Chapter 5: Changing the metal in the Grubbs 2 metal carbene metathesis catalyst framework – a DFT study

5.1 Motivation

The four main types of metal carbenes tested and used for alkene metathesis since the breakthrough of the mechanism by Chauvin all have different metal centres. Tungsten, titanium, molybdenum and ruthenium all are in different positions in the periodic table. However, Mo and W share a group and Mo and Ru share a period. Ti is an early-transition metal in the third period. The position of the transition metals in the periodic table has an influence on the number and type of empty d-orbitals available for possible [2+2] cycloaddition reactions with alkenes. If the criteria for metathesis is empty d-orbitals, in the form of the LUMO, changing the metal might have a profound effect on catalyst activity. Therefore, all transition metals except the radioactive Tc, were substituted into the Gr2 ligand framework to elucidate the effect that changing the metal will have on the electronic properties of the metal carbene.

5.2 Article

Changing the metal in the Grubbs 2 metal carbene metathesis catalyst framework– a DFT study

Abstract

By changing the metal atom of the second generation Grubbs catalyst, the properties of the metal carbene and subsequent activity of the catalyst for alkene metathesis will change. Screening of all possible transition metals for substitution with ruthenium led to new avenues of research for the development of better alkene metathesis catalysts. Chromium, cobalt, rhodium, rhenium, osmium and iridium complied with the criteria defined for possible metathesis activity. Osmium has the added advantage of showing potential metathesis activity in the precatalyst form.

Keywords

Frontier orbitals, alkene metathesis, transition metals, DFT

Introduction

"The alkene metathesis reaction is one of the most original and unusual transformations in chemistry. Remarkably, the strongest bond in the alkene, the C=C double bond, is broken during the reaction" [1]. Alkene metathesis has come a long way since the first observation by Eleuterio in 1956 [2]. Chauvin's metal carbene mechanism [3] paved the way for researchers to develop new catalysts. From the first used Fischer-type metal carbenes [4] to the discovery of the highly active Schrock- [5] and Grubbs-type [6] metal carbenes; alkene metathesis proved itself as a powerful synthesis technique. However, "the full potential of olefin metathesis will be realized only when additional catalysts are discovered that are truly practical and afford exceptional selectivity for a significantly broader range of reactions" [7]. Up to date the second generation Grubbs catalyst is found to be the most widely used of all developed metal carbene catalysts, because of its stability and usability. In this chapter

we aim to use the ligand framework of this catalyst as basis for investigating possible transition metals as viable substitutions for ruthenium.

The second generation Grubbs catalyst comprises two major role playing ligands: a phosphine ligand bound on one side of the metal and a NHC ligand bound on the other side of the metal atom. Phosphine is a common spectator ligand with a lone pair on the central atom that can be donated to the metal [1],[8]. The aryl phosphine promotes slight π acidity, and the σ* antibonding orbitals of the P-Cy bonds play the role of acceptor in PCy_3 [9]. Bulky PCy_3 ligands favor the formation of low-coordinate metals with a Tolman cone angle of 170° [1]. On the other hand, the N-heterocyclic carbene (NHC) ligand tends to be a stronger electron donor than the PR_3 ligand. Furthermore, the thermodynamic instability of free NHCs causes dissociation of the ligand to be strongly disfavored. Therefore, because of the high trans effect of the NHC the PCy_3 ligand is labilized. This loss of the PCy_3 is necessary for the activity of the second generation Grubbs precatalyst [1].

If we now change the metal in the precatalyst and catalyst framework the properties of the resulting complex also change. This can be attributed in part to the increase in electronegativity from left to right in the periodic table, which means the energy of the orbitals decreases from left to right [1]. Ligand back donation as well as tolerance to organic functionality is also changed [1]. Both properties are important in catalysis. The thermal alkene metathesis [2+2] cycloaddition reaction is only possible because of the empty d-orbitals of transition metals [10],[11]. Therefore, the role of the metal atom is very important.

In a previous paper [12] we showed that the frontier molecular orbital theory (FMOT) can be used for the Gr2 catalyst to follow the mechanism of the alkene metathesis reaction. We found the reaction to be frontier orbital-controlled rather than charge-controlled. The location of atom orbital coefficients of the LUMO on both the metal atom and the carbene atom then becomes important for knowing the site of primary overlap of the alkene. In this regard the presence of a positive charge on the metal can

also be used as a criterion for primary overlap. In this paper we will test the effect of the metal by evaluating the transition metals in the Grubbs 2 framework by DFT calculations according to the following criteria: availability of empty metal d-orbitals, location of the AO coefficients of the LUMO, NPA charge of metal and carbene carbon, availability of metal atom as shielded by the ligands and π-π* attraction [13],[14] through space.

Method

All group 4-10 transition metals (Table 1) were calculated as possible substitutions for the ruthenium atom in the second generation Grubbs-metal carbene catalyst framework (Fig. 1). However, technetium (Tc) was not considered for substitution as it is radioactive. Group 3, 11 and 12 transition metals were left out of consideration because of a lack of unpaired valence electrons for chlorine bonding.

Table 1 Possible metals for substitution into Gr2 metal framework based on availability of 2 electrons for binding of chlorine atoms

Group	Metals	d-block valence electrons					M(II) metal configuration in Gr2 framework
~~3~~	~~Sc, Y, La~~	~~1~~					
4	Ti, Zr, Hf	1	1				d^2
5	V, Nb, Ta	1	1	1			d^3
6	Cr, Mo, W	1	1	1	1		d^4
7	Mn, -, Re	1	1	1	1	1	d^5
8	Fe, **Ru**, Os	**2**	**1**	**1**	**1**	**1**	**d^6**
9	Co, Rh, Ir	2	2	1	1	1	d^7
10	Ni, Pd, Pt	2	2	2	1	1	d^8
~~11~~	~~Cu, Ag, Au~~	~~2~~	~~2~~	~~2~~	~~2~~	~~1~~	
~~12~~	~~Zn, Cd, Hg~~	~~2~~	~~2~~	~~2~~	~~2~~	~~2~~	

*Red block most probable metals according to open d-orbitals and electrons available for back bonding.

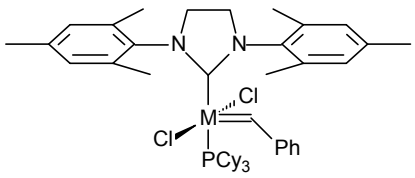


Fig. 1. The Grubbs 2 metal carbene framework.

Geometry optimizations of all the metal atoms substituted in the precatalyst and catalyst frameworks were done with the DFT DMol^3 module of Materials Studio 5.5 [15] at the GGA PW91 level with the DNP basis set. Energy calculations of the LUMO were also done with Materials Studio. Molecular energy values, LUMO energy values and LUMO pictures for all transition metals, except technetium, for both the precatalyst and catalyst frameworks are given in Appendix A. Fig. 2 shows the important area of the LUMO of the precatalysts and catalysts that were investigated as criteria for possible new catalysts.

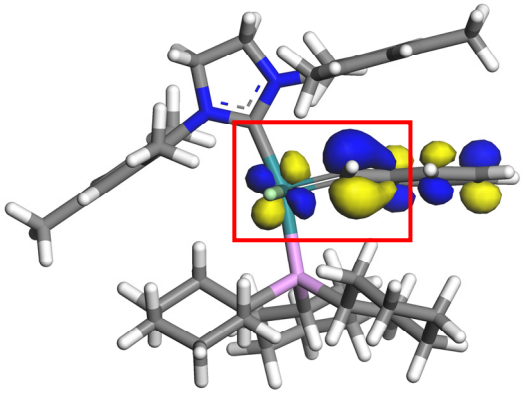


Fig. 2. Selection used in LUMO pictures tables.

There should be sufficient orbital lobes on both the metal and the carbene carbon for possible overlap with an alkene. Primary overlap of the alkene should be able to occur at the metal atom for formation of the metallacyclobutane intermediate. For the calculation of the atomic orbital (AO) coefficients of the molecular orbitals (MO) a different software package had to be used. Materials Studio only gives final energy values without providing a detailed table of the composition of the molecular orbitals. For this purpose Gaussian 03 [16] was used at the B3LYP/LanL2DZ level.

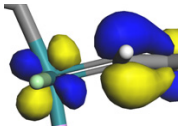
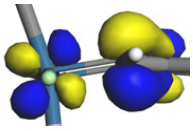
Chemissian [17], a visualization program that can open Gaussian output, makes it possible to investigate the contribution of each AO to the MO by using the following input in Gaussian: #P B3LYP/LanL2DZ pop=full GFInput. The shielding percentage (G(M)) of the metal atom by the ligands was calculated with Solid Angle [18]. Furthermore, the natural population analysis (NPA) [19] of all molecules was also calculated using Gaussian 03 with the following input: #P B3LYP/LanL2DZ pop=(full,NPA).

To investigate the possibility of π-π* interaction between the C_{ipso} carbon and the carbene carbon, the AO coefficients of the two interacting carbon atoms were investigated using Chemissian. The MOs, with AO coefficients for these two carbons exceeding |0.20|, were identified for a possible stabilization interaction. All bond lengths are taken from the geometry optimized structures in Materials Studio.

Results and Discussion

From the calculated metal atom substituted second generation precatalyst frameworks (see Appendix B), only osmium qualified as potential substitute in the precatalyst framework. Table 2 shows the comparison of the LUMO properties with respect to the metal carbene double bond of Os to Ru. All properties of Os are closely related to Ru. The LUMO energy difference is only 0.1eV, with the position and size of the AO coefficients almost exactly the same. Both metal precatalysts have a fairly large d_{xy} coefficient on the metal and a p_y coefficient on the carbon.

Table 2 LUMO properties of Ru and Os in the Grubbs second generation precatalyst framework

Ru	(-2.8eV)		
			
C	p_y	0.41	
Ru	d_{xy}	-0.41	
C	p_y	0.31	
Os	(-2.7eV)		
			
Os	d_{xy}	0.41	
C	p_y	-0.40	
C	p_y	-0.31	
Os	d_{xy}	0.22	

A deeper look at other electronic and steric properties shed some more light on the feasibility of Os as a replacement for Ru in the precatalyst framework (Table 3).

Table 3 Electronic and steric properties of the second generation Grubbs precatalyst framework

Ru
2.20
74.88%
Ru 0.26
C -0.08
Os
2.20
71.93%
Os 0.36
C -0.16

Key
é neg[a]
G(M)[b]
NPA M
NPA C

[a] Pauling electronegativity with that of C 2.55

[b] Percentage of the metal's surface shielded by the ligated atoms only

The Pauling electronegativity of both Ru and Os is 2.20, but the Os metal atom is 3% less shielded by ligands than Ru. Furthermore, the natural atomic charge of Os is also more positive than Ru, with the charge on the carbene carbon slightly more negative than Ru. These factors all contribute to the possibility of Os as metal substitute for the Ru atom in the precatalyst framework. In Fig. 3 it can be seen that the difference in the shielding of the atom can be ascribed to the slightly longer bond lengths in the Os substituted precatalyst. The metal-carbene double bond for Os is significantly longer than the Ru=C bond.

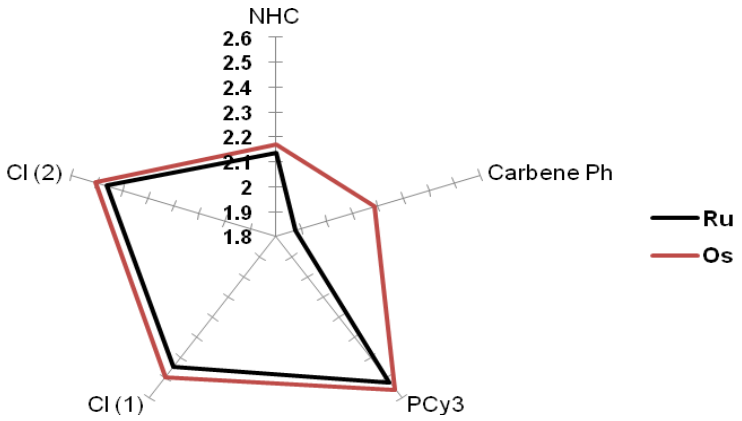
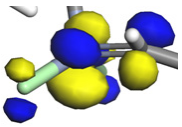
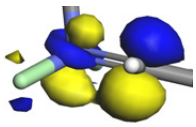


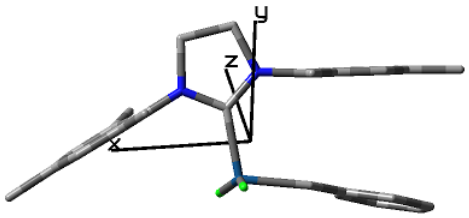
Fig. 3. Metal-ligand bondlengths in precatalyst framework.

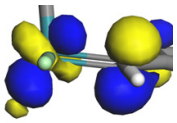
The moment the PCy_3 is dissociated from the precatalyst to form the active catalyst in the case of Ru, more transition metals are available as replacement for Ru in the catalyst framework. From the LUMO screening (see Appendix B) chromium, cobalt, rhodium, rhenium, osmium and iridium proved to be potential substitutes for ruthenium (Table 4).

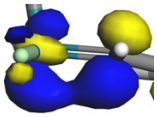
Table 4 LUMO properties of transition metals in the Grubbs second generation catalyst framework

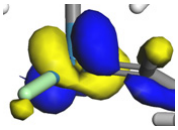
Cr (-3.0eV)		
		
Cr	d_{xy}	0.36
C	p_y	0.32
Cr	d_{yz}	0.31
Cr	d_{xz}	-0.24
C	p_y	0.23
Cr	d_{3z2-r2}	0.20

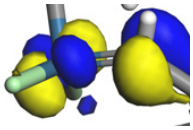
Co (-3.3eV)		
		
C	p_y	0.37
Co	d_{yz}	0.28
Co	d_{xy}	0.25
Co	d_{x2-y2}	-0.24
C	p_y	0.24

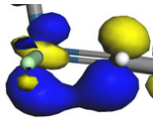


Ru (-3.3eV)		
		
Ru	*d_{xy}*	*0.44*
CC	*p_y*	*0.37*
CC	*p_y*	*0.26*
Ru	*d_{yz}*	*0.21*

Rh (-3.4eV)		
		
Rh	d_{yz}	0.34
C	p_y	-0.31
C	p_y	-0.22
C	p_z	-0.21

Re (-3.4eV)		
		
Re	d_{xy}	0.45
Re	d_{xz}	-0.35
Re	d_{xy}	0.23
Re	d_{x2-y2}	0.23
Re	d_{yz}	0.21
C	p_y	0.20

Os (-3.0eV)		
		
Os	d_{3z2-r2}	0.35
Os	d_{xz}	0.30
C	p_z	0.29
C	p_y	0.24
C	p_y	0.24
Os	d_{xy}	0.20

Ir (-3.3eV)		
		
Ir	d_{yz}	0.31
C	p_y	-0.31
C	p_y	-0.22
Ir	d_{xy}	-0.21

All of these metals have an E_{LUMO} between -3.0eV and -3.4eV with the order ranging from Cr, Os < Co, Ru, Ir < Rh, Re. Furthermore, the presence of AOs on both the metal and the carbene carbon makes coordination of the alkene and subsequent formation of the metallacyclobutane intermediate possible. As seen from the internal Cartesian axis of the molecules assigned by Gaussian, AOs with a coefficient along the y-axis are most suitable for overlap of the alkene from the bottom [20]. Of the selected metal substituted catalyst frameworks presented in Table 4 only Os has as biggest coefficients no AOs with a lobe directed along the y-axis. All of the rest have a p_y AO on the carbene carbon, and a d_{xy} or d_{yz} AO on the metal atom. In order of the largest AO coefficient on the metal atom the selected transition metals can be arranged as follows: Re > Ru > Cr > Os > Rh > Ir > Cr.

Regarding the electronic and steric properties of the metal substituted catalyst framework (Table 5) the following trends can be observed. With respect to the Pauling electronegativity Os and Ir have the same electronegativity with those of Cr, Co and Re being less and that of Rh being more than Ru. Moreover, the shielding of the metal atoms by the ligands also differs greatly from Ru. It can be seen that Co is the most shielded (73.56%) and Ir the least shielded (60.10%), with the rest being in order from smallest to largest Re < Os < Rh < Ru < Cr. Further considering the natural atomic charge of the metal atoms in the catalyst framework the order is changed considerably with Re the most positive (0.74e) followed by Ir, Co, Os, Rh, Cr and finally Ru being the least positive (0.46e). All of the carbene carbon atoms in the precatalyst frameworks have a slightly negative charge.

Tabel 5 Electronic and steric properties of the second generation Grubbs catalyst framework

Cr 1.66 68.77% Cr 0.53 C -0.20		**Co** 1.88 73.56% Co 0.69 C -0.17	
	Ru 2.20 65.28% Ru 0.46 C -0.06	**Rh** 2.28 63.17% Rh 0.61 C -0.18	**Key** é neg[a] G(M)[b] NPA M NPA C
Re 1.90 62.32% Re 0.74 C -0.31	**Os** 2.20 62.37% Os 0.66 C -0.20	**Ir** 2.20 60.10% Ir 0.70 C -0.25	

[a] Pauling electronegativity with that of C 2.55

[b] Percentage of the metal's surface shielded by the ligated atoms only

Indeed, when considering the metal ligand bond lengths of the catalyst frameworks (Fig. 4) further selection of the metal replacement of Ru is possible. With the exception of Cr and Co all frameworks have similar metal-chlorine bond lengths. However, a sizeable difference can be observed for the NHC and carbene ligands. Taking into account the atomic radius of the metal atoms, the difference in bond lengths is caused by electronic properties.

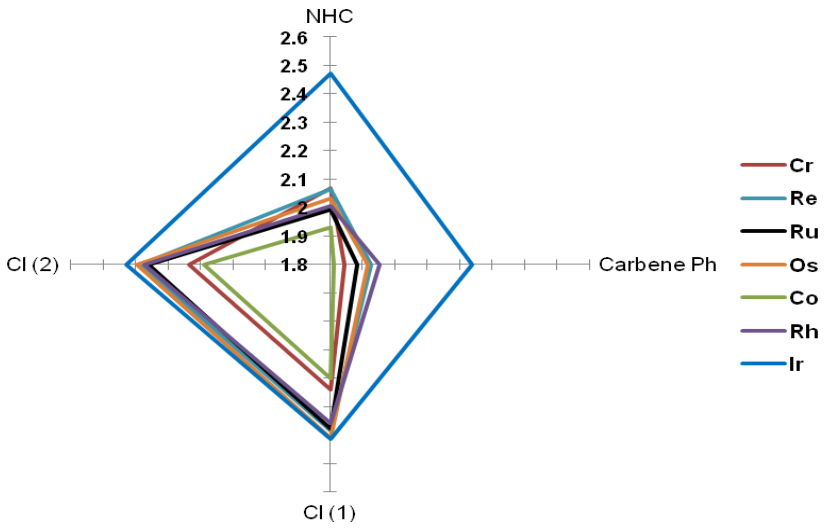


Fig. 4. Metal-ligand bond lengths in the second generation Grubbs catalyst framework.

Fig. 5 gives the variation in metal ligand bond lengths from Ru for each catalyst framework. The baseline is the Ru-ligand bond lengths, with a positive deviation indicating shorter bond lengths and a negative deviation indicating longer bond lengths.

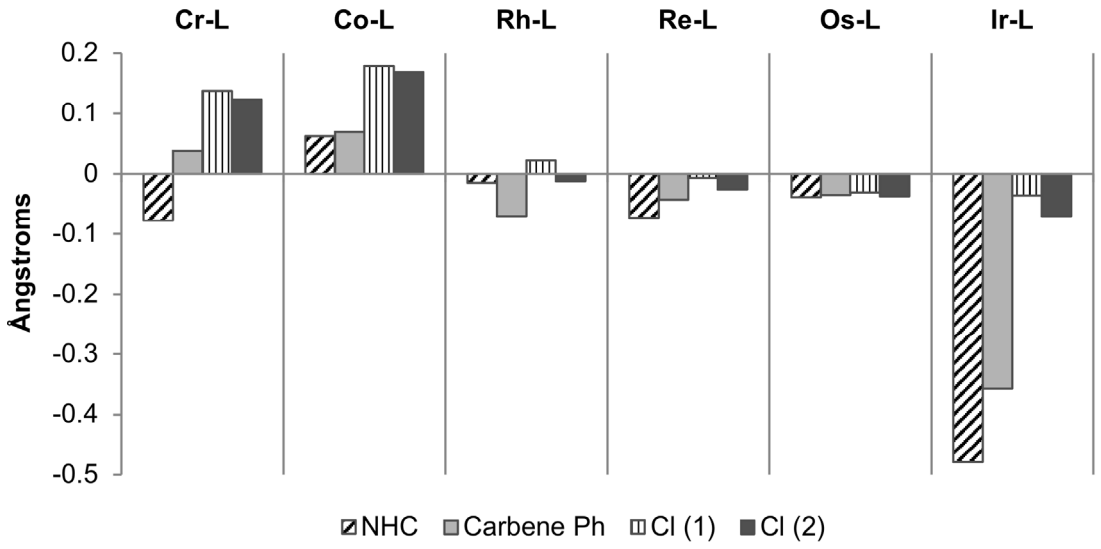


Fig. 5. The difference in bond lengths of the substituted metals versus ruthenium in the second generation Grubbs catalyst framework.

Cr and Co have shorter M=C bonds than Ru; Rh, Re and Os have slightly longer M=C bond lengths and Ir has a much longer M=C bond than Ru. Considering the NHC-M bond, the presence of the π back bonding from the metal to the NHC is among other factors indicated by the length of the bond [21],[22]. All of the metals have a longer NHC-M bond length except for Co which is shorter and Rh which is almost similar. In addition, consideration of the bond dissociation energy (BDE) of the PCy_3 for each catalyst framework (Table 6) leads to further insights. Again taking Ru as baseline it can easily be seen for which metal PCy_3 will dissociate faster (Fig. 6). For all the metals the BDE are smaller than Ru apart from Os.

Table 6 Bond dissociation energies (kcal/mol) for the PCy_3 ligand of the second generation Grubbs catalyst frameworks

Cr 24.8				**Co** 17.6	
			Ru 36.1	**Rh** 30.7	
		Re 31.4	**Os** 40.7	**Ir** 34.4	

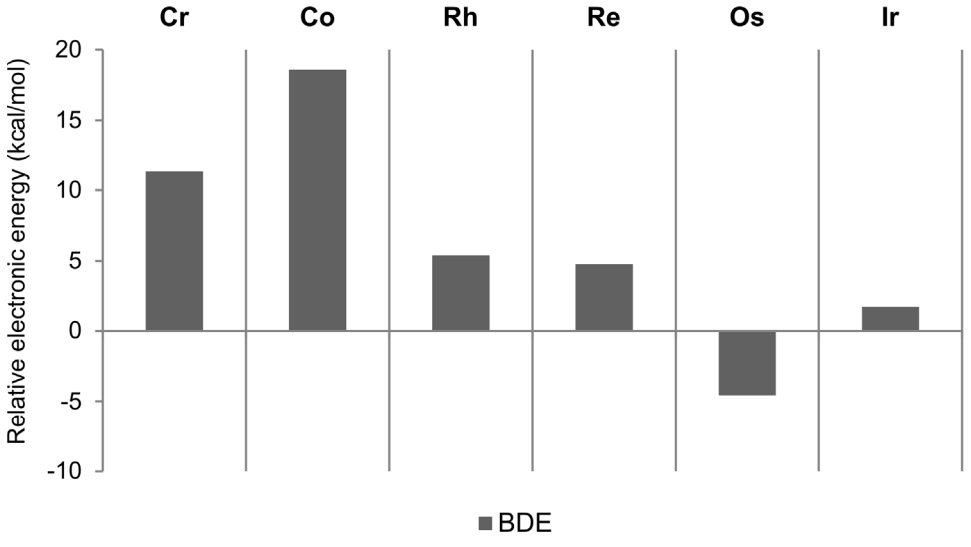


Fig. 6. The difference of bond dissociation energies (kcal/mol) of the substituted metals versus ruthenium in the second generation Grubbs catalyst framework.

According to a recent publication by Fernández, Lugan and Lavigne [13] and work done by Credendino, Falivene and Cavallo [14] supporting this, a π-π* interaction between the $C_{ipso(N\text{-}Aryl)}$ carbon of the NHC ligand aryl group and the carbene carbon in the second generation Grubbs framework is present. This interaction was found to stabilize the active carbene orientation proposed by Straub [23] thereby positively effecting the catalytic activity of the complexes [13]. Fig. 7 shows an example of such an interaction observable in our Os-substituted catalyst framework. The interaction is indicated by the red circle in the figure and comprises the stabilizing overlap of the LUMO and the HOMO-7 orbitals.

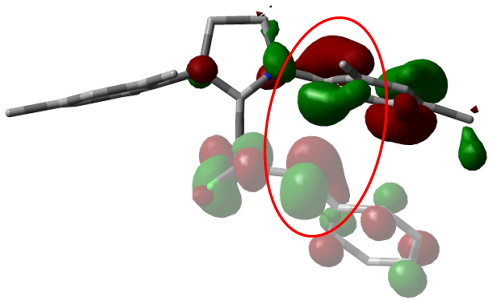


Fig. 7. The possible π-π* interaction along the y-axis between the HOMO-7 and the LUMO circled in red, in the case of Os substituted in the Grubbs 2 catalyst framework.

We found the stabilizing interaction possible in all of the metal-substituted precatalyst and catalyst frameworks (Table 7). A screening was done of the AO coefficients on the $C_{ipso(N\text{-}Aryl)}$ atom showing potential for such an interaction. In most of the frameworks the AO orbitals on the $C_{ipso(N\text{-}Aryl)}$ and $C_{carbene}$ atoms are orientated along the same axis (y-axis) for interaction to occur.

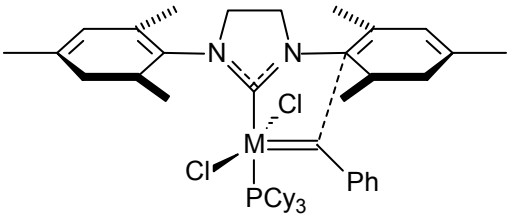
Table 7 The molecular orbitals responsible for possible π-π* stabilization between the carbene carbon and the $C_{ipso(N\text{-}Aryl)}$

Metal	MO C(carbene)	AO C(carbene)	Coeff C(carbene)	MO C(ipso)	AO C (ipso)	Coeff C (ipso)
Precatalyst framework						
Ru	LUMO	py	0.41	H[a]-8	py	0.32
Os	LUMO	py	0.40	H-7	py	0.27
Catalyst framework						
Cr	LUMO	py	0.32	H-6	py	0.39
Co	LUMO	py	0.37	H-7	py	0.31
Ru	LUMO	py	0.37	H-7	pz	0.22
Rh	LUMO	py	0.22	H-6	py	0.34
Re	LUMO	py	0.25	H-7	py	0.33
Os	LUMO	pz	0.29	H-7	py	0.39
Ir	LUMO	py	0.24	H-5	py	0.35

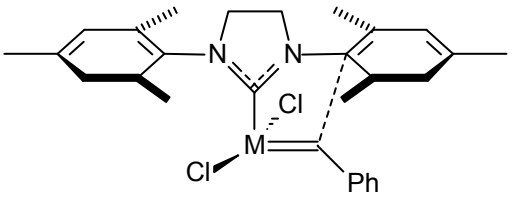
[a] HOMO

The effect of the stabilization is also reflected in the distance between the $C_{ipso(N\text{-}Aryl)}$ and $C_{carbene}$ atoms shown in Table 8 for both the precatalyst and catalyst frameworks.

Table 8 The bond lengths between the carbene carbon and the $C_{ipso(N\text{-}Aryl)}$ indicating possible π-π* stabilization



Precatalyst framework



Catalyst framework

Ru 3.01
Os 3.04

Cr 3.09		**Co** 3.10
	Ru 3.20	**Rh** 3.12
Re 3.03	**Os** 2.93	**Ir** 3.18

Fernández, Lugan and Lavigne [13] reported a distance of 3.11 Å as remarkably short. In all our calculated metal-substituted precatalyst and catalyst frameworks, except for Rh (3.12 Å) and Ir (3.18 Å), the distance is even shorter than they reported. Arranging the complexes in order of smaller to larger $C_{ipso(N\text{-}Aryl)}$ - $C_{carbene}$ distance yields for the catalyst framework: Os < Re < Cr < Co < Rh < Ir < Ru.

Conclusion

In conclusion it was found for the precatalyst framework that Os is a testable option for substitution of Ru. Os is less shielded by its ligand environment and furthermore has a LUMO similar to Ru. With the dissociation of the PCy_3 ligand, Os stays in contingency for substitution of Ru. According to the criteria named for good metathesis catalysts, Os has almost similar and in some cases better electronic and steric properties than Ru, i.e. Os is less shielded than Ru and slightly more positive on the metal atom. In a paper by Occhipinti and Jensen [24] on the nature of the transition metal-carbene bond, they found the properties of Os substituted in a first generation and second generation Grubbs-type framework to be quite similar to Ru. Both Ru and Os compounds could be classified as weakly to moderately electrophilic rendering them “electrophilic Schrock” carbenes [24]. Regarding the rest of the screened transition metals: all comply with the given criteria, especially Re, and will be tested experimentally in future work.

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