.3; 27.8	1.95–1.33	29.5; 27.9
PCy_3	1.30–1.23	26.6; 26.5	1.2–1.00	26.6

[a] The arbitrary numbering is depicted in Figure 1. Chemical shifts are quoted in ppm.

137.0, 132.2, 132.0, 131.5, 130.5, 129.3, 128.9, 128.5, 128.4, 128.3, 127.4, 126.5, 126.2, 123.0, 118.0, 117.4, 116.7, 35.7, 34.9, 33.5, 33.2, 31.8, 31.4, 29.9, 29.3, 28.0, 27.9, 27.8, 27.6, 27.2, 27.0, 26.8, 26.4, 26.1, 25.8, 20.4, 18.2; ^{31}P NMR ($CDCl_3$): $\delta = 44.2$; anal. calcd. (%) for $C_{48}H_{56}ClN_2O_3PRu$ (876.48): C 65.78, H 6.44, N 3.20; found: C 65.38, H 6.37, N 3.46.

3d: Anal. calcd. (%) for $C_{46}H_{51}Cl_2N_2O_3PRu$ (882.87): C 62.58, H 5.82, N 3.17; found: C 62.24, H 5.78, N 3.42.

3e: ^{1}H NMR ($CDCl_3$): $\delta = 8.98$, 8.32, 7.88, 7.71, 7.61, 7.31, 7.11, 7.04, 6.93, 6.78, 5.75, 4.22, 3.52, 2.55, 2.18, 1.84, 1.53, 1.16, 1.06, 0.82, 0.80, 0.24; ^{13}C NMR ($CDCl_3$): $\delta = 295.9$, 295.0, 174.8, 174.4, 167.2, 143.6, 140.0, 135.9, 135.8, 135.4, 135.0, 134.9, 132.2, 132.0, 131.1, 129.1, 128.9, 128.5, 128.4, 128.2, 128.1, 126.5, 123.0, 118.0, 117.5, 116.8, 35.7, 34.9, 33.5, 33.2, 32.0, 31.4, 29.9, 29.3, 28.0, 27.9, 27.8, 27.6, 27.2, 27.0, 26.8, 26.4, 26.1, 25.8, 21.0, 20.3, 18.1; ^{31}P NMR ($CDCl_3$): $\delta = 44.2$; anal. calcd. (%) for $C_{49}H_{58}ClN_2O_3PRu$ (890.50): C 66.09, H 6.56, N 3.15; found: C 65.93, H 6.53, N 3.15.

3f: ^{1}H NMR ($CDCl_3$): $\delta = 8.62$, 8.59, 7.57, 7.45, 7.36, 7.32, 7.30, 6.94, 6.68, 6.58, 6.41, 6.29, 6.23, 6.07, 5.88, 5.38, 3.38, 3.14, 2.92, 2.39, 2.13, 1.82, 1.53, 1.42, 1.17, 0.98, 0.69, 0.48, 0.36, 0.23, 0.19, 0.14; ^{13}C NMR ($CDCl_3$): $\delta = 295.2$, 295.0, 293.1, 293.0, 174.8, 168.1, 167.6, 148.8, 148.0, 144.9, 143.6, 141.8, 141.6, 141.1, 140.7, 140.6, 140.3, 140.2, 140.1, 139.4, 136.2, 136.0, 135.2, 135.1, 134.0, 132.2, 132.1, 131.9, 130.0, 129.8, 129.3, 129.2, 129.1, 128.8, 128.6, 128.3, 127.0, 126.4, 126.3, 126.0, 123.4, 123.2, 123.1, 122.9, 122.5, 118.0, 117.3, 116.5, 116.4, 35.9, 35.0, 33.6, 33.5, 33.3, 33.2, 31.6, 30.6, 30.0, 29.5, 29.4, 28.1, 27.9, 27.8, 27.6, 27.4, 27.3, 27.0, 26.9, 26.5, 26.2, 25.6, 25.3, 23.6, 22.9, 22.8, 22.7, 21.3, 14.1; ^{31}P NMR ($CDCl_3$): $\delta = 48.1$, 47.22, 46.83; anal. calcd. (%) for $C_{52}H_{64}ClN_2O_3PRu$ (932.58): C 66.97, H 6.92, N 3.00; found: C 66.78, H 7.36, N 2.37.

Acknowledgements

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