

Chapter 6: Rhenium and Osmium as replacement metals in the second generation Grubbs metal carbene catalyst

6.1 Motivation

The success of alkene metathesis catalysts seems to be strongly connected to the type of metal used as metal carbene. From the previous article we saw what effect of only the metal in the Gr₂ framework can have on the electronic properties of the metal carbene. Of the six transition metals that complied with the criteria for alkene metathesis activity, rhenium and osmium stood out as possible candidates for substitution of ruthenium. They are close in properties and position in the periodic table to ruthenium. This appears to give these metals the advantage for substitution into the Gr₂ framework, without having to change the ligands. By comparing the reaction of a known experimental reaction with part of the reaction already calculated, the effect of the change of metal could be elucidated. As this work is only a preliminary testing of the viability of the method, the results are presented as a communication.

6.2 Communication

Rhenium and Osmium as replacement metals in the second generation Grubbs metal carbene catalyst

Computational results have shown the viability of substituting the ruthenium in the second generation Grubbs catalyst with rhenium and osmium. Both metals show a similar bonding scheme in terms of the molecular orbitals to ruthenium, as well as exhibiting a comparable reaction energy profile.

Starting from the accidental discovery of alkene metathesis in the 1950s and 1960s [1], a lot of research has been done and applications found for alkene metathesis. After the discovery of the highly active Grubbs [2] and Schrock-type [3] metal carbene catalysts, the field was opened for the design and development of new catalysts. Still, “a truly practical and exceptionally selective catalyst” [4] has yet to be found. In this regard, osmium and rhenium have been substituted into the second generation Grubbs catalyst (Gr2) framework, replacing the ruthenium, to elucidate the effect of changing the metal and to verify the possibility of using these two metals in future catalyst design.

A screening was done of all transition metals as possible metal substitute in the Gr2 framework [5]. According to the criteria of having a larger atomic orbital coefficient on the metal atom than the carbene carbon atom in the LUMO of the catalyst, as well as having a slightly positive charge, rhenium and osmium were selected. In a study regarding the classification of metal carbenes [6], osmium has been theoretically tested and found to be similar in classification to ruthenium. Both are termed “electrophilic Schrock” [6] type carbenes, rendering osmium a possible substitution for ruthenium. According to the authors, no known computational and experimental metathesis work has been done on the substitution of either metals specifically in the Gr2 framework.

In an experimental reaction done by Chatterjee *et al.* [7], the cross metathesis reaction of allylbenzene and an allylic alcohol with Gr2 gave a cross product yield of 80% after 12 hours at 40°C. In former work [8] this reaction was investigated theoretically to assess the capability of the frontier molecular orbitals (FMO) to predict and explain the experimental results. Because we wanted to know whether the FMO as reactivity indicator could be useful in the initial steps, the reaction was only investigated up to the metallacyclobutane intermediate (MCB). Fig. 1 shows the calculated reaction scheme. The energy profile was drawn considering all structures up to the MCB, but the in-depth study of the FMO was only done for steps **D1**, **D2-D3** and **D3**. The calculations were then repeated for comparison by first substituting the ruthenium with rhenium and then with osmium.

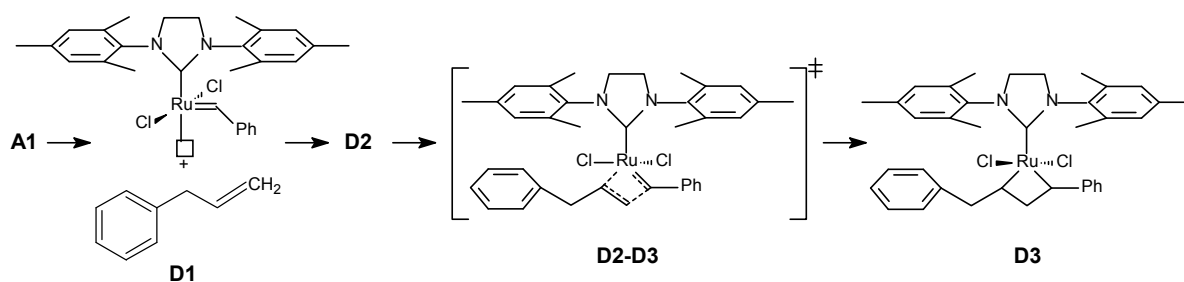


Fig. 1. The reaction scheme studied according to the work of Chatterjee *et al.* [7] and a previous study [8], with **A1** the precatalyst and **D2** the coordinated alkene-catalyst-complex.

In all instances the initial geometry optimizations were done with Materials Studio 5.0 [9] using the GGA PW91/DNP method, as well as the potential energy surface (PES) scans. Further energy calculations were done with Gaussian 03 [10] using the B3LYP/LanL2DZ method.

In all instances for reaction step **D1** (Table 1), the site of the metal atom should be the favored site for primary overlap of the HOMO of the alkene with the LUMO of the catalyst with Ru AOC 0.44, Re AOC 0.35 and Os AOC 0.38. Secondary overlap at the carbene carbon is also possible with Ru C-atom AOC 0.37, Re C-atom AOC 0.25 and Os C-atom AOC 0.29.

Table 1 Atomic orbital coefficients (AOC) of the LUMO molecular orbital of reaction step **D1** of Ru, Os and Re in the Gr2-type catalyst framework

Ru			Os			Re		
Atom	AO	coefficient	Atom	AO	coefficient	Atom	AO	coefficient
Ru	d_{xy}	0.44	Os	$d_{z^2-r^2}$	0.35	Re	d_{xy}	0.45
C	p_y	0.37	Os	d_{xz}	0.30	Re	d_{xz}	-0.35
C	p_y	0.26	C	p_z	0.29	Re	d_{xy}	0.23
Ru	d_{yz}	0.21	C	p_y	0.24	Re	$d_{x^2-y^2}$	0.23
			C	p_y	0.24	Re	d_{yz}	0.21
			Os	d_{xy}	0.20	C	p_y	0.20

All molecular orbitals, with an AOC for the metal atom, carbene carbon atom and the two carbons of the alkene in the molecule, with a value higher or equal to |0.20| indicate the bonding in the transition state and MCB that leads to further metathesis products. The bonding orbitals of the Re and Os substituted species that comply with this criteria (see Appendix C), have been found to be similar to those of Ru [8]. In Fig. 2 the MO diagrams of the selected bonding orbitals are shown. All bonding orbitals are lower in energy than the HOMO leading to stable bonding and are again quite similar to Ru.

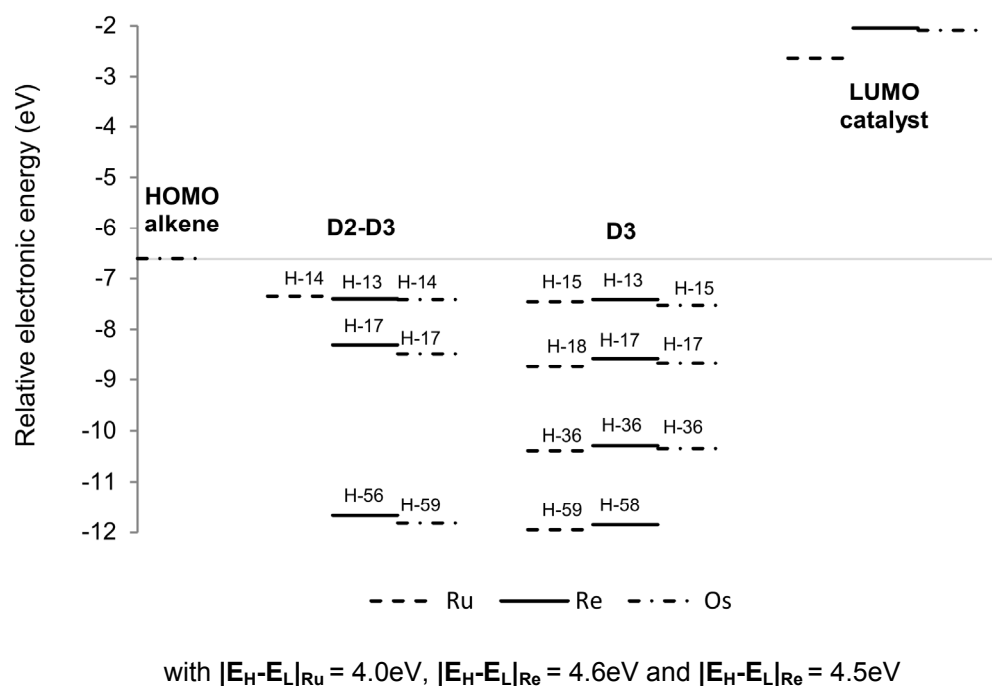


Fig. 2. The MO diagrams of the Ru, Re and Os substituted metals in Gr2 ligand framework with the relative electronic energy in eV.

In the reaction energy profile (Fig. 3) all catalysts have the dissociation of the PCy_3 -ligand as rate-limiting step. Rhenium has the overall lowest energy profile, with osmium having the highest energy profile. Both compare well with the profile of ruthenium. Thus, for the alkene metathesis reaction up to the formation of MCB the reaction pathway with rhenium as metal substitution in the Gr2 framework will be favored.

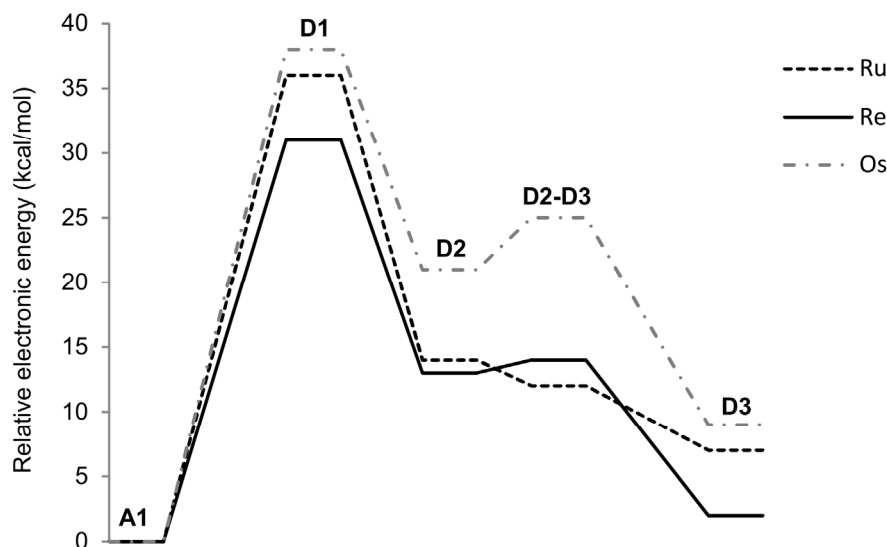


Fig. 3. Reaction energy profile of the studied reaction scheme with the different substituted metals in the Gr2 catalyst framework, with the relative electronic energy in kcal/mol.

To conclude, we have calculated the reaction of Chatterjee *et al.* [7] with the exception of substituting the ruthenium in the Gr2 catalyst with osmium and rhenium. Preliminary results show the possibility of using these metals successfully as alkene metathesis catalysts. However, further investigations and experimental testing will be done to elucidate fully the potential of osmium and rhenium as future metals in a second generation Grubbs-type framework.

Notes and references

- [1] A.M. Rouhi, Chem. Eng. News (Washington) 80 (2002) 34.
- [2] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J. Am. Chem. Soc. 114 (1992) 3974.
- [3] R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. DiMare, M. O'Regan, J. Am. Chem. Soc. 112 (1990) 3875.
- [4] A. Hoveyda, A. Zhugralin, Nature 450 (2007) 243.
- [5] J.I. Du Toit, C.G.C.E. Van Sittert, H.C.M. Vosloo, J. Organomet. Chem. (2012) Submitted. (Chapter 5 Article in thesis)
- [6] G. Occhipinti, V.R. Jensen, Organometallics 30 (2011) 3522.

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- [7] A.K. Chatterjee, T. Choi, D.P. Sanders, R.H. Grubbs, *J. Am. Chem. Soc.* 125 (2003) 11360.
- [8] J.I. Du Toit, C.G.C.E. Van Sittert, H.C.M. Vosloo, *J. Organomet. Chem.* (2012) Submitted. (Chapter 4 Article in thesis)
- [9] Accelrys Software Inc, Materials Studio Modeling Environment, Release 5.5.0.0. San Diego, Accelrys Software Inc, 2010.
- [10] M.J. Frisch, G.W. Trucks, H.B. Schlegel *et al.*, Gaussian 03, Revision B.03. Gaussian Inc, Pittsburgh PA, 2003.