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Unprecedented Selectivity of Ruthenium Iodide Benzylidenes in Olefin Metathesis Reactions

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Abstract: The development of selective olefin metathesis catalysts is crucial to achieve new synthetic pathways. Here we show that cisdiiodo sulfur chelated ruthenium benzylidenes do not react with strained cycloalkenes and internal olefins, but can effectively catalyze metathesis reactions of terminal dienes. Surprisingly, internal olefins may partake in olefin metathesis reactions once the ruthenium methylidene intermediate is generated. This unexpected behavior allows the facile formation of strained *cis*-cyclooctene by the RCM reaction of 1,9-undecadiene. Moreover, cis-1,4-polybutadiene may be transformed to small cyclic molecules, including its smallest precursor, 1,5-cyclooctadiene, by the use of this novel sequence. Norbornenes, including the reactive DCPD, remain unscathed even in the presence of terminal olefin substrates; being too bulky to approach the diiodo ruthenium methylidene. The impressively latent catalyst was activated by addition of an external chloride source, unveiling a novel method for controlled polymerization of DCPD. The experimental results are accompanied by thorough DFT calculations that provide insights towards further developments.

The remarkable versatility of ruthenium olefin metathesis catalysts has led to valuable and efficient reactions on a great variety of alkene substrates.1 Indeed, thoughtful modifications in the ligand sphere have expanded the catalytic properties of ruthenium alkylidenes. In this manner, asymmetric and stereoselective reactions were put forth and even alternating copolymers could be made.² An important contribution has been the development of latent precatalysts,³ mainly achieved by sulfur chelation.⁴ Latency is important in the field of polymerization, and it can be used for 3-D printing and to selectively guide orthogonal photochemical pathways.⁵ Undoubtedly, tinkering with the ligand sphere has been the prevalent approach towards tuning olefin metathesis catalysts' properties. As such, the anionic ligands have had a great influence on the efficiency and selectivity of ruthenium catalysts for olefin metathesis reactions.⁶ However, Slugovc et al. have shown that full exchange of the chloride ligands in HG-2nd-CI can be challenging.⁷ On the other hand, the trans effect in cis-dichloro ruthenium precatalysts greatly facilitates the substitution of the anionic ligands, disclosing a unique pathway for halide exchange, e.g. Ru-S-I, (Figure 1).8 Ru-S-I was shown to be an efficient latent catalyst for ring-closing metathesis (RCM) reactions; whereas it was completely inert for the ring opening metathesis polymerization (ROMP) of 1,5cyclooctadiene (COD).8c This unprecedented behavior led us to investigate the perplexing paradox of a complex that can only catalyze olefin metathesis of seemingly less reactive substrates9 by screening the reactivity of Ru-S-I towards other ROMP monomers (Figure 2). Herein, we disclose the unprecedented behavior displayed by Ru-S-I, which shows excellent reactivity for terminal alkenes, promotes metathesis of cyclooctenes only after producing the methylidene derivative and is completely inactive towards norbornene substrates, unless external chloride is added. By taking advantage of this selectivity, strained cycloolefins that are usually polymerized by other ruthenium catalysts could be efficiently synthesized and unusually reactive substrates could be obtained from the controlled depolymerization of polybutadiene.







Figure 2. ROMP and RCM substrates.

Table 1 summarizes the preliminary scope conducted following the typical reaction protocols (for latent complexes), i.e. 0.1M monomer with 1 mol% of Ru-S-I in toluene-d₈ at 80°C for 1h. Indeed, several strained ROMP monomers, including the usually highly reactive dicyclopentadiene (DCPD), did not react (Table 1, entries 2-6) even when heated. Previous literature reports with ruthenium diiodo olefin metathesis catalysts, revealed that ringopening at room temperature occurred only when the reaction was carried out in a chlorinated solvent,¹⁰ hinting that a partial halogen exchange was in effect.⁷ Moreover, ROMP initiated by another diiodo derivative had to be carried out at high temperatures, but RCM in this case could not be achieved.11 Notably, when norbornenes and **DEDAM** were mixed together, all the norbornene derivatives (DCPD, NDC and NAn) remained unaffected, even though RCM was efficiently achieved (Table 1, entries 7-9). Thus, to the best of our knowledge, Ru-S-I is the first catalyst that can efficiently promote RCM while being completely inert to ROMP of very reactive norbornenes in situ, even under trying conditions (high temperature and relatively high catalyst

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loading). The uniqueness of this sulfur-chelated system was further emphasized by a control experiment designed to compare Ru-S-I with HG-2nd-I. Indeed, also in our hands HG-2nd-I polymerized **COE** as previously reported;¹⁰ perhaps due to the partial presence of a monochloro-monoiodo impurity that could not be removed, even after several attempts. So, although the actual catalytic active species for Ru-S-I and pure HG-2nd-I are probably identical (because the initial benzylidene is lost after the first catalytic cycle of the RCM), the fact that we could not isolate pure Ru-S-I does not allow for a direct comparison between these catalysts. Another intriguing outcome of these exploratory studies was obtained in entries 10 and 11. Thus, mixing equimolar amounts of COE or COD with DEDAM and Ru-S-I resulted in the complete consumption of both metathesis substrates. Given that norbornene derivatives are highly strained and are usually more reactive than cyclooctenes for ROMP (especially DCPD, one of the most reactive ROMP monomers known), these results were quite puzzling. NMR of entry 10 clearly revealed the successful RCM of **DEDAM** and the appearance of new terminal vinylic hydrogens (SI, Fig. S10a). The observed broadness of these peaks hinted at the presence of oligomers. This assumption was readily confirmed by MALDI-TOF-MS analysis, where a distribution of oligomers with mass intervals of 110 daltons was observed (SI, Fig. S10d). Indeed, the resulting mixture was reminiscent of the product obtained from a typical ADMET reaction of 1,9-decadiene,¹² even though the monomer used in this case was cis-cyclooctene.

Table 1. Selective RCM and ROMP reactions.

entry	ROMP/RCM	ROMP	RCM
	Substrate	Conv.	Conv.
1	none/DEDAM	-	>99%
2	DCPD/none	o%	
3	NDC/none	о%	-
4	NAn/none	0%	-
5	COE/none	0%	- 6
6	COD/none	0%	-
7	DCPD/DEDAM	0%	75%
8	NDC/DEDAM	0%	90%
9	NAn/DEDAM	0%	93%
10	COE/DEDAM	>98%	>99%
11	COD/DEDAM	>99%	>99%

[a] Reaction conditions: 0.1M substrates, 1 mol% **Ru-S-I**, 1h at 80°C in toluened8. Conversions were monitored by 1H NMR. No conversions were observed for entries 2-6 also after 24h.



Scheme 1 Proposed methylene transfer mechanism.

The presence of terminal alkenes in the final product led us to envision a mechanism where the terminal methylene of the DEDAM was being transferred to COE by a crossmetathesis/ring-opening type mechanism (Scheme 1). The RCM reaction of **DEDAM** produces a methylidene complex, which is the least hindered diiodo ruthenium species. We propose that this basic intermediate can coordinate also non-terminal olefins, such as COE, and insert them into the metathesis catalytic cycle. Moreover, the Ru diiodo alkylidenes (not methylidenes) can only react with olefin substrates that are unobstructed (terminal alkenes or ethylene). Naturally, the 1,9-decadiene produced by this manner is itself a terminal alkene which can continue to react with the alkylidenes formed and produce the oligomers observed in the reaction mixture. The reaction was then repeated with different amounts of **DEDAM**. As expected, excess **DEDAM** led mainly to the selective production of 1,9-decadiene (SI, Fig. S12). Conversely, a 10:1 ratio of COE to DEDAM produced small amounts of "methylene initiator" that led to much larger oligomers (Figure 3). COD was also probed as the monomer and also produced the expected oligomeric species (SI, Fig. S21). As previously stated, the ADMET polymerization reaction, pioneered by Wagener et al.,^{12a} allows for the precise synthesis of welldefined polymers; however, as it is a condensation process, part of the monomer is lost during the reaction. However, in this special case (where a catalytic amount of **DEDAM** is added), the oligomerization proceeds through cross-metathesis reactions, as an ADMET does; but no material is lost during the process.

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Figure 3. MALDI-TOF MS analysis for the reaction of 10eq COE and 1eq DEDAM in the presence of Ru-S-I after 24h.

The ability of Ru-S-I to promote "ethenolysis" with DEDAM was also tested with jojoba oil. The oil was mixed with Ru-S-I in toluene for 1 hour at 80°C without any visible reaction. Then, addition of excess **DEDAM** led to efficient cleavage of the jojoba molecule; proving that also non-strained internal olefins may react by this mechanism (SI, Fig. S22). Previous literature reports have shown that specialized complex catalytic systems are needed to produce strained cycloalkenes by olefin metathesis.¹³ Having established that internal olefins cannot coordinate to Ru-S-I alkylidenes, we imagined that inhibition of methylidene formation could be achieved by having a terminal olefin only on one side of an RCM substrate. Then, the formed cycloalkenes should not be able to react further (see supporting information for proposed mechanistic cycles, Fig. S30). To test this hypothesis, a mixture of E,Z-1,9-undecadiene was synthesized as a precursor to ciscyclooctene. To our great satisfaction, COE was efficiently produced (together with small amounts of the expected dimer byproduct) even at relatively high concentrations (Figure 5 and SI). Control experiments with HG-2nd-CI showed that, under the same reaction conditions, oligomers are the main products and only traces of cis-cyclooctene can be observed (SI, Fig. S31). Further experiments were conducted with two additional substrates, 1,9-decadiene and 2-methyl-1,9-undecadiene. While the former expectedly afforded oligomers; the latter was completely unreactive, highlighting the susceptibility of the catalyst to steric hindrance (SI, Fig. S32 and 33 respectively). Depolymerization of the widely used industrial polymer, cis-1,4polybutadiene (PBD) by olefin metathesis is a well-studied reaction that usually produces cyclic alkenes.¹⁴ As expected for a non-terminal olefin, no reaction occurred when Ru-S-I was added to a PBD solution in hot toluene. But, if a small amount of DEDAM was also added, depolymerization readily took place. Remarkably, GC-MS analysis of the mixture of cyclic olefins revealed the presence of reactive COD, together with other macrocycles (SI, Fig. S37). A control experiment with HG-2nd-CI under the same conditions also induced the depolymerization of PBD; however, a much more complex mixture of oligomers was obtained, and no COD was seen in the mixture (SI, Fig. S38). Even though these first results only produced a minor amount of COD, having a catalyst that has the ability to depolymerize a polymer to its pristine monomer is a highly desirable goal to achieve unspoiled recycling.¹⁵



Figure 5. a) ¹HNMR of 1,9-undecadiene. b) ¹HNMR of reaction of 1,9-undecadiene (4 mM) with **Ru-S-I** after 24h. The olefin signals for **COE** are observed at 5.63 ppm and for the dimer byproduct at 5.40-5.50 ppm.

We then turned our attention to the norbornenes. The lack of reactivity observed for norbornene molecules is most likely due to a more congested coordination site caused by the bicyclic framework. Indeed, when mixing neat DCPD with 0.1% Ru-S-I, the liquid mixture remained completely fluid for periods longer than ten days; highlighting the impressive latency for this important industrial monomer. Knowing that Ru-S-CI is not latent for DCPD, we decided to attempt to induce ROMP by an in situ exchange of the anionic ligands. To our great satisfaction, a mixture of DCPD and Ru-S-I could be readily polymerized following addition of (Bu)₄NCI (SI, Fig. S41). Given the need to discover new strong materials for use in added manufacturing applications,¹⁶ the fact that this reactive monomer can be mixed with its precatalyst for very long periods without reacting and can be quickly polymerized by the addition of chloride is of great interest. Density functional theory calculations (DFT) were conducted to answer several experimental insights that were not obvious to rationalize. First, we wished to describe why the methylidene can react with a non-terminal alkene and an alkylidene cannot. Thus, the energy profiles for methylidene and ethylidene with COE were calculated (Figure 6). The energy profile is thermodynamically worse for ethylidene by more than 10 kcal/mol, and more interestingly, the kinetics for the ethylidene system are also worse for the opening of the metallacycle (9.3 kcal/mol) than for its closure (3.9 kcal/mol), which supports the extraordinary results observed in Table 1. Overall the upper energy barriers are 14.6 and 22.1 kcal/mol from the methylidene and ethylidene species, respectively. On the other hand, with chlorides, the energy values are more favorable (the upper energy barriers drop to 5.0 and 15.0 kcal/mol, respectively) and probably justify why CI is usually preferred over I in typical Ru catalysts. Moreover, the latter energy barriers are not for the precatalysts, but for the 14e species. Thus, there is an additional energy cost (14.1 kcal/mol, see SI for further details) that needs to be accounted for. Next, we also wanted to show that the diiodo alkylidene can react with a terminal alkene. Overall, DFT showed that metathesis of terminal alkenes catalyzed by Ru-S-I is valid not only with the methylidene species, but also with the ethylidene species, which keeps the catalytic cycle alive.

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Figure 6. Reaction mechanism of COE with the methylidene (R = H) and ethylidene (R = Me) for **Ru-S-I** catalyst. Relative free energies in kcal/mol calculated at B3LYP-d3/cc-pVTZ~SDD//BP86/SVP~SDD (in black for R = H and in green for R = Me, in parentheses the values for **Ru-S-CI**).



Figure 7. Topographic steric maps for the active catalytic methylidene species a) with iodides or b) chlorides. The linking C atom of the NHC is on the z axis, and the metal atom is 2 Å below the plane described by the metal and both halide atoms. The isocontour curves of the steric maps are given in Å.

Finally, to unveil the different behavior of the ruthenium catalysts bearing iodides or chlorides, the steric properties by calculation of the buried volume (%V_{Bur}) by means of the SambVca2.1 package developed by Cavallo and coworkers were studied.¹⁷ This computational tool has been used here to describe crowding of the metal center when including the more sterically demanding iodides, putting the eye on the plane placed 2 Å away from the plane that holds the metal and both halide atoms, to describe better the interaction between the metal center and the entering olefin. In particular, the quantitative comparison of the catalytic trans species with or without the Ru-S bond confirms that iodides impose a %V_{Bur} increase of 3.4 and 4.3%, respectively (Figure 7 and SI). In conclusion, the exchange of chlorides by iodides in sulfur chelated benzylidenes brings about an impressive change in olefin metathesis activity and selectivity. Both catalytic experimental results and extensive DFT calculations were used to investigate this phenomenon. Indeed, Ru-S-I is completely unreactive towards non-terminal olefins. The formation of the methylidene derivative subsequently enables metathesis with unobstructed internal olefins. On the other hand, if formation of the methylidene is discouraged by substitution on one end of the diene, then strained cycloolefins may be synthesized with unprecedented efficiency. Related to this behavior. depolymerization of PBD afforded cyclic oligomers, with the singular result that the mixture included COD. Finally, the extreme reluctance of Ru-S-I to react with norbornenes, provides the possibility to activate the latent catalyst by the addition of chloride ions even after prolonged periods of time. We are continuing to explore novel applications for this surprising new catalyst, such as its activation by photoinduced chloride release and studying the generality of the iodo effect on diverse latent Ru alkylidenes.

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The ISF is gratefully acknowledged for financial support. A. P. is a Serra Húnter Fellow, and thanks the Spanish MINECO for a project PGC2018-097722-B-I00. Keywords: Olefin Metathesis • Latent Catalyst • ROMP • DFT • RCM

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