

## On the electronic structure of second generation Hoveyda–Grubbs alkene metathesis precursors

Francisco Nuñez-Zarur<sup>a</sup>, Jordi Poater<sup>b</sup>, Luis Rodríguez-Santiago<sup>a</sup>, Xavier Solans-Monfort<sup>a</sup>, Miquel Solà<sup>b,\*</sup>, Mariona Sodupe<sup>a,\*</sup>

<sup>a</sup> Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Cerdanyola del Vallès, Spain

<sup>b</sup> Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain

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### ABSTRACT

Hoveyda–Grubbs complexes are commonly used catalysts in alkene metathesis. They are precursors of the catalytic species and need to be activated before entering into the real catalytic cycle. This activation can determine in a large extent the performance of the catalyst and thus, it is important to understand the factors that influence their activation and stability. In the present work, the electronic structure of 15 different Hoveyda–Grubbs precatalysts is analyzed by means of DFT quantum chemical calculations. Electronic delocalization measures and aromaticity indices have been used to study the influence of the Hoveyda ligand substituents on the Ru···O interaction and the metal carbene bond, and to analyze whether or not the 5-membered metal containing ring exhibits metalloaromaticity. Results show that these complexes do not exhibit any metalloaromaticity, although delocalization measures indicate that there is a certain  $\pi$  electron delocalization on the Hoveyda ligand. On the other hand, present study shows that the Ru···O interaction is mainly electrostatic and that the influence of the substituents not only depends on the changes occurred at the O atom but also on the metal site. Substituents *para* to the alkoxy group (*meta* to the carbene) mainly tune the electronic structure of the chelating ligand in such a way that electron donor substituents strengthen the Ru···O interaction whereas electron withdrawing ones induce the reverse effect. However, substituents in *para* to the carbene (*meta* to the alkoxy) mainly tune the electronic structure of the ruthenium carbene bond modifying the Ru <sup>$\delta^-$</sup> –C <sup>$\delta^+$</sup> <sub>ene</sub> bond polarization and producing the opposite effect.

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### 1. Introduction

Olefin metathesis is considered to be one of the most important reactions in organic synthesis since it allows the formation of new carbon–carbon double bonds even in the presence of functional groups [1,2]. In fact, many polymers [3], natural products [1,2] and others substances are obtained through synthetic routes that involve at least one alkene metathesis step. The reaction implies two alkene molecules that exchange their substituents through the cleavage and formation of carbon–carbon double bonds as shown in Scheme 1 [3–8]. The process, however, only takes place in the presence of an appropriate catalyst [5,6]. In homogeneous reactions, two main families of catalysts are distinguished, namely the  $d^0$  alkylidene complexes [5,9] and the Ru-based carbene ones [10,11]. The present work deals with Ru-based carbene complexes of general formula Ru(=CHR<sup>1</sup>)Cl<sub>2</sub>L<sup>1</sup>L<sup>2</sup>, which are usually referred as Grubbs type catalysts [6,12–15] (**1** in Scheme 2). Initially, these

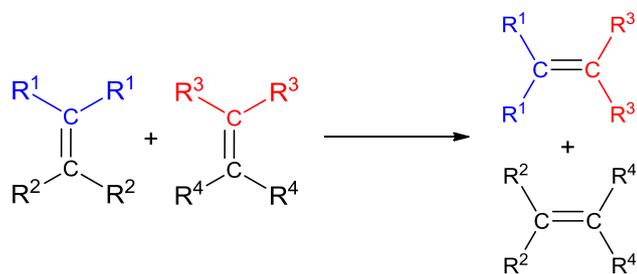
complexes enclosed a phosphine as L<sup>2</sup> ligand [13,14,16] but more recently a variety of complexes presenting a chelating carbene have been synthesized. They are referred to Hoveyda–Grubbs catalysts and, among the alkene metathesis catalysts, are the most commonly used [11,17–21]. Here we will focus on complex **2** in Scheme 2, which bears a N-heterocyclic carbene (NHC) as L<sup>1</sup> ligand [18], and on some of its derivative species [19,20,22] (**3–12** in Scheme 2).

It is now well accepted that Hoveyda–Grubbs complexes are precursors of the catalytic species and thus, they need to be activated before they enter into the real catalytic cycle. Since the catalytic species is the same for all the precursors, it is thought that their stability and activation determine in a large extent the performance of the catalyst [11,23]. The activation process implies (i) the loss of the L<sup>2</sup> ligand, which is the chelating alkoxy in the Hoveyda–Grubbs complex, and (ii) a cross metathesis process that exchanges the initial metal–carbene substituents by those of the reactant alkene involved in the catalytic cycle (Scheme 3) [11,23–30].

Several factors have been suggested to be relevant on the Hoveyda–Grubbs precursor activation and stability. It has been proposed that the interaction between the ruthenium center and the

\* Corresponding authors.

E-mail address: [Mariona.sodupe@uab.cat](mailto:Mariona.sodupe@uab.cat) (M. Sodupe).

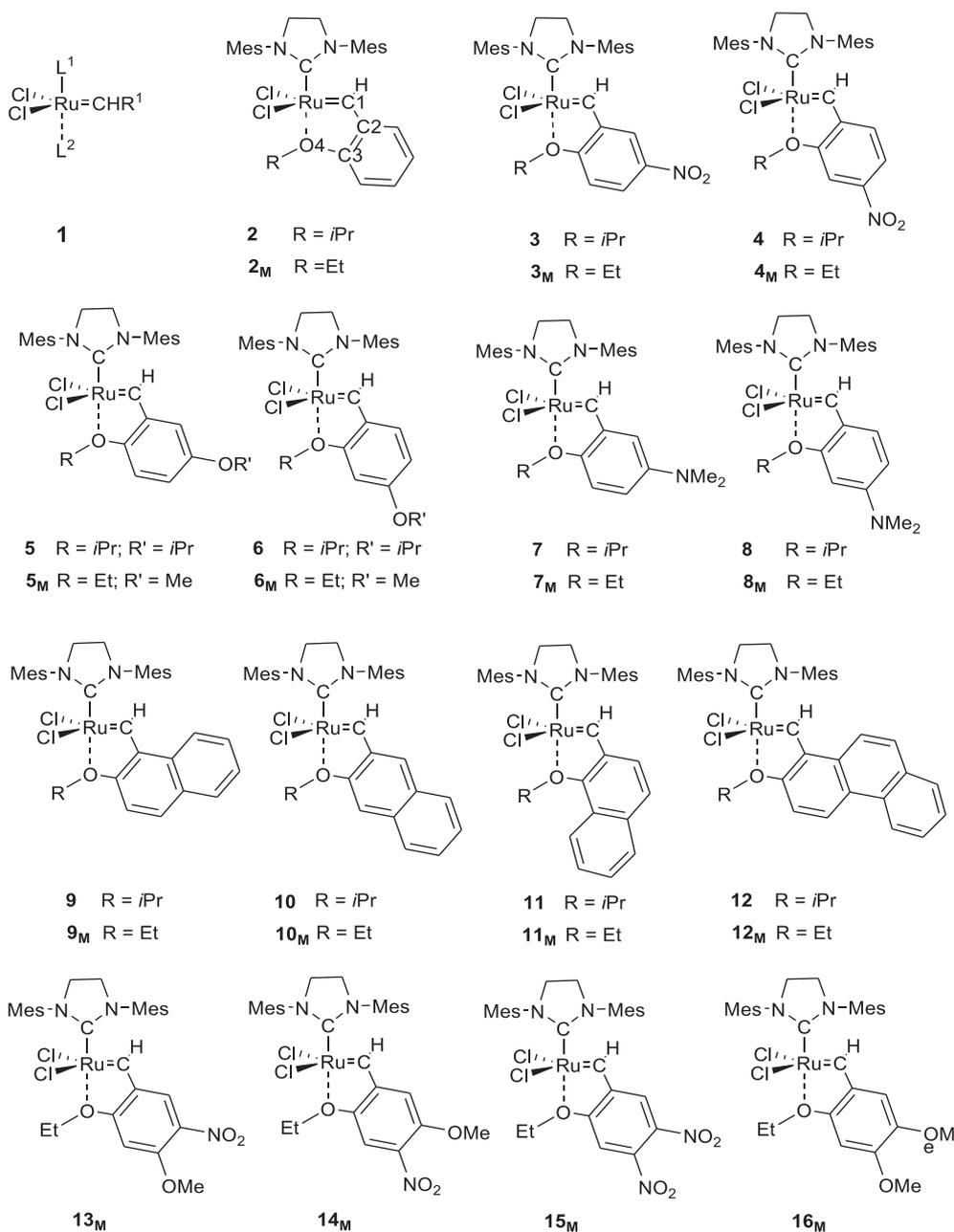


Scheme 1.

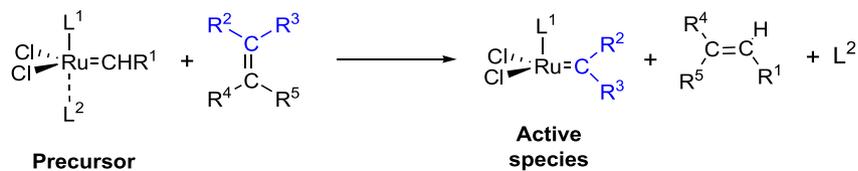
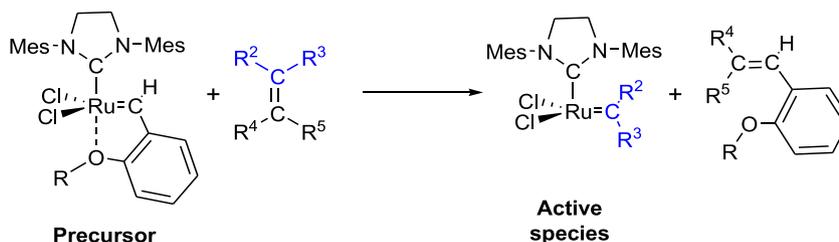
alkoxy ligand has an important role [19,20]. Accordingly, the addition of electron withdrawing groups such as  $-\text{NO}_2$  in the Hoveyda ligand (**3** and **4** in Scheme 2) decreases the electron density at the chelating O atom, which weakens the  $\text{Ru}\cdots\text{O}$  bond. Consequently,

complexes **3** and **4** usually activate faster than the original Hoveyda–Grubbs precatalyst (**2** in Scheme 2). Similarly, when the Hoveyda ligand presents electron donor groups, such as  $-\text{O}i\text{Pr}$  (**5** and **6** in Scheme 2), the  $\text{Ru}\cdots\text{O}$  interaction becomes stronger, which would explain the slower precatalyst activation [20].

The synthesis of ruthenium complexes wearing a naphthalene or phenanthrene based chelating ligand (**9–12** in Scheme 2) and the study of their catalytic performance in the ring closing olefin metathesis reaction of *N,N*-diallyltosylamine led to an alternative explanation about the origin of the key factors controlling the Hoveyda–Grubbs precatalyst activation [21]. The authors proposed that the metal containing cycle formed by Ru,  $\text{C}_{\text{ene}}$ , C2, C3 and O (see **2** in Scheme 2 for labeling) exhibit some aromatic character and that the stability arising from this metalloaromaticity controls, at least in part, the catalytic activity of complexes **9–12**. In the same direction, some of us have recently studied the ring closing reaction for a model of the same *N,N*-diallyltosylamine diene cata-



Scheme 2.

**(a) Ru-based precursors activation process****(b) Grubbs-Hoveyda derivative precursors activation process**

Scheme 3.

lyzed by several Hoveyda–Grubbs derivatives (2–6 in Scheme 2) [31] and found that the energy barrier corresponding to the Ru···O dissociation process does not show any relationship with the Ru···O bond length but, in contrast, it correlates relatively well with the C<sub>ene</sub>–C2 bond length; that is, with the double bond character of this bond.

The olefin metathesis reaction catalyzed by Ru-based complexes has been widely studied from a computational point of view [32–43]. Nevertheless, few works have focused on the Hoveyda–Grubbs derivatives [31,44–47] and, to our knowledge, a detailed investigation on the electronic properties of these complexes has not been reported. The aim of this study is to get a deeper understanding on the electronic structure of Hoveyda–Grubbs precatalysts. In particular, we analyze the influence of the Hoveyda ligand substituents on (i) the Ru···O interaction, (ii) the metalloaromaticity in the 5-membered metal containing ring and (iii) the metal carbene bond, by means of electronic delocalization measures and aromaticity criteria. This will help understand the activation process of these precursors and thus, their catalytic activity.

## 2. Computational details

### 2.1. Models

The Hoveyda–Grubbs precatalysts have been represented by simplified models (Scheme 2) in which the isopropyl alkoxy substituent has been replaced by an ethoxy (EtO) group and the O<sup>i</sup>Pr group of the Hoveyda ligand by a OMe group. The inclusion of **M** in the nomenclature is used to emphasize that we are referring to the model (and not the real) system.

### 2.2. Structure optimization

All calculations have been performed with the B3LYP [48,49] hybrid density functional as implemented in the Gaussian03 package [50]. The optimized geometries have been obtained using the quasi relativistic effective core pseudo-potentials (RECPs) of the Stuttgart group and the associated basis sets augmented with a polarization function for Ru [51,52]. All other atoms are represented with a 6-31G(d, p) [53–55] basis sets. We have verified that all structures are minima on the potential energy surface by

performing vibrational analysis. This level of theory has been used by us in previous studies and shown to be a cost-effective methodology [31,46,47]. In particular, we have verified the effect of increasing the basis sets as well as the effect of changing the density functional used in a very recent work on the activation of these complexes [47] and we found that main trends are not affected by improving the basis sets nor changing the functional.

### 2.3. Electron delocalization measurements

For the analysis of the electronic delocalization of the 5-membered metal containing ring and the contiguous benzene-like rings we have used different indexes. As a magnetic measure of aromaticity, we have used the nucleus-independent chemical shift (NICS) index, proposed by Schleyer and co-workers [56,57]. NICS is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system. In particular, the GIAO method [58] has been used to perform calculations of NICS at ring centers (NICS(0)) determined by the non-weighted mean of the heavy atoms coordinates, as well as the out-of-plane component of it, the NICS(0)<sub>zz</sub> [59].

In previous works, some authors have criticized the use of NICS indices to analyze the aromaticity in metallabenzenes [60] and in benzenes coordinated to metal centers [61]. For this reason, the multicenter index (MCI) [62,63] have also been employed as an electronic-based aromaticity measure. MCI is a particular extension of the  $I_{ring}$  index [64] defined as:

$$I_{ring}(\mathcal{A}) = \sum_{i_1, i_2, \dots, i_N} n_{i_1} \cdots n_{i_N} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \cdots S_{i_N i_1}(A_N) \quad (1)$$

$n_i$  being the occupancy of molecular orbital (MO)  $i$  and  $A = \{A_1, A_2, \dots, A_N\}$  a string containing the set of  $N$  atoms forming the ring structure. Summing up all  $I_{ring}$  values resulting from the permutations of indices  $A_1, A_2, \dots, A_N$  the mentioned MCI index is obtained:

$$MCI(\mathcal{A}) = \frac{1}{2N} \sum_{P(\mathcal{A})} I_{ring}(\mathcal{A}) \quad (2)$$

where  $P(A)$  stands for a permutation operator which interchanges the atomic labels  $A_1, A_2, \dots, A_N$  to generate the  $N!$  permutations of the elements in the string  $A$  [65]. MCI and  $I_{ring}$  give an idea of the electron sharing between all atoms in the ring.

The electronic reorganization in the rings has been further analyzed by means of the delocalization index (DI) between atoms  $A$  and  $B$ ,  $\delta(A, B)$ , which is obtained by the double integration of the exchange–correlation density ( $\Gamma_{xc}(\vec{r}_1, \vec{r}_2)$ ) over the space occupied by atoms  $A$  and  $B$  [66,67]:

$$\delta(A, B) = -2 \int_A \int_B \Gamma_{xc}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (3)$$

For single-determinant closed-shell wave functions one obtains:

$$\delta(A, B) = 4 \sum_{ij}^{N/2} S_{ij}(A) S_{ij}(B) \quad (4)$$

The sums in Eq. (4) run over all the  $N/2$  occupied MOs.  $S_{ij}(A)$  is the overlap between MOs  $i$  and  $j$  within the basin of atom  $A$ . We have made use of the AIM atomic partition [68,69] defined from the condition of zero-flux gradient in one-electron density  $\rho(\mathbf{r})$  to compute  $S_{ij}(A)$  values.

Calculation of atomic overlap matrices ( $S_{ij}(A)$ ) and computation of MCI have been performed with the AIMPAC [70] and ESI-3D [71] collection of programs. These indices derived from the electronic density have been calculated at the B3LYP/3-21G level in order to avoid the non-nuclear attractors that appear due to the use of effective core pseudo-potentials. It is well-known that interatomic surfaces have to be computed from densities containing core electrons [72]. On the other hand, NICS have been calculated at the same level as the geometry optimization and energetics. For the indices considered, the higher the aromaticity (electronic delocalization), the larger the MCI and the lower the NICS(0) and NICS(0)<sub>zz</sub> values.

### 3. Results

#### 3.1. Geometries

The optimized geometries of all considered complexes are shown in Fig. 1. With respect to our previous work [31], we have considered two new complexes presenting electron donor groups (**7<sub>M</sub>** and **8<sub>M</sub>**), four hypothetical disubstituted benzene based species (**13<sub>M</sub>**–**16<sub>M</sub>**) and the naphthalene and phenanthrene containing catalysts (**9<sub>M</sub>**–**12<sub>M</sub>**) synthesized by Grela and co-workers [21]. The naphthalene and phenanthrene complexes are mainly added to evaluate the metalloaromatic character of the metal containing ring as proposed by Grela and co-workers [21].

Metal coordination in Hoveyda–Grubbs like precursors lies between that of an ideal square based pyramid (SBP) and that of an ideal trigonal bipyramid (TBP). Taking SBP geometry as reference, the carbene ligand is at the apical position (Fig. 1) and the two chlorine ligands, the N-heterocyclic carbene (NHC) and the alkoxy group in the basal plane. The largest deviation from the ideal SBP structure comes from the Cl–Ru–Cl angle which is at least 20° smaller than the 180° of the ideal structure (i.e. it varies from 153.6° to 158.0°). Noteworthy, these features are equivalent to those reported in previous computational works [31] and are in very good agreement with the available X-ray data for complexes **2**, **3**, **9**, **10** and **12** and other related systems (see Table S1 in the ESI for details) [17,18,21,73]. The largest difference between X-ray and computed data is observed for the Ru···O distance, calculations predicting always a longer value of at least 0.1 Å. More interestingly, computed and experimental L–Ru–L angles and the M–L distances of the different catalysts fairly follow the same trends, thereby suggesting that the level of theory used in this work is able to account for most of the subtle variations induced by the substituents. The Ru=C<sub>ene</sub> distance varies from 1.825 to 1.838 Å, the Ru–Cl from 2.356 to 2.387 Å (not shown in Fig. 1), the Ru–C<sub>NHC</sub> from 1.980 to 1.996 Å and the Ru···O distance ranges

from 2.300 to 2.384 Å. The major effect induced by the Hoveyda ligand substituents is thus, centered on the weakest Ru···O bond, the fluctuation being larger than 0.08 Å.

Noteworthy, the metal containing ring formed by Ru, C<sub>ene</sub>, C2, C3 and O (see Scheme 2) is almost planar, the Ru–C<sub>ene</sub>–C2–C3 torsion angle being always smaller than 0.7° regardless the presence of substituents in the Hoveyda ligand. The only exception is **11<sub>M</sub>** that shows a Ru–C<sub>ene</sub>–C2–C3 torsion angle of 6.5°. This complex, however, presents some particularities. Note that for all catalysts but **11<sub>M</sub>** the alkyl chain of the EtO group is essentially coplanar with the phenyl ring of the Hoveyda ligand. In contrast, for **11<sub>M</sub>**, the ethyl group is rotated by about 60° to avoid repulsion between the pending chain of the alkoxy group (Et) and the second benzene ring of the Hoveyda ligand. Actually, the minimum structure with the ethoxy chain co-planar with the phenyl ring lies 3.5 kcal mol<sup>−1</sup> above the non-planar one. The main consequence of this deviation is that the Ru···O distance becomes substantially longer ( $d_{\text{Ru}\cdots\text{O}} = 2.384$  Å), probably due to the fact that the non-planar configuration disfavors the electron donation from the alkoxy group to the metal.

#### 3.2. Effect of the substituents on the precursor electronic structure

As previously mentioned, three different factors have been proposed to influence the catalytic activity of the Hoveyda–Grubbs type catalysts: (i) the Ru···O interaction strength [20], (ii) the metalloaromaticity of the 5-membered ring formed by Ru, C<sub>ene</sub>, C2, C3 and O [21] and (iii) the electron delocalization around the metal carbene evidenced by the C<sub>ene</sub>–C2 double bond character [31]. Here we analyze how the substituents in the Hoveyda ligand tune the first two factors and the metal carbene bond, using several indicators of electron delocalization and aromaticity criteria. The analysis of the electronic delocalization is made by computing the delocalization indices ( $\delta(A, B)$ ) between adjacent atoms of the metal containing ring, as well as the magnetic-based NICS(0) and the electronic-based MCI aromaticity criteria of this ring and the contiguous benzene-like one. Computed values for the metal containing and benzene rings are shown in Tables 1 and S2, respectively.

In our previous work on catalysts **2<sub>M</sub>**–**6<sub>M</sub>**, we showed that the Ru···O distance is significantly influenced by the presence of substituents either at sites *para* to the alkoxy or *para* to the metal carbene [31]. Here we observe similar effects. In particular, with respect to the unsubstituted Hoveyda–Grubbs precatalyst **2<sub>M</sub>**, electron withdrawing substituents *para* to the alkoxy group cause an elongation of the Ru···O bond distance (**3<sub>M</sub>**) whereas electron withdrawing substituents in *meta* (**4<sub>M</sub>**) slightly decrease this distance. The reverse situation is observed for electron donor substituents in *para* (**5<sub>M</sub>** and **7<sub>M</sub>**) and *meta* (**6<sub>M</sub>** and **8<sub>M</sub>**) sites to the alkoxy group. These general trends are even made more evident when considering the hypothetical disubstituted systems. For instance, complex **13<sub>M</sub>** has an electron withdrawing group *para* to the alkoxy ligand and a donor OMe substituent in *meta*. The individual contribution of each substituent is to weaken the Ru···O interaction and, as a result, the Ru···O distance is significantly longer than that of the parent compound **2<sub>M</sub>**. In contrast, in complex **14<sub>M</sub>** the substituents are interchanged and thus, they strengthen the Ru···O interaction, leading to a shorter Ru···O distance. Finally, the disubstituted compounds presenting two electron withdrawing or two electron donor groups (**15<sub>M</sub>** and **16<sub>M</sub>**) present intermediate Ru···O distances to those computed for **13<sub>M</sub>** and **14<sub>M</sub>**, as expected due to the compensation effects originated by the two groups.

Similar trends are observed when analyzing the delocalization index  $\delta(\text{Ru}, \text{O})$  of the Ru···O bond. This delocalization index should, in principle, depend on the Ru···O interaction strength in such a way that the stronger the interaction the larger the  $\delta(\text{Ru}, \text{O})$  value (the DI has been identified by many authors as a covalent bond order) [67]. Indeed, it is observed that the largest  $\delta(\text{Ru}, \text{O})$  values are

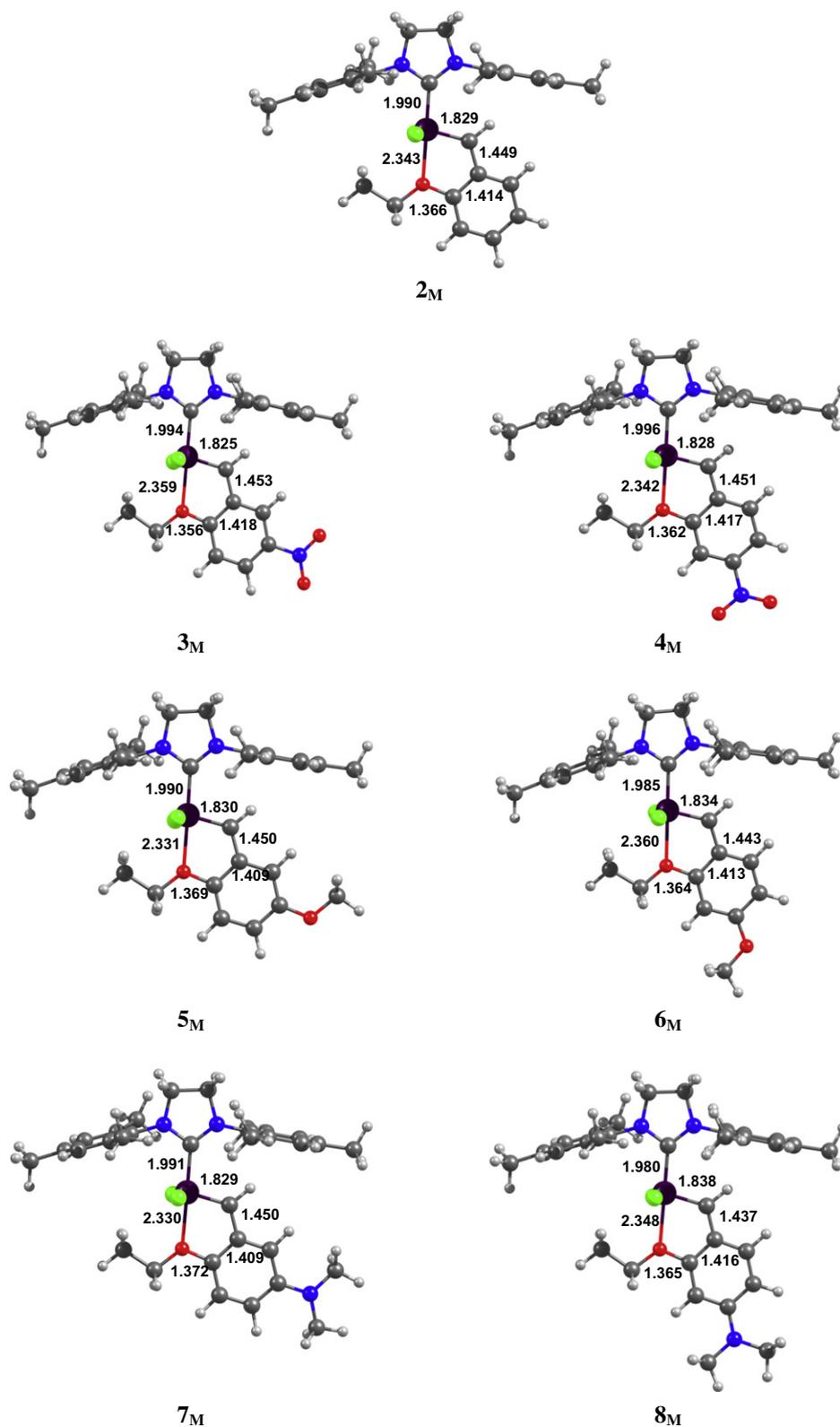


Fig. 1. B3LYP optimized geometries for the Grubbs-Hoveyda-type precatalysts. Distances in Å.

obtained for catalysts having the shortest Ru···O distances (complexes  $9_M$  and  $12_M$ ) whereas the smallest  $\delta(\text{Ru},\text{O})$  values are computed for the systems presenting the largest Ru···O distances (complexes  $3_M$ ,  $6_M$ ,  $13_M$  and  $15_M$ ). Overall, the two criteria go in the same direction and thus, all evidences point toward the fact

that the Ru···O strength depends not only on the nature of the substituents (electron withdrawing or electron donor) but also on their position (*para* or *meta* to the alkoxy) indicating that the synthesis of complexes wearing electron withdrawing groups does not necessarily imply weaker Ru···O strength. The contrary is also true,

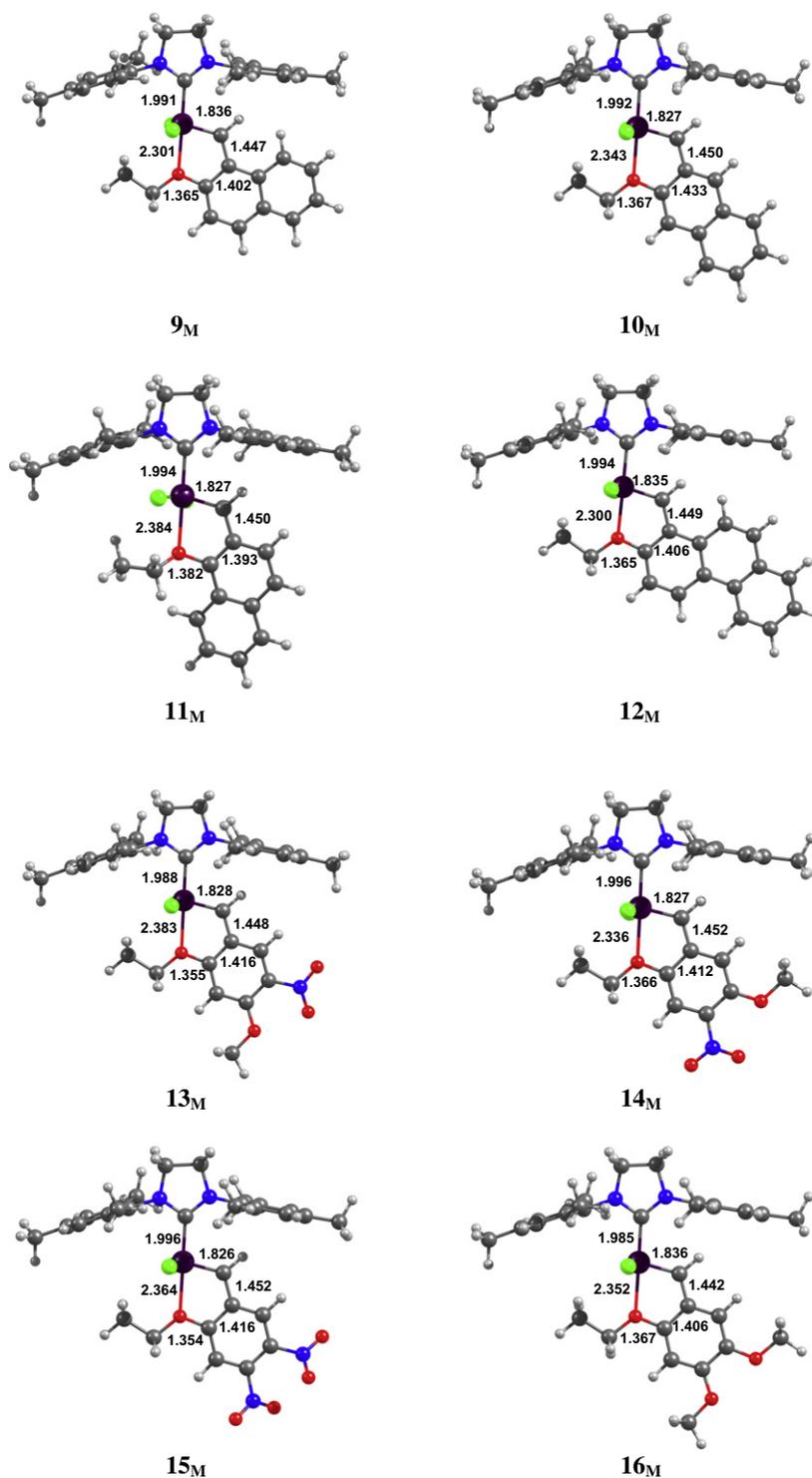


Fig. 1 (continued)

electron donor groups do not mandatorily lead to stronger Ru···O interactions.

Regarding the metalloaromaticity of the ruthenafurane cycle, several evidences point out that the metallacycle ring is nonaromatic or antiaromatic. These evidences apply to all considered compounds and thus, none of them can be considered aromatic. This nonaromaticity can be understood considering the molecular orbital diagram of the Ru=C and Ru···O interactions shown in Scheme 4. This scheme describes the interaction of the two fragments that

form the precursor as if it arises from: i) the triplet Cl<sub>2</sub>Ru(NHC) metal moiety and ii) the triplet carbene Hoveyda C–Ph–O–Et one. That is, we have considered that the Ru=C bond is mainly covalent and thus, both the metal fragment and the ligand contribute to the bond with two electrons, one  $\sigma$  and one  $\pi$ . The metal fragment has six electrons on ruthenium, i.e.  $d_{xy}$  and  $d_{yz}$  orbitals are doubly occupied while the  $d_z^2$  and  $d_{xz}$ , responsible of the Ru=C<sub>ene</sub> bond, are monooccupied. Noteworthy, we have also analyzed the relevant Kohn–Sham orbitals, shown in Fig. S1, to ensure the validity of the

**Table 1**  
NICS(0) and NICS(0)<sub>zz</sub> (in ppm), MCI (in a.u.) aromaticity values and delocalization indices (in a.u.) of the contiguous atoms of the metal containing ring.

Catalyst	NICS(0)	NICS(0) <sub>zz</sub>	MCI	δ(Ru,C1)	δ(C1,C2)	δ(C2,C3)	δ(C3,O)	δ(Ru,O)
<b>2<sub>M</sub></b>	4.46	14.51	0.005	1.651	1.146	1.209	0.974	0.239
<b>3<sub>M</sub></b>	4.07	13.72	0.005	1.664	1.131	1.197	0.994	0.227
<b>4<sub>M</sub></b>	3.78	13.69	0.005	1.654	1.141	1.201	0.982	0.238
<b>5<sub>M</sub></b>	3.91	14.70	0.005	1.648	1.146	1.225	0.966	0.247
<b>6<sub>M</sub></b>	3.55	15.00	0.005	1.626	1.166	1.205	0.979	0.228
<b>7<sub>M</sub></b>	4.00	14.62	0.004	1.649	1.144	1.213	0.960	0.247
<b>8<sub>M</sub></b>	3.33	14.89	0.005	1.600	1.187	1.182	0.973	0.232
<b>9<sub>M</sub></b>	3.94	15.76	0.007	1.621	1.167	1.269	0.974	0.264
<b>10<sub>M</sub></b>	4.57	16.23	0.003	1.654	1.142	1.134	0.972	0.234
<b>11<sub>M</sub></b>	-7.52 <sup>a</sup>	16.38	0.004	1.646	1.149	1.286	0.957	0.261
<b>12<sub>M</sub></b>	3.96	15.77	0.006	1.628	1.161	1.247	0.973	0.263
<b>13<sub>M</sub></b>	3.67	13.94	0.005	1.648	1.144	1.183	0.995	0.213
<b>14<sub>M</sub></b>	3.76	13.38	0.004	1.656	1.136	1.204	0.971	0.243
<b>15<sub>M</sub></b>	3.68	12.53	0.006	1.659	1.133	1.199	1.000	0.226
<b>16<sub>M</sub></b>	3.40	14.85	0.005	1.616	1.170	1.224	0.970	0.235

<sup>a</sup> NICS(0) of compound **11<sub>M</sub>** may be not reliable as having the ethyl group very close.

schematic molecular orbital diagram. First, it can be observed in Scheme 4 that the metal *d* orbital involved in the  $\pi$  metal–carbene bond ( $d_{xz}$ ) exhibits very small overlap with the  $\pi$  orbital centered on the oxygen atom of the alkoxy fragment ( $p_x$ ). Indeed, the overlap would be strictly zero if the oxygen atom lies on the *y* axis. The metal *d* orbital that overlaps with the  $p_x$  orbital of the oxygen atom is the  $d_{xy}$ , which is doubly occupied. The  $\pi$  Ru··O interaction involves 4 electrons and thus, it is not stabilizing. As a result, none of the  $\pi$ -orbitals is fully delocalized in the whole metallacycle as it happens, for instance, in the classical aromatic compounds such as polycyclic aromatic hydrocarbons or in the [(C<sub>5</sub>H<sub>5</sub>)Rh(PH<sub>3</sub>)<sub>3</sub>(Cl)<sub>2</sub>] metallabenzene studied by Fernández and Frenking [74]. The  $\pi$ -system of the present complexes involves 8 $\pi$ -electrons, which confers antiaromaticity according to the Hückel's rule. Note that, apart from the 6 $\pi$  electrons of the Ru=C<sub>ene</sub> and Ru··O interactions there are two additional electrons coming from the C2 and C3 carbons. Moreover, there is no  $\pi$ -orbital having a change of phase typical of Möbius aromatic compounds [75–77] like twisted 4N annulenes [78]. Finally, all computed aromaticity indices (NICS(0), NICS(0)<sub>zz</sub> and MCI) show that the metallacycle exhibits an antiaromatic or nonaromatic character.

The presence of substituents in the phenyl ring produces small variations on the electron delocalization index  $\delta(\text{Ru},\text{C}_{\text{ene}})$  and, consequently, on the metal carbene bond distance. In general, and regardless of their position, the presence of electron withdrawing groups (complexes **3<sub>M</sub>** and **4<sub>M</sub>**) leads to shorter Ru=C<sub>ene</sub> bond distances and slightly higher  $\delta(\text{Ru},\text{C}_{\text{ene}})$  values. These variations are usually associated with a decrease of the  $\delta(\text{C}_{\text{ene}},\text{C}2)$  index and a lengthening of the C<sub>ene</sub>–C2 bond. The opposite effect is observed when electron donor groups are included in the phenyl ring (**5<sub>M</sub>**–**8<sub>M</sub>**): the Ru=C<sub>ene</sub> bond is lengthened, the  $\delta(\text{Ru},\text{C}_{\text{ene}})$  values decrease and concomitantly the delocalization indexes associated with C<sub>ene</sub> and C2 bond marginally increase. Interestingly, the same features are observed for the disubstituted complexes. Complex **15<sub>M</sub>**, which has two electron withdrawing groups, presents the shortest Ru=C<sub>ene</sub> distance as well as the highest  $\delta(\text{Ru},\text{C}_{\text{ene}})$  value of all benzene-based complexes. Precatalyst **16<sub>M</sub>** has two electron donor groups and thus, it presents the longest Ru=C<sub>ene</sub> bond and the smallest  $\delta(\text{Ru},\text{C}_{\text{ene}})$  index. Finally, complexes **13<sub>M</sub>** and **14<sub>M</sub>** that have one electron donor and one electron withdrawing groups present intermediate Ru=C<sub>ene</sub> bond distances as compared to **15<sub>M</sub>** and **16<sub>M</sub>**.

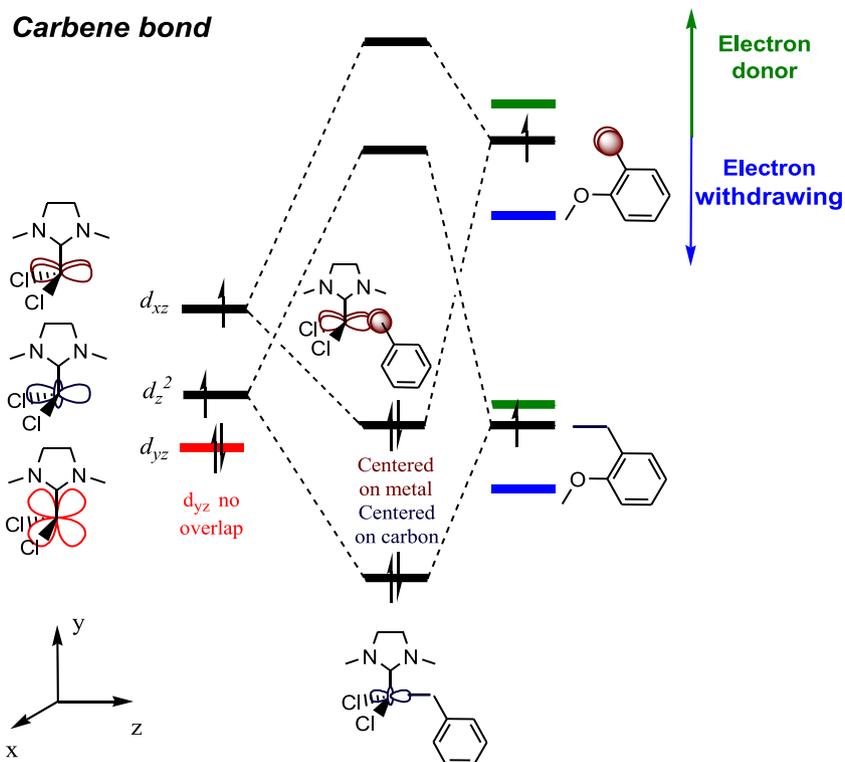
#### 4. Discussion

The origin of the  $\delta(\text{Ru},\text{C}_{\text{ene}})$  variations as a function of the Hoveyda ligand substituents may be understood considering the

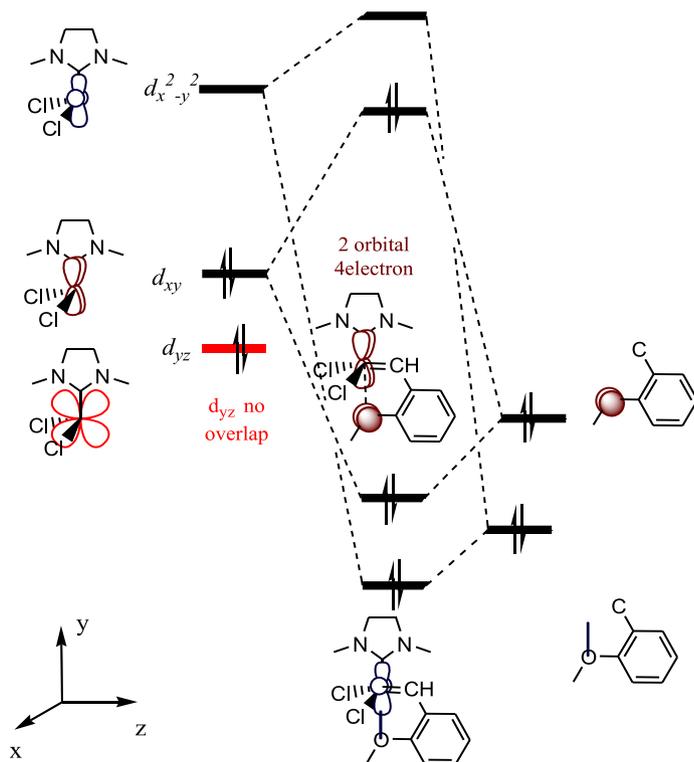
nature of the Ru=C bond and how the Hoveyda ligand substituents tune the electron density around this bond. According to the recent work of Occhipinti and Jensen [79], the electron density of the Ru=C  $\sigma$ -bond is polarized towards the carbon while the electron density of the  $\pi$  bond is polarized towards the metal. The NBO analysis shown in Table 2 goes in the same direction.

The Ru=C  $\sigma$ -polarization is almost not affected by the presence of substituents in the Hoveyda ligand. However, the effect of the substituents is more pronounced on the Ru=C  $\pi$ -bond polarization. Note that the contribution of the metal at the  $\pi$  Natural Bond Orbital varies between 62.8% and 71.1%. This can be rationalized from the qualitative energy diagram of molecular orbitals represented in Scheme 4. The molecular orbitals of the ligand with the appropriate symmetry to form the  $\pi$  Ru=C bond lie above those of the metal fragment (Table 3), which explains the polarization towards the metal. The addition of electron withdrawing groups in the ligand decreases the energy of the ligand orbitals (see Table 3), which become closer to those of the metal fragment. As a result, the  $\pi$  orbital is less polarized toward the metal and the Ru=C  $\pi$ -bond becomes more covalent (shorter Ru=C distance and higher  $\delta(\text{Ru},\text{C}_{\text{ene}})$  index). In contrast, the addition of electron donor groups increases the energy of the ligand orbitals enhancing the polarization toward the metal and the Ru <sup>$\delta^-$</sup> –C<sub>ene</sub> <sup>$\delta^+$</sup>  character. In summary, the nature of the carbene fragment seems to be mainly tuned by the nature of the substituents in the Hoveyda ligand rather than by their position. In this way, the presence of electron withdrawing groups favors the covalent character of the Ru=C<sub>ene</sub> bond while the presence of the electron donor groups favors a more polarized Ru <sup>$\delta^-$</sup> –C<sub>ene</sub> <sup>$\delta^+$</sup>  bond.

The Ru··O interaction cannot be rationalized considering a single effect. In fact, it seems to be influenced by the effects of the substituents on both the Ru=C<sub>ene</sub> bond and the O electron density. As shown in Scheme 4 there is a large energy span between the ruthenium empty *d* orbital and the lone pair of the oxygen atom able to interact with it. As a consequence, the Ru··O interaction is mainly electrostatic, which is evidenced by the small  $\delta(\text{Ru},\text{O})$  index. Thus, at first glance one would expect that this interaction will mainly depend on the electron density at the alkoxy oxygen. Natural population analysis shows that the electron density of this oxygen (Table 3) decreases in the presence of electron withdrawing groups in the ligand, which becomes less negative, whereas the opposite effect is observed when adding electron donor groups. Not surprisingly, the *para* effect is more important than the *meta* one as it is described in Scheme 5 [80,81]. Consequently, generally weaker Ru··O interactions are expected when electron withdrawing groups are present and stronger ones when the added substituents are electron donor. However, this is not the case since other factors play a key role. In fact, a second important factor is the variation on the electronic



**Ru...O interaction**



**Scheme 4.**

charge at the ruthenium center. As just mentioned, the presence of substituents in the benzylidene based ligand also tunes the electron density on the metal–carbene. That is, electron withdrawing groups favor the covalent character of the Ru=C<sub>ene</sub> bond by decreasing the Ru<sup>δ-</sup>–C<sub>ene</sub><sup>δ+</sup> polarization, whereas electron donor ones enhance bond

polarization. As a result, an electron withdrawing substituent in the Hoveyda ligand influences the Ru...O interaction in two opposite ways, it decreases the electron density at the chelating oxygen, weakening the Ru...O interaction, and it also decreases the electron density at Ru, increasing its positive charge and strengthening the

**Table 2**  
Percentage of Ru and C contribution to the Natural Bond Orbitals of Ru=C.

	$\sigma$ -NBO		$\pi$ -NBO	
	Ru	C	Ru	C
<b>2<sub>M</sub></b>	44.7	55.3	65.9	34.1
<b>3<sub>M</sub></b>	44.7	55.3	64.2	35.8
<b>4<sub>M</sub></b>	44.9	55.1	63.5	36.5
<b>5<sub>M</sub></b>	44.7	55.3	65.7	34.3
<b>6<sub>M</sub></b>	44.3	55.7	67.2	32.8
<b>7<sub>M</sub></b>	44.8	55.2	66.5	33.5
<b>8<sub>M</sub></b>	44.2	55.8	68.3	31.7
<b>13<sub>M</sub></b>	44.4	55.6	65.7	34.3
<b>14<sub>M</sub></b>	44.8	55.2	63.4	36.6
<b>15<sub>M</sub></b>	44.7	55.3	62.8	37.2
<b>16<sub>M</sub></b>	48.0	52.0	71.1	34.3

**Table 3**  
Net atomic charges and energies (in a.u.) of the orbitals involved in the Ru=C bond. See Scheme 4.

	qO	qRu	$\sigma$	$\pi$
<b>2<sub>M</sub></b> -fragment	-0.532		-0.27078	-0.17472
<b>3<sub>M</sub></b> -fragment	-0.518		-0.29222	-0.20118
<b>4<sub>M</sub></b> -fragment	-0.526		-0.29868	-0.20661
<b>5<sub>M</sub></b> -fragment	-0.535		-0.26999	-0.17051
<b>6<sub>M</sub></b> -fragment	-0.530		-0.26462	-0.15751
<b>7<sub>M</sub></b> -fragment	-0.537		-0.26509	-0.16286
<b>8<sub>M</sub></b> -fragment	-0.532		-0.25424	-0.14004
<b>13<sub>M</sub></b> -fragment	-0.518		-0.29438	-0.18389
<b>14<sub>M</sub></b> -fragment	-0.530		-0.29907	-0.20148
<b>15<sub>M</sub></b> -fragment	-0.515		-0.32290	-0.22342
<b>16<sub>M</sub></b> -fragment	-0.533		-0.26250	-0.15228
Ru-fragment		+0.463	-0.25946	-0.23073

Ru···O interaction. Overall, since the *para* effect is more important than the *meta* one (Scheme 5), the strengthening or weakening of the Ru···O interaction with respect to that of the parent compound depends on the position of the substituent. If the substituent is *para* to the chelating alkoxy, its effect on the alkoxy will be major and will determine the strengthening (electron donor groups) or

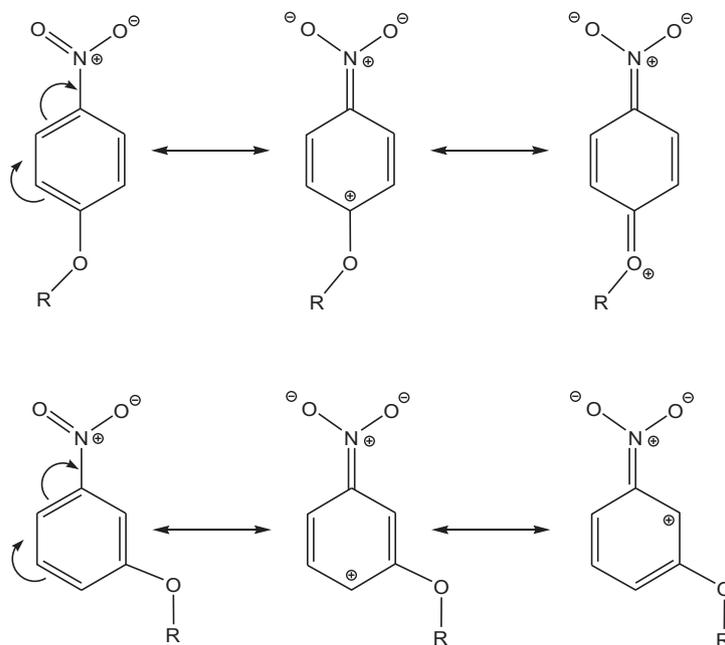
weakening (electron withdrawing groups) of the Ru···O interaction. In contrast, if the substituent is *para* to the metal carbene, its influence on the metal center electron density will be dominant and thus, the complex will exhibit stronger Ru···O interaction when adding electron withdrawing groups and weaker ones when adding electron donors.

## 5. Conclusions

The electronic structure of 15 different Hoveyda–Grubbs precatalysts has been analyzed by means of DFT quantum chemical calculations. Electronic delocalization measures and aromaticity indices have been used to analyze the influence of the Hoveyda ligand substituents on the Ru···O interaction, the metal carbene bond, and whether or not the 5-membered metal containing ring exhibit metalloaromaticity, as previously suggested.

Results show that these complexes do not exhibit any aromatic character on the metal containing ring although delocalization measures indicate that there is a certain  $\pi$  electron delocalization on the Hoveyda ligand.

More importantly, present study shows that the Ru···O interaction is mainly electrostatic and that the influence of the substituents not only depends on the changes occurred at the O atom but also on the metal site. In general substituents *para* to the alkoxy group (*meta* to the carbene) mainly tune the electronic structure of the chelating oxygen atom in such a way that substituents with an electron donor character increase the electron density at the O atom whereas electron withdrawing ones induce the opposite effect. Thus, electron donor groups *para* to the alkoxy will strengthen the Ru···O interaction hindering the activation process of the precatalyst whereas electron withdrawing groups will facilitate it. However, substituents in *para* to the carbene (*meta* to the alkoxy) mainly tune the electronic structure of the ruthenium carbene bond modifying the Ru $^{\delta-}$ –C $_{ene}^{\delta+}$  bond polarization and producing the opposite effect. Electron withdrawing groups strengthen the Ru···O interaction due to a decrease of the electron density at the metal center and electron donor ones weakens it. Overall, the synthesis of Hoveyda–Grubbs-type complexes for olefin metathesis must account for a good compromise between the



**Scheme 5.**

nature of the benzylidene ligand and the position of the substituents in order to favor the activation process.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2012.07.015>.

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