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The Influence of Phosphane Ligands on the Versatility of Ruthenium–Indenylidene Complexes in Metathesis

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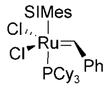
Abstract: The aim of the present study is to develop readily available and stable pre-catalysts that could be easily prepared on large scale from simple starting materials. Based on the hypothesis that substitution of classical PCy_3 with phosphanes of varying electron-donating properties could be a straightforward manner to improve catalytic activity, a methodical study dealing with the effect of phosphane fine-tuning in ruthenium–indenylidene catalysts was performed. Challenged to establish how the electronic properties of *para*-substituted phosphane ligands translate into catalyst activity, the versatile behaviour of these new ruthenium–indenylidene complexes was investigated for a number of metathesis reactions.

Keywords: N-heterocyclic carbenes · metathesis · phosphanes · ruthenium–indenylidene

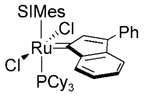
Introduction

In a quest to synthesise ever better performing, well defined, ruthenium-based catalysts for olefin metathesis,[1] design efforts have focused on modulation of the organic fragments around the Ru centre. The first significant breakthrough in this area appeared with the introduction of N-heterocyclic carbenes (NHC)[2] on ruthenium–benzylidene complexes by Herrmann et al. in 1998.[3] Although they were found in some instances to be more active, these two NHC-containing complexes were in most cases less efficient than their bisphosphane analogues. The real breakthrough, however, came with the synthesis of more active mixed phosphane–NHC complexes, so-called second-generation catalysts, such as **1**[4].



1

Ru–benzylidene



2

Ru–indenylidene

These early examples clearly illustrate the crucial role played by the NHC ligand.[5,6] Since then, numerous pre-catalysts have permitted the evolution of metathesis reactions into a powerful carbon–carbon double-bond-forming tool and as a consequence numerous industrial and therapeutic applications have benefited from this success story.[7]

Mechanistic and computational studies of **1** and the related complexes $[Ru(X)_2(SIMes)(PR_3)({=}CHR)]$ (SIMes = *N*,*N′*-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, X = halogen, PR_3 = aryl- or alkylphosphane, =CHR = alkylidene) have revealed that ancillary ligands dramatically affect the rates of initiation and propagation in olefin metathesis reactions.[8,9] Recently, variations on the core architecture of ruthenium complexes have consisted mainly in the introduction of new NHCs[6,10] and in the modification of the alkylidene ligand[11] in order to produce new metathesis catalysts with improved stability, activity, selectivity and functional group tolerance.[12] Among the latter modification type, ruthenium–indenylidene complexes, such as **2**, have emerged

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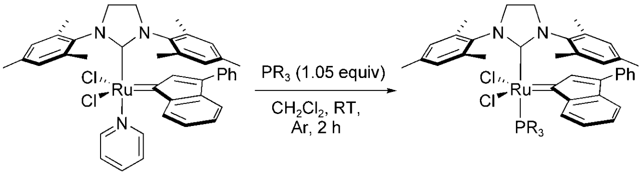
as efficient tools for olefin metathesis transformations and are an attractive alternative to benzylidene congeners.[13] These pre-catalysts are straightforwardly synthesised in large scale with readily available and stable precursors, and demonstrate an enhanced stability to harsh reaction conditions and exhibit catalytic activity equal to/or better than their benzylidene counterparts.[14] Similarly to other ruthenium families, the main research activity in ruthenium–indenylidene chemistry has focused on modifying the carbene moiety,[13,15] or on substituting the phosphane by other ligands, such as, for example, Schiff bases[16] or pyridine,[17] underlining the poor attention paid to the effects of varying the phosphane ligand. This is intriguing as, ever since Tolman quantified their electronic and steric parameters,[18] the variation of phosphane ligands on metal centres has become a valuable approach to modulate the catalytic activity of catalytic systems[19] and metathesis is no exception. By using magnetisation transfer experiments to investigate the first step of the olefin metathesis mechanism, studies of Grubbs et al. have demonstrated that changing the phosphane bound to the ruthenium centre affects phosphane dissociation and recoordination of free PR_3 to ruthenium and, therefore, has a profound and complex influence on the catalytic activity.[8b,20] Hence, first-generation catalysts require more electron-donating phosphanes,[21] whereas second-generation catalysts benefit from the use of poorer coordinating ligands.[8,20] On the other hand, although first-generation catalysts have higher phosphane exchange rates than second-generation complexes, the latter are more active. This observation was rationalised by the higher affinity of NHC-containing catalysts for olefin coordination compared to rebinding of the phosphane leading to a higher rate of propagation into the catalytic cycle. Earlier work from our group on first- and second-generation benzylidene systems showed that replacing tricyclohexylphosphane (PCy_3) with triphenylphosphane (PPh_3)[5a] or phosphabicyclononane (Phoban)[22] resulted in more rapid ring-closing metathesis (RCM). Nevertheless, even though faster phosphane exchange was observed with PPh_3,[20] its high lability and its lack of bulkiness translated into a decrease in stability of the corresponding complex.[5a] Thus, PCy_3 still appeared as a more viable ligand and has been predominantly used in spite of its cost. Recently, Verpoort and co-workers have reported a comparative study of ruthenium–indenylidene complexes **2**, **3** and **4** (Table 1) versus first-, second- and third-generation Grubbs' catalysts.[23] The replacement of the PCy_3 ligand with the more labile PPh_3 ligand drastically improved the catalytic performance as **4** displayed similar activities as second-generation catalysts for RCM and initiated ring-opening metathesis polymerisation (ROMP) significantly faster. This is in line with our original observations on the second-generation ruthenium–benzylidene system.

Table 1. Synthesis of phosphane-tuned SIMes–Ru–indenylidene complexes.



3 → **4–9**

Complex	PR_3	Yield [%]	σ_P[a]	pK_a[a]
4	PPh_3	78	0	2.73
5	$P(p\text{-}CH_3OC_6H_4)_3$	75	−0.27	4.57
6	$P(p\text{-}CH_3C_6H_4)_3$	77	−0.17	3.84
7	$P(p\text{-}FC_6H_4)_3$	90	0.06	1.97
8	$P(p\text{-}ClC_6H_4)_3$	90	0.23	1.03
9	$P(p\text{-}CF_3C_6H_4)_3$	73	0.52	[b]

[a] Values taken from reference [20]. [b] Unknown.

The choice of the ancillary ligand remains a crucial parameter in finding the adequate compromise between lability of the dissociating ligand and stabilisation of the pre-catalyst. The aforementioned modifications to NHC ligands or alkylidene moiety often involve complicated and expensive multistep synthesis with low overall yields. As part of our ongoing research towards the development of more active metathesis systems, we aimed to develop readily available and stable pre-catalysts that could be prepared easily on large scale and did not require elaborate and/or expensive starting materials. Based on the hypothesis that the substitution of classical PCy_3 by phosphanes with different electron-donating properties could be an efficient and easy way to improve the catalytic activity, we also decided to explore in a methodical approach the effect of phosphane modification in ruthenium–indenylidene catalysts. Challenged to establish how the electronic properties of *para*-substituted phosphane ligands translate into catalyst activity, the versatile behaviour of these new ruthenium–indenylidene complexes was investigated for a number of metathesis reactions: RCM of dienes or enynes, ring-rearrangement metathesis (RRM), cross-metathesis (CM) and ROMP.

Results and Discussion

Synthesis and structural characterisation: Keeping in mind that increased initiation would permit higher catalysis rate, lower catalyst loadings and reaction temperatures, five new ruthenium–indenylidene complexes were synthesised and fully characterised. These have the general formula $[RuCl_2(SIMes)(PR_3)(Ind)]$ (Ind = 3-phenylindenylid-1-ene) and bear less electron-donating phosphanes than PCy_3. A *para*-substituted triphenylphosphane ligand series was selected as it possesses members displaying different electronic properties that should influence the phosphane dissociation/rebinding rates (Table 1). Of note, these phosphanes all have the same cone angle of 145°, whereas PCy_3 has a cone angle of 170°.

Ruthenium–mono pyridine adducts have proven to be versatile precursors in the synthesis of new complexes by facile ligand substitution reactions.[15b,20,23,24] Starting from the commercially available $[RuCl_2(SIMes)(pyridine)(Ind)]$ (**3**), complexes **4**–**9** were obtained in one step through exchange of pyridine by the appropriate phosphane at room temperature (Table 1). They were isolated on scales that reached up to 1.5 g with good yields and high purity by simple precipitation and/or washing. Of note, the same previously reported steric and electronic limitations were encountered while attempting to use phosphane ligands that are bulky (such as *ortho*-substituted phosphanes) or electron poor such as $P(C_6F_5)_3$.[24] ^1H NMR spectra of **4**–**9** showed a characteristic resonance at $\delta = 4$ ppm for the imidazolidine protons. ^{13}C NMR spectra displayed characteristic low-field resonances for N-heterocylic carbenic carbons around $\delta = 215$ ppm with $^2J(C,P)$ between 89 and 86 Hz that clearly indicated a mutually *trans* arrangement of the phosphane and NHC ligands. In each case, the signal at $\delta = 300$ ppm is characteristic of a Ru=C carbenic carbon with $^2J(C,P) = 13$ Hz, indicating, this time, relative *cis* arrangement to the phosphane. ^{31}P NMR spectra showed single resonances between $\delta = 22$ and 27 ppm. Elemental analysis also confirmed the composition and bulk purity of the new compounds. Complexes **4**–**9** were found to be perfectly stable in the solid state and could be easily handled in air. In [D$_2$]dichloromethane (CD_2Cl_2) under N_2 at 40 °C, analysis of the NMR spectra showed that all complexes were stable for more than 4 h and complete decomposition was not observed after 24 h. In [D$_8$]toluene under N_2 at 80 °C, major degradation occurred within 1 h and was complete after 4 h for **4**, **5**, **6** and **7**, but not for complexes **8** and **9** that showed improved stability and were not entirely degraded after 4 h under these conditions. Complexes **8** and **9** could also be kept several days in CD_2Cl_2 under N_2 at room temperature without any sign of decomposition.

The structures of the Ru–indenylidene complexes **5** and **6** were unambiguously confirmed by X-ray crystallography and are graphically presented in Figures 1 and 2 with a selection of bond distances and angles. The solid-state structures of **5** and **6** are quite similar, despite containing different phosphane ligands. Bond distances were all within the expected range of similar Ru–benzylidene,[20] including **1**, and Ru–indenylidene complexes[15a] ($Ru{-}C^{NHC} \approx 2.09$ Å, $Ru{-}C^{Ind} \approx 1.86$ Å). They show the expected distorted square-pyramidal geometry around the metal centre with a slight tilt of the NHC (C(1)-Ru(1)-P(1) = 164 and 162°, respectively). Bond angles in these SIMes-containing Ru–indenylidenes were more closely related to those reported for $[RuCl_2(SIPr)(PCy_3)(Ind)]$[15a] bearing the 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr) ligand than for those found in SIMes–Ru–benzylidenes,[20] underlining the important effect of the alkylidene group on the geometry of the complex.

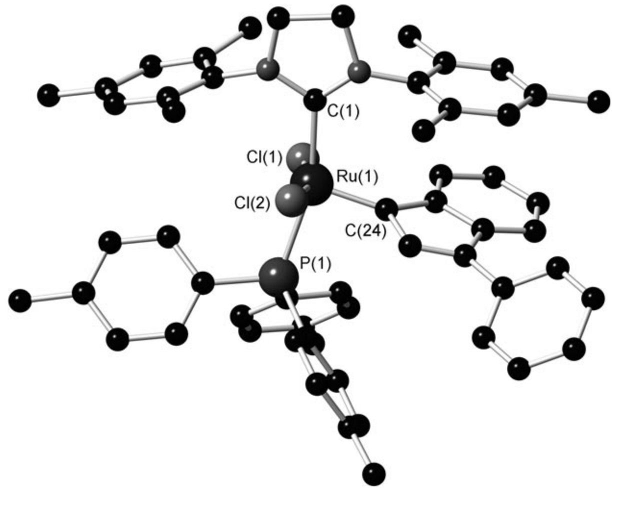


Figure 1. Ball-and-stick representation of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)−C(24) 1.870(5), Ru(1)−C(1) 2.086(5), Ru(1)−P(1) 2.3975(15), Ru(1)−Cl(1) 2.3619(16), Ru(1)−Cl(2) 2.4040(16), C(24)-Ru(1)-C(1) 104.3(2), C(1)-Ru(1)-P(1) 164.73(15), Cl(1)-Ru(1)-Cl(2) 161.28(5).

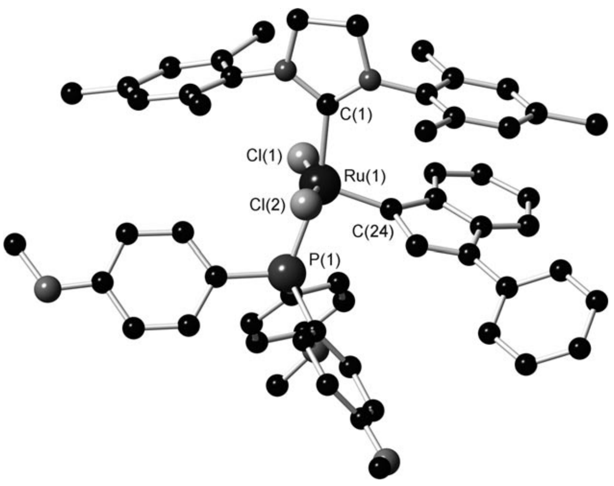
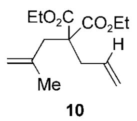
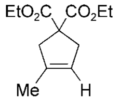
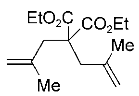
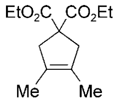


Figure 2. Ball-and-stick representation of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)−C(24) 1.867(6), Ru(1)−C(1) 2.090(6), Ru(1)−P(1) 2.4069(16), Ru(1)−Cl(1) 2.3750(17), Ru(1)−Cl(2) 2.4035(18); C(24)-Ru(1)-C(1) 105.4(2), C(1)-Ru(1)-P(1) 162.71(17), Cl(1)-Ru(1)-Cl(2) 162.84(5).

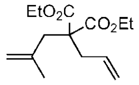
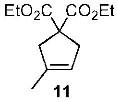
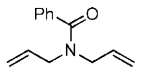
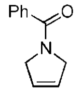
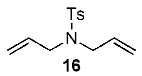
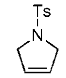
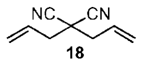
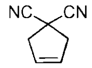
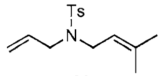
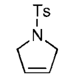
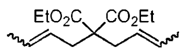
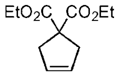
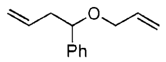
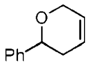
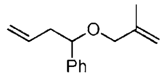
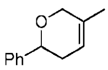
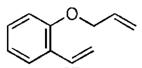
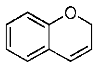
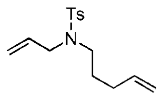
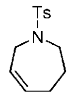
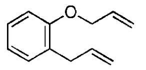
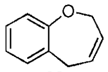
Catalytic activity in ring-closing metathesis (RCM): The reactivity of the catalysts series **4**–**9** was investigated for a number of metathesis reactions (RCM, RRM, CM and ROMP) and compared to the second-generation benzylidene catalyst **1**, the second-generation indenylidene catalyst **2** and the third-generation catalyst **3**. Benchmarks, as well as, original substrates featuring diverse functional groups and steric encumbrance were studied. Catalytic activities of **1**–**9** were first evaluated in the ring-closing metathesis of allyl malonate substrates with low (**10**) or high (**12**) steric hindrance (Table 2). As expected for RCM of **10**, the novel catalysts **4**–**9** bearing more labile phosphanes were all more active than the commercially available complexes **1**, **2** and **3**, affording complete conversion to **11** in shorter reaction times. Within the indenylidene class, a drastic difference in term of efficiency was observed between alkyl (**2**, 82 % in 5 h) and aryl phosphanes (**4**–**9**, >99 % in 0.5–1.5 h). Hence, it appears clear that dissociation/rebinding rates of aryl phosphanes, associated to their stereoelectronic parameters, allow for more rapid kinetics in RCM. The catalytic activity

Table 2. Comparison of pre-catalysts **1**–**9** in ring closing metathesis with model substrates.[a]

Entry	Substrate	Product	[Ru]	t [h]	Conv. [%]
1	 **10**	 **11**	**1**	1.5	>99
2			**2**	5	82
3			**3**	5	38
4			**4**	0.75	>99
5			**5**	1.5	>99
6			**6**	1.25	>99
7			**7**	0.75	>99
8			**8**	0.75	>99
9			**9**	0.5	>99
10	 **12**	 **13**	**1**		30
11			**2**		58
12			**3**		10
13			**4**		18
14			**5**	5[b]	22
15			**6**		21
16			**7**		22
17			**8**		22
18			**9**		23

[a] Reaction conditions: substrate (0.5 mmol), [Ru] complex (1 mol %), CH_2Cl_2 (0.1 M), N_2, RT. [b] [Ru] complex (5 mol %), toluene (0.1 M), N_2, 80 °C.

Table 3. Catalytic performance of complexes **4** and **9** in RCM of dienes.[a]

Entry	Substrate	Product	[Ru]	t [h]	Yield [%]
1	 **10**	 **11**	**4**	0.75	97
2			**9**	0.5	97
3	 **14**	 **15**	**4**	0.5	98
4			**9**	0.25	98
5	 **16**	 **17**	**4**	1	95
6			**9**	0.5	95
7	 **18**	 **19**	**4**	3	82
8			**9**	1	84
9	 **20**	 **17**	**4**	0.25	95
10			**9**	0.25	95
11	 **21**	 **22**	**4**	1.5	95
12			**9**	1	94
13	 **23**	 **24**	**4**	1.5	93
14			**9**	0.75	94
15	 **25**	 **26**	**4**	1	90
16			**9**	0.5	91
17	 **27**	 **28**	**4**	1.0	97
18			**9**	0.5	97
19	 **29**	 **30**	**4**	1.5	95
20			**9**	0.75	96
21	 **31**	 **32**	**4**	3	91[b]
22			**9**	1.5	92[b]

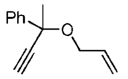
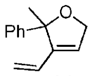
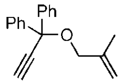
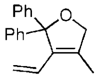
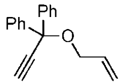
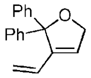
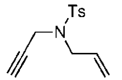
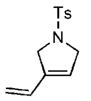
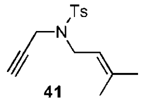
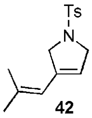
[a] Reaction conditions: substrate (0.5 mmol), [Ru] complex (1 mol %), CH_2Cl_2 (0.1 M), N_2, RT. [b] CH_2Cl_2 (0.05 M).

found is the following: **2** (Cy) < **5** (OCH_3) < **6** (CH_3) < **4** (H) ≈ **7**(F) ≈ **8** (Cl) < **9** (CF_3) and correlates with the decreasing phosphane pK_a or the increasing Hammett constant (σ_p) of the aryl substituent.[2] Complex **9** bearing the extremely electron-poor phosphane $P(p\text{-}CF_3C_6H_4)_3$ was the most active pre-catalyst for RCM of **10**. Interestingly, an opposite trend was obtained in the case of the encumbered substrate **12**, since PCy_3-containing **2** afforded the highest conversion (58 %) outperforming by far its benzylidene counterpart **1** (30 %). The higher thermal stability of **2** is no doubt the cause for the ability to perform under harsh reaction conditions. Of note, the successful formation of challenging tetrasubstituted olefins is usually reached with Hoveyda–Grubbs catalysts requiring multistep and low-yielding synthesis.[10e,25] All triarylphosphane-bearing complexes (**4**–**9**) exhibited the same low reactivity at this temperature. Even though third-generation catalyst **3** with an indenylidene scaffold has been reported to surpass the best third-generation Grubbs catalyst, its performance in RCM is quite inferior to second-generation complexes.[23]

Highly active complex **9** was then subjected to a representative set of RCM reactions in order to study its scope and compatibility with functional groups or ring sizes (Table 3). For comparison, metathesis reactions were also accomplished with **4** bearing the economical PPh_3. By using only 1 mol % of ruthenium at room temperature, all dienes were completely converted to the corresponding cyclic product with excellent yields (82–98 %) in short reaction times (0.25–3 h). The effect of the more labile $P(p\text{-}CF_3C_6H_4)_3$ ligand on the catalytic activity translated into a more active complex **9** that performed twice as fast as **4**. Ester, ether, amine, nitrile and amide functional groups were well tolerated and did not affect the catalytic outcome. Complete conversions to di- or trisubstituted cycloalkenes were obtained starting either from terminal, 1,2-, 2,2′-disubstituted or 1,1′,2-trisubstituted olefins. As generally encountered in RCM, the only problematic substrates were tetrasubstituted dienes that lead to poor yields (Table 2). The straightforward formation of five-, six- and seven-membered rings that are mono- or bicyclic was also achieved. During the progress of the study of the scope, the formation of self-cross-metathesis products was not observed. Nonetheless, RCM of diene **31** leading to the seven-membered bicyclic ring **32** had to be carried out under higher dilution conditions to avoid polymer formation (Table 3, entries 21 and 22).

The reactivity profile of pre-catalysts **4**–**9** also proved to be very attractive in the ring-closing metathesis of enynes as outlined in Table 4. Comparison of substrates **33** and more hindered **35** revealed analogies to the RCM of dienes (Table 4, entries 1–18). All triarylphosphane-bearing com-

Table 4. Catalytic performance of pre-catalysts **1**–**9** in RCM of enynes.[a]

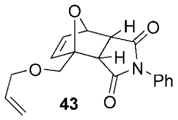
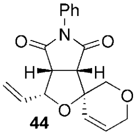
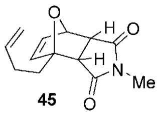
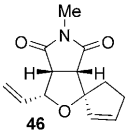
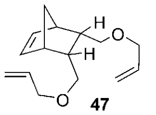
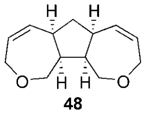
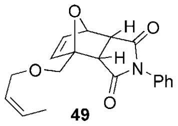
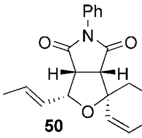
Entry	Substrate	Product	[Ru]	t [h]	Conv. (Yield) [%]
1	 **33**	 **34**	**1**	0.5	>99
2			**2**	24	63
3			**3**	24	12
4			**4**	0.75	>99 (95)
5			**5**	3	>99
6			**6**	0.75	>99
7			**7**	1.25	>99
8			**8**	0.75	>99
9			**9**	0.3	>99 (96)
10	 **35**	 **36**	**1**	5[b]	75
11			**2**		74
12			**3**		5
13			**4**		38 (32)
14			**5**		42
15			**6**		37
16			**7**		22
17			**8**		55
18			**9**		52 (50)
19	 **37**	 **38**	**4**	0.5	>99 (95)
20			**9**	0.3	>99 (95)
21	 **39**	 **40**	**4**	24	<2
22			**9**	24	<2
23	 **41**	 **42**	**4**	5	57 (53)
24			**9**	5	40 (37)

[a] Reaction conditions: substrate (0.5 mmol), [Ru] complex (1 mol%), CH_2Cl_2 (0.1 M), N_2, RT. [b] [Ru] complex (5 mol%), toluene (0.1 M), 80 °C.

plexes **4**–**9**, particularly **9**, performed significantly faster and more competently than **2** at room temperature whereas the stability of tricyclohexylphosphane benefited **2** under harsher conditions. Interestingly, the alkylidene appears to also play a crucial role in enabling smooth reactions, as Ru–benzylidene **1** (Table 4, entry 1) performed much better than **2** (Table 4, entry 2). Despite complex **1** contains PCy_3, its efficiency was found comparable to the arylphosphane complexes. In the case of the encumbered substrate **35**, no performance difference was observed between the two catalysts (Table 4, entries 10 and 11). The reaction scope of **4** and **9** was then extended to the synthesis of selected exocyclic 1,3-dienes. For substrates **33** and **37**, excellent yields were obtained at room temperature in 20 min by using 1 mol% of **9** (Table 4, entries 9 and 20). On the other hand, the cyclisation of **39** was found to be problematic, and the desired product could not be isolated (Table 4, entries 21 and 22), whereas RCM carried out on a similar substrate **41**, possessing two additional methyl groups, by using the same reaction conditions led to the formation of 53% and 37% of **42**, respectively (Table 4, entries 23 and 24). Surprisingly, in this latter case, complex **4** performed better than **9**.

Ring-rearrangement metathesis (RRM): Ring-rearrangement metathesis, combining ring-opening/ring-closing metathesis steps, allows for the straightforward construction of complex scaffolds.[26] Ruthenium–indenylidene complexes were already established in RRM reactions allowing for a large spectrum of rearrangements.[27] A brief examination of catalyst activity revealed that **9** lead to the best performance. Oxabicyclo[2.2.1]heptene and norbornene *exo*-derivatives were subjected to ring rearrangement by using 1 mol% of **4** or **9** in a diluted solution (Table 5). To avoid polymerisation during low-pressure solvent reduction, the completed reactions were quenched with ethyl vinyl ether.[28] The formation of five- and six-membered rings was easily achieved in good yields and short reaction times (Table 5, entries 1–4). On the other hand, RRM leading to the seven-membered ring product **48** was hindered by polymerisation side reactions (Table 5, entries 5 and 6). In this particular case, pre-catalyst **4**, which has a lower activity in RRM, permitted a reduction in polymer formation by slowing the reaction rate (Table 5, entry 5). Substitution of the exocyclic C=C bond engendered a significant increase in the reaction time leading to a decrease in the yield (Table 5, entries 7 and 8 vs. entries 1 and 2).

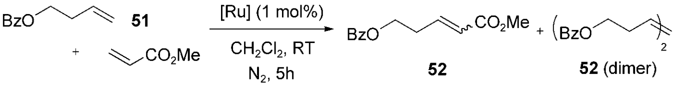
Table 5. Catalytic performance of pre-catalysts **4** and **9** in RRM.[a]

Entry	Substrate	Product	[Ru]	t [h]	Yield [%]
1			**4**	5	80
2			**9**	1.5	92
3			**4**	0.25	91
4			**9**	0.25	96
5			**4**	5	56[b]
6			**9**	1	42[b]
7			**4**	5	53[c]
8			**9**	5	66[c]

[a] Reaction conditions: substrate (0.5 mmol), [Ru] complex (1 mol%), CH_2Cl_2 (0.01 M), N_2, RT. [b] Polymer accounts for mass balance. [c] Reaction products are an inseparable mixture of the expected product and the starting material. ^1H NMR conversion.

Cross-metathesis (CM): Complexes **1**–**9** (1 mol%) were then compared in the cross-metathesis reaction of but-3-enyl benzoate (**51**) with 2 equivalents of methyl acrylate at room temperature (Table 6). Once again, our series of triarylphosphane-containing Ru catalysts **4**–**9** was more active and stereoselective than complexes **1**, **2** and **3**. The exchange of

Table 6. Comparison of pre-catalysts **1–9** in cross-metathesis.[a]



[Ru]	PR_3	Conv. [%]	**52** [%][b]	*E*/*Z* ratio	**52** (dimer) [%][b]
1	PCy_3	80	69	>20:1	11
2	PCy_3	29	26	16:1	3
3	–	8	5	7:1	3
4	PPh_3	80	73	>20:1	7
5	$P(p\text{-}CH_3OC_6H_4)_3$	77	60	>20:1	17
6	$P(p\text{-}CH_3C_6H_4)_3$	82	74	>20:1	8
7	$P(p\text{-}FC_6H_4)_3$	81	74	>20:1	7
8	$P(p\text{-}ClC_6H_4)_3$	81	77	>20:1	4
9	$P(p\text{-}CF_3C_6H_4)_3$	75	69	>20:1	6

[a] Reaction conditions: substrate **51** (0.5 mmol), methyl acrylate (1 mmol), [Ru] (1 mol%), CH_2Cl_2 (0.1 M), N_2, RT, 5 h. [b] ^1H NMR conversion.

PCy_3 for a more labile phosphane provided a radical improvement in terms of conversion and stereoselectivity. Although CM by using **1** or **4–9** resulted in similar high conversions of the starting material, a favoured distribution for the cross-metathesis product **52** over the self-metathesis dimer of **52** was found with Ru–indenylidenes (except with **5**).

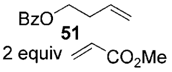
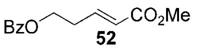
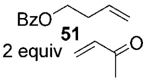
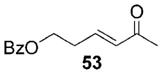
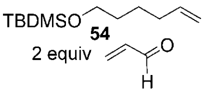
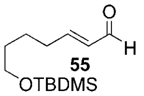
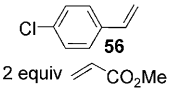
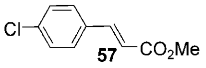
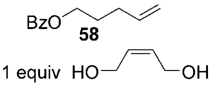
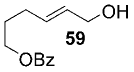
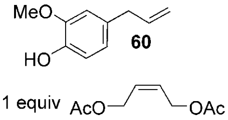
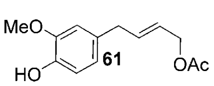
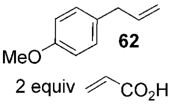
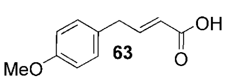
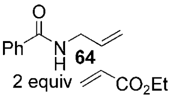
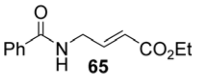
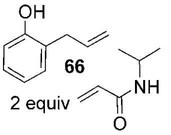
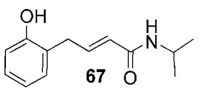
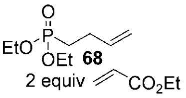
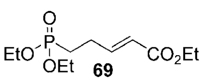
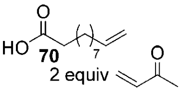
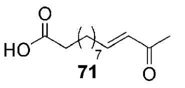
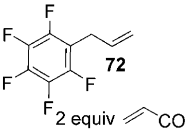
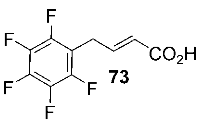
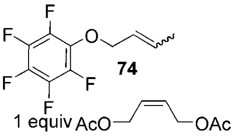
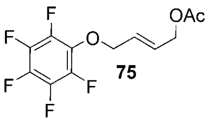
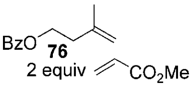
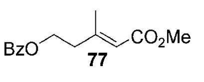
Unexpectedly, the activity trend found for CM is: **2** (Cy) < **5** (OCH_3) < **9** (CF_3) < **4** (H) < **6** (CH_3) ≈ **7** (F) < **8** (Cl), which does not fit to the electronic properties of the phosphanes and strongly differed with the trend observed in RCM. [$RuCl_2$(SIMes)$P(p\text{-}ClC_6H_4)_3$(Ind)] (**8**) was, under the studied conditions, the most efficient and selective pre-catalyst within the series. The overall stability of the catalyst in the reaction medium is probably the most important factor dictating catalyst efficiency in such time-demanding CM.

We then extended the scope of cross-metathesis reactions to a wider range of benchmark and original substrates by using 1 mol% of **4** or **8** under mild conditions (Table 7). Special attention was paid to functional group tolerance, as well as, to the influence of chain length and olefin substitution. Optimisation of the reaction conditions revealed that the coupling preceded better in more concentrated solution and favoured the CM product. Hence, compared to conversions reported in Table 6, cross-product **52** was obtained with 82 and 90% yields by using **4** and **8**, respectively, in a 1 M dichloromethane solution and only traces of **51** or the dimer of **52** were observed (Table 7, entries 1 and 2). As for the RCM, the Ru–indenylidene catalysts were robust and tolerant to several polar substituents including esters, silyl ethers, ethers, aryl halides, alcohols, acids and phosphonates, leading to the synthesis of the corresponding products in moderate to good yields. Unfortunately, compound **65** bearing an unprotected amide was produced in low yields along with a significant amount of dimer (Table 7, entries 15 and 16). The examination of several unactivated olefin partners bearing various functionalities indicated a strong substrate dependence of our catalytic systems. Whereas ester-, ketone-, alcohol-, acetate- and acid-containing olefins led to good yields and high *E*/*Z* ratios, the coupling of aldehyde (Table 7, entries 5 and 6) or amide groups (Table 7, entries 17 and 18) conjugated to the C=C double bond were found more problematic. The use of cross-metathesis dimers as partners was also successful (Table 7, entries 9–12). Even the 1,2-disubstituted olefin **74** could be coupled (Table 7, entries 25 and 26), CM of the more challenging ψ,ψ-disubstituted olefin **76** with methyl acrylate failed with both catalysts and only starting materials were recovered even when the reaction was conducted under harsher reaction conditions (Table 7, entries 27 and 28). Finally, comparison of pre-catalysts **4** and **8** on the entire screening scope shows that both complexes are equipotent for cross-metathesis reactions. In all cases, similar yields were achieved in the same time range and with high regioselectivity, underlining the weak influence of the nature of the phosphane in CM compared to its influence in RCM.

Ring-opening metathesis polymerisation (ROMP): Improved initiation has significant implications in metathesis polymerisation giving access to higher control over polymer molecular weights, therefore, the scope of **4–9** as initiators in ring-opening metathesis polymerisation was evaluated. For this purpose, we used two norbornene derivatives, namely dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**78**) and 5,6-bis(methoxymethyl)bicyclo[2.2.1]hept-2-ene (**79**). Catalysts (or initiators, in the polymerisation jargon) **2** and **3** were selected as reference initiators because of their extremely different initiation behaviour, providing a reasonable benchmark for all initiators under investigation. In a first approximation, the average number molecular weight (M_n) is determined by the ratio of initiation rate to propagation rate (k_i/k_p) of a given initiator and monomer combination. Provided that no secondary metathesis reaction affects the double bonds of the formed polymer (i.e., back-biting), determination of M_n will allow for an indirect, qualitative comparison of k_i/k_p for the initiators under investigation.[29] For example, **3** shows fast and complete initiation with most monomers (estimation for $k_i/k_p > 10–1000$ depending on the monomer) and thus, every initiator molecule starts a growing chain. Therefore, polymers characterised by low M_n values and low polydispersity indices (PDIs) are obtained.[30] In contrast, slow and incomplete initiation is a characteristic feature of **2** in ROMP (estimation for $k_i/k_p < 1–0.01$ depending on the monomer), resulting in high M_n and high PDI values of the corresponding polymers.[30]

The initiator **2–9** (1 equiv) were treated with monomers **78** or **79** (300 equiv) and results are summarised in Table 8 and Figure 3. All polymerisations were completed in 1 h; except for catalysts **5** (2 h) and **9** (30 min). M_n values range from 102 100–356 200 $g\,mol^{-1}$ and from 88 700–302 800 $g\,mol^{-1}$ for polymers obtained from monomer **78** and **79**, respectively. A correlation between donor property of the phosphane (expressed by their electronegativity χ or Hammett constant σ_p)[31,20] and the experimental M_n values are depicted in Figure 4 and Figure 5. Correlations in the linear fits are not perfect but show the same general trends for both monomers, confirming the above-established trend

Table 7. Scope of cross-metathesis reactions for pre-catalysts **4** and **8**.[a]

Entry	Substrate	Product	[Ru]	t [h]	Yield [%]	E/Z ratio	Yield (dimer) [%]
1 2	 **51** 2 equiv	 **52**	**4** **8**	2 2	82 90	>20:1 >20:1	– –
3 4	 **51** 2 equiv	 **53**	**4** **8**	7 7	66 69	>20:1 >20:1	– –
5 6	 **54** 2 equiv	 **55**	**4** **8**	2 2	25 26	>20:1 >20:1	– –
7 8	 **56** 2 equiv	 **57**	**4** **8**	3 3	50 52	>20:1 >20:1	39 42
9 10	 **58** 1 equiv	 **59**	**4** **8**	3 3	65 63	9:1 9:1	– –
11 12	 **60** 1 equiv	 **61**	**4** **8**	1 1	71 74	9:1 9:1	19 26
13 14	 **62** 2 equiv	 **63**	**4** **8**	3 3	76 72	>20:1 >20:1	16 16
15 16	 **64** 2 equiv	 **65**	**4** **8**	2 2	3 10	>20:1 >20:1	10 23
17 18	 **66** 2 equiv	 **67**	**4** **8**	2 2	23 20	8:2 8:2	<2 <2
19 20	 **68** 2 equiv	 **69**	**4** **8**	3 3	75 76	>20:1 >20:1	25 24
21 22	 **70** 2 equiv	 **71**	**4** **8**	2 2	84 81	>20:1 >20:1	– –
23 24	 **72** 2 equiv	 **73**	**4** **8**	3 3	35 33	>20:1 >20:1	32 27
25 26	 **74** 1 equiv	 **75**	**4** **8**	2 2	58 50	>20:1 >20:1	21 21
27[b] 28[b]	 **76** 2 equiv	 **77**	**4** **8**	5 5	– –	– –	– –

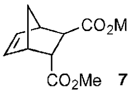
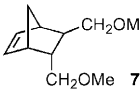
[a] Reaction conditions: substrate (0.5 mmol), cross partner (1–2 equiv), [Ru] (1 mol%), CH_2Cl_2 (1 M), N_2, RT.[b] [Ru] (5 mol%), toluene (0.1 M), 80 °C.

for RCM. Electron-poor PPh_3 derivatives show an easier dissociation, leading to high initiation rates, whereas complexes bearing electron-rich phosphane ligands exhibit lower initiation rates. This trend is also illustrated by the PDI values of the polymers. Electron-rich phosphane-bearing complexes afford polymers with high PDIs, whereas the PDI values decrease with an increasing χ of the phosphane.[30] All initiators under investigation showed improved initiation efficiency when compared to **2**, which bears PCy_3, and produce polymers with lower M_n and PDI values with both monomers (see Table 8 and Figure 3).[30] Complex **9** featuring the most electron-withdrawing group, that is, the CF_3 group, showed the best results. Regardless of the phopshane used, none of the complexes under investigation outperform the pyridine bearing initiator **3** in this respect. The presented results are in line with previous work carried out by Grubbs et al. who compared initiation constants in polymerisation of 1,4-cyclooctadiene (COD) with analogous benzylidene complexes.[32]

Conclusion

It is now well established that there is no universal catalyst for all categories of metathesis reactions. Considering the substrate dependence on catalysis, we investigated various phosphane-bearing ruthenium–indenylidene complexes in model reactions and examined which was their preferred niche. By using a simple method to modify the phosphane around the SIMes–Ru–indenylidene scaffold, a toolbox of catalysts featuring different stability, dissociation rate and activity in olefin metathesis was readily achieved. As an overall trend, $[RuCl_2(SIMes)\{P(p\text{-}CF_3C_6H_4)_3\}(Ind)]$ bearing an extremely electron-poor phosphane was found to be the most active catalyst for poorly hindered substrates in diene and enyne RCM, RRM and ROMP, whereas

Table 8. Electronic parameters (electronegativity, χ) of the phosphane ligands and results from ROMP of monomers **78** and **79**.[a]

		 **78**			 **79**		
[Ru]	χ	M_n[c]	PDI[c]	Yield [%][b]	M_n[c]	PDI[c]	Yield [%][b]
2	1.4	654400	2.0	89	967200	2.3	87
3	n.a.	45400	1.1	72	64700	1.1	74
4	13.25	155000	1.4	74	177800	1.4	66
5	10.5	356200	1.5	84	302800	1.8	85
6	11.5	273900	1.5	78	296000	1.5	86
7	17.5	151400	1.3	61	170200	1.4	96
8	16.8	129200	1.3	87	140000	1.4	70
9	20.5	102100	1.3	67	88700	1.3	68

[a] Reaction conditions: $c_{Mon}=0.2\ mol\,L^{-1}$, monomer/initiator=300:1, CH_2Cl_2, RT, quenching with ethyl vinyl ether. [b] Isolated yield after repeated precipitation from methanol. [c] Determined by GPC relative to polystyrene standards, THF.

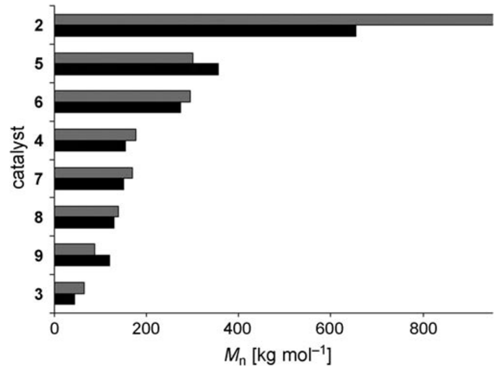


Figure 3. M_n values of the polymers obtained from **78** (black bars) and **79** (grey bars) by using initiators **2**–**9**.

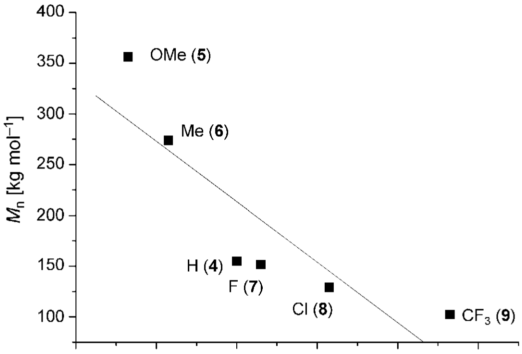


Figure 4. Correlation between the Hammett constant (σ_p) of the phosphane substituent and the M_n values of the polymers obtained from **78**.

its bulkier PCy_3-containing congener was highly efficient for encumbered substrates. On the other hand, in cross-metathesis similar conversions were achieved by using the new series of catalysts. [$RuCl_2$(SIMes)(PPh_3)(Ind)] appeared as middle-of-the-road catalyst giving good results in all olefin reaction types examined. Since such a significant effect is obtained by simply modulating the *para*-functional group of the phenyl group on a triphenylphosphane scaffold, we are currently examining the effects of further modifications on this and related architectures.

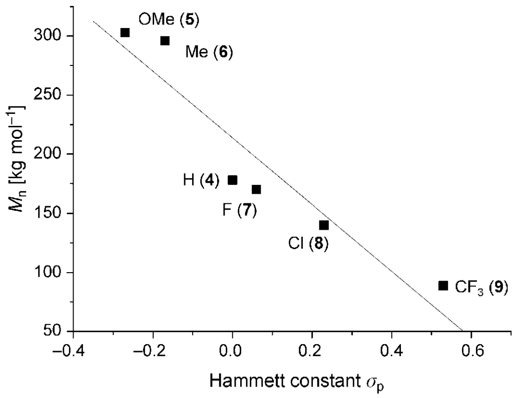


Figure 5. Correlation between the Hammett constant (σ_p) of the phosphane substituent and the M_n values of the polymers obtained from **79**.

Experimental Section

General considerations: All reagents were used as received. Dichloromethane was dispensed from a solvent purification system from Innovative Technology. Catalyst syntheses were performed in an MBraun glovebox containing dry argon and less than 1 ppm oxygen. Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^1H, ^{31}P, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker Avance 300 or Bruker Avance II 400 Ultrashield NMR spectrometers. High-resolution mass spectrometry (HRMS) analyses were performed by the Mass Spectrometry Service of the University of St Andrews and by EPSRC National Mass Spectrometry Service Centre (Swansea University). Complexes **2** and **3** are commercially available from Umicore AG or Strem Chemicals Inc. Substrates **10**,[13c] **12**,[13c] **14**,[13c] **16**,[13c] **20**,[33] **21**,[34] **23**,[13c] **25**,[13c] **27**,[35] **29**,[13c] **31**,[13c] **33**,[13c] **35**,[5d] **37**,[13c] **39**,[13c] **41**,[13c] **43**,[27] **45**,[27] **47**,[27] **49**,[27] **51**,[36] **54**,[37] **58**,[38] **76**,[36] **78**[29] and **79**[39] have previously been described in the literature.

[$RuCl_2$(SIMes)(PPh_3)(3-phenylinden-1-ylidene)] (4): In a glovebox, complex **3** (1.5 g, 2.0 mmol) and PPh_3 (526 mg, 2.0 mmol, 1 equiv) were dissolved in dichloromethane (10 mL) and stirred for 3 h at room temperature. The volatiles were removed in vacuum and the residue was recrystallised from dichloromethane/hexane (1:5, 18 mL). Filtration and washing with methanol (10 mL) and pentane (2×10 mL) afforded the ruthenium complex **4** as an ochre coloured solid (1.45 g, 78%). ^1H and ^{31}P NMR were similar to the literature data.[23] ^1H NMR (300 MHz, CD_2Cl_2): $\delta=7.78$ (d, $J=7.2$ Hz, 1H; H^{Ind}), 7.46–7.38 (m, 3H; H^{Ar}), 7.30–7.26 (m, 2H; H^{Ar}), 7.18–7.11 (m, 4H; H^{Ar}), 7.02–6.87 (m, 16H; H^{Ar}), 6.47 (s, 1H; *m*-CH^{SIMes}), 6.32 (s, 1H; *m*-CH^{SIMes}), 5.94 (s, 1H; *m*-CH^{SIMes}), 4.02–3.95 (m, 2H; CH_2-CH_2), 3.84–3.70 (m, 2H; CH_2-CH_2), 2.60 (s, 3H; CH_3^{SIMes}), 2.57 (s, 3H; CH_3^{SIMes}), 2.39 (s, 3H; CH_3^{SIMes}), 2.05 (s, 3H; CH_3^{SIMes}), 1.93 (s, 3H; CH_3^{SIMes}), 1.76 ppm (s, 3H; CH_3^{SIMes}); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta=25.96$ ppm.

[$RuCl_2$(SIMes)(P(*p*-MeOPh)$_3$)(3-phenylinden-1-ylidene)] (5): In a glovebox, complex **3** (1.0 g, 1.34 mmol) and tris(*p*-methoxyphenyl)phosphane (490 mg, 1.4 mmol, 1.05 equiv) were dissolved in dichloromethane (10 mL) and stirred for 3 h at room temperature. The volatiles were removed in vacuum and the residue was washed with methanol (10 mL) and pentane (2×10 mL), affording the ruthenium complex **5** as a burgundy solid (1.03 g, 75%). ^1H NMR (300 MHz, CD_2Cl_2): $\delta=7.93$ (d, $J=$

7.2 Hz, 1H; H^{Ind}), 7.54–7.46 (m, 3H; H^{Ar}), 7.36 (t, J=7.4 Hz, 2H; H^{Ar}), 7.24 (td, J=7.3, 0.9 Hz, 1H; H^{Ar}), 7.13 (bs, 2H; H^{Ar}), 7.06–6.92 (m, 8H; H^{Ar}), 6.58 (dd, J=8.8, 1.5 Hz, 6H; H^{Ar}), 6.49 (s, 1H; m-CH^{SIMes}), 6.40 (s, 1H; m-CH^{SIMes}), 6.02 (s, 1H; m-CH^{SIMes}), 4.11–4.04 (m, 2H; CH_2-CH$_2$), 3.95–3.78 (m, 2H; CH_2-CH$_2$), 3.71 (s, 9H; OCH$_3$), 2.72 (s, 3H; CH$_3^{SIMes}$), 2.65 (s, 3H; CH$_3^{SIMes}$), 2.49 (s, 3H; CH$_3^{SIMes}$), 2.12 (s, 3H; CH$_3^{SIMes}$), 2.04 (s, 3H; CH$_3^{SIMes}$), 1.84 ppm (s, 3H; CH$_3^{SIMes}$);. ^{13}C NMR (75.5 MHz, CD$_2$Cl$_2$): d=299.0 (d, J(C,P)=12.9 Hz, C), 216.1 (d, J(C,P)=86.3 Hz, C), 160.9 (3C), 143.4 (C), 141.4 (C), 140.6 (C), 139.9 (C), 139.5 (C), 138.6 (C), 138.3 (C), 138.2 (C), 137.3 (C), 137.0 (C), 136.9 (CH), 136.7 (C), 136.1 (CH), 136.0 (3CH), 135.8 (3CH), 130.1 (CH), 130.0 (CH), 129.3 (CH), 129.2 (3CH), 129.0 (CH), 128.9 (CH), 128.2 (CH), 126.6 (4C), 123.9 (CH), 123.3 (CH), 116.4 (CH), 113.3 (3CH), 113.2 (3CH), 55.4 (3CH$_3$), 52.7 (CH$_2$), 52.4 (CH$_2$), 21.5 (CH$_3$), 21.0 (CH$_3$), 20.6 (CH$_3$), 20.4 (CH$_3$), 18.9 (CH$_3$), 18.7 ppm (CH$_3$); ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ= 22.41 ppm; elemental analysis calcd (%) for C$_{57}$H$_{57}$Cl$_2$N$_2$O$_3$PRu (1021.02): C 67.05, H 5.63, N 2.74; found: C 66.98, H 5.70, N 2.75.

[RuCl$_2$(SIMes)(P(p-Tolyl)$_3$)(3-phenylinden-1-ylidene)] (6): In a glovebox, complex **3** (1.0 g, 1.34 mmol) and tri-p-tolylphosphane (427 mg, 1.4 mmol, 1.05 equiv) were dissolved in dichloromethane (10 mL) and stirred for 2 h at room temperature. The volatiles were removed in vacuum and the residue was recrystallised from dichloromethane/cold pentane (1:5, 18 mL) at −20°C. Of note, the complex is soluble in pentane at room temperature. After cold filtration, the orange-red solid was dissolved in cyclohexane (30 mL) and filtered to remove insoluble impurities. After evaporation of solvent in vacuum, the ruthenium complex **6** was obtained as a orange-red solid (1.00 g, 77%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ= 7.93 (d, J=7.2 Hz, 1H; H^{Ind}), 7.53–7.22 (m, 6H; H^{Ar}), 7.12–6.85 (m, 16H; H^{Ar}), 6.43 (s, 1H; m-CH^{SIMes}), 6.39 (s, 1H; m-CH^{SIMes}), 6.03 (s, 1H; m-CH^{SIMes}), 4.07 (t, J=7.2 Hz, 2H; CH_2-CH$_2$), 3.83 (sextuplet, J=7.2 Hz, 2H; CH_2-CH$_2$), 2.72 (s, 3H; CH$_3^{SIMes}$), 2.64 (s, 3H; CH$_3^{SIMes}$), 2.49 (s, 3H; CH$_3^{SIMes}$), 2.24 (s, 9H; p-CH$_3$), 2.09 (s, 3H; CH$_3^{SIMes}$), 2.04 (s, 3H; CH$_3^{SIMes}$), 1.84 ppm (s, 3H; CH$_3^{SIMes}$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ=299.4 (d, J(C,P)=13.1 Hz, C), 215.9 (d, J(C,P)=85.7 Hz, C), 143.4 (C), 141.4 (C), 140.6 (C), 139.9 (3C), 139.5 (C), 138.7 (C), 138.3 (C), 138.2 (C), 137.3 (C), 137.1 (C), 136.9 (CH), 136.7 (C), 136.0 (C), 134.5 (3CH), 134.4 (3CH), 130.1 (CH), 130.0 (CH), 129.3 (CH), 129.2 (CH), 129.17 (2CH), 129.0 (CH), 128.99 (CH), 128.8 (CH), 128.6 (CH), 128.5 (3CH), 128.4 (3CH), 128.1 (2CH), 126.6 (4C), 116.4 (CH), 52.7 (CH$_2$), 52.5 (CH$_2$), 21.5 (CH$_3$), 21.3 (3CH$_3$), 21.0 (CH$_3$), 20.6 (CH$_3$), 20.4 (CH$_3$), 18.9 (CH$_3$), 18.6 ppm (CH$_3$); ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ= 24.08 ppm; elemental analysis calcd (%) for C$_{57}$H$_{57}$Cl$_2$N$_2$PRu (973.03): C 70.36, H 5.90, N 2.88; found: C 70.29, H 5.94, N 3.08.

[RuCl$_2$(SIMes)(P(p-FPh)$_3$)(3-phenylinden-1-ylidene)] (7): In a glovebox, complex **3** (1 g, 1.34 mmol) and tris(p-fluorophenyl)phosphane (444 mg, 1.4 mmol, 1.05 equiv) were dissolved in dichloromethane (10 mL) and stirred for 2 h at room temperature. The volatiles were removed in vacuum and the residue was washed with methanol (10 mL) and pentane (2×10 mL), affording the ruthenium complex **7** as a maroon solid (1.18 g, 90%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ=7.83 (d, J=7.4 Hz, 1H; H^{Ind}), 7.57–7.51 (m, 3H; H^{Ar}), 7.40 (t, J=7.5 Hz, 2H; H^{Ar}), 7.24 (t, J=7.2 Hz, 1H; H^{Ar}), 7.09–6.97 (m, 10H; H^{Ar}), 6.78 (td, J=8.8, 1.4 Hz, 6H; H^{Ar}), 6.58 (s, 1H; m-CH^{SIMes}), 6.43 (s, 1H; m-CH^{SIMes}), 6.04 (s, 1H; m-CH^{SIMes}), 4.11–4.04 (m, 2H; CH_2-CH$_2$), 3.95–3.76 (m, 2H; CH_2-CH$_2$), 2.66 (s, 6H; CH$_3^{SIMes}$), 2.48 (s, 3H; CH$_3^{SIMes}$), 2.17 (s, 3H; CH$_3^{SIMes}$), 2.00 (s, 3H; CH$_3^{SIMes}$), 1.82 ppm (s, 3H; CH$_3^{SIMes}$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ=300.8 (d, J(C,P)=12.4 Hz, C), 215.0 (d, J(C,P)=88.3 Hz, C), 164.0 (d, J(C,F)=250.6 Hz, 3C), 143.4 (C), 141.3 (C), 141.2 (C), 139.8 (C), 139.7 (C), 138.9 (C), 138.2 (C), 137.5 (C), 137.0 (C), 136.7 (d, J(C,F)=11.5 Hz, 3CH), 136.6 (d, J(C,F)=11.6 Hz, 3CH), 136.2 (C), 135.8 (C), 130.09 (CH), 130.06 (CH), 129.4 (CH), 129.35 (3CH), 129.3 (CH), 129.1 (CH), 129.0 (CH), 128.7 (CH), 128.6 (CH), 127.6 (d, J(C,F)=3.2 Hz, CH), 127.2 (d, J(C,F)=3.2 Hz, CH), 126.6 (4C), 116.8 (CH), 115.2 (d, J(C,F)= 10.7 Hz, 3CH), 114.9 (d, J(C,F)=10.6 Hz, 3CH), 52.7 (d, J(C,P)=3.5 Hz, CH$_2$), 52.4 (d, J(C,P)=2.3 Hz, CH$_2$), 21.4 (CH$_3$), 21.0 (CH$_3$), 20.5 (CH$_3$), 20.4 (CH$_3$), 18.8 (CH$_3$), 18.7 ppm (CH$_3$); ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ=24.89 ppm. ^{19}F NMR (376 MHz, CD$_2$Cl$_2$): δ=−111.82 ppm; elemental analysis calcd for C$_{54}$H$_{48}$Cl$_2$F$_3$N$_2$PRu (M_W 984.92): C 65.85, H 4.91, N 2.84; found: C 65.64, H 4.72, N 2.63.

[RuCl$_2$(SIMes)(P(p-ClPh)$_3$)(3-phenylinden-1-ylidene)] (8): In a glovebox, complex **3** (1.5 g, 2.0 mmol) and tris(p-chlorophenyl)phosphane (770 mg, 2.1 mmol, 1.05 equiv) were dissolved in dichloromethane (10 mL) and stirred for 3 h at room temperature. The volatiles were removed in vacuum and the residue dissolved in hexane (20 mL). The red solution was cooled and filtrated to remove insoluble impurities. After evaporation of solvent in vacuum, the remaining solid was washed with methanol (10 mL) and pentane (2×10 mL), affording the ruthenium complex **8** as a dark red solid (1.86 g, 90%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ=7.83 (d, J=7.2 Hz, 1H; H^{Ind}), 7.57–7.34 (m, 6H; H^{Ar}), 7.27–7.20 (m, 2H; H^{Ar}), 7.10–6.97 (m, 14H; H^{Ar}), 6.52 (s, 1H; m-CH^{SIMes}), 6.42 (s, 1H; m-CH^{SIMes}), 6.05 (s, 1H; m-CH^{SIMes}), 4.07 (t, J=10.0 Hz, 2H; CH_2-CH$_2$), 3.93–3.78 (m, 2H; CH_2-CH$_2$), 2.67 (s, 3H; CH$_3^{SIMes}$), 2.63 (s, 3H; CH$_3^{SIMes}$), 2.50 (s, 3H; CH$_3^{SIMes}$), 2.14 (s, 3H; CH$_3^{SIMes}$), 2.02 (s, 3H; CH$_3^{SIMes}$), 1.84 ppm (s, 3H; CH$_3^{SIMes}$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ=301.1 (d, J(C,P)=12.5 Hz, C), 214.7 (d, J(C,P)=88.2 Hz, C), 143.3 (C), 141.7 (C), 141.2 (C), 139.9 (C), 139.6 (C), 139.0 (C), 138.3 (C), 138.2 (C), 137.5 (C), 136.9 (2C), 136.5 (2C), 136.1 (C), 135.8 (3CH), 135.7 (3CH), 130.08 (CH), 130.04 (CH), 129.9 (CH), 129.5 (CH), 129.45 (3CH), 129.4 (CH), 129.3 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.2 (3CH), 128.1 (3CH), 126.6 (4C), 116.8 (CH), 52.7 (d, J(C,P)=3.5 Hz, CH$_2$), 52.5 (d, J(C,P)=1.8 Hz, CH$_2$), 21.4 (CH$_3$), 21.0 (CH$_3$), 20.5 (CH$_3$), 20.4 (CH$_3$), 18.8 (CH$_3$), 18.6 ppm (CH$_3$); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$): δ=25.82 ppm; elemental analysis calcd for C$_{54}$H$_{48}$Cl$_5$N$_2$PRu (M_W 1034.28): C 62.71, H 4.68, N 2.71; found: C 62.40, H 4.60, N 2.76.

[RuCl$_2$(SIMes)(P(p-CF$_3$Ph)$_3$)(3-phenylinden-1-ylidene)] (9): In a glovebox, complex **3** (1.14 g, 1.53 mmol) and tris(p-fluoromethylphenyl)phosphane (750 mg, 1.61 mmol, 1.1 equiv) were dissolved in dichloromethane (10 mL) and stirred for 3 h at room temperature. The volatiles were removed in vacuum and the residue dissolved in hexane (20 mL). The red solution was cooled and filtrated to remove insoluble impurities. After evaporation of solvent in vacuum, the remaining solid was purified by silica gel chromatography (hexane/diethyl ether 8:2) affording the ruthenium complex **9** as a dark red solid (1.27 g, 73%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ=7.74 (d, J=7.0 Hz, 1H; H^{Ind}), 7.58–7.52 (m, 1H; H^{Ar}), 7.44–7.34 (m, 10H; H^{Ar}), 7.27–7.11 (m, 9H; H^{Ar}), 6.99–6.93 (m, 2H; H^{Ar}), 6.49 (s, 1H; m-CH^{SIMes}), 6.42 (s, 1H; m-CH^{SIMes}), 6.05 (s, 1H; m-CH^{SIMes}), 4.13–4.06 (m, 2H; CH_2-CH$_2$), 3.96–3.78 (m, 2H; CH_2-CH$_2$), 2.68 (s, 3H; CH$_3^{SIMes}$), 2.65 (s, 3H; CH$_3^{SIMes}$), 2.49 (s, 3H; CH$_3^{SIMes}$), 2.14 (s, 3H; CH$_3^{SIMes}$), 2.01 (s, 3H; CH$_3^{SIMes}$), 1.83 ppm (s, 3H; CH$_3^{SIMes}$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ=302.6 (d, J(C,P)=12.8 Hz, C), 214.0 (d, J-(C,P)=89.9 Hz, C), 143.3 (C), 142.4 (C), 141.1 (C), 140.1 (C), 139.8 (C), 139.1 (C), 138.3 (C), 137.7 (C), 137.0 (d, J(C,F)=2.3 Hz, CH), 136.8 (CH), 135.8 (C), 135.7 (C), 135.5 (C), 135.1 (CH), 135.0 (3CH), 134.9 (3CH), 131.9 (q, J(C,F)=33,6 Hz, 3C-CF$_3$), 130.3 (CH), 130.2 (CH), 129.5 (CH), 129.4 (3CH), 129.37 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 126.6 (4C), 124.9–124.7 (m, 6CH), 124.2 (d, J(C,F)=272.5 Hz, 3CF$_3$), 117.0 (CH), 52.7 (d, J(C,P)=3.6 Hz, CH$_2$), 52.4 (d, J(C,P)= 1.6 Hz, CH$_2$), 21.2 (CH$_3$), 21.0 (CH$_3$), 20.6 (CH$_3$), 20.5 (CH$_3$), 18.8 (CH$_3$), 18.6 ppm (CH$_3$); ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ=26.98 ppm; ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ=−63.86 ppm; elemental analysis calcd for C$_{57}$H$_{48}$Cl$_2$F$_9$N$_2$PRu (M_W 1134.94): C 60.32, H 4.26, N 2.47; found: C 60.40, H 4.52, N 2.31.

General procedure for RCM reactions: A Schlenk flask under nitrogen was charged with the substrate (0.5 mmol) and dry dichloromethane (5 mL, c=0.1 M), then pre-catalyst **4** or **9** (5×10^{-6} mol) was added. The reaction mixture was magnetically stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the volatiles were removed under vacuum and the crude residue was purified by flash column chromatography (pentane/ether 9:1) to yield the pure product.

General procedure for ring-rearrangement metathesis reactions: A Schlenk flask, fitted with a magnetic stir bar, under nitrogen, was charged with the substrate (0.5 mmol) and dry dichloromethane (50 mL, c= 0.01 M). The pre-catalyst **4** or **9** (5×10^{-6} mol) was then added. The reaction mixture was stirred at room temperature and the progress was monitored by TLC. After completion, ethyl vinyl ether (0.1 mL) was added and the solution was further stirred 30 min. The volatiles were removed under vacuum and the crude product was purified by flash column chromatography to yield the pure product.

General procedure for cross-metathesis reactions: A Schlenk flask, under nitrogen, was charged with the substrate (0.5 mmol), the olefin partners (1 mmol unless otherwise stated) and dry dichloromethane (0.5 mL, $c = 1\,\text{M}$). The pre-catalyst **4** or **7** (5×10^{-6} mol) was then added. The reaction mixture was magnetically stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under vacuum and the crude residue was purified by flash column chromatography (pentane/ether 1:1) to yield the pure product.

General procedure for ROMP reactions: The initiator **2**–**9** (1 equiv) was weighed into a Schlenk flask with a stirring bar and dissolved in dry and degassed CH_2Cl_2 (1 mL). Monomer **78** or **79** (300 equiv) was dissolved in the corresponding amount of solvent to reach a total concentration of $0.2\,\text{mol}\,\text{L}^{-1}$. The monomer solution was added to the initiator solution. The reaction mixture was stirred until polymerisation was complete, which was monitored by thin layer chromatography. After completion, the polymerisation reaction was quenched by addition of an excess of ethyl vinyl ether (200 μL). After 15 min of additional stirring, the solvent was reduced to approximately 1 mL. The reaction mixture was then slowly added to vigorously stirred, cold methanol to precipitate the polymer, which was collected and dried in vacuum. Provided yields refer to the amount of isolated polymer. A sample of each polymer was subjected to GPC for analysis of M_n and PDI.

CCDC-767344 (**5**) and 767343 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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