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Nitrenium ions and trivalent boron ligands as analogues of N-heterocyclic carbenes in olefin metathesis; a computational study

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We used the density functional theory to evaluate the suitability of nitrenium ions and trivalent boron ligands as analogues of N-heterocyclic carbenes in ruthenium-based metathesis catalysts. We demonstrate that these analogues induce only minor structural changes in the Hoveyda-Grubbs-like precatalysts, but have major impact on the precatalysts initiation. Nitrenium ions-modified precatalysts are characterized by a weak Ru-N bond resulting in relatively strong Ru-O bond and large free energy barriers for initiation, making them good candidates for efficient latent Ru-based catalysts. On the other hand the trivalent boron ligand, bearing a formal -1 charge, bind strongly to the Ruthenium ion, weakening the Ru-O bond and facilitating its dissociation, to promote fast reaction initiation. We show that the calculated bond dissociation energy of the Ru-C/N/B bond may serve as an accurate indicator of the Ru-O bond strength and the rate of metathesis initiation.

Introduction

Metathesis reaction, named as "emerging green technology" by the Royal Academy of Science during the 2005 Nobel Prize award, is a versatile tool for the formation of C-C bonds. The introduction of metal-based metathesis catalysts resulted in an enormous scientific progress and enabled wide industrial applications of this reaction.[1] Ruthenium catalysts, developed first by Grubbs, are particularly valued for their high stability and fast initiation in a range of metathesis reactions. The 2nd generation Grubbs ruthenium complex bearing the N-Heterocyclic carbene (NHC) and its modification suggested by Hoveyda (**1**) were the milestones in olefin metathesis and allowed to extend the scope of this reaction.[2] It was soon realized that the activity and selectivity of the catalyst can be directly controlled by the choice of a N-heterocyclic carbene ligand. Today there are numerous examples of 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (SIMes) and 1,3-bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene (IMes) derivatives that can act as potent catalyst in various metathesis reactions.[1c,d]

In the recent years there have been many attempts to synthesize new metathesis catalysts based on Hoveyda catalyst, by introducing various structural modifications in its structure. There are numerous examples of structural changes in the benzylidene part and isopropyl moiety altering the catalytic activities of such compounds, often to a large degree.[1,3] New generations of olefin metathesis catalysts with some major structural changes have also been recently suggested based on computational results. New carbene-replacing moieties for olefin metathesis have been suggested recently using an evolutionary algorithm for *de novo* ligand optimization.[4] Similarly, Cavallo and Slugovc showed promising DFT results for ruthenium bis-ylidene complexes as potential catalysts for olefins metathesis.[5] There have been also some studies showing that Grubbs-type catalysts with Ru replaced by Fe might be a viable option in olefin metathesis and result and cheaper and more environment-friendly catalysts.[6] These studies show that the computational approach is a feasible option in exploring the vast space of molecular structures when searching for new catalysts to help in their design and synthesis.

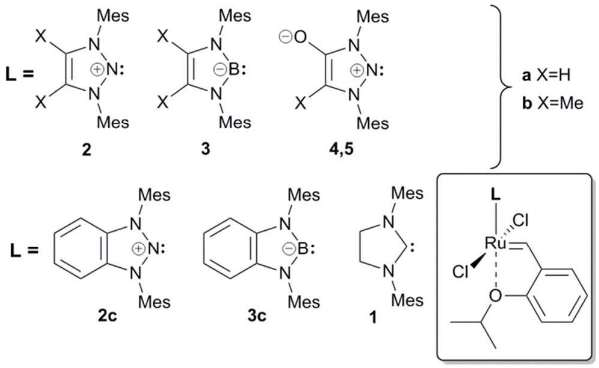

Fig. 1 Structure of the catalysts investigated in this work. For the asymmetric ligand system **4** corresponds to the enolate group positioned on the same side as the benzylidene part of the catalyst, while **5** corresponds to the enolate group positioned on the same side as the isopropyl part of the catalyst.

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Interestingly, the replacement of the entire NHC by another member of the Arduengo-type ligand with a different atom bonding the metal cation has been rarely suggested. Recently, however, new types of such ligands and their complexes with metal ions has been reported: these include the N-heterocyclic nitrenium ion (NHN)[7] and the trivalent boron compounds (denoted here as NHBs).[8] The nitrogen-derived analogue of NHC (Fig. 1, structures **2a**-**c**) is isoelectronic to the N-heterocyclic carbene, but is significantly different in its ligation behaviour. For NHCs, the interactions with transition metals are dominated by the σ-donation;[9] this is specifically clear for the systems with ruthenium ions.[10] On the other hand NHNs show mostly π-acceptor properties, due to the presence of cationic nitrogen centre with a vacant p-orbital. Crystal structures with the triazolium ligands bound to transition metal ions were obtained for Rh, Ru,[7a] Pt[7b] and Ni,[11] yet the potential catalytic activity for none of these compounds has yet been examined.

The boron derivatives of NHC (Fig. 1: structures **3a**-**c**) may be viewed as system laying on the opposite side of the electronic structure spectrum, due to its -1 formal charge. Trivalent boron compounds are in general considered as Lewis acids, due to boron atom empty p-orbital perpendicular to the molecular plane.[8] However, boron atom can change its character to more nucleophilic upon a substitution with an electron donating groups.[12] These compounds are considered very reactive, with great σ-donation capability, therefore they need an additional stabilization to be bound to transition metal as a ligand. Moreover, ^{11}B NMR experiments suggest anionic character of the ligand which is preserved also in the diamino-substituted boryllithium.[12a] Unfortunately, to our knowledge no ruthenium olefin metathesis catalysts with NHBs are known.

Both NHNs and NHBs offer new functionalities and new potential catalysts in tandem with Ru^{2+} and other transition metal cations. Regrettably, the synthesis of metal complexes ligated by NHNs and NHBs proceeds slowly due to various difficulties in experimental handling of these moieties. Due to this fact we decided to employ computational methods to asses, whether they are a viable option for new, potent metathesis catalysts. In this work we present a computational, density functional-based study of hypothetical Hoveyda-type Ruthenium catalysts with the original NHC group replaced by either NHN or NHB moieties. The calculations have been performed using a computational protocol similar to our previous studies (see Experimental section for details).[13] We have analysed the impact of the changes on the structural and electronic properties of six hypothetical catalysts: three bearing different NHN groups (**2a**-**c**) and three with the NHB groups (**3a**-**c**). The structure of these precatalysts was based on the known Hoveyda catalyst **1**. We also performed calculations for the initiation step of the catalytic cycle of these systems and compared them to the original Hoveyda catalyst. Additionally, we performed calculations for NHN-containing catalysts modified with enolates, resulting in neutral systems (Fig. 1, **4**-**5**), based on previously synthesized, enolate-substituted NHC rhodium complexes.[14] In the case of BHN-containing catalysts we also performed additional calculations with a Na$^+$ ion acting as an counterion.

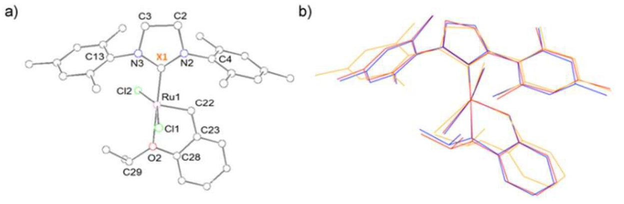

Fig. 2 (a) Labelling scheme of precatalysts; X1 stands for C(1) in Hov, N(1) for NHNs and B(1) for NHBs and (b) molecular overlay of structures of investigated precatalysts: 1 (red) vs 2a (blue) and 3a (orange).

Results and discussion

Structural studies

We started our analysis of the new, hypothetical catalysts by finding the energy minima for the isomers with the chlorides in either the cis or trans positions. In the case of 1 it is known that the trans geometry is favoured over the cis one not only for the precatalyst, but throughout the entire catalytic reaction.[15] On the other hand some similar compounds with a different NHC and other structural modification can adopt the cis conformation.[16] In the case of all NHNs (structures **2**, **4** and **5**) we found that the trans stereoisomers were favored by 3-7 kcal/mol (see Geometry of precatalysts in the ESI†). On the other hand in the NHBs case the energy differences between trans and cis isomers were below 1 kcal/mol and on the level of the M06 method accuracy. Further in this work we decide to analyze only the trans isomer, but such a small difference is worth keeping in mind as it may negatively affect the catalytic potency of NHBs.

The structural differences introduced with the change of the C carbene into N or B, between Hoveyda catalyst (**1**) and its NHN (**2**) and NHB (**3**) derivatives are presented in Fig. 2 and Table 1. The largest differences between the three precatalyst can be observed for the Ru1-O2 bond (see Figure 2 for labelling), which is elongated by 0.2 Å for the boryl-substituted system and shortened by ca. 0.14 Å for the triazolium-substituted one. An opposite trend may be observed for the Ru1-C22 and O2-C29 bonds, which are slightly longer in the NHN case, but shorter for the NHB-modified system. Additionally, the Ru1-X1 bond is elongated with respect to **1** for both modifications. Such a result is surprising, since we expected a longer and weaker bond for the NHN-modified catalysts, but a shorter and stronger bond for the NHB-modified system. All other geometric parameters are rather conserved and the differences between them are close to negligible. In the case of systems **4** and **5** we expected that the neutralization of the NHN ligand charge would yield geometries more similar to the original Hoveyda catalyst **1**. This hypothesis was found to be true for the Ru1-C22 bond length; additionally the Ru1-O2 bond became elongated while the O2-C29 bond became shortened with respect to system 2. On the other hand, the Ru1-X1 bond became even more elongated with respect to **2**, yielding the value of 2.1 Å. We can attribute this effect to the

Table 1. The comparison of structural parameters of investigated compounds.

	1	**1** x-ray[2b]	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**4a**	**4b**	**5a**	**5b**
						Bond length (Å)						
Ru1-C22	1.833	1.829(1)	1.848	1.848	1.850	1.823	1.824	1.824	1.831	1.830	1.832	1.831
Ru1-X1	1.972	1.979(1)	2.033	2.052	2.010	2.016	2.023	2.023	2.103	2.108	2.099	2.101
Ru1-O2	2.328	2.256(1)	2.183	2.183	2.192	2.540	2.546	2.546	2.200	2.206	2.202	2.202
O2-C28	1.352	1.370(2)	1.359	1.359	1.358	1.350	1.349	1.349	1.359	1.360	1.358	1.358
O2-C29	1.449	1.469(2)	1.471	1.471	1.471	1.430	1.430	1.430	1.458	1.457	1.460	1.460
						Plane angle (degrees)						
N1-X1-N2	106.71	107.20(1)	104.50	104.50	105.86	101.68	101.67	102.32	104.05	103.84	104.15	103.89
X1-Ru1-C22	102.68	101.34(6)	102.34	102.34	102.28	98.90	99.59	99.48	102.10	102.27	102.78	102.91
Cl1-Ru1-Cl2	160.26	156.25(1)	163.37	163.37	163.30	149.45	150.03	150.34	162.14	162.38	163.09	163.25
						BDE (kcal/mol)						
Ru1-X1	80.86	-	41.31	41.10	43.24	126.40	126.46	125.05	41.84	41.92	57.29	42.09

presence of the electron donating group in the aromatic ring, which weakens the π-acceptor ligation properties of NHN, but maintains the σ-donation at the similar level.

Performance in metathesis initiation

There are three possible initiation pathways of olefin metathesis precatalysts activation. In the dissociative mechanism the entire catalytic process is initiated by the dissociation of the Ru1-X2 bond, followed by the olefin association. Such a mechanism is prevalent in the case of the first and second generation Grubbs precatalysts, triggered by the Ru-P bond dissociation.[17] In the associative mechanism the entire catalytic process commences with the olefin association followed by Ru1-X2 (X = P or O depending on the catalyst) bond dissociation. A third possibility is the interchange mechanism, where both events (olefin association and Ru1-X2 bond dissociation) occur simultaneously. The most recent theoretical and experimental results suggest that for all investigated Hoveyda-like and Grubbs-like systems the associative mechanism is always characterized by the highest energy barrier.[18] On the other hand the interchange mechanism is often a viable pathway and in many cases and depending on both the catalyst and the olefin substrate, the initiation may follow either the dissociative, interchange or both mechanisms in parallel. In all known cases precatalyst initiation is the rate-limiting step of the olefin metathesis catalytic cycle at low and moderate olefin concentrations.[19] As a result, in this study we have only considered the dissociative and interchange mechanisms as valid initiation pathways for the new hypothetical precatalysts.

The results of the initiation energy barriers for all three NHN precatalysts (see Fig. 3) **2a**-**c** clearly suggest that these hypothetical systems are poor candidates for potent and fast metathesis catalyst. The commonly used catalysts, including **1**, are characterized by energy barriers of approx. 19-21 kcal/mol,[20] yielding moderately fast initiation at ambient temperature. Our calculations for the NHN-modified precatalyst give us free energy barriers of 27-28 kcal/mol for the interchange mechanism. The 8 kcal/mol difference in activation free energy translates at room temperature, using Eyring equation, to roughly $2 \cdot 10^{-6}$ times slower reaction. In the case of the dissociative path we were not able to obtain the transition states for the dissociative path with the proper geometry and the correct number of imaginary frequencies. Nevertheless, we can estimate the free energy barriers based on the free energy of products to be at least 23 kcal/mol for **2c** and at least 26-27 kcal/mol for **2a**-**b**. These values give differences of 3-7 kcal/mol between the activation free energies of **1** and **2a**-**c**, which at room temperature translates into 5-3000 times lower initiation rate constant.

On the other hand the NHB-modified precatalysts have completely different and much lower activation free energies. For all three considered precatalysts the free energy barrier is lower for the dissociative path then the interchange path by several kcal/mol. The most interesting results are, however, the low estimated values of these barriers. In the case of **3c** the free energy barrier is estimated at 12.83 kcal/mol, while for **3a**-**b** they are 1-2 kcal/mol higher (Fig. 3). Such low values should in this case translate to a very low initiation rate constant and very fast reaction rate. We can compare them to one of the fastest initiating metathesis catalyst, the 6-coordinated [(H2IMes)(3-Br-py)2(Cl)2Ru=CHPh designed by Grubbs in 2002.[21] The experimental lower limit of the initiation rate constant of this Grubbs catalyst was estimated to be 4 s^{-1} at 5^{o}C. We have previously shown that this value corresponds to the $\Delta G^{\ddagger}$ of 15.5 kcal/mol.[13c] As a result we can realistically expect that **3c** should initiate at a similar rate or faster. Inspired by these results we made an attempt to find the relationship between the obtained $\Delta G^{\ddagger}$ values of the new, hypothetical catalysts and their structure.

The obvious difference between **1**, **2** and **3** is the different formal charge of the ligating group bound to Ruthenium cation. We first evaluated the Ru1-X1 bond dissociation energy (BDE) of all studied compounds. As expected, the BDE and bond strength depend on the formal charge of the ligating group and is the lowest for NHNs-modified precatalyst, estimated between 41 and 43 kcal/mol (see Table 1). The relative weakness of the bond comes naturally from the electrostatic repulsion between the Ru^{2+} ion and the NHN group bearing the +1 formal charge. NHB-modified precatalysts **3a**-**c** are on the other side of the spectrum with an additional attractive force between the Ru^{2+} ion and the ligating group with the -1 formal charge. For these systems the

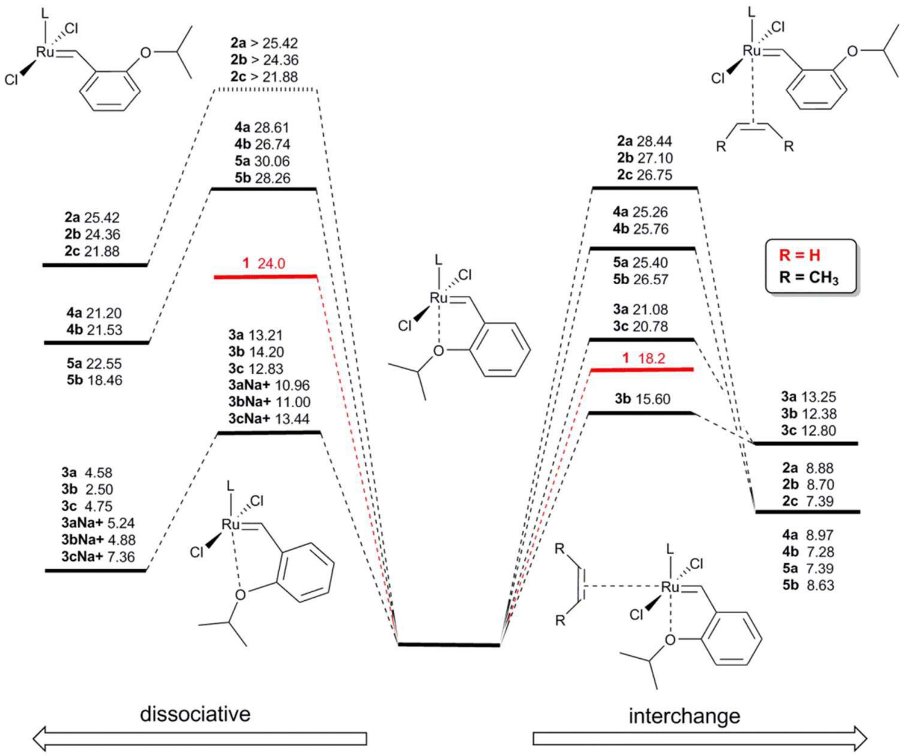

Fig. 3 Free energies (in kcal/mol) for the initiation step for NHN and NHB Hoveyda-derivatives precatalysts following the dissociative or interchange mechanism. Reference values (red) for Hoveyda catalyst 1 are taken from ref. 18.

BDE estimates are between 125 and 127 kcal/mol. These values may be directly compared to the BDEs of Grubbs catalyst, Hoveyda-Grubbs catalyst **1** (both estimated previously at 80 kcal/mol), and to other, similar catalysts with acyclic carbenes (69-74 kcal/mol).[13b]

These results are interesting since there have been attempts to connect the σ/π-donation with the strength of the Ru-carbene bond. Our study is the second example of the correlation between the high BDE and low-energy barrier for this type of catalysts. Here, however, we can clearly see that a stronger Ru1-X1 bond corresponds directly to a longer, and therefore weaker Ru-O2 bond, which makes the precatalyst less stable and the reaction initiation more likely to occur.

In the final step of this study we modified the NHN precatalysts by adding an enolate group in two different positions to yield neutral catalysts **4a**-**b** and **5a**-**b**. The goal of this step was to see whether the neutralization of the NHN ligand by forming a zwitterion-like structure, but retaining the formal +1 charge on the N atom directly bonded to Ru^{2+}, allows us to lower free energy barrier for the initiation. The results, presented in Table 1 show that this is not the case. In all four studied cases (**4a**-**b**, **5a**-**b**) the free energy barriers of both the dissociative and interchange path remain relatively high, at 25-30 kcal/mol. The Mulliken population analysis of systems **2**, **4** and **5** reveals that the N1 partial charge is very similar for all these catalysts, irrespective of the NHN formal charge. In this case we can again see that the high free energy barriers correlate with the low BDE of the Ru1-N1 bond. Similar results were obtained in the case of calculations for NHB-containing systems **2a**-**c** in the presence of the Na^+ counterion, where the neutralization of the entire catalytic system does not affect much free energy barriers.

Conclusions

There are numerous studies on the ruthenium-based catalyst showing that they can be tuned by introducing small structural changes to their benzylidene or carbene part (e.g. by adding electron-donating or electron-withdrawing groups), adding new ligands/molecules to the first coordination centre of ruthenium or substituting chlorine atoms by other atoms/moieties.[22] This work is the first attempt to gain knowledge about the impact of replacing the carbene carbon atom by either nitrogen or boron atom on the structure and reactivity of Hoveyda-Grubbs type precatalyst. We show that we can tune the free energy barrier of the precatalyst initiation reactions by altering the Ru1-X1 bond strength, which in turn affects the ease of the Ru1-O2 bond dissociation. These two bonds work in opposition to each other, therefore the stronger Ru1-X1 bond corresponds to the easier Ru1-O2 bond dissociation and vice versa. As a result, the nitrenium ions-modified precatalysts with a weak Ru1-N1 bond show difficult Ru1-O2 bond dissociation and large free energy barriers of initiation which makes them poor candidates for fast metathesis catalysts, but potentially good candidates for latent catalysts.[23] On the other hand NHB-modified precatalysts, possessing strong Ru1-B1 bond, are excellent candidates for very fast and efficient metathesis catalysts. We also show that the Ru1-X1 BDE is an excellent and easy to obtain indicator of the suitability of the precatalyst as a rapid/latent olefin metathesis catalyst.

Experimental

Computational details

In this study we used density functional theory (DFT) calculations to study the structures of investigated complexes and possible pathways of their initiation mechanisms. The calculations have been performed using a computational protocol similar to our previous studies.[13] We have used an all-atom model for all studied catalysts and the cis-2-butene molecule to model the substrate of olefin metathesis. Starting models for precatalyst were prepared on the basis of available CSD crystal structures of a well-known Hoveyda precatalyst (refcode: ABEJUM01).[24] In the first step, all structures were modelled using the M06-D3 density functional with the 6-31G** basis set for all atoms except the Ru atom, which was described by the Los Alamos angular momentum projected effective core potential (ECP) using the double-ζ contraction of valence functions (denoted as LACVP**).[25] We have chosen M06 functional, since it was also shown to perform particularly well for ruthenium-based catalysts, giving accurate energies for a number of Grubbs and Hoveyda systems.[26] Since the M06 functional has already medium-range dispersion implemented, M06-D3 may overestimate the effect of dispersion due to double-counting of these effects.[27] On the other hand the addition of D3 correction to M06 was shown to improve the results for many organic reactions when calculating the differences in relative energies.[25]

We have used the standard energy convergence criterion of $5 \cdot 10^{-5}$ Hartree. For each structure frequencies were calculated to verify the nature of each stationary point. In the second step we calculated solvation energies using the Poisson-Boltzmann self-consistent polarizable continuum method (PBF) as implemented in Jaguar v.7.9 (Schrodinger, 2013) to represent dichloromethane, using the dielectric constant of 8.93 and the effective radius 2.33 Å. The solvation calculations were performed using the M06-D3/LACVP** level of theory and the gas-phase optimized structures. For all stationary points we have also performed single-point energy calculations using the same M06 functional, but with a larger basis set: here Ru was described with the triple-ζ contraction of valence functions augmented with two f functions, and the core electrons were described by the same ECP; the other atoms were described with the 6-311++G** basis set.

Energies discussed in this work for stationary points are free energies, calculated as the sum of electronic energy (single-point, using the larger 6-311++G** basis set), solvation energy, zero-point energy correction, thermal correction to enthalpy, and the negative product of temperature and entropy (at 298 K). In the case of bond dissociation energies we used the same 6-311++G** basis set and counterpoise correction using the standard Boys-Bernardi scheme.[28]

In the case of complexes **3** with Na^+ counterion, we have started with the previously optimized geometry of **3a** pre-catalyst and prepared five different systems with the Na^+ ion in different positions. Upon geometry optimization the system with the lowest total energy had the Na^+ ion positioned close to the B atom of the NHB group and one of the chlorides (see ESI† for details). We used this optimized position of the Na^+ ion in further calculations of all stationary points for the **3a**-**c** complexes with the counterion.

Acknowledgements

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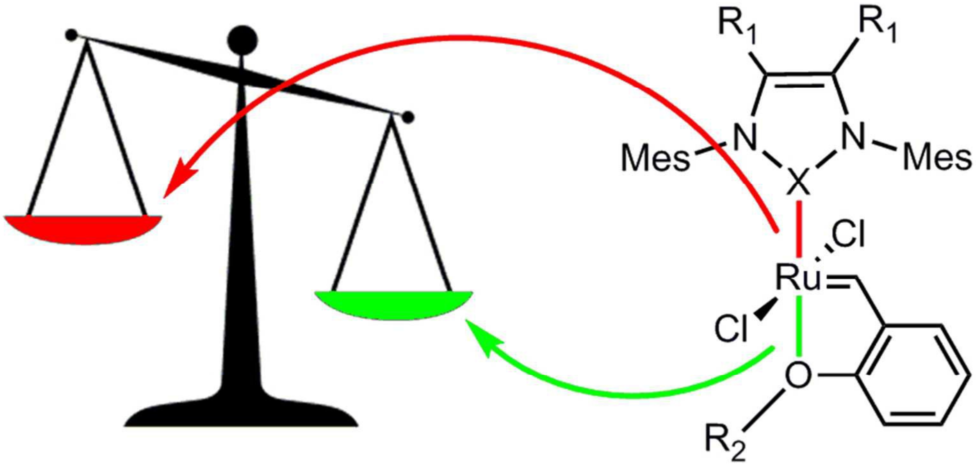
TOC text:

A DFT mechanistic study reveals that nitrenium ions-modified Hoveyda-like complexes are good candidates for latent metathesis catalysts, while boron-modified systems are candidate for very fast metathesis catalysts.



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