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.

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8   **Introduction**

9   Olefin metathesis represents one of the most important tools in

10   organometallic chemistry and catalysis [1-7]. Its relevance is highlighted

11   by its increasing importance at the industrial level. In addition, the award of

12   the Nobel Prize in 2005 to Y. Chauvin, R. H. Grubbs and R. R. Schrock for

13   their respective involvement in the discovery of olefin metathesis,

14   showcases its significance [8-10]. Since their pioneering work on

15   molybdenum (Schrock) and ruthenium (Grubbs) catalysts, numerous

16   studies have been performed to enhance the activity and lifetime of the

17   catalysts. Despite the importance of the molybdenum chemistry [11, 12],

18   this review will focus on the development of ruthenium complexes as they

19   have shown to be more user-friendly, thus far.

20   Since the discovery of a ruthenium vinylcarbene complex able to

21   catalyze the olefin metathesis reaction in 1992 [13], several developments

22   have led to ever more efficient catalysts. In particular, the introduction of a

23   benzylidene moiety led to the well-known Grubbs first-generation catalyst

1   [14]. Next significant breakthroughs were the introduction of the 2-

2   isopropoxybenzylidene [15, 16] or 3-phenylinden-1-ylidene [17-20]

3   moieties in place of the benzylidene to furnish even more stable catalysts

4   (Figure 1).

5

6   < Fig. 1 >

7

8   Diversification of the catalyst structures was also performed by

9   replacement of one of the phosphane ligand with a *N*-heterocyclic carbene

10   (NHC). Since their discovery in 1991 by Arduengo [21], well-defined

11   NHCs have received significant attention as organocatalysts and ancillary

12   transition metal ligands. Indeed, these strongly σ-donating ligands

13   represent suitable replacements for tertiary phosphanes in numerous

14   organometallic complexes [22]. Diversification of their structure is

15   convenient and allows for the generation of families of tunable ligands in

16   terms of sterics and electronics. In ruthenium-catalyzed olefin metathesis,

17   the introduction of NHCs has had a critical and direct impact on catalyst

18   stability and efficiency, giving rise to second-generation catalysts [23-25].

19   SIMes (*N,N'*-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene)

20   and   SIPr   (*N,N'*-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolin-2-

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

2 2).

3

4 < Fig. 2 >

5

6 Another possibility to enhance catalysts stability and activity was to

7 tune the so-called throwaway ligand. Numerous studies have been reported

8 on the substitution of the commonly used tricyclohexylphosphine by other

9 phosphanes [26-29], NHCs [30-33], pyridine [18, 34], and Schiff bases

10 [35-37] in the benzylidene and indenylidene families. The search for even

11 more stable and efficient catalysts led to studies based on the known

12 synergistic effect between strongly σ donating NHCs and strongly π acidic

13 phosphites on transition metals [38-41]. This short review will present and

14 discuss the synthesis of this new family of ruthenium NHC/phosphite

15 complexes, their catalytic efficiency and summarize mechanistic insights

16 into their stability and reactivity.

17

18 *Synthesis of ruthenium NHC phosphites complexes*

19 As stated above, the original thoughts behind these novel complexes were

20 to combine phosphites and NHC ligands around a ruthenium center to

21 obtain unreported structures. Consequently, several ruthenium complexes

1 were synthesized, featuring various phosphites and NHCs in the

2 benzylidene and indenylidene series. In addition, the specific properties of

3 NHC/phosphite ruthenium complexes allowed for the generation of a

4 highly interesting cationic species via halogen abstraction.

5   Initial studies were performed using commercially available

6 indenylidene complex **Ind-III**, bearing SIMes and a pyridine ligand.

7 Simple substitution reactions involving **Ind-III** with different phosphites in

8 dichloromethane led to the displacement of the pyridine moiety (Table 1)

9 [42, 43]. Four phosphites featuring different sterics (Tolman cone angle

10 [44]) were evaluated, namely trimethyl, triethyl, triisopropyl and

11 triphenylphosphite, giving complexes *cis*-**Caz-1a-d** [45, 46]. Interestingly,

12 during the course of the reaction, two different complexes were observed

13 and assigned as the *trans*- and *cis*-dichloro isomers. In all cases, the *trans*

14 isomer was found to be the kinetic product of the reaction, which converted

15 upon heating and prolonged reaction times into the thermodynamic

16 product, the *cis* isomer. These structures still represent rare examples of

17 *cis*-dichloro ruthenium complexes for metathesis in which a monodentate

18 phosphorus ligand is involved [47, 48], and the first examples of

19 indenylidene-type complexes displaying such configuration. The *cis*-

20 dichloro geometry has been found more common in Hoveyda-type

21 complexes featuring bidentate ligands [49-58].

1

2   < Table 1 >

3

4   Formation of complexes *cis*-**Caz-1a-d** proceeded smoothly and

5   could be correlated to the phosphite steric hindrance. Indeed, phosphites

6   with a large cone angle such as P(OiPr)$_3$ and P(OPh)$_3$, required longer

7   reaction times than the smaller P(OMe)$_3$ and P(OEt)$_3$ (Table 1). Isolation

8   and study of the *trans* isomer was only possible when P(OiPr)$_3$ was used.

9   Kinetic studies conducted using NMR spectroscopy of the *trans*/*cis*

10 isomerization for **Caz-1a** concluded that this process follows a

11 mononuclear and non-dissociative mechanism [42]. In addition, DFT

12 calculations demonstrated that for all P(OR)$_3$-based systems, the *cis*

13 isomers were more stable than the *trans* relatives. This was found to

14 contrast with PR$_3$-based complexes for which the *trans* isomer is favored

15 [59]. Thanks to this *cis*-dichloro configuration, *cis*-**Caz-1a-d** were also

16 shown to be significantly more thermally and bench stable than their

17 tricyclohexylphosphine analogs.

18   The introduction of a phosphite ligand in ruthenium-based

19 metathesis complexes led to a strong enhancement of stability due to a

20 phosphite/NHC synergism. Since then, attempts to introduce phosphites in

21 catalysts, which are known to decompose but also activate faster than **Ind-**

1   **II** [RuCl$_2$(Ind)(PCy$_3$)(SIMes)], have been carried out. Thus, focus was

2   placed on tuning of **Ind-II'** [RuCl$_2$(Ind)(PCy$_3$)(SIPr)] and **G-II**

3   [RuCl$_2$(=CHPh)(PCy$_3$)(SIMes)]   and   replacement   of   the

4   tricyclohexylphosphine ligand. A similar synthetic strategy was applied to

5   obtain the corresponding complexes. The ruthenium pyridine adducts **Ind-**

6   **III'**,   [RuCl$_2$(Ind)(Py)(SIPr)],   and   **G-III**,   [RuCl$_2$(=CHPh)(Py)$_2$(SIMes)]

7   were reacted with P(OEt)$_3$ or P(OiPr)$_3$ to yield respectively *trans*-**Caz-2a-b**

8   and *trans*-**Caz-3a-b** [60] (Scheme 1).

9

10   < Scheme 1 >

11

12   In contrast to previous results, the *trans*/*cis* isomerization could not

13   be easily achieved. Such isomerization could only be observed in the case

14   of **Caz-2b,** with concomitant decomposition. In the case of SIPr congeners,

15   this lack of isomerization was assigned to the increased steric bulk of the

16   SIPr ligand compared to SIMes, for which % V_{bur} are respectively 32.5 and

17   30.0 [61-64]. This steric cause for reactivity was correlated with the fact

18   that the *cis* isomer was only observed with the complex bearing the

19   smallest phosphite P(OEt)$_3$. Interestingly, X-ray data analysis showed that

20   in all cases, Ru-P(OR)$_3$ complexes presented *ca.* 0.10 Å shorter Ru-P bond

21   than Ru-PCy$_3$ analogs. Even if phosphites are less σ-donating than

1   phosphanes, their π-accepting character combined with strong σ-donor

2   NHC ligands resulted in stronger Ru-P bonds. This character could once

3   more be correlated to the increased stability of complexes **Caz-2a-b** when

4   compared to the parent compound [RuCl$_2$(Ind)(PCy$_3$)(SIPr)] **Ind-II'**.

5   The excellent stability and catalytic activity of *cis*-**Caz-1a** prompted

6   the Cazin group to develop cationic derivatives of this compound [65].

7   Indeed, if neutral NHC ruthenium complexes are widely reported in the

8   literature, disclosures of syntheses describing related cationic systems

9   remain scarce [56, 66-69]. Reaction of *cis*-**Caz-1a** with 1 equivalent of

10   silver hexafluoroantimonate furnished cleanly **Caz-1a$^+$** in 95% yield, in

11   which a chlorine atom was abstracted (Scheme 2) [65]. The resulting four-

12   coordinate 14-electron complex displays a sawhorse configuration with the

13   new vacant site being *cis* to the NHC and *trans* to the phosphite ligand.

14

15   < Scheme 2 >

16

17   When an additional equivalent of silver hexafluoroantimonate was added to

18   the reaction mixture to attempt a second chlorine abstraction, oxidation of

19   Ru(II) to Ru(III) with concomitant reduction of Ag(I) to Ag(0) resulted in

20   the formation of **Caz-1a^{2+}** [65]. This structure represents a rare example of

21   a Ru(III) four-coordinate bis-cationic complex. Interestingly, during the

1   oxidation process, a *cis/trans* isomerization (related to P(OiPr)$_3$) of the

2   chlorine atom was observed.

3   The crucial role of the phosphite was highlighted by 1) the extremely high

4   thermal stability of **Caz-1a$^+$**, 2) the fact that chlorine abstraction from

5   phosphine or pyridine-containing analog complexes gave complex

6   mixtures of compounds.

7   Ten new ruthenium compounds bearing a NHC and a phosphite were thus

8   been readily synthesized and characterized. The beneficial effect of the

9   phosphite, when compared to parent phosphane, on the stability of the

10   complexes was unambiguously demonstrated. This improved stability was

11   shown to be an advantage in solution since the catalysts exhibited excellent

12   activity and prolonged lifetimes.

13

14   *Catalytic activity of ruthenium NHC phosphite complexes*

15   In order to understand the differences between the phosphite-containing

16   catalysts, reported data on ring-closing metathesis (RCM) have been

17   gathered in Table 2. Among the large range of examples studied for the

18   scope and application of these compounds, focus was placed on

19   compounds **6** and **8**, known to be easy and difficult substrates in RCM,

20   respectively. In all cases, enhanced stability discussed in the previous

21   section directly translated in terms of catalytic activity when compared to

1   phosphane analogs and allowed to conduct the catalytic reactions at very

2   low catalyst loadings. Among these, the general order of activity observed

3   with phosphane congeners is respected, that is **Caz-1a,d** and **Caz-1⁺** were

4   efficient for difficult transformation and **Caz-2a,b** and **Caz-3a,b** for easy

5   substrates since they decompose faster at elevated temperatures.

6

7   < Table 2 >

8

9   Catalysts **Caz-1a,d**, featuring an unusual *cis*-dichloro arrangement,

10 were shown to have a latent character [43]. Indeed, when RCM of **8** in

11 toluene at 80°C catalyzed by *trans*-**Caz-1a** and *cis*-**Caz-1a** were monitored

12 by NMR spectroscopy, *cis*-**Caz-1a** clearly showed an activation period of

13 approximately 30 min [42]. The same behavior was witnessed with the

14 other [RuCl$_2$(Ind){P(OR)$_3$}(SIMes)] catalysts. As shown in Tables 1 and 2,

15 catalytic activity in this series is directly linked to phosphite bulk.

16 Complexes bearing bulky phosphites, namely P(OiPr)$_3$ and P(OPh)$_3$, were

17 found to activate faster than those bearing smaller phosphites, giving rise to

18 better conversions for easy and difficult substrates (Table 2, entries 1-4 and

19 12-15). As a comparison, the tricyclohexylphosphane analog **Ind-II** gave

20 only 61% conversion when the use of *cis*-**Caz-1a** permitted to reach

21 complete conversion of hindered substrate **8**. Among this series of

1   catalysts, *cis*-**Caz-1a** proved to be the most efficient and allowed to

2   perform RCM of various benchmark substrates with catalyst loadings as

3   low as 0.05 mol% and 0.1 mol% for easy and difficult substrates,

4   respectively [42, 43].

5   The same latent character was demonstrated for **Caz-1$^+$**, which is

6   even more thermally stable than *cis*-**Caz-1a** [65]. In order to obtain high

7   conversions reactions required to be carried out at 140°C in xylene. After

8   15 min with only 0.1 and 0.2 mol% of **Caz-1$^+$**, cyclized products **7** and **9**

9   were obtained with 99% and 90% conversion, respectively (Table 2, entries

10 5 and 17). It is important to note that at 140°C, even *cis*-**Caz-1a**

11 decomposed rapidly while **Caz-1$^+$** still proved active. Such stability and

12 catalytic activity (down to 0.1 mol%) has never been reported for cationic

13 ruthenium complexes in olefin metathesis.

14   Catalysts **Caz-2a,b** and **Caz-3a,b** are derived from complexes **Ind-**

15 **II'** and **G-II** which activate rapidly but also decompose at rather low

16 temperatures (50°C). However, as stability was enhanced by the

17 introduction of phosphites, RCM reactions had to be conducted at 50°C to

18 ensure good catalyst activation [59]. If the fastest initiation of **Ind-II'** was

19 shown evident by the results on unhindered substrate **6** (Table 2, entries 6-

20 8), the superiority of **Caz-2a,b** was obvious when hindered compound **10**

21 was cyclized (Table 2, entries 21-23). **Caz-3a,b** were also found to be

1   slightly more active than **G-II** on RCM of **6** (Table 2, entry 9-11) but their

2   higher stability could be used as an advantage with substrate **8** [60]. After

3   8h in MTBE at 50°C, tetra-substituted cyclized product **9** was obtained

4   with 25%, 63% and 42% conversion in the presence of 2 mol% of **G-II**,

5   **Caz-3a** and **Caz-3b**, respectively (Table 2, entries 18-20). As for **G-II**,

6   heating reactions at higher temperature did not allow for better results and

7   led to decomposition of complexes **Caz-3a,b**.

8   The best catalysts of each series were also evaluated in enyne RCM

9   (EYRCM) and cross metathesis (CM) at low catalyst loading (Tables 3 and

10   4). In EYRCM, latent catalysts **Caz-1a** and **Caz-1a$^+$** were not as efficient

11   as for RCM [43, 65]. Indeed, RCM of enynes **12** and **14** into dienes **13** and

12   **15**, respectively, did not produce more than an 80% yield (Table 3, entries

13   1-3). Such yields, even though not optimal, were obtained with as low as

14   0.075 mol% of catalyst. On the contrary, **Caz-2b**, featuring SIPr and

15   P(OEt)$_3$ ligands, gave excellent results and allowed to isolate **15** in 94%

16   yield with only 0.1 mol% of catalyst (Table 3, entry 4) [59]. Finally, even if

17   working at lower temperature, **Caz-3a** gave similar results as **Caz-1a** and

18   **Caz-1$^+$**. However, **Caz-3a** was demonstrated to be more efficient than **G-II**

19   on difficult EYRCM substrates [60].

20

21   < Table 3 >

12

1

2   To study CM, substrates **16** and **18** were reacted with 5 equivalents

3   of methyl acrylate. All phosphite-containing catalysts were able to promote

4   this reaction efficiently (Table 4). Indeed, alkene **16** was readily converted

5   with yields of up to 79% when 0.2 mol% of **Caz-1**^{+} were used (Table 4,

6   entry 2) [65]. Interestingly, **Caz-3a** was found as efficient as **G-II** for this

7   transformation [60]. Compound **17** was obtained in 72% yield (Table 4,

8   entries 3 and 4). **Caz-1a** permitted the use of even lower catalyst loading

9   since only 0.075 mol% catalyst afforded 68% isolated yield of the desired

10   product (Table 4, entry 1) [43]. Finally, compound **19** could be isolated in

11   good yield when using **Caz-1a** and **Caz-2b** at 0.2 mol% (Table 4, entries 5

12   and 6) [42, 43, 59].

13

14   < Table 4 >

15

16   Since *cis*-**Caz-1a** possesses this particular reactivity, it was screened

17   in recent studies and compared to other commercially available catalysts.

18   Lamaty and co-workers showed that *cis*-**Caz-1a** was able to promote RCM

19   of dienes **20** and **22** under microwave activation in polyethylene glycol

20   (PEG) as green solvent for metathesis [70]. However, it was necessary to

21   use methylated PEG (MeO-PEG-2000-OMe) in order to avoid the

1 formation of a Ru-hydride species, which promoted isomerization of

2 olefins, and thus formation of undesired side-products (Scheme 3).

3

4 < Scheme 3 >

5

6 Caijo *et al.* evaluated *cis*-**Caz-1a** in the synthesis of precursors of

7 fragrances, namely δ-decalactone and exaltolide, and compared it to a

8 series of standard and fast initiation commercially available precatalysts

9 [71]. Even though *cis*-**Caz-1a** is latent and thus initiates slowly, it was

10 shown highly active in the RCM of diene **24** and led to the highest yield of

11 69% in the macrolactonization/hydrogenation of **25** (Scheme 4). The

12 authors highlighted the fact that the latter result was, in terms of catalyst

13 efficiency and concentration, a significant improvement over the state-of-

14 the-art [72-74].

15 Latent and highly stable catalysts are interesting in ring-opening

16 metathesis polymerization (ROMP) since they allow control of

17 polymerization by controlling the initiation trigger (e.g. heat, light,

18 mechanical force). Thus, phosphite-containing complexes *cis*-**Caz-1a** and

19 **Caz-2a** were evaluated in the ROMP of model substrate endo,exo-

20 bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**Mon-1**) and

21 endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-diphenyl ketone (**Mon-2**) [59]. At

1   room temperature, *cis*-**Caz-1a** gave less than 10% conversion after 24h of

2   reaction and **Caz-2a** revealed to be a slower initiator than phosphane

3   analog **Ind-II'** (Table 5, entries 1, 2 and 4). **Caz-2a** gave a polymer

4   characterized by a number-average molecular weight (M_n) value of 131000

5   g/mol and a polydiversity index (PDI) of 1.6. As a comparison, **Ind-II** and

6   **Ind-III** featuring a SIMes ligand were much better initiators (Table 5,

7   entries 3 and 5). At higher temperature, *cis*-**Caz-1a** was able to initiate

8   polymerization to furnish a polymer with M_n value of 106000 g/mol and a

9   PDI of 1.8 (Table 5, entry 6). Even at 80°C, *cis*-**Caz-1a** proved less active

10   than **Caz-2a**.

11   Kinetic study of the polymerization of **Mon-2** at 25°C confirmed

12   that i) *cis*-**Caz-1a** to be less active than **Caz-2a**, ii) **Caz-2a** was less active

13   than the phosphane parent compound **Ind-II'**. Such information is in

14   agreement with the fact that phosphites have a higher re-coordination

15   ability than phosphanes during catalysis, thus explaining the higher

16   stability but also lower activity of $P(OR)_3$-containing initiators.

17

18   < Table 5 >

19

20   In a parallel study, **Ind-II** and *cis*-**Caz-1a** were evaluated in the

21   ROMP of dicyclopentadiene (DCPD), an inexpensive by-product of C5

1   stream of naphtha crackers [75]. The corresponding polymer pDCPD is

2   highly valuable and its use is becoming more prevalent in view of its

3   outstanding properties, *i.e.* chemical resistance, high rigidity and

4   robustness. The synthetic approach to pDCPD involving ROMP is

5   generally performed using Grubbs first or second-generation catalysts. The

6   use of an air and moisture stable initiator such as *cis*-**Caz-1a** would provide

7   a competitive approach to this polymer. It has been established that 20 ppm

8   of **Ind-II** or 25 ppm of *cis*-**Caz-1a** were sufficient to furnish pDCPD with

9   similar mechanical properties to industrially made pDCPD, *i.e.* Young's

10   modulus (E) of 1.78 ± 0.1, and a maximal stress R_m value of 50 ± 3 MPa

11   (values for pDCPD obtained with *cis*-**Caz-1a**). In addition, involvement of

12   **Ind-II** and thermally latent initiator *cis*-**Caz-1a** instead of **G-II** widened

13   the processing window of the DCPD/initiator formulation, at room

14   temperature, to minutes and several hours before curing, respectively.

15

16   *Mechanistic investigation*

17   Among the phosphite-containing catalysts described above, the peculiar

18   *cis*-dichloro arrangement in **Caz-1a-d** raised numerous mechanistic

19   questions. In particular, investigations addressing the higher stability of

20   these complexes over phosphane analogs and on the catalytic mechanism

21   have been carried out.

1   DFT calculations of the relative energy of the *cis* and *trans* isomer

2   showed that the *cis* isomer was more stable [43]. Moreover, this relative

3   energy is in linear correlation with Tolman cone angle of the phosphite

4   ligands. Similar calculations on phosphane-containing complexes

5   confirmed that, in this case, the *trans* isomer was the most stable.

6   Calculations of absolute bond dissociation energies (DBE) were performed

7   on $P(OMe)_3$ and PMe_3 as model ligands to minimize steric influence. In the

8   *trans* isomers, values obtained for the phosphite (14.6 kcal/mol) were

9   smaller than for the phosphane (22.3 kcal/mol), showing that the less

10 donating $P(OMe)_3$ should dissociate more rapidly than PMe_3. However, in

11 the *cis* isomer, the BDE values for $P(OMe)_3$ (21.8 kcal/mol) were higher

12 than for PMe_3 (20.5 kcal/mol), indicating a stronger binding of the

13 phosphite. In addition, structural analysis showed that the average P-O

14 bond in the *cis* isomer was 0.01 Å longer than in the *trans* isomer. This

15 difference is a clear indication of back-donation from the metal into the π^*

16 orbitals corresponding to P-O bonds [76], and explains the difference in

17 binding strength between phosphites and phosphanes.

18   Such data provided some insight into the activation mechanism of

19 *cis*-**Caz-1a-d**. Indeed, BDE calculations suggest that dissociation of the

20 phosphite, if it occurs, would be favored when $P(OR)_3$ is *trans* to the NHC.

21 In addition, when bulkier olefins than ethylene are involved in the

1   metathesis, the possibility of an activation step through an associative-

2   displacement mechanism as suggested for Hoveyda-Grubbs catalysts was

3   ruled out [77]. The energies associated with complexes in which

4   coordination of ethylene prior to dissociation of a phosphite ligand was

5   involved were found too high to be reasonable.

6   All these data seem to indicate that the *cis* isomer of **Caz-1a-d** plays

7   the role of a reservoir for the *trans* isomer. Thus, when *cis*-**Caz-1a-d** pre-

8   catalysts are used in catalysis in toluene, throughout the reaction, the *cis*

9   isomer releases progressively *trans*-**Caz-1a-d**. Then the *trans* isomer can

10   follow the classical metathesis mechanism, *i.e.* first initiation by release of

11   the throwaway ligand, in this case, the phosphite, and metathesis with the

12   substrate that generates the 14-electron active species that can enter the

13   catalytic cycle to afford the desired metathesis product (Scheme 5).

14

15   < Scheme 5 >

16

17   **Conclusion**

18   In summary, the synthesis of new ruthenium complexes featuring a NHC

19   and a phosphite ligand has been reviewed. The expected synergism

20   between σ-donating NHC and π-acidic phosphite was unambiguously

21   demonstrated in olefin metathesis as all novel complexes showed an

1 enhanced stability when compared to PCy$_3$-containing congeners. In

2 particular, the original *cis*-dichloro configuration in the **Caz-1a-d** series

3 gave rise to latent and highly stable catalysts. The phosphite catalysts

4 showed excellent activities in RCM, EYRCM and CM and their superiority

5 over phosphane analogs became apparent as soon as "difficult" substrates

6 were tested, especially at low catalyst loading. In addition, **Caz-2a**,

7 featuring SIPr and P(OiPr)$_3$ ligands, and *cis*-**Caz-1a**, featuring SIMes and

8 P(OiPr)$_3$ ligands, showed interesting activities in ROMP. In the case of

9 **Caz-1a-d**, calculations and kinetic experiments demonstrated that *cis*/*trans*

10 isomerization proceeded through a mononuclear non-dissociative

11 mechanism. During catalysis, such isomerization might occur prior to the

12 initiation and propagation steps.

13

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14

1   *Figure Captions*

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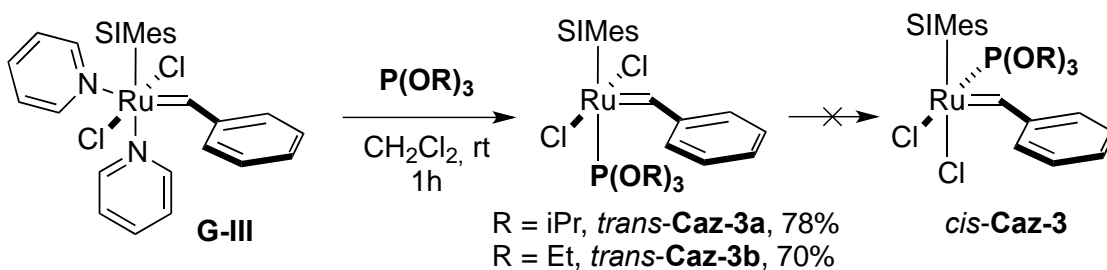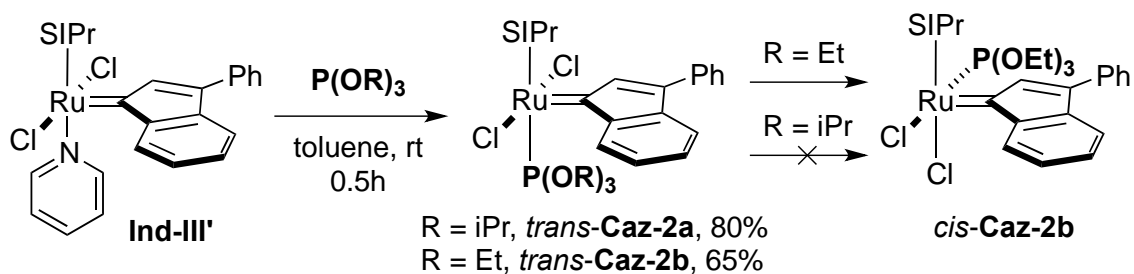
3   metathesis

4   *Vinylcarbene*   *Benzylidene*   *Boomerang-type*   *Indenylidene*
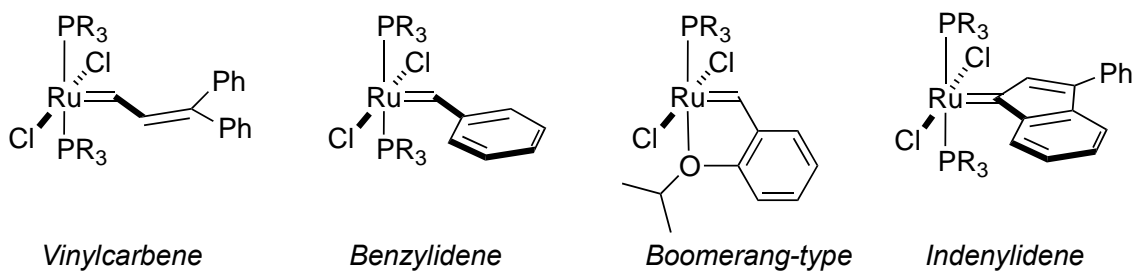
5

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

7   catalysts

8   **SIMes**   **SIPr**   **G-II**   **Ind-II**   **Ind-II'**

9

1

2   *Schemes*

3   **Scheme 1**

R = iPr, *trans*-**Caz-2a**, 80%
R = Et, *trans*-**Caz-2b**, 65%

cis-**Caz-2b**

R = iPr, *trans*-**Caz-3a**, 78%
R = Et, *trans*-**Caz-3b**, 70%

cis-**Caz-3**

4

5   **Scheme 2**

cis-**Caz-1a**   **Caz-1a⁺**, 95%   **Caz-1a⁺⁺**, 95%

6

7

8   **Scheme 3**

cis-**Caz-1a** (5 mol%)

PEG, MW
100 °C, 1h

n = 1, **20**
n = 2, **22**
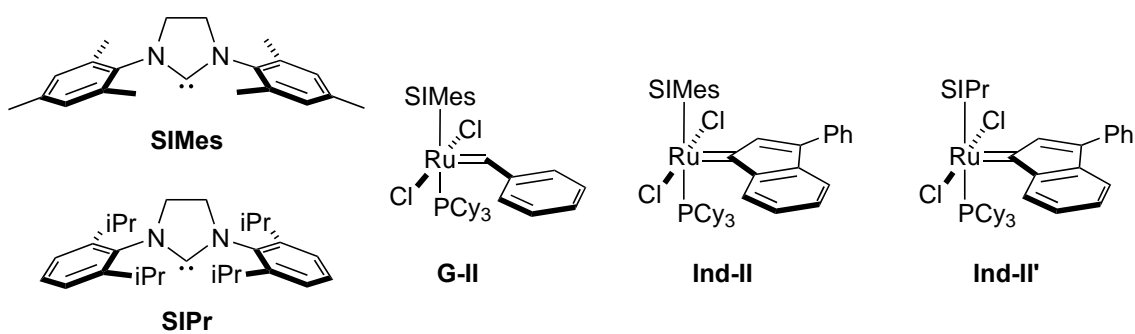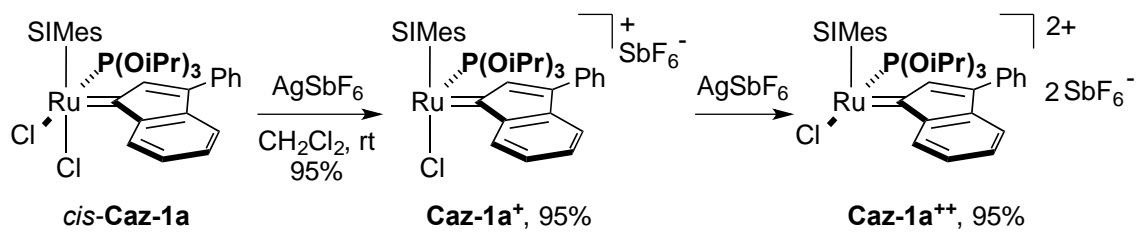
21
23

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

1

2 **Scheme 4**

cis-**Caz-1a** (0.1 mol%)

toluene (0.02M)
80°C, 2h
77%

24

d-decalactone

1) cis-**Caz-1a** (1 mol%)
toluene (0.01M)
80°C, 4h

2) Pd/C, H$_2$

25

69%

exaltolide
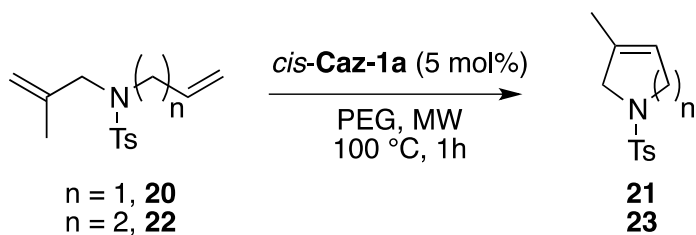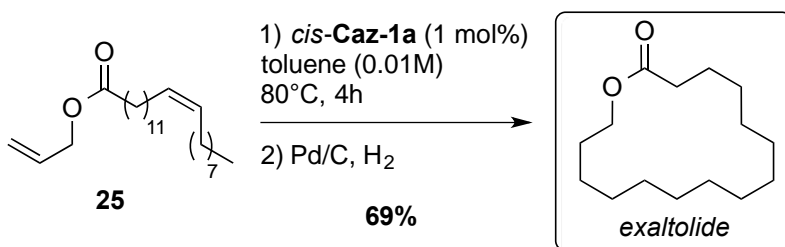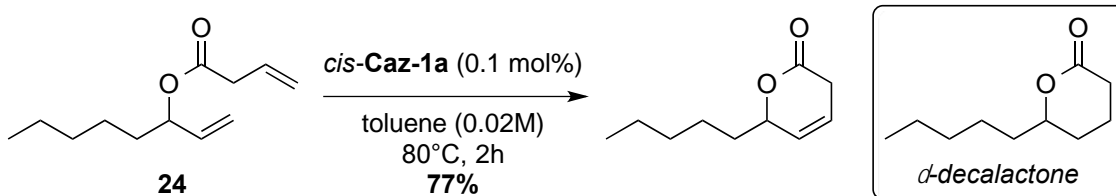
3

4

5 **Scheme 5**
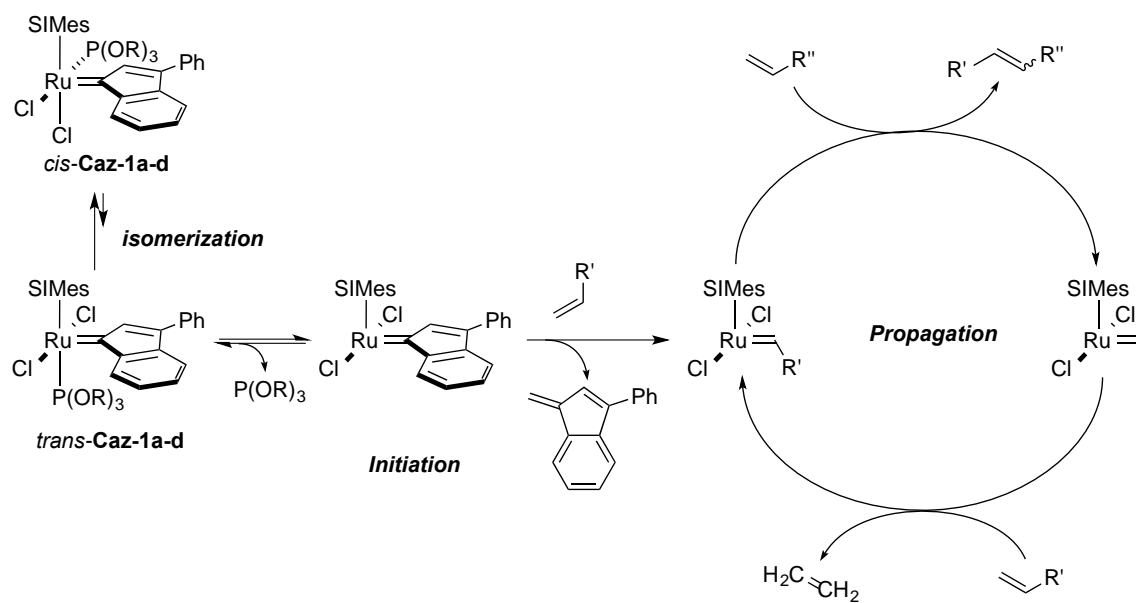
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2

3

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

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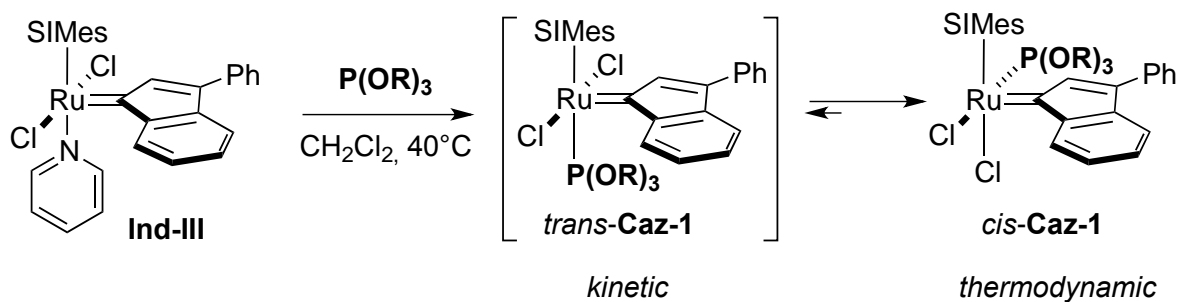
Entry	P(OR)$_3$ (equiv.)	θ (°)[a]	Time (h)	Yield (%)	Complex
1	P(OMe)$_3$ (1)	107	3	57	*cis*-**Caz-1b**
2	P(OEt)$_3$ (1)	109	5	88	*cis*-**Caz-1c**
3	P(OiPr)$_3$ (1)	128	15	84	*cis*-**Caz-1a**
4	P(OPh)$_3$ (4)	130	15	76	*cis*-**Caz-1d**

8   [a] *Tolman cone angle.*

9

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

2
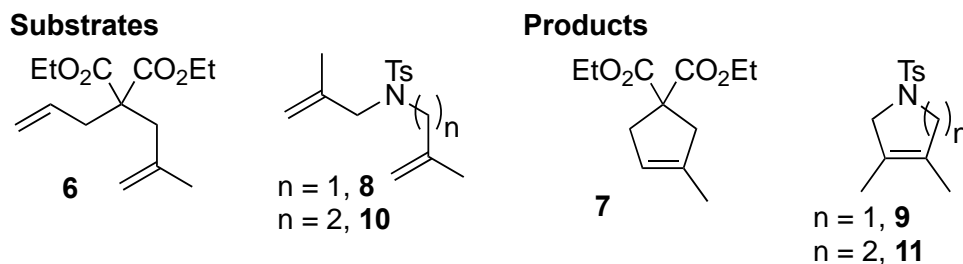
Entry	Substrate	Cat (mol%)	Conditions	Conv. (%)	Lit.
1		**Caz-1a** (1/0.075)[a]		> 99 / >99[b]	42
2		**Caz-1b** (1)[a]	toluene, 80°C, 0.5h	78	43
3		**Caz-1c** (1)[a]		35	
4		**Caz-1d** (1)[a]		98	
5	**6**	**Caz-1a**^{+} (0.1)	xylene, 140°C, 15 min	99	65
6		**Caz-2a** (0.025)	CH$_2$Cl$_2$, 50°C, 2h	96	59
7		**Caz-2b** (0.025)		>99	
8		**Ind-II'** (0.025)	CH$_2$Cl$_2$, 30°C, 1h	99	
9		**G-II** (0.025)		91	60
10		**Caz-3a** (0.025)	MTBE, 50°C, 8h	95	
11		**Caz-3b** (0.025)		93	
12		**Caz-1a** (0.5 / 0.1)[a]		>99 / 96[c]	42
13		**Caz-1b** (0.5)[a]	toluene, 80°C, 5h	27	43
14		**Caz-1c** (0.5)[a]		22	
15	**8**	**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$_2$Cl$_2$, 50°C, 2h	46	59
22		**Caz-2b** (2)		47	
23		**Ind-II'** (5)	toluene, 80°C, 1h	23	

3 [a] *Cis* isomers were used for compounds **caz-1a-d**. [b] Solvent-free, 120°C,

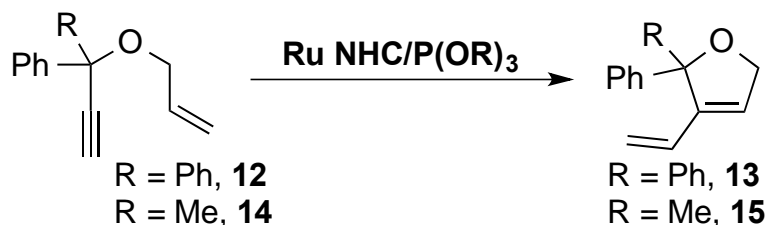4 15h, 0.075 mol% Ru. [c] Refluxing toluene, 5h, 0.1 mol% Ru.

5

6

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

2 RCM

3

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$_2$Cl$_2$, 50°C, 3h	94	59
5		**Caz-3a** (0.1)	MTBE, 50°C, 8h	78	60

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

5

6 **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**
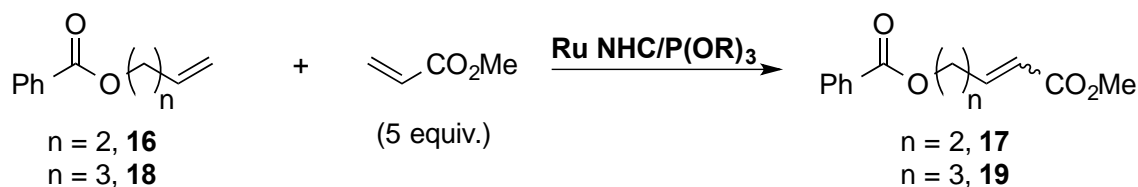
7

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$_2$Cl$_2$, 50°C, 3h	77	59

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

9 used.

10

11

1
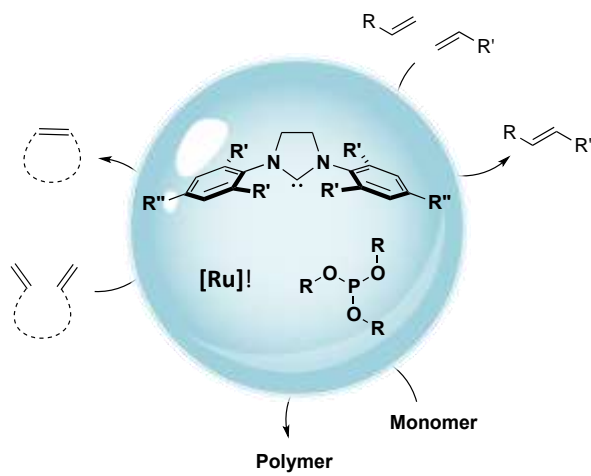2   **Table 5** Polymerization with different initiators
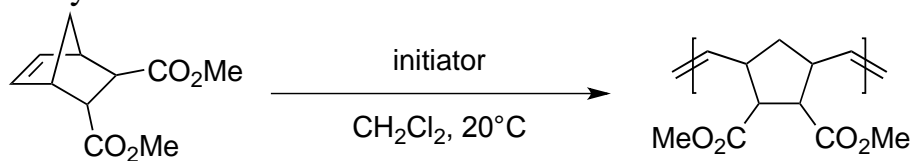
3

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

4   [a] Toluene, 80°C.
5

1   **Graphics for use in the Table of Contents**

2