**σ/π Plasticity of NHCs on the Ruthenium–Phosphine and Ruthenium=Ylidene Bonds in Olefin Metathesis Catalysts**

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**ABSTRACT:** The nature of the Ru bonding environment in a set of Grubbs catalysts has been studied by means of density functional theory (DFT). On the one hand, for a set of 20 [Ru(=CH2)(NHC)(PCy3)][Cl]2 second-generation adducts, the results show that calculated 31P NMR shieldings exhibit a good correlation with the calculated R(Ru−P) bond lengths, which are in turn strongly correlated with the calculated PCy3 ligand dissociation energies. Bond energy decomposition analysis (EDA) also indicates that there is a strong correlation between the σ and π orbital interaction energies of the Ru−PCy3 bond, while no correlation was found for the case of the bond between the Ru moiety and the N-heterocyclic carbene (NHC) ligands, Ru−NHC. Furthermore, π orbital interaction energies of the Ru−PCy3 bond were found to be strongly correlated with the calculated PCy3 ligand dissociation energies, as well as with the R(Ru−P) bond lengths, confirming the significance of the π back-donation component from Ru to PCy3 in determining the lability of the PCy3 ligand in the studied adducts. On the other, for a set of 17 [Ru(=CHR)(NHC)(PCy3)x−1][Cl]2 first (x = 0)- and second-generation (x = 1) complexes, DFT results show that changes occurring in the 13C NMR shielding of the Ru−ylidene bond are mainly due to σ(Ru≡C) → π*(Ru=C) molecular orbital (MO) transitions. Good correlations are observed between σ(13C) and the energy gaps of the MOs involved in such transitions, between the binding energies of the ylidene moiety and the rest of the Ru fragment, as well as with the R(Ru=C) bond lengths. Finally, our novel preliminary results suggest that, once the metallacycle intermediate is formed by reaction with ethylene, 13C(β) NMR shielding retains the NMR information from σ(13C) in the 16e species, in contrast to what happens with the 13C(α) NMR shielding.

**INTRODUCTION**

In the less than three decades since Arduengo reported the synthesis of the first crystalline N-heterocyclic carbene (NHC), the use of this organic species as a ligand in organometallic complexes has increased exponentially. In a mimetic manner, NHCs have often been a perfect substitute for phosphines in organometallic catalysts, in which changes in the steric and/or electronic properties have resulted in an improved catalytic activity.

Apart from the recent advances in organocatalysis, the effect of the NHCs in catalysis has been basically circumvented when they are linked to metals. Particularly, as a ligand of organometallic complexes, the inclusion of an NHC ligand by Grubbs in exchange for a phosphine provoked the definitive impulse for the olefin metathesis to be recognized soon after, in 2005, with the Nobel Prize, together with Chauvin and Schrock. Further, this represented the switch from first- to second-generation Grubbs catalysts.

Several methods have been developed for the characterization and rationalization of specific properties in NHC ligands, with special emphasis on the electronic and steric properties, such as the Tolman electronic parameter (TEP) and the percent buried volume (%Vbur). In this context, the metal–ligand electronic parameter (MLEP) also includes the metal in the analysis, apart from the extended view that steric maps also provide.

With regard to the electronic part, NHCs have been assumed to be purely σ donors, although subsequent studies confirmed that the contributions of π bonding are not insignificant. In this context, while the σ donor effect in NHCs is prominent, an important dose of π back-donation is observed when NHCs are complexed, thus accepting electron density or even behaving as π donor agents.

Scheme 1a exemplifies how the back-donation works with any metal (M), involving a d orbital of M and the π* orbital from the NHC. Actually, it consists of the in-phase combination between a filled d orbital on the metal with an empty π* orbital of the NHC, whereas the interaction of the same orbitals also generates the corresponding antibonding orbital.

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With regard to the π bonding nature of NHCs, Nolan,21 Bertrand,22 and Ganter23 overcame small inconsistencies of the TEP using NMR coupling constants on the Pt−C bond for [PtCl2(DMSO)(NHC)] complexes and the phosphorus and selenium signals of phosphinidene adducts24 and selenourea compounds, respectively. In this context, Nolan and co-workers also probed the π back-bonding abilities to NHC of phosphinidene and selenium adducts and the capabilities of selenoureas to be deployed as ligands for Au(I).25 The theoretical interpretation derived from these compounds is insufficient, and therefore it is not fully valid for metallic complexes bearing NHC ligands, only for NHC−PPh and NHC−Se.20 In this sense, Belpassi and Zuccaccia examined the σ donation and the π back-donation in Au(NHC)-based complexes, taking into account the trans ligand to the NHC,26 continuing the work of Ciancaleoni and Belpassi in the same sense, although the latter only considered the use of phosphine ligands.27 More recently, the π back-donation has been analyzed to distinguish between cationic Au-NHC complexes and their isolobal NHC-proton compounds.28 However, for the case of Grubbs olefin metathesis catalysts, in order to properly define the NHC ligand, its description should be in combination with, at least, the trans Ru−P bond.

Thus, in order to understand the nature of the Ru−P and Ru−NHC bonds, and also to shed light onto the mode of communication between the phosphine (PCy3) and NHC ligands (Scheme 1b), a total of 20 [Ru(===CH2)(NHC)-(PCy3)]2 second-generation adducts (Figure 1), of which 14 contain standard NHCs covering derivatives of imidazol-2-ylidene and 4,5-dihydroimidazol-2-ylidene, 3 include triazol-2-ylidene carbenes, and 3 contain cyclic alkylaminocarbenes (CAAC), were investigated. In a second part, an analysis of the bonding and NMR properties for the Ru═ylidene bond has been performed for a set of 17 [Ru(===CHR)-(NHC)x(PCy3)2x][Cl2] first (x = 0)- and second-generation adducts considered in the first part of this study, where [Ru] (red) = [Ru(===CH2)(PCy3)][Cl] and 31P magnetic shieldings, σ(31P), are shown in ppm (blue).

Figure 1. Set of 20 [Ru(===CH2)(NHC)(PCy3)]2 Cl2 second-generation adducts considered in the first part of this study, where [Ru] (red) = [Ru(===CH2)(PCy3)][Cl] and 31P magnetic shieldings, σ(31P), are shown in ppm (blue).
(x = 1) Grubbs catalysts, in which different ylidene moieties, \( \equiv \text{CHR} \), from previously synthesized complexes have been studied (\textit{vide infra}, Figure 7). In this sense, our objective is to provide a comprehensive view of the connectivity between the most important functional groups linked to the central metal atom in ruthenium-based olefin metathesis catalysts: i.e., what is the communication mode in terms of energy, orbital, and NMR analysis?

\section*{COMPUTATIONAL DETAILS}

The structures and energies for a set of second-generation \([\text{Ru} (\equiv \text{CH})_2 (\text{NHC}) (\text{PCy}_3)]_{2-}[\text{Cl}]_2\) and first \((x = 0)\) and second-generation \((x = 1)\) \([\text{Ru}(\equiv \text{CHR})_2 (\text{NHC}) (\text{PCy}_3)]_{2-}[\text{Cl}]_2\) Grubbs catalysts have been studied through the use of density functional theory (DFT) via the spin-restricted Kohn–Sham (RKS) formalism. The generalized gradient approximation (GGA) has been used via the BP86 functional\[^{33}\] together with the TZ2P Slater-type orbital (STO) basis set, which is augmented by one polarization function for both light (hydrogen) and heavy atoms. The DHS procedure was applied for the self-consistent field (SCF) convergence with the Becke fuzzy cell integration scheme (quality good)\[^{31}\].

The zeroth order regular approximation (ZORA)\[^{32}\] to the Dirac equation was applied during the optimization calculations in the gas phase in order to include relativistic effects (scalar) and freeze the inner-core orbitals. Nuclear magnetic resonance (NMR) chemical shifts were calculated using the gauge-including atomic orbitals (GIAO) method\[^{33}\] through all-electron basis sets and inclusion of relativistic spin–orbit coupling.

Energy decomposition analysis (EDA)\[^{34}\] has been performed over \(C_i\)-symmetrized complexes by rigid fragmentation into the two respective moieties. In the framework of EDA, the total binding energy (BE) is divided into deformation energy and interaction energy \((\Delta E_{\text{tot}} = \Delta E_{\text{int}} + \Delta E_{\text{def}})\). The interaction energy \((\Delta E_{\text{int}})\) is the energy released when the two free deformed fragments are brought to the position that they have in the joint complex between both moieties, whereas the deformation energy \((\Delta E_{\text{def}})\) is the energy needed to modify the geometry of the ground state free fragments to attain the geometry that they have together. Next, in a second decomposable level \(\Delta E_{\text{def}}\) can be split into electrostatic, Pauli repulsion, and orbital interaction terms \((\Delta E_{\text{def}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}})\). The attractive term \(\Delta E_{\text{elstat}}\) corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments. The also attractive orbital interaction term, \(\Delta E_{\text{Pauli}}\), accounts for charge transfer and polarization, while the repulsive Pauli term, \(\Delta E_{\text{Pauli}}\), comprises the destabilizing interactions between occupied orbitals and is responsible for the steric repulsion. In the present study, we will focus on an analysis of values derived from \(\Delta E_{\text{def}}\).

All calculations were carried out through the facilities provided by the Amsterdam Density Functional (ADF) modeling suite package (revision 2016.102).

\section*{RESULTS AND DISCUSSION}

\textbf{Ruthenium–Phosphine Bond.} The calculated magnetic shielding of the P atom in the 20 complexes of Figure 1 spans a window of 21.9 ppm, with the complexes CAAC3 and 1PrPMe\[^{34}\] presenting the highest and lowest calculated \(^{31}\)P magnetic shielding (349.8 vs 327.9 ppm, respectively). This narrow range is somewhat surprising, despite the fact that the considered N-heterocyclic carbene (NHC) are remarkably different in terms of both steric and electronic properties. In detail, unsaturated imidazol-2-ylidene bearing secondary alkyl N substituents exhibit the lowest DFT calculated \(^{31}\)P magnetic shielding (328–334 ppm), followed by unsaturated \(N,N'\)-dialkylimidazol-2-ylidene and one example of a saturated \(N,N'\)-dialkyl-4,5-dihydroimidazol-2-ylidene (335–338 ppm). Triazoles also appear in the same region. On the other hand, saturated \(N,N'\)-diaryl species exhibit higher \(\sigma^{(31)P}\) values (339–341 ppm). Interestingly, CAAC complexes exhibit the highest \(^{31}\)P magnetic shielding (346–350 ppm).

Decomposition of the total isotropic magnetic shielding into paramagnetic and diamagnetic terms (plus spin–orbit–orbit), \(\sigma = \sigma_p + \sigma_d + (\sigma_{SO})\), indicates that the main variable is the paramagnetic shielding term, \(\sigma_p\), which varies over a range of 22 ppm, while the diamagnetic shielding term \(\sigma_d\) covers a range of only 2 ppm (see Table S1 in the Supporting Information). This observation is consistent with our recent findings for selonoureas and phosphinidine adducts\[^{20}\].

We start the analysis by examining the correlation between the \(^{31}\)P magnetic shielding and one of the most trivial geometrical parameters in these complexes, the Ru–PCy\(_3\) distance. As shown in Figure 2, an excellent correlation \((R^2 = 0.88)\) is obtained, with higher magnetic shielding corresponding to longer Ru–PCy\(_3\) distances. A point worth mentioning here is that, similarly to the calculated magnetic shielding of the P atom, Ru–PCy\(_3\) distances also span a rather small window of about 0.12 Å\[^{36}\]. On the other hand, we did not find any reasonable correlation between the Ru–PCy\(_3\) and the Ru–NHC distances and, consequently, between the Ru–NHC distance and the calculated \(^{31}\)P shielding, with \(R^2\) values of 0.59 and 0.53, respectively (see Figure S1 in the Supporting Information).

The calculated \(R(\text{Ru–P})\) and \(R(\text{Ru–C})\) distances can be good indicators of the corresponding bond strengths. Therefore, we estimated the Ru–PCy\(_3\) and Ru–NHC bond energies as the ligand dissociation energies \((\Delta E_L, \text{where } L = \text{PCy}_3, \text{NHC})\), i.e., the difference in potential energies of the optimized geometries of products and reactants, as shown in eqs 1 and 2:

\[
\Delta E_{\text{PCy}_3} = (E_{[\text{NHC} + \text{Ru(\text{CH}_2)(\text{Cl})_2}]} + E_{\text{PCy}_3}) - (E_{[\text{NHC} + \text{Ru(\text{CH}_2)(\text{Cl})_2}]} + E_{\text{PCy}_3})
\]

\[
\Delta E_{\text{NHC}} = (E_{[\text{Ru(\text{CH}_2)(\text{Cl})_2}]} + E_{\text{PCy}_3}) - (E_{[\text{Ru(\text{CH}_2)(\text{Cl})_2}]} + E_{\text{PCy}_3})
\]

For the 20 ruthenium adducts studied, in a plot of the calculated \(\Delta E_{\text{PCy}_3}\) vs \(R(\text{Ru–P})\), a strong correlation \((R^2 = \ldots)\) is observed.
These observations together, we hypothesize that PCy3 and ERu between ERu and NHC ligands interconvert, thereby affecting the coordination of NHC to the Ru metal and thus the strength of the Ru–NHC bond.

At this point, a bond energy decomposition analysis (EDA) of the considered ruthenium adducts, rigidly fragmented into [Ru(≡CH2)(NHC)][Cl]2 and PCy3 moieties and the [Ru(≡CH2)(PCy3)][Cl]2 and NHC moieties, was performed to unravel the nature of the Ru–PCy3 and Ru–NHC bonds, with the main focus on the extent of π-back donation from a filled Ru dπ orbital to the empty PCy3 or NHC π* orbital. To this end, the geometries of all the complexes were reoptimized under the constraint of C2 symmetry, with the NHC ring lying in the σp plane. This allows the orbital interaction energy contribution of the A' and A'' irreducible representations to be associated with the σ and π Ru–PCy3 and Ru–NHC bonds (Eσ and Eπ), respectively.

Focusing on the nature of the Ru–PCy3 bond in Figure 4a, we found an excellent correlation (R2 = 0.93) between Eσ(PCy3 → Ru) and Eπ(Ru–PCy3), indicating that a stronger Ru–PCy3 σ bond means a stronger Ru–PCy3 π bond. On the other hand, for the Ru–NHC bond, in Figure 4b correlating Eσ(NHC → Ru) vs Eπ(Ru → NHC) there was a poor correlation (R2 = 0.23), which is in line with our earlier findings for selenoureas and phosphinidines. Additionally, we observed an excellent correlation (R2 = 0.94) between Eσ(Ru → PCy3) and the calculated 31P magnetic shielding (see Figure S3 in the Supporting Information).

With these insights into the nature of the Ru–PCy3 and the Ru–NHC bonds in hand, we then explored the mode of communication between PCy3 and NHC ligands interconnected via the Ru metal. Figure 5 shows those orbitals of each moiety involved in the σ and π bonding of the Ru–PCy3 and Ru–NHC bonds. Then, we searched for a correlation between the estimated Eσ and Eπ of Ru–PCy3 and Ru–NHC bonds (Figure 6); a strong correlation (R2 = 0.91) was observed between Eσ(Ru → NHC) and Eπ(Ru → PCy3) (Figure 5a), whereas a poor correlation (R2 = 0.47) was found between Eσ(NHC → Ru) and Eπ(PCy3 → Ru) (Figure 5b). Taking these observations together, we hypothesize that PCy3 and NHC ligands in the considered ruthenium adducts communicate through π bonding: i.e., the weaker the Ru–PCy3 π bond, the stronger the Ru–NHC π bond and vice versa. In other words, when there is less π electron density available for PCy3, the NHC is more π accepting, and thus the Ru–PCy3 bond is weaker.

For example, among the 20 studied ruthenium adducts, complexes CAAC1–3 presented the highest Eπ for the Ru–NHC bond (22.7–23.7 kcal mol⁻¹) and the lowest Eσ for the Ru–PCy3 bond (7.3–7.5 kcal mol⁻¹). On the other hand, IPrPrMe presented the lowest Eσ for the Ru–NHC bond (10.3 kcal mol⁻¹) and the highest Eπ for the Ru–PCy3 bond (11.0 kcal mol⁻¹). As an end result, in support of our hypothesis, complexes CAAC1–3 presented weaker Ru–PCy3 bonds (ΔEPCy3 = 7.0–8.2 kcal mol⁻¹), while IPrPrMe presented a stronger Ru–PCy3 bond (ΔEPCy3 = 20.2 kcal mol⁻¹). Additionally, as further evidence for our hypothesis, in the studied 20 ruthenium adducts we observed a reasonably good correlation (R2 = 0.82) between Eσ(Ru → PCy3) and ΔEPCy3 and an excellent correlation (R2 = 0.86) between Eσ(Ru → PCy3) and R(Ru–P) bond lengths, suggesting that the R(Ru–P) distances are indicative of the amount of Ru to PCy3 back donation, which in turn determines the lability of the PCy3 ligand (see Figure S4 in the Supporting Information).

As additional remarks, for the cases of ruthenium adducts Imes, SIMes, IPr, and SIPr, it is possible to do a comparison among the different NHCs and their influence on the corresponding Ru–PCy3 bond strength, ΔEPCy3. At first, it is...
evident from Table 1 that the calculated $R$(Ru–P) distances are slightly shorter in the case of unsaturated NHCs than in the saturated NHCs. This observed trend in bond lengths is in turn reflected in the estimated PCy$_3$ dissociation energies, $\Delta E_{PCy3}$, as the Ru–PCy$_3$ bond is stronger ($\sim$2 kcal mol$^{-1}$) in the case of unsaturated NHCs than in the saturated NHCs.$^{37}$ As pointed out in our EDA discussion, the differential strength of the Ru–PCy$_3$ bonds can be explained from an orbital interaction standpoint. According to EDA, the sum of $E_a$ and $E_c$ of Ru–PCy$_3$ bonds ($E_{PCy3}$) for unsaturated NHCs ($\sim$60 kcal mol$^{-1}$) is around 2 kcal mol$^{-1}$ larger than for saturated NHCs ($\sim$58 kcal mol$^{-1}$).

Next, for ruthenium adducts IMes, SIMes, IPr, and SIPr, we substituted PCy$_3$ by PPh$_3$ and investigated the corresponding Ru–PPh$_3$ bond strength, $E_a$(Ru–PPh$_3$). The calculated $\Delta E_{PPh3}$ values (21.0–23.0 kcal mol$^{-1}$) are around 7.0 kcal mol$^{-1}$ higher in energy than the corresponding $\Delta E_{PCy3}$ values (13.5–16.0 kcal mol$^{-1}$). In case of Ru–PCy$_3$ and Ru–PPh$_3$-containing adducts, we observed a strong correlation ($R^2 = 0.90$) between the calculated ruthenium and P bond dissociation energies and $R$(Ru–P) distances. Additionally, similarly to Ru–PCy$_3$, a strong correlation ($R^2 = 0.90$) was observed between $E_c$(Ru $\rightarrow$ NHC) and $E_a$(Ru $\rightarrow$ PPh$_3$) in the four considered Ru–PPh$_3$ adducts (Figure 6).

**Ruthenium Ylidene Bond.** In order to elucidate the bonding and NMR properties of the Ru–ylidene bond for the set of 17 [Ru(CHR)(NHC)(PCy$_3$)$_2$][Cl$_2$] first ($x = 0$)- and second-generation ($x = 1$)-intercept (13C) = 0) complexes (see Figure 7), our DFT results indicate that the calculated magnetic shielding of the carbene C atom spans a window of 92.8 ppm, complexes PCy$_3$-a (R = CHEt) and PCy$_3$-g (carbazole derivative) being the ones with the lowest and highest calculated $^{13}$C magnetic shielding ($-139.4$ vs $-46.7$ ppm, respectively). Further, their experimental chemical shifts have been compared with the calculated shifts, giving an excellent correlation ($R^2 = 0.97$). This is also added to the fact that the slope and $y$-intercept variables from the correlation are close to 1 and 0, respectively, which validates the methodology employed by us (including relativistic spin–orbit effects) and provides an almost exact correspondence between the observed and calculated $^{13}$C magnetic shieldings. Furthermore, comparison of the DFT vs experimental $^1$H chemical shifts in this selected set of 17 complexes containing the CHR ylidene motif also exhibits a very good correlation ($R^2 = 0.93$), with the complex IMes-e (R = CHPh) being somewhat out of the trend (see Figure 8 and Figure S7 in the Supporting Information).

As was also observed for the Ru–PCy$_3$ and Ru–NHC bonds, the main term contributing to the $\sigma^{(13)}C$ of ylidene C in the Ru–ylidene bond is due to the paramagnetic term, $\sigma_p$, spanning a range of 85.7 ppm (diamagnetic and spin–orbit terms exhibit minor contributions).

Since changes in the paramagnetic shielding are due to occupied–occupied but mainly to occupied–virtual molecular orbital (MO) transitions, Figure 9 rationalizes the most important of these for a simple [Ru(==CHR)(NHC)(PMe$_3$)$_2$][Cl$_2$] model, with NHC = 2,3-dihydro-1H-imidazol-4-ylidene. As can be seen, optimization under the constraint of Cs symmetry, with the NHC ring lying in the $\sigma_p$ plane, indicates that for this system $\sigma^{(13)}C$ = $-113.9$ ppm and $\sigma_p^{(13)}C$ = $-364.5$ ppm. Paramagnetic shielding tensors reveal that the main contributions for $\sigma^{(13)}C$ come from MO transitions projected along the Ox (occupied) and Oy (virtual) axes, with a shielding answer along the Oz axis: $\sigma^{(13)}C$ = $-711.8$ ppm. This corresponds with the transition between the occupied $\sigma$ Ru==C bond to the empty $\pi^*$ Ru==C bond, contributing with a total of $-69.4$ ppm and an energy gap, $\Delta E$, of 6.0 eV. In addition, a smaller but also significant contribution comes from

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**Figure 5.** (a) $E_c$(Ru $\rightarrow$ NHC) vs $E_a$(Ru $\rightarrow$ PCy$_3$) and (b) $E_a$(NHC $\rightarrow$ Ru) vs $E_c$(PCy$_3$ $\rightarrow$ Ru) in the ruthenium complexes shown in Figure 1.

**Figure 6.** Calculated $E_c$(Ru $\rightarrow$ NHC) vs $E_a$(Ru $\rightarrow$ PPh$_3$), where X = Cy (black) or Ph (blue), for the ruthenium adducts IMes, SIMes, IPr, and SIPr.
a transition from the filled π Ru=C bond to the virtual σ* Ru=C bond, participating with −14.5 ppm and an energy gap of 5.0 eV.

A complete analysis requires the elucidation of the main MOs transitions that respond to the changes occurring in the shielding answer along the Ox axis, since σ_{Ox}^{(13)C} = −315.0 ppm. In this case, a π_{Ox} Ru=C bond → π_{Ox}^* Ru=C bond transition is showed as the main transition explaining the σ_{Ox}^{(13)C} contribution with −10.3 ppm and an energy gap of 7.8 eV. Finally, the very low value of σ_{Ox}^{(13)C} = −66.6 ppm suggests practically no participation of MOs projected along the Oy and Oz axes.

When we focus on the main σ Ru=C bond → π_{Oz} Ru=C bond transition for the set of 17 Ru adducts shown at Figure 7 plus the first- and second-generation (NHC = IMes) complexes for methylene and phenyl-indenylidene, there is a clear relationship between the energy gap of the MOs involved in such transitions and the calculated 13C magnetic shielding. This reveals the dominant role that they play, exhibiting that the smaller the Δε, the stronger the coupling (deshielded) and vice versa. Interestingly, similar adducts that are only differentiated by the presence of two PCy3 ligands (first generation) or one PCy3 and one NHC ligand (second generation) present close values of both Δε and σ^{(13)C}, showing that there is a

Table 1. Comparison of Bonding Properties in Ruthenium Adducts IMes, IPr, SIMes, and SIPr

<table>
<thead>
<tr>
<th>complex</th>
<th>R_{(Ru-P)}/Å</th>
<th>ΔE_{PCy3}/kcal mol⁻¹</th>
<th>E_{(PCy3 → Ru)}/kcal mol⁻¹</th>
<th>E_{(Ru → PCy3)}/kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMes</td>
<td>2.503</td>
<td>15.7</td>
<td>50.1</td>
<td>9.7</td>
</tr>
<tr>
<td>IPr</td>
<td>2.497</td>
<td>15.6</td>
<td>50.3</td>
<td>9.9</td>
</tr>
<tr>
<td>SIMes</td>
<td>2.517</td>
<td>13.4</td>
<td>48.6</td>
<td>9.0</td>
</tr>
<tr>
<td>SIPr</td>
<td>2.513</td>
<td>13.4</td>
<td>49.0</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Figure 7. Set of 17 [Ru(═CHR)(NHC)(PCy3)]_2[Cl]_2 first (x = 0)- and second-generation (x = 1) adducts considered in the second part of this study. [Ru] moieties refer to [Ru(PCy3)][Cl]_2 (blue), [Ru(IMes)(PCy3)][Cl]_2 (red), [Ru(SIMes)(PCy3)][Cl]_2 (purple), and [Ru[1,3-bis(2,6-difluorophenyl)imidazolidine][PCy3]][Cl]_2 (green). The nomenclature is consistent with these [Ru] moieties. The first- and second-generation (NHC = IMes) complexes for methylene and phenyl-indenylidene are also included: PCy3-CH2, PCy3-PhInd, IMes-CH2, and IMes-PhInd.

Figure 8. Comparison of experimental vs calculated 13C chemical shifts for the complexes in Figure 7 containing the =CHR motif, using tetramethylsilane (TMS) as reference: δ = σ_{ref} − σ.

Figure 9. The most significant MO transitions explaining σ_{Ox} for the simplest [Ru(═CH2)(NHC)(PMes)][Cl]_2 model, NHC = 2,3-dihydro-1H-imidazole.
minor influence of such ligands in the NMR response of the ylidene C atom.\(^{38}\) In addition to this, \(^{13}\)C magnetic shieldings can be grouped on the basis of the nature of the alkylidine group; thus ylidene C atoms directly attached to aromatic C atoms are less shielded than those in which these atoms are bonded to a chalcogen atom such as O or S, and these are less shielded than those directly bonded to a N atom, such as the carbazole and pyrrolidone derivatives. The energy of the empty MOs of the \(\pi\) \(\beta\) Ru\(=\)C bond range 1.68 eV over the 21 adducts studied, while the occupied MOs of the \(\sigma\) Ru\(=\)C bond range 0.83 eV; thus a larger range of energy is spanned by the virtual MOs. Finally, when both first- and second-generation [Ru] \(=\)CH\(_2\) and PCY\(_3\)-a complexes are excluded, a good correlation (\(R^2 = 0.78\)) can be seen, as shown in Figure 10.

In support of these observations, EDA analyses also shed light on the nature of the Ru\(=\)ylidene bond and its relationship with \(\sigma\)(\(^{13}\)C). For the 21 ruthenium adducts considered, rigidly fragmented into the \([\text{Ru-(NHC)}]_x(\text{PCY}_3)_2-\text{Cl}_x\) \((x = 0, 1)\) and the CHR moieties (including [Ru] \(=\)CH\(_2\) and [Ru] \(=\)PhInd complexes), it can be seen that the stronger the coupling (low field), the stronger the bond and vice versa, [Ru(NHC)]\(_x\)(PCY\(_3\))\(_{2-x}\)[Cl]\(_x\) \((x = 0, 1)\) moieties being triplet multiplicity fragments in all cases, while for CHR moieties the singlet vs triplet stability depends on the fragment. This relationship also exhibits a good correlation (\(R^2 = 0.89\)), excluding [Ru] \(=\)CH\(_2\) and [Ru] \(=\)PhInd adducts), with shielding being grouped by alkylidenes and exhibiting a minor influence of the PCY\(_3\) and NHC ligands (see Figure 11).

Previously described by us, calculated Ru–PCY\(_3\) and Ru–NHC bond lengths were found to be good indicators of the corresponding bond strengths. For the case of the Ru\(=\)ylidene bond, it is observed that the calculated Ru–C distances also correlate with calculated \(^{13}\)C magnetic shielding, showing two different correlation behaviors: either those adducts in which the carbene C atom is directly attached to another C atom (aromatic or not) presents \(R^2 = 0.93\), with the two [Ru] \(=\) PhInd complexes (PCY\(_3\)-PhInd and IMes-PhInd) excluded from this correlation (see Figure 12) or for those cases in which the ylidene C atom is bonded with another heteroatom (O, S, N) or for the two [Ru] \(=\)CH\(_2\) complexes (PCY\(_3\)-CH\(_2\) and IMes-CH\(_2\)), a very good correlation is also obtained (\(R^2 = 0.97\)). On the basis of these two groups, it is seen that a lower field means stronger and shorter Ru\(=\)C bonds. However, it is worth mentioning that, for a given Ru\(=\)C distance, \(\sigma\)(\(^{13}\)C) for the Ru\(=\)C–X motif is more deshielded than for the case of Ru\(=\)C–X \((X = O, S, N)\).

Once the basis of the connectivity between the NMR shielding of the ylidene C atom with the orbital, bonding, and structural properties of the Ru\(=\)ylidene bond in the [Ru(=CHR)(NHC)]\(_x\)(PCY\(_3\))\(_{2-x}\)[Cl]\(_x\) \((x = 0, 1)\) 16e species is elucidated, an extension of our DFT findings to the initialization process of olefin metathesis establishes some interesting relations.

First of all, Scheme 2 gathers the general mechanism for the formation of the metallacycle compound from the 16e species, passing through PCY\(_3\) dissociation (leading to the so-called 14e species) and through the insertion of one ethylene molecule (coordination intermediate). The metallacycle compound is characterized to have a four-membered ring constituted by the Ru metal, the former ylidene C atom, one C(\(\alpha\)), and C(\(\beta\)) from C\(_2\)H\(_4\).

![Figure 10. Comparison of energy gap, \(\Delta\varepsilon\), vs the calculated \(^{13}\)C magnetic shielding, \(\sigma\)(\(^{13}\)C), for the MOs involved in the \(\sigma\) Ru\(=\)C bond transition. Points in red are excluded from the regression analysis.](https://dx.doi.org/10.1021/acs.organomet.0c00536)

![Figure 11. Comparison of the binding energy, \(\Delta E_{bind}\), vs the calculated \(^{13}\)C magnetic shielding, \(\sigma\)(\(^{13}\)C), of the [Ru] and \(=\)CHR ylidene fragments. Points in red are excluded from the regression analysis.](https://dx.doi.org/10.1021/acs.organomet.0c00536)

![Figure 12. Comparison of the calculated \(^{13}\)C magnetic shielding, \(\sigma\)(\(^{13}\)C), vs R(Ru=C) bond length. Two correlation behaviors are seen: for those adducts in which carbene C atom is directly attached to another C atom (aromatic or not, blue) and those in which it is bonded with a different heteroatom (red). Points in violet are excluded from the regression analysis.](https://dx.doi.org/10.1021/acs.organomet.0c00536)
In contrast to what has been recently observed by Gordon et al. in some transition-metal olefin metathesis catalyst complexes, it seems that \( \sigma^{13}\text{C}(\alpha) \) in the metallacycle does not retain some of the alkylidene character (Figure 13a). Although our work is focused on complexes using the same metal but different bonding environments by modifying the ylidene moiety, we do not observe any trend allowing the correlation of \( \sigma^{13}\text{C}(\alpha) \) before and after cyclization. Indeed, what is observed is that \( \sigma^{13}\text{C}(\alpha) \), ranging in a shielding window of ca. 50 ppm, is distributed by groups, highlighting the importance of the atoms directly bonded to \( \text{C}(\alpha) \). However, surprising information can be extracted from Figure 13b, in which with the exception of some complexes such as \( \text{PCy}_3\text{-CH}_2 \), IMes-CH\(_2\), PCy\(_3\)-PhInd, and IMes-PhInd and complexes with sulfur-containing ylidenes a good correlation can be seen \( (R^2 = 0.94) \) for \( \sigma^{13}\text{C}(\beta) \) in the metallacycle and \( \sigma^{13}\text{C}(\delta) \) in the 16e species. However, does this relationship mean that \( \text{C}(\beta) \) has the capacity to retain the information from the precatalyst? An additional comparison between \( \sigma^{13}\text{C}(\beta) \) and \( \sigma^{13}\text{C}(\delta) \) in the isolated \( \text{C}(\beta)\text{H}_2\equiv\text{C}(\delta)\text{HR} \) alkynes demonstrates that this correlation does not come from the entering olefin, which points to validation of our hypothesis.

In this sense, the very low window of \( \sigma^{13}\text{C}(\beta) \) \((\text{ca.} \ 20 \ \text{ppm})\) as well as the large number of MO transitions contributing to \( \sigma^{13}\text{C}(\beta) \) does not allow us to establish a clear correlation as we did in Figure 10 between \( \Delta \varepsilon \) and \( \sigma^{13}\text{C}(\beta) \). However, it seems that the nature of this shielding covers \( \sigma \text{ C–H bond} \) to \( \pi^* \text{ C–H bond} \) transitions mainly involving \( \text{C}(\alpha) \) and \( \text{C}(\beta) \) atoms with p orbitals from X at \( \text{C}(\beta)\text{–C}(\alpha)\text{–X} \) playing some role in the up- or downfield shielding of \( \sigma^{13}\text{C}(\beta) \).

**CONCLUSIONS**

In summary, using DFT calculations we have investigated the electronic nature of Ru–PCy\(_3\) and the Ru–NHC bonds, probing a possible mode of communication between the PCy\(_3\) and NHC ligands for a set of 20 \([\text{Ru}(\equiv\text{CH})\text{(NHC)}(\text{PCy}_3)]^{-}\)–[Cl\(_2\)] adducts. Phosphorus NMR shielding derived from calculations correlated well \( (R^2 = 0.87) \) with the calculated \( R(\text{Ru–P}) \) bond lengths. The latter was strongly correlated \( (R^2 = 0.86) \) with the calculated PCy\(_3\) ligand dissociation energies, indicating that the calculated bond lengths are good indicators of the corresponding bond strengths. However, this explanation does not hold for the Ru–NHC bond, as no correlation \( (R^2 = 0.09) \) was observed between \( R(\text{Ru–NHC}) \) bond lengths and NHC ligand dissociation energies.

Bond energy decomposition analysis (EDA) indicated a strong correlation \( (R^2 = 0.93) \) between \( \sigma \) and \( \pi \) orbital interaction energies for the Ru–PCy\(_3\) bond, while a poor correlation \( (R^2 = 0.23) \) for the Ru–NHC bond was seen. Additionally, we observed an excellent correlation \( (R^2 = 0.91) \) between \( \pi \) orbital interaction energies of the Ru–PCy\(_3\), and the Ru–NHC bonds, suggesting that both ligands communicate through \( \pi \)-bonding: i.e., a stronger Ru–NHC \( \pi \) bond means a weaker Ru–PCy\(_3\) \( \pi \) bond and vice versa. Furthermore, \( \pi \) orbital interaction energies of the PCy\(_3\) ligand were found to be strongly correlated to \( \Delta E_{\text{PCy3}} \) \( (R^2 = 0.82) \), as well as to the \( R(\text{Ru–P}) \) bond lengths \( (R^2 = 0.95) \). These observations indeed reflect the importance of Ru to PCy\(_3\) back-donation, which in turn is regulated by the \( \pi \)-accepting ability of NHCs, in determining the lability of the PCy\(_3\) ligand for the 20 studied ruthenium adducts.

Furthermore, for the set of 17 \([\text{Ru}(\equiv\text{CH})\text{(NHC)}(\text{PCy}_3)_{x=0}]^{-}\)–[Cl\(_2\)] \( x = 0 \) - and second-generation \( (x = 1) \) complexes, our DFT findings hypothesize that changes occurring in the \( ^{13}\text{C} \) NMR shielding of the Ru=ylide bond are mainly due to \( \sigma(\text{Ru=C}) \rightarrow \pi^*(\text{Ru=C}) \) molecular orbital (MO) transitions. In this regard, \( \sigma^{13}\text{C} \) for carbene C of the ylidene moiety correlates with the energy gap of the MOs involved in the aforementioned transition, with the binding energy between the alkylidene and the rest of the Ru fragment, and with the \( R(\text{Ru=C}) \) bond lengths.

Finally, novel preliminary results shown by us also hypothesize that, during the initial stage of the olefin metathesis reaction, \( ^{13}\text{C}(\beta) \) NMR shielding from the metallacycle compound retains the NMR information from the
σ(13C) in the 16e species, although it surprisingly does not with the 13C(α) NMR shielding, C(α) being the former carbene C form the ylidene moiety.

[ASSOCIATED CONTENT]

1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.organomet.0c00536.

Extended computational data (PDF)
Cartesian coordinates (XYZ)

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Notes
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