Phosphite ligands in Ru-based olefin metathesis catalysts

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Abstract In this short review, we focus on the synthesis and applications of new phosphite-bearing ruthenium complexes in olefin metathesis. These complexes were designed to take advantage of a known synergistic effect between strong σ-donating NHC ligands and π-acidic phosphites. The resulting catalysts display higher stability compared to their phosphine-containing congeners. A comparative summary of their use in ring-closing metathesis, cross metathesis and ring-opening metathesis polymerization is presented as well as DFT calculations describing our mechanistic understanding.

Keywords Phosphite ● Metal Complexes ● Metathesis ● Coordination Chemistry

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Introduction

Olefin metathesis represents one of the most important tools in organometallic chemistry and catalysis [1-7]. Its relevance is highlighted by its increasing importance at the industrial level. In addition, the award of the Nobel Prize in 2005 to Y. Chauvin, R. H. Grubbs and R. R. Schrock for their respective involvement in the discovery of olefin metathesis, showcases its significance [8-10]. Since their pioneering work on molybdenum (Schrock) and ruthenium (Grubbs) catalysts, numerous studies have been performed to enhance the activity and lifetime of the catalysts. Despite the importance of the molybdenum chemistry [11, 12], this review will focus on the development of ruthenium complexes as they have shown to be more user-friendly, thus far.

Since the discovery of a ruthenium vinylcarbene complex able to catalyze the olefin metathesis reaction in 1992 [13], several developments have led to ever more efficient catalysts. In particular, the introduction of a benzylidene moiety led to the well-known Grubbs first-generation catalyst

[14]. Next significant breakthroughs were the introduction of the 2-isopropoxybenzylidene [15, 16] or 3-phenylinden-1-ylidene [17-20] moieties in place of the benzylidene to furnish even more stable catalysts (Figure 1).

< Fig. 1 >

Diversification of the catalyst structures was also performed by replacement of one of the phosphane ligand with a *N*-heterocyclic carbene (NHC). Since their discovery in 1991 by Arduengo [21], well-defined NHCs have received significant attention as organocatalysts and ancillary transition metal ligands. Indeed, these strongly σ-donating ligands represent suitable replacements for tertiary phosphanes in numerous organometallic complexes [22]. Diversification of their structure is convenient and allows for the generation of families of tunable ligands in terms of sterics and electronics. In ruthenium-catalyzed olefin metathesis, the introduction of NHCs has had a critical and direct impact on catalyst stability and efficiency, giving rise to second-generation catalysts [23-25]. SIMes (*N,N'*-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene) and SIPr (*N,N'*-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolin-2-

ylidene) represent two of the most used NHC ligands for metathesis (Fig. 2).

< Fig. 2 >

Another possibility to enhance catalysts stability and activity was to tune the so-called throwaway ligand. Numerous studies have been reported on the substitution of the commonly used tricyclohexylphosphine by other phosphanes [26-29], NHCs [30-33], pyridine [18, 34], and Schiff bases [35-37] in the benzylidene and indenylidene families. The search for even more stable and efficient catalysts led to studies based on the known synergistic effect between strongly σ donating NHCs and strongly π acidic phosphites on transition metals [38-41]. This short review will present and discuss the synthesis of this new family of ruthenium NHC/phosphite complexes, their catalytic efficiency and summarize mechanistic insights into their stability and reactivity.

Synthesis of ruthenium NHC phosphites complexes

As stated above, the original thoughts behind these novel complexes were to combine phosphites and NHC ligands around a ruthenium center to obtain unreported structures. Consequently, several ruthenium complexes

were synthesized, featuring various phosphites and NHCs in the benzylidene and indenylidene series. In addition, the specific properties of NHC/phosphite ruthenium complexes allowed for the generation of a highly interesting cationic species via halogen abstraction.

Initial studies were performed using commercially available indenylidene complex **Ind-III**, bearing SIMes and a pyridine ligand. Simple substitution reactions involving **Ind-III** with different phosphites in dichloromethane led to the displacement of the pyridine moiety (Table 1) [42, 43]. Four phosphites featuring different sterics (Tolman cone angle [44]) were evaluated, namely trimethyl, triethyl, triisopropyl and triphenylphosphite, giving complexes *cis*-**Caz-1a-d** [45, 46]. Interestingly, during the course of the reaction, two different complexes were observed and assigned as the *trans*- and *cis*-dichloro isomers. In all cases, the *trans* isomer was found to be the kinetic product of the reaction, which converted upon heating and prolonged reaction times into the thermodynamic product, the *cis* isomer. These structures still represent rare examples of *cis*-dichloro ruthenium complexes for metathesis in which a monodentate phosphorus ligand is involved [47, 48], and the first examples of indenylidene-type complexes displaying such configuration. The *cis*-dichloro geometry has been found more common in Hoveyda-type complexes featuring bidentate ligands [49-58].

< Table 1 >

Formation of complexes *cis*-**Caz-1a-d** proceeded smoothly and could be correlated to the phosphite steric hindrance. Indeed, phosphites with a large cone angle such as $P(OiPr)_3$ and $P(OPh)_3$, required longer reaction times than the smaller $P(OMe)_3$ and $P(OEt)_3$ (Table 1). Isolation and study of the *trans* isomer was only possible when $P(OiPr)_3$ was used. Kinetic studies conducted using NMR spectroscopy of the *trans*/*cis* isomerization for **Caz-1a** concluded that this process follows a mononuclear and non-dissociative mechanism [42]. In addition, DFT calculations demonstrated that for all $P(OR)_3$-based systems, the *cis* isomers were more stable than the *trans* relatives. This was found to contrast with PR_3-based complexes for which the *trans* isomer is favored [59]. Thanks to this *cis*-dichloro configuration, *cis*-**Caz-1a-d** were also shown to be significantly more thermally and bench stable than their tricyclohexylphosphine analogs.

The introduction of a phosphite ligand in ruthenium-based metathesis complexes led to a strong enhancement of stability due to a phosphite/NHC synergism. Since then, attempts to introduce phosphites in catalysts, which are known to decompose but also activate faster than **Ind-**

II [$RuCl_2$(Ind)(PCy_3)(SIMes)], have been carried out. Thus, focus was placed on tuning of **Ind-II'** [$RuCl_2$(Ind)(PCy_3)(SIPr)] and **G-II** [$RuCl_2$(=CHPh)(PCy_3)(SIMes)] and replacement of the tricyclohexylphosphine ligand. A similar synthetic strategy was applied to obtain the corresponding complexes. The ruthenium pyridine adducts **Ind-III'**, [$RuCl_2$(Ind)(Py)(SIPr)], and **G-III**, [$RuCl_2$(=CHPh)$(Py)_2$(SIMes)] were reacted with $P(OEt)_3$ or $P(OiPr)_3$ to yield respectively *trans*-**Caz-2a-b** and *trans*-**Caz-3a-b** [60] (Scheme 1).

< Scheme 1 >

In contrast to previous results, the *trans*/*cis* isomerization could not be easily achieved. Such isomerization could only be observed in the case of **Caz-2b**, with concomitant decomposition. In the case of SIPr congeners, this lack of isomerization was assigned to the increased steric bulk of the SIPr ligand compared to SIMes, for which $\%V_{bur}$ are respectively 32.5 and 30.0 [61-64]. This steric cause for reactivity was correlated with the fact that the *cis* isomer was only observed with the complex bearing the smallest phosphite $P(OEt)_3$. Interestingly, X-ray data analysis showed that in all cases, Ru-$P(OR)_3$ complexes presented *ca.* 0.10 Å shorter Ru-P bond than Ru-PCy_3 analogs. Even if phosphites are less σ-donating than

phosphanes, their π-accepting character combined with strong σ-donor NHC ligands resulted in stronger Ru-P bonds. This character could once more be correlated to the increased stability of complexes **Caz-2a-b** when compared to the parent compound [$RuCl_2$(Ind)(PCy_3)(SIPr)] **Ind-II'**.

The excellent stability and catalytic activity of *cis*-**Caz-1a** prompted the Cazin group to develop cationic derivatives of this compound [65]. Indeed, if neutral NHC ruthenium complexes are widely reported in the literature, disclosures of syntheses describing related cationic systems remain scarce [56, 66-69]. Reaction of *cis*-**Caz-1a** with 1 equivalent of silver hexafluoroantimonate furnished cleanly **Caz-1a**$^+$ in 95% yield, in which a chlorine atom was abstracted (Scheme 2) [65]. The resulting four-coordinate 14-electron complex displays a sawhorse configuration with the new vacant site being *cis* to the NHC and *trans* to the phosphite ligand.

< Scheme 2 >

When an additional equivalent of silver hexafluoroantimonate was added to the reaction mixture to attempt a second chlorine abstraction, oxidation of Ru(II) to Ru(III) with concomitant reduction of Ag(I) to Ag(0) resulted in the formation of **Caz-1a**$^{2+}$ [65]. This structure represents a rare example of a Ru(III) four-coordinate bis-cationic complex. Interestingly, during the

oxidation process, a *cis*/*trans* isomerization (related to $P(OiPr)_3$) of the chlorine atom was observed.

The crucial role of the phosphite was highlighted by 1) the extremely high thermal stability of **Caz-1a**$^+$, 2) the fact that chlorine abstraction from phosphine or pyridine-containing analog complexes gave complex mixtures of compounds.

Ten new ruthenium compounds bearing a NHC and a phosphite were thus been readily synthesized and characterized. The beneficial effect of the phosphite, when compared to parent phosphane, on the stability of the complexes was unambiguously demonstrated. This improved stability was shown to be an advantage in solution since the catalysts exhibited excellent activity and prolonged lifetimes.

Catalytic activity of ruthenium NHC phosphite complexes

In order to understand the differences between the phosphite-containing catalysts, reported data on ring-closing metathesis (RCM) have been gathered in Table 2. Among the large range of examples studied for the scope and application of these compounds, focus was placed on compounds **6** and **8**, known to be easy and difficult substrates in RCM, respectively. In all cases, enhanced stability discussed in the previous section directly translated in terms of catalytic activity when compared to

phosphane analogs and allowed to conduct the catalytic reactions at very low catalyst loadings. Among these, the general order of activity observed with phosphane congeners is respected, that is **Caz-1a,d** and **Caz-1**$^{+}$ were efficient for difficult transformation and **Caz-2a,b** and **Caz-3a,b** for easy substrates since they decompose faster at elevated temperatures.

< Table 2 >

Catalysts **Caz-1a,d**, featuring an unusual *cis*-dichloro arrangement, were shown to have a latent character [43]. Indeed, when RCM of **8** in toluene at 80°C catalyzed by *trans*-**Caz-1a** and *cis*-**Caz-1a** were monitored by NMR spectroscopy, *cis*-**Caz-1a** clearly showed an activation period of approximately 30 min [42]. The same behavior was witnessed with the other [$RuCl_2$(Ind){$P(OR)_3$}(SIMes)] catalysts. As shown in Tables 1 and 2, catalytic activity in this series is directly linked to phosphite bulk. Complexes bearing bulky phosphites, namely $P(OiPr)_3$ and $P(OPh)_3$, were found to activate faster than those bearing smaller phosphites, giving rise to better conversions for easy and difficult substrates (Table 2, entries 1-4 and 12-15). As a comparison, the tricyclohexylphosphane analog **Ind-II** gave only 61% conversion when the use of *cis*-**Caz-1a** permitted to reach complete conversion of hindered substrate **8**. Among this series of

catalysts, *cis*-**Caz-1a** proved to be the most efficient and allowed to perform RCM of various benchmark substrates with catalyst loadings as low as 0.05 mol% and 0.1 mol% for easy and difficult substrates, respectively [42, 43].

The same latent character was demonstrated for **Caz-1**$^{+}$, which is even more thermally stable than *cis*-**Caz-1a** [65]. In order to obtain high conversions reactions required to be carried out at 140°C in xylene. After 15 min with only 0.1 and 0.2 mol% of **Caz-1**$^{+}$, cyclized products **7** and **9** were obtained with 99% and 90% conversion, respectively (Table 2, entries 5 and 17). It is important to note that at 140°C, even *cis*-**Caz-1a** decomposed rapidly while **Caz-1**$^{+}$ still proved active. Such stability and catalytic activity (down to 0.1 mol%) has never been reported for cationic ruthenium complexes in olefin metathesis.

Catalysts **Caz-2a,b** and **Caz-3a,b** are derived from complexes **Ind-II'** and **G-II** which activate rapidly but also decompose at rather low temperatures (50°C). However, as stability was enhanced by the introduction of phosphites, RCM reactions had to be conducted at 50°C to ensure good catalyst activation [59]. If the fastest initiation of **Ind-II'** was shown evident by the results on unhindered substrate **6** (Table 2, entries 6-8), the superiority of **Caz-2a,b** was obvious when hindered compound **10** was cyclized (Table 2, entries 21-23). **Caz-3a,b** were also found to be

slightly more active than **G-II** on RCM of **6** (Table 2, entry 9-11) but their higher stability could be used as an advantage with substrate **8** [60]. After 8h in MTBE at 50°C, tetra-substituted cyclized product **9** was obtained with 25%, 63% and 42% conversion in the presence of 2 mol% of **G-II**, **Caz-3a** and **Caz-3b**, respectively (Table 2, entries 18-20). As for **G-II**, heating reactions at higher temperature did not allow for better results and led to decomposition of complexes **Caz-3a,b**.

The best catalysts of each series were also evaluated in enyne RCM (EYRCM) and cross metathesis (CM) at low catalyst loading (Tables 3 and 4). In EYRCM, latent catalysts **Caz-1a** and **Caz-1a**$^+$ were not as efficient as for RCM [43, 65]. Indeed, RCM of enynes **12** and **14** into dienes **13** and **15**, respectively, did not produce more than an 80% yield (Table 3, entries 1-3). Such yields, even though not optimal, were obtained with as low as 0.075 mol% of catalyst. On the contrary, **Caz-2b**, featuring SIPr and $P(OEt)_3$ ligands, gave excellent results and allowed to isolate **15** in 94% yield with only 0.1 mol% of catalyst (Table 3, entry 4) [59]. Finally, even if working at lower temperature, **Caz-3a** gave similar results as **Caz-1a** and **Caz-1**$^+$. However, **Caz-3a** was demonstrated to be more efficient than **G-II** on difficult EYRCM substrates [60].

< Table 3 >

To study CM, substrates **16** and **18** were reacted with 5 equivalents of methyl acrylate. All phosphite-containing catalysts were able to promote this reaction efficiently (Table 4). Indeed, alkene **16** was readily converted with yields of up to 79% when 0.2 mol% of **Caz-1**$^{+}$ were used (Table 4, entry 2) [65]. Interestingly, **Caz-3a** was found as efficient as **G-II** for this transformation [60]. Compound **17** was obtained in 72% yield (Table 4, entries 3 and 4). **Caz-1a** permitted the use of even lower catalyst loading since only 0.075 mol% catalyst afforded 68% isolated yield of the desired product (Table 4, entry 1) [43]. Finally, compound **19** could be isolated in good yield when using **Caz-1a** and **Caz-2b** at 0.2 mol% (Table 4, entries 5 and 6) [42, 43, 59].

< Table 4 >

Since *cis*-**Caz-1a** possesses this particular reactivity, it was screened in recent studies and compared to other commercially available catalysts. Lamaty and co-workers showed that *cis*-**Caz-1a** was able to promote RCM of dienes **20** and **22** under microwave activation in polyethylene glycol (PEG) as green solvent for metathesis [70]. However, it was necessary to use methylated PEG (MeO-PEG-2000-OMe) in order to avoid the

formation of a Ru-hydride species, which promoted isomerization of olefins, and thus formation of undesired side-products (Scheme 3).

< Scheme 3 >

Caijo *et al.* evaluated *cis*-**Caz-1a** in the synthesis of precursors of fragrances, namely δ-decalactone and exaltolide, and compared it to a series of standard and fast initiation commercially available precatalysts [71]. Even though *cis*-**Caz-1a** is latent and thus initiates slowly, it was shown highly active in the RCM of diene **24** and led to the highest yield of 69% in the macrolactonization/hydrogenation of **25** (Scheme 4). The authors highlighted the fact that the latter result was, in terms of catalyst efficiency and concentration, a significant improvement over the state-of-the-art [72-74].

Latent and highly stable catalysts are interesting in ring-opening metathesis polymerization (ROMP) since they allow control of polymerization by controlling the initiation trigger (e.g. heat, light, mechanical force). Thus, phosphite-containing complexes *cis*-**Caz-1a** and **Caz-2a** were evaluated in the ROMP of model substrate endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**Mon-1**) and endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-diphenyl ketone (**Mon-2**) [59]. At

room temperature, *cis*-**Caz-1a** gave less than 10% conversion after 24h of reaction and **Caz-2a** revealed to be a slower initiator than phosphane analog **Ind-II'** (Table 5, entries 1, 2 and 4). **Caz-2a** gave a polymer characterized by a number-average molecular weight (M_n) value of 131000 g/mol and a polydiversity index (PDI) of 1.6. As a comparison, **Ind-II** and **Ind-III** featuring a SIMes ligand were much better initiators (Table 5, entries 3 and 5). At higher temperature, *cis*-**Caz-1a** was able to initiate polymerization to furnish a polymer with M_n value of 106000 g/mol and a PDI of 1.8 (Table 5, entry 6). Even at 80°C, *cis*-**Caz-1a** proved less active than **Caz-2a**.

Kinetic study of the polymerization of **Mon-2** at 25°C confirmed that i) *cis*-**Caz-1a** to be less active than **Caz-2a**, ii) **Caz-2a** was less active than the phosphane parent compound **Ind-II'**. Such information is in agreement with the fact that phosphites have a higher re-coordination ability than phosphanes during catalysis, thus explaining the higher stability but also lower activity of $P(OR)_3$-containing initiators.

< Table 5 >

In a parallel study, **Ind-II** and *cis*-**Caz-1a** were evaluated in the ROMP of dicyclopentadiene (DCPD), an inexpensive by-product of C5

stream of naphtha crackers [75]. The corresponding polymer pDCPD is highly valuable and its use is becoming more prevalent in view of its outstanding properties, *i.e.* chemical resistance, high rigidity and robustness. The synthetic approach to pDCPD involving ROMP is generally performed using Grubbs first or second-generation catalysts. The use of an air and moisture stable initiator such as *cis*-**Caz-1a** would provide a competitive approach to this polymer. It has been established that 20 ppm of **Ind-II** or 25 ppm of *cis*-**Caz-1a** were sufficient to furnish pDCPD with similar mechanical properties to industrially made pDCPD, *i.e.* Young's modulus (E) of 1.78 ± 0.1, and a maximal stress R_m value of 50 ± 3 MPa (values for pDCPD obtained with *cis*-**Caz-1a**). In addition, involvement of **Ind-II** and thermally latent initiator *cis*-**Caz-1a** instead of **G-II** widened the processing window of the DCPD/initiator formulation, at room temperature, to minutes and several hours before curing, respectively.

Mechanistic investigation

Among the phosphite-containing catalysts described above, the peculiar *cis*-dichloro arrangement in **Caz-1a-d** raised numerous mechanistic questions. In particular, investigations addressing the higher stability of these complexes over phosphane analogs and on the catalytic mechanism have been carried out.

DFT calculations of the relative energy of the *cis* and *trans* isomer showed that the *cis* isomer was more stable [43]. Moreover, this relative energy is in linear correlation with Tolman cone angle of the phosphite ligands. Similar calculations on phosphane-containing complexes confirmed that, in this case, the *trans* isomer was the most stable. Calculations of absolute bond dissociation energies (DBE) were performed on $P(OMe)_3$ and PMe_3 as model ligands to minimize steric influence. In the *trans* isomers, values obtained for the phosphite (14.6 kcal/mol) were smaller than for the phosphane (22.3 kcal/mol), showing that the less donating $P(OMe)_3$ should dissociate more rapidly than PMe_3. However, in the *cis* isomer, the BDE values for $P(OMe)_3$ (21.8 kcal/mol) were higher than for PMe_3 (20.5 kcal/mol), indicating a stronger binding of the phosphite. In addition, structural analysis showed that the average P-O bond in the *cis* isomer was 0.01 Å longer than in the *trans* isomer. This difference is a clear indication of back-donation from the metal into the π^* orbitals corresponding to P-O bonds [76], and explains the difference in binding strength between phosphites and phosphanes.

Such data provided some insight into the activation mechanism of *cis*-**Caz-1a-d**. Indeed, BDE calculations suggest that dissociation of the phosphite, if it occurs, would be favored when $P(OR)_3$ is *trans* to the NHC. In addition, when bulkier olefins than ethylene are involved in the

metathesis, the possibility of an activation step through an associative-displacement mechanism as suggested for Hoveyda-Grubbs catalysts was ruled out [77]. The energies associated with complexes in which coordination of ethylene prior to dissociation of a phosphite ligand was involved were found too high to be reasonable.

All these data seem to indicate that the *cis* isomer of **Caz-1a-d** plays the role of a reservoir for the *trans* isomer. Thus, when *cis*-**Caz-1a-d** pre-catalysts are used in catalysis in toluene, throughout the reaction, the *cis* isomer releases progressively *trans*-**Caz-1a-d**. Then the *trans* isomer can follow the classical metathesis mechanism, *i.e.* first initiation by release of the throwaway ligand, in this case, the phosphite, and metathesis with the substrate that generates the 14-electron active species that can enter the catalytic cycle to afford the desired metathesis product (Scheme 5).

< Scheme 5 >

Conclusion

In summary, the synthesis of new ruthenium complexes featuring a NHC and a phosphite ligand has been reviewed. The expected synergism between σ-donating NHC and π-acidic phosphite was unambiguously demonstrated in olefin metathesis as all novel complexes showed an

enhanced stability when compared to PCy_3-containing congeners. In particular, the original *cis*-dichloro configuration in the **Caz-1a-d** series gave rise to latent and highly stable catalysts. The phosphite catalysts showed excellent activities in RCM, EYRCM and CM and their superiority over phosphane analogs became apparent as soon as "difficult" substrates were tested, especially at low catalyst loading. In addition, **Caz-2a**, featuring SIPr and $P(OiPr)_3$ ligands, and *cis*-**Caz-1a**, featuring SIMes and $P(OiPr)_3$ ligands, showed interesting activities in ROMP. In the case of **Caz-1a-d**, calculations and kinetic experiments demonstrated that *cis*/*trans* isomerization proceeded through a mononuclear non-dissociative mechanism. During catalysis, such isomerization might occur prior to the initiation and propagation steps.

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Figure Captions

Fig. 1 General structures of the families of ruthenium catalysts for olefin metathesis

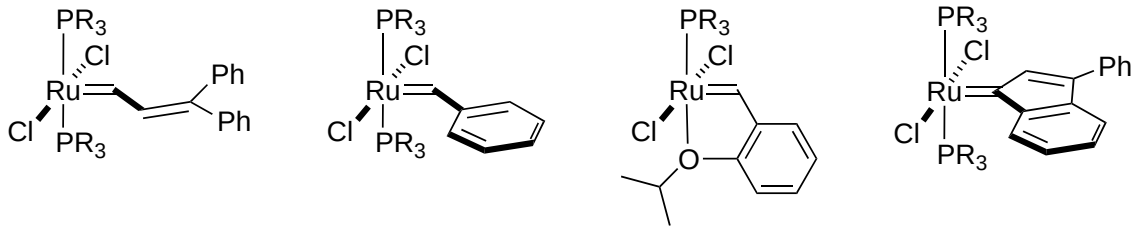
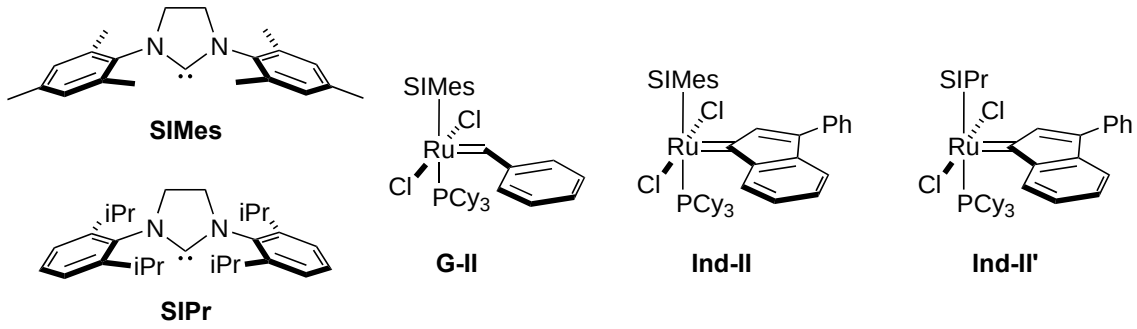
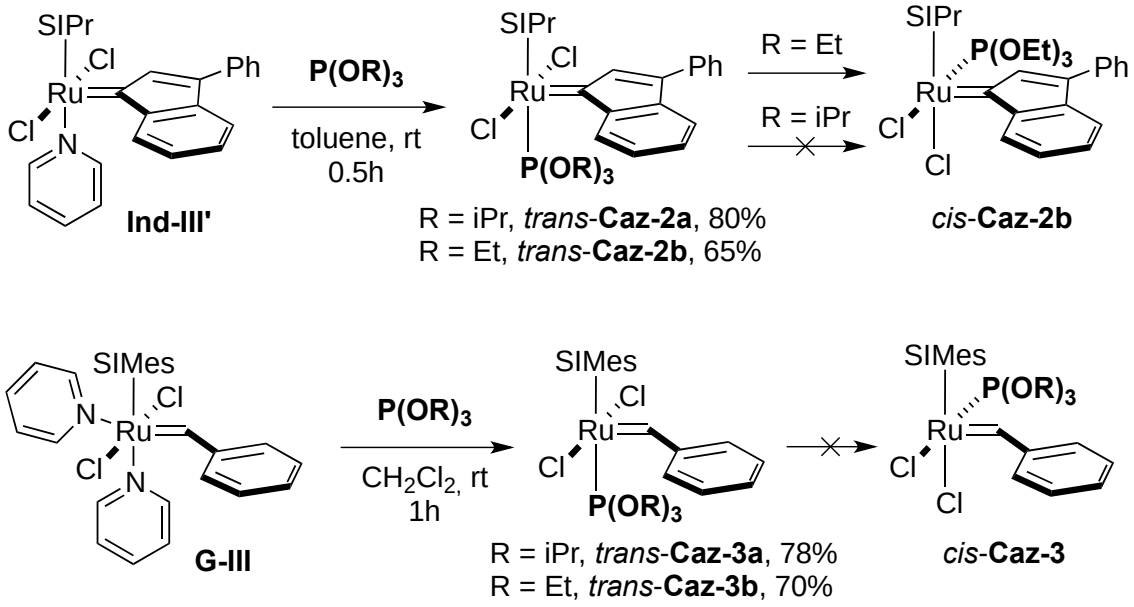


Fig. 2 Structure of SIMes and SIPr and derived ruthenium olefin metathesis catalysts

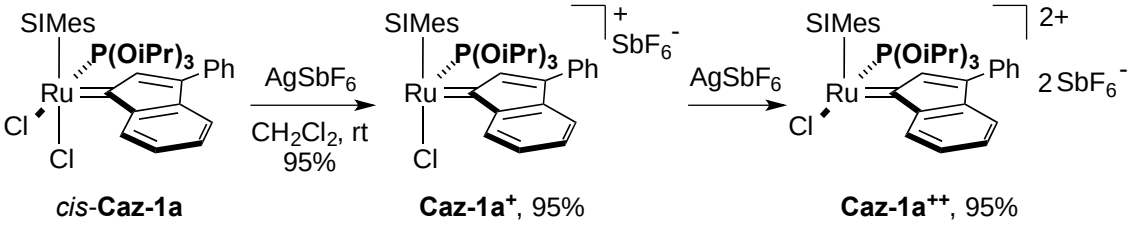


Schemes

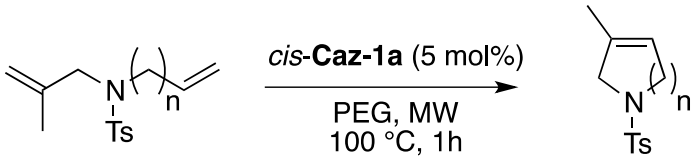
Scheme 1



Scheme 2



Scheme 3

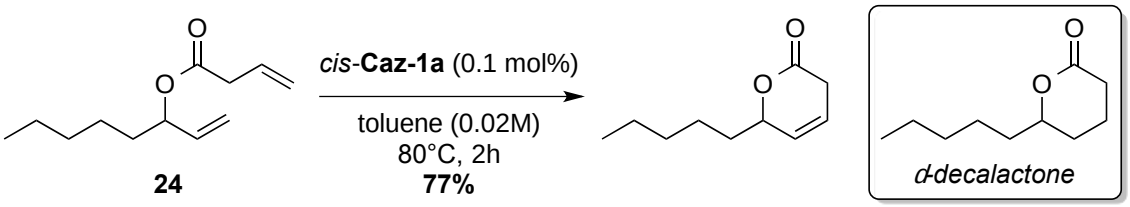


n = 1, **20**
n = 2, **22**

21
23

	PEG-3400	**MeO-PEG-2000-OMe**
n = 1,	30% + isomers	93%
n = 2,	34% + isomers	83%

Scheme 4



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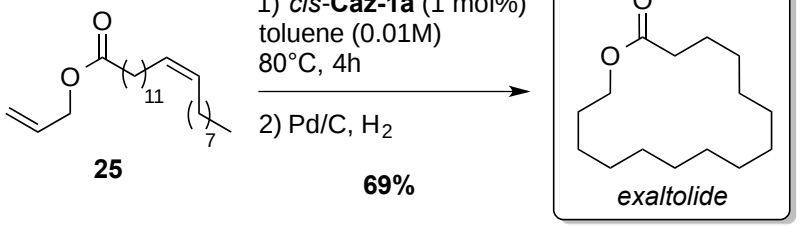

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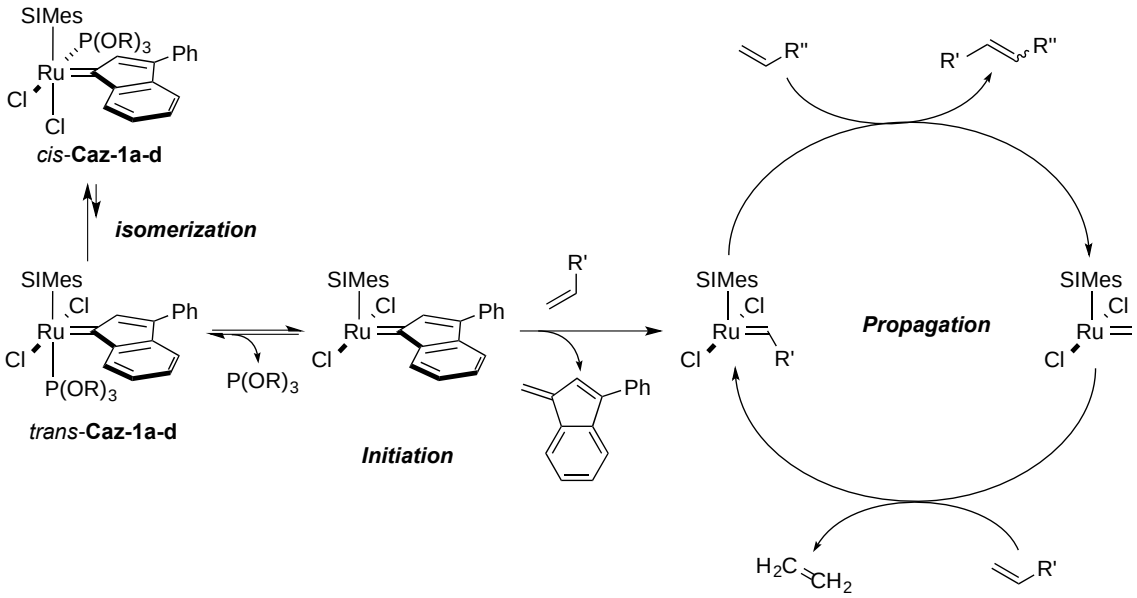
Scheme 5

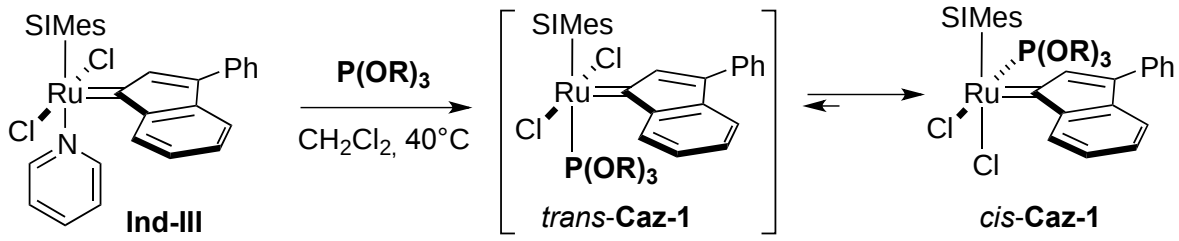

SIMes
P(OR)3
Ph
Ru
Cl
Cl
cis-Caz-1a-d
isomerization
trans-Caz-1a-d
P(OR)3
Initiation
R'
Ph
Propagation
R"
R'
R"
H2C
CH2
R'

1

2

3

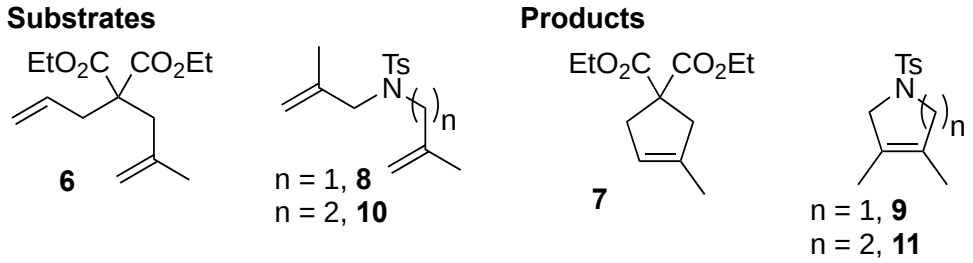
Table 1 Synthesis of complexes *cis*-**Caz-1a-d**



Entry	$P(OR)_3$ (equiv.)	θ (°)[a]	Time (h)	Yield (%)	Complex
1	$P(OMe)_3$ (1)	107	3	57	*cis*-**Caz-1b**
2	$P(OEt)_3$ (1)	109	5	88	*cis*-**Caz-1c**
3	$P(OiPr)_3$ (1)	128	15	84	*cis*-**Caz-1a**
4	$P(OPh)_3$ (4)	130	15	76	*cis*-**Caz-1d**

[a] *Tolman cone angle.*

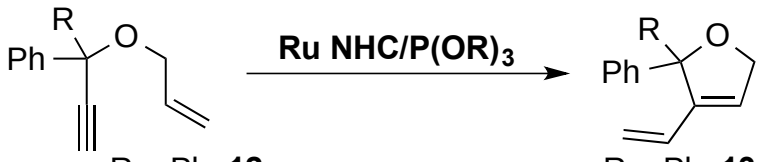
Table 2 Comparative evaluation of Ru NHC/$P(OR)_3$ complexes in RCM



Entry	Substrate	Cat (mol%)	Conditions	Conv. (%)	Lit.
1	**6**	**Caz-1a** (1/0.075)[a]	toluene, 80°C, 0.5h	> 99 / >99[b]	42
2		**Caz-1b** (1)[a]		78	43
3		**Caz-1c** (1)[a]		35	
4		**Caz-1d** (1)[a]		98	
5		**Caz-1a**$^+$ (0.1)	xylene, 140°C, 15 min	99	65
6		**Caz-2a** (0.025)	CH_2Cl_2, 50°C, 2h	96	59
7		**Caz-2b** (0.025)		>99	
8		**Ind-II'** (0.025)	CH_2Cl_2, 30°C, 1h	99	
9		**G-II** (0.025)	MTBE, 50°C, 8h	91	60
10		**Caz-3a** (0.025)		95	
11		**Caz-3b** (0.025)		93	
12	**8**	**Caz-1a** (0.5 / 0.1)[a]	toluene, 80°C, 5h	>99 / 96[c]	42
13		**Caz-1b** (0.5)[a]		27	43
14		**Caz-1c** (0.5)[a]		22	
15		**Caz-1d** (0.5)[a]		98	
16		**Ind-II** (0.5)		61	
17		**Caz-1a**$^+$ (0.2)	xylene, 140°C, 15 min	90	65
18		**G-II** (2)	MTBE, 50°C, 8h	25	60
19		**Caz-3a** (2)		63	
20		**Caz-3b** (2)		42	
21	**10**	**Caz-2a** (2)	CH_2Cl_2, 50°C, 2h	46	59
22		**Caz-2b** (2)		47	
23		**Ind-II'** (5)	toluene, 80°C, 1h	23	

[a] *Cis* isomers were used for compounds **caz-1a-d**. [b] Solvent-free, 120°C, 15h, 0.075 mol% Ru. [c] Refluxing toluene, 5h, 0.1 mol% Ru.

Table 3 Comparative evaluation of Ru NHC/$P(OR)_3$ complexes in enyne RCM



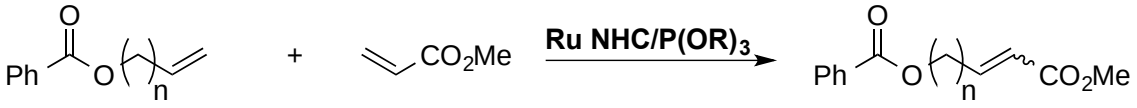
R = Ph, **12**
R = Me, **14**

R = Ph, **13**
R = Me, **15**

Entry	Substrate	Cat (mol%)[a]	Conditions	Yield (%)	Lit.
1	**12**	**Caz-1a** (0.075)	toluene, reflux, 15h	68	43
2		**Caz-1a** (1)	toluene, 80°C, 0.5h	75	43
3	**14**	**Caz-1a**$^+$ (0.2)	xylene, 140°C, 15 min	79	65
4		**Caz-2b** (0.1)	CH_2Cl_2, 50°C, 3h	94	59
5		**Caz-3a** (0.1)	MTBE, 50°C, 8h	78	60

[a] *Cis* isomers were used for compounds **caz-1a**.

Table 4 Comparative evaluation of Ru NHC/$P(OR)_3$ complexes in CM



n = 2, **16**
n = 3, **18**

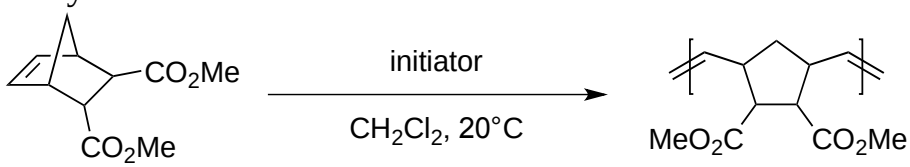
(5 equiv.)

n = 2, **17**
n = 3, **19**

Entry	Substrate	Cat (mol%)	Conditions	Yield (%)[a]	Lit.
1		**Caz-1a** (0.075)[b]	toluene, reflux, 15h	68	43
2	**16**	**Caz-1a**$^+$ (0.2)	xylene, 140°C, 15 min	79	65
3		**Caz-3a** (0.2)	MTBE, 50°C, 8h	72	60
4		**G-II** (0.2)	MTBE, 50°C, 8h	72	60
5	**18**	**Caz-1a** (0.2)[b]	toluene, reflux, 15h	81	43
6		**Caz-2b** (0.2)	CH_2Cl_2, 50°C, 3h	77	59

[a] In all cases, diastereomeric ratio was > 20:1. [b] *Cis* isomer of **caz-1a** was used.

Table 5 Polymerization with different initiators

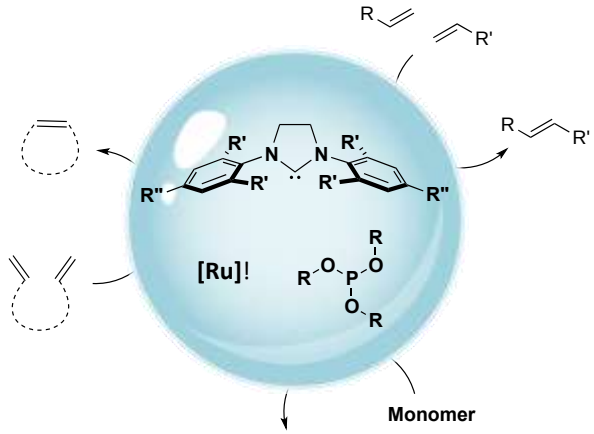


Mon-1 monomer/initiator 300:1

Entry	Cat	Time (h)	M_n	PDI
1	*cis*-**Caz-1a**	24	n.d.	n.d.
2	**Caz-2a**	8	131000	1.6
3	**Ind-II**	4	300000	2.0
4	**Ind-II'**	2	52000	1.3
5	**Ind-III**	0.25	48000	1.05
6[a]	*cis*-**Caz-1a**	1	106000	1.8

[a] Toluene, 80°C.

1 Graphics for use in the Table of Contents



2