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)]Cl₂ second-generation adducts, 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 for 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 π -backdonation 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)_x(PCy₃)_{2-x}][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=yldiene bond are mainly due to $\sigma(\text{Ru}=\text{C}) \rightarrow \pi^*(\text{Ru}=\text{C})$ molecular orbitals (MO) transitions. Good correlations are observed between $\sigma(^{13}\text{C})$ and the energy gaps of the MOs involved in such transition, 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 the $\sigma(^{13}\text{C})$ in the 16e species, contrary to what happen with the ¹³C(α) NMR shielding.

INTRODUCTION

In less than three decades since Arduengo reported the synthesis of the first crystalline *N*-heterocyclic carbene (NHC),¹ the use of this organic species as a ligand in organometallic complexes has increased exponentially.² In a mimetic manner, NHCs have been often a perfect substitute of phosphines in organometallic catalysts, in which changes in the steric and/or electronic properties³ have resulted in an improved catalytic activity.

Apart from the recent advances in organocatalysis,⁴ the impact of the NHCs in catalysis has been basically circumscribed when linked to metals.⁵ 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,⁶ together with Chauvin⁷ and Schrock.⁸ Further, this represented the switch from first⁹ to second Grubbs' catalysts generation.¹⁰

Several methods have been developed for the characterization and rationalization of specific properties in NHC ligands, with special emphasis in the electronic and steric properties,¹¹ such as the Tolman Electronic Parameter (TEP)¹² and the Percent Buried Volume (%V_{bur}).¹³ In this context, the Metal–Ligand Electronic Parameter (MLEP) also includes the metal into the analysis,¹⁴ apart from the extended view that steric maps also provide.¹⁵

Regarding the electronic part, NHCs were assumed as purely σ -donors,^{5g, 16} although subsequent studies confirmed that the contributions of the π -bonding are not insignificant.^{3a, 17} In this context, while the σ -donor effect in NHCs is prominent, an important dose of π -backdonation is observed when NHCs are complexed, thus accepting electron density or even behaving as π -donor agents.¹⁸

Scheme 1. (a) Simple Representation of the Frontier Molecular Orbitals involving the $M(d)$ and $\text{NHC}(\pi)$ Orbitals. Ru to NHC Back-bonding gathers a Filled d Orbital on Ru with an Empty π Orbital of the NHC (Note: M refers to Metal). (b) Previously Studied Systems²⁰ and Overview of this Investigation.

Scheme 1a exemplifies how the backdonation works with any metal (M),¹⁹ involving a d orbital of M and the π^* orbital from the NHC. Actually, it consists in 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 anti-bonding orbital.²⁰

In 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 $[\text{PtCl}_2(\text{DMSO})(\text{NHC})]$ complexes, and the phosphorous and selenium signals of phosphinidene adducts²⁴ and selenourea compounds, respectively. In this context, Nolan and co-workers also probed the π -backbonding abilities to NHC of phosphinidene and selenium adducts and the capabilities of selenoureas to be deployed as ligands for $\text{Au}(\text{I})$.²⁵

The theoretical interpretation derived from these compounds is insufficient and therefore it is not fully valid for metallic complexes bearing NHC ligands,³ but only for $\text{NHC}=\text{PPh}$ and $\text{NHC}=\text{Se}$.²⁰ In this sense, Belpassi and Zuccaccia examined the σ -donation and the π -backdonation in $\text{Au}(\text{NHC})$ 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 -backdonation 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 (PCy_3) and NHC ligands (Scheme 1b), a total of 20 $[\text{Ru}(\text{=CH}_2)(\text{NHC})(\text{PCy}_3)[\text{Cl}]_2]$ second-generation adducts (Figure 1), from which 14 contains standard NHCs covering derivatives of imidazol-2-ylidenes and 4,5-dihydroimidazol-2-ylidenes, 3 includes triazol-2-ylidenes carbenes, and 3 contains cyclic alkyl amino carbenes (CAAC), were investigated. In a second part, an analysis of the bonding and NMR properties for the Ru=ylidene bond has been performed in a set of 17 $[\text{Ru}(\text{=CHR})(\text{NHC})_x(\text{PCy}_3)_{2-x}][\text{Cl}]_2$ first- ($x = 0$) and second-generation ($x = 1$) Grubbs' catalysts, in which different ylidene moieties, =CHR , from previously synthesized complexes have been studied (*vide infra*, Figure 7). In this sense, our objective is to provide a comprehensive view about the connectivity between the most important functional groups linked to the central metal atom in ruthenium-based olefin metathesis catalysts, *i.e.*, which is the communication mode in terms of energy, orbital, and NMR analysis?

COMPUTATIONAL DETAILS

The structures and energies for a set of second-generation $[\text{Ru}(\text{=CH}_2)(\text{NHC})(\text{PCy}_3)[\text{Cl}]_2]$ and first- ($x = 0$) and second-generation ($x = 1$) $[\text{Ru}(\text{=CHR})(\text{NHC})_x(\text{PCy}_3)_{2-x}][\text{Cl}]_2$ 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 functional²⁹ together with the TZ2P Slater-Type Orbital (STO) basis set,³⁰ which is augmented by one polarization function for both light (hydrogen) and heavy atoms. The DIIS procedure was applied for the Self-Consistent Field (SCF) convergence with the Becke fuzzy cells integration scheme (quality good).³¹

The Zeroth Order Regular Approximation (ZORA)³² to the Dirac equation was applied during the optimization calculations in gas phase in order to include relativistic effects (scalar) and freezing the inner-core orbitals. Nuclear Magnetic Resonance (NMR) chemical shifts were calculated using the Gauge-Including Atomic Orbitals (GIAO) method³³ through all electrons basis set and including relativistic spin-orbit coupling.

Energy Decomposition Analysis (EDA)³⁴ has been performed over C_s -symmetrized complexes by rigid fragmentation into the respective two moieties. In the framework of EDA, the total binding energy (BE) is divided into deformation energy and interaction energy ($\text{BE} = \Delta E_{\text{int}} + \Delta E_{\text{def}}$). The interaction energy (ΔE_{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 (ΔE_{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 ΔE_{int} can be splitted into electrostatic, Pauli repulsion, and orbital interaction terms ($\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}}$). The attractive term ΔE_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments. The also attractive orbital interaction term, ΔE_{oi} , accounts for charge

transfer and polarization while the repulsive Pauli term, ΔE_{Pauli} , comprises the destabilizing interactions between occupied orbitals and is responsible for the steric repulsion. In the present study, we will focus on the analysis of values derived from ΔE_{oi} .

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

Figure 1. Set of 20 $[\text{Ru}(\text{=CH}_2)(\text{NHC})(\text{PCy}_3)][\text{Cl}]_2$ second-generation adducts considered in the first part of this study, being $[\text{Ru}]$ (red) = $[\text{Ru}(\text{=CH}_2)(\text{PCy}_3)][\text{Cl}_2]$. ^{31}P magnetic shieldings, $\sigma(^{31}\text{P})$, are shown in ppm (blue).

RESULTS AND DISCUSSION

1. 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 **CAAC3** and **IPr^{Me}** complexes presenting the highest and lowest calculated ^{31}P magnetic shielding (349.8 vs. 327.9 ppm, respectively). This narrower range is somewhat surprising; despite the considered *N*-heterocyclic carbenes (NHC) are remarkably different in terms of both steric and electronic properties. Going into details, unsaturated imidazol-2-ylidenes bearing secondary alkyl *N*-substituents exhibit the lowest DFT calculated ^{31}P magnetic shielding (328–334 ppm), followed by unsaturated *N,N'*-diarylimidazol-2-ylidenes 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 $\sigma(^{31}\text{P})$ (339–341 ppm). Interestingly, **CAAC** complexes exhibit highest ^{31}P magnetic shielding (346–350 ppm).

Decomposition of the total isotropic magnetic shielding into paramagnetic and diamagnetic terms (plus spin-orbit),³⁵ $\sigma = \sigma_{\text{p}} + \sigma_{\text{d}} (+\sigma_{\text{so}})$, indicates that the main variable is the paramagnetic shielding term, σ_{p} , which varies in a range of 22 ppm, while the diamagnetic shielding term σ_{d} covers a range of only 2 ppm. (see Table S1 of the Supporting Information). This observation is consistent with our recent findings for selenoureas and phosphindine 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–PCy₃ distance. As shown in Figure 2, an excellent correlation ($R^2 =$

0.88) is obtained, with higher magnetic shielding corresponding to longer Ru–PCy₃ distances. A point worth mentioning here that similar to the calculated magnetic shielding of the P atom, Ru–PCy₃ 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–PCy₃ and the Ru–NHC distances and, consequently, between the Ru–NHC distance and the calculated ^{31}P shielding, with R^2 of 0.59 and 0.53, respectively (see Figure S1 in the Supporting Information).

Figure 2. Calculated ^{31}P magnetic shielding, $\sigma(^{31}\text{P})$, vs. the distance between the Ru and P atoms, $R(\text{Ru}-\text{P})$, in the ruthenium complexes shown in Figure 1.

The calculated R(Ru–P) and R(Ru–C) distances can be good indicators of the corresponding bond strengths. Therefore, we estimated the Ru–PCy₃ and Ru–NHC bond energies as the ligand dissociation energies (ΔE_L , where L = PCy₃ or NHC), *i.e.*, the difference in potential energies of the optimized geometries of products and reactants, as shown in Eqns. (1) and (2) below:

$$\Delta E_{\text{PCy}_3} = (E_{[\text{NHC-Ru}(\text{CH}_2)(\text{Cl})_2]} + E_{\text{PCy}_3}) - (E_{[\text{NHC-Ru}(\text{CH}_2)(\text{Cl})_2\text{-PCy}_3]}) \quad (1)$$

$$\Delta E_{\text{NHC}} = (E_{[\text{Ru}(\text{CH}_2)(\text{Cl})_2\text{-PCy}_3]} + E_{\text{NHC}}) - (E_{[\text{NHC-Ru}(\text{CH}_2)(\text{Cl})_2\text{-PCy}_3]}) \quad (2)$$

For the studied 20 ruthenium adducts, plotting the calculated ΔE_{PCy_3} *vs.* R(Ru–P), a strong correlation ($R^2 = 0.86$) is gratifyingly achieved (Figure 3). On the contrary, no correlation ($R^2 = 0.09$) was observed for the calculated ΔE_{NHC} *vs.* R(Ru–C) (Figure S2 in the Supporting Information). This observation can be attributed to the fact that different NHCs presented in the considered ruthenium adducts possess different steric and electronic properties, which strongly influence the coordination of NHC to the Ru metal and thus the strength of the Ru–NHC bond.

Figure 3. Interatomic distance between the Ru and P atoms, R(Ru–P), *vs.* calculated Ru–PCy₃ dissociation energies, ΔE_{PCy_3} , in the ruthenium complexes shown in Figure 1.

At this point, a Bond Energy Decomposition Analysis (EDA) on the considered ruthenium adducts, rigidly fragmented into the [Ru(=CH₂)(NHC)][Cl]₂ and PCy₃ moieties, and the [Ru(=CH₂)(PCy₃)]Cl₂ and NHC moieties, was performed to unravel the nature of the Ru–PCy₃ and Ru–NHC bonds, with main focus on the extent of π -backdonation from a filled Ru *dz* orbital to the empty PCy₃ or NHC π^* orbital. To this end, the geometries of all the complexes were re-optimized under the constraint of C_s symmetry, with the NHC ring lying in the σ_{XY} 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 (E_σ and E_π), respectively. Focusing on the nature of the Ru–PCy₃ bond in Figure 4a, an excellent correlation ($R^2 = 0.93$) was found between $E_\sigma(\text{PCy}_3 \rightarrow \text{Ru})$ and $E_\pi(\text{Ru} \rightarrow \text{PCy}_3)$, 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 $E_\sigma(\text{NHC} \rightarrow \text{Ru})$ *vs.* $E_\pi(\text{Ru} \rightarrow \text{NHC})$ resulted in poor correlation ($R^2 = 0.23$), which is in line with our earlier findings for selenoureas and phosphinidine adducts.²⁰ Additionally, we

observed an excellent correlation ($R^2 = 0.94$) between $E_\pi(\text{Ru} \rightarrow \text{PCy}_3)$ and the calculated ³¹P magnetic shielding (see Figure S3 in the Supporting Information).

Figure 4. (a) $E_\sigma(\text{PCy}_3 \rightarrow \text{Ru})$ *vs.* $E_\pi(\text{Ru} \rightarrow \text{PCy}_3)$ for the Ru–PCy₃ bond; and (b) $E_\sigma(\text{NHC} \rightarrow \text{Ru})$ *vs.* $E_\pi(\text{Ru} \rightarrow \text{NHC})$ for the Ru–NHC bond in the ruthenium complexes shown in Figure 1.

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 E_σ and E_π of Ru–PCy₃ and Ru–NHC bonds (Figure 6); a strong correlation ($R^2 = 0.91$) was observed between $E_\pi(\text{Ru} \rightarrow \text{NHC})$ and $E_\pi(\text{Ru} \rightarrow \text{PCy}_3)$ (Figure 5a), whereas a poor correlation ($R^2 = 0.47$) was found between $E_\sigma(\text{NHC} \rightarrow \text{Ru})$ and $E_\sigma(\text{PCy}_3 \rightarrow \text{Ru})$ (Figure 5b). Taking together these observations, we hypothesize that PCy₃ and NHC ligands in the considered ruthenium adducts communicate through π -bonding, *i.e.*, the weaker Ru–PCy₃ π -bond, the stronger Ru–NHC π -bond and *vice versa*. In other words, the less is the π -electron density available for PCy₃, the more π -accepting is the NHC, and thus the weaker is the Ru–PCy₃ bond.

Figure 5. (a) $E_{\pi}(\text{Ru} \rightarrow \text{NHC})$ vs. $E_{\pi}(\text{Ru} \rightarrow \text{PCy}_3)$; and (b) $E_{\sigma}(\text{NHC} \rightarrow \text{Ru})$ vs. $E_{\sigma}(\text{PCy}_3 \rightarrow \text{Ru})$ in the ruthenium complexes shown in Figure 1.

For example, among the 20 studied ruthenium adducts, **CAAC1-3** complexes presented the highest E_{π} for the Ru-NHC bond (22.7-23.7 kcal mol⁻¹), and thus the lowest E_{π} for the Ru-PCy₃ bond (7.3-7.5 kcal mol⁻¹). On the other hand, **IPr**^{Me} presented the lowest E_{π} for Ru-NHC bond (10.3 kcal mol⁻¹), and the highest E_{π} for Ru-PCy₃ bond (11.0 kcal mol⁻¹). As an end result, in support to our hypothesis, **CAAC1-3** complexes presented weaker Ru-PCy₃ bonds ($\Delta E_{\text{PCy}_3} = 7.0$ -8.2 kcal mol⁻¹), while **IPr**^{Me} presented a stronger Ru-PCy₃ bond ($\Delta E_{\text{PCy}_3} = 20.2$ kcal mol⁻¹). Additionally, as a further evidence to our hypothesis, in the studied 20 ruthenium adducts we observed a reasonable good correlation ($R^2 = 0.82$) between $E_{\pi}(\text{Ru} \rightarrow \text{PCy}_3)$ and ΔE_{PCy_3} , and an excellent correlation ($R^2 = 0.86$) between $E_{\pi}(\text{Ru} \rightarrow \text{PCy}_3)$ and $R(\text{Ru}-\text{P})$ bond lengths, suggesting that the $R(\text{Ru}-\text{P})$ distances are indeed indicative of amount of Ru to PCy₃ backdonation, which in turn determines the liability of 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 between different NHCs and their influence on the corresponding Ru-PCy₃ bond strength, ΔE_{PCy_3} . At first, it is evident from Table 1 that the calculated $R(\text{Ru}-\text{P})$ distances are

slightly shorter in case of unsaturated NHCs than in the saturated ones. This observed trend in bond lengths is in turn reflected in the estimated PCy₃ dissociation energies, ΔE_{PCy_3} , as the Ru-PCy₃ bond is stronger (≈ 2 kcal mol⁻¹) in case of unsaturated NHCs than the saturated ones.³⁷ As pointed in the EDA section, the differential strength of the Ru-PCy₃ bonds can be explained from an orbital interaction standpoint. According to EDA, the sum of E_{σ} and E_{π} of Ru-PCy₃ bonds (E_{sum}) for unsaturated NHCs (≈ 60 kcal mol⁻¹) is around 2 kcal mol⁻¹ larger than for saturated ones (≈ 58 kcal mol⁻¹).

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

Complex	$R(\text{Ru}-\text{P}) / \text{\AA}$	$\Delta E_{\text{PCy}_3} / \text{kcal mol}^{-1}$	$E_{\sigma}(\text{PCy}_3 \rightarrow \text{Ru}) / \text{kcal mol}^{-1}$	$E_{\pi}(\text{Ru} \rightarrow \text{PCy}_3) / \text{kcal mol}^{-1}$
IMes	2.503	15.7	50.1	9.7
IPr	2.497	15.6	50.3	9.9
SIMes	2.517	13.4	48.6	9.0
SIPr	2.513	13.4	49.0	9.3

Next, for ruthenium adducts **IMes**, **SIMes**, **IPr**, and **SIPr**, we substituted PCy₃ by PPh₃ and investigated the corresponding Ru-PPh₃ bond strength, ΔE_{PPh_3} , and $E_{\pi}(\text{Ru} \rightarrow \text{PPh}_3)$. The calculated ΔE_{PPh_3} values (21.0-23.0 kcal mol⁻¹) are around 7.0 kcal mol⁻¹ higher in energy than the corresponding ΔE_{PCy_3} values (13.5-16.0 kcal mol⁻¹). In case of Ru-PCy₃ and Ru-PPh₃ containing adducts, we observed a strong correlation ($R^2 = 0.90$) between the calculated ruthenium and P bond dissociation energies and $R(\text{Ru}-\text{P})$ distances. Additionally, similar to Ru-PCy₃ adducts, a strong correlation ($R^2 = 0.90$) was observed between $E_{\pi}(\text{Ru} \rightarrow \text{NHC})$ and $E_{\pi}(\text{Ru} \rightarrow \text{PPh}_3)$ in the considered four Ru-PPh₃ adducts (Figure 6).

Figure 6. Calculated $E_{\pi}(\text{Ru} \rightarrow \text{NHC})$ vs. $E_{\pi}(\text{Ru} \rightarrow \text{PX}_3)$, where X = Cy (black) or Ph (blue), for the ruthenium adducts **IMes**, **SIMes**, **IPr**, and **SIPr**.

2. Ruthenium=Ylidene Bond

In order to elucidate the bonding and NMR properties of the Ru=yldiene bond for the set of 17 $[\text{Ru}(\text{=CHR})(\text{NHC})_x(\text{PCy}_3)_{2-x}][\text{Cl}]_2$ first- ($x = 0$) and second-generation ($x = 1$) 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, being complexes **PCy₃-a** ($R = \text{CHet}$) and **PCy₃-g** (carbazole derivative) the ones with the lowest and highest calculated ¹³C magnetic shielding, -139.4 vs. -46.7 ppm,

respectively). Further, their experimental chemical shifts have been compared with the calculated shifts observing 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 ^1H 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 complex **IMes-e** ($R = \text{CHPh}$), somewhat out of the trend (see Figure 8 and Figure S7 in the Supporting Information).

Figure 7. Set of 17 $[\text{Ru}(=\text{CHR})(\text{NHC})_x(\text{PCy}_3)_{2-x}][\text{Cl}_2]$ first- ($x = 0$) and second-generation ($x = 1$) adducts considered in the second part of this study. $[\text{Ru}]$ moieties refer to $[\text{Ru}(\text{PCy}_3)_2][\text{Cl}]_2$ (blue), $[\text{Ru}(\text{IMes})(\text{PCy}_3)][\text{Cl}]_2$ (red), $[\text{Ru}(\text{SIMes})(\text{PCy}_3)][\text{Cl}]_2$ (purple) and $\{\text{Ru}[1,3\text{-bis}(2,6\text{-difluorophenyl})\text{imidazolidine}](\text{PCy}_3)\}[\text{Cl}]_2$ (green), respectively. Nomenclature is consistent with these $[\text{Ru}]$ moieties. The first- and second-generation ($\text{NHC} = \text{IMes}$) complexes for methylene and phenyl-indenylidene are also included: $\text{PCy}_3\text{-CH}_2$, $\text{PCy}_3\text{-PhInd}$, IMes-CH_2 , and IMes-PhInd .

Figure 8. Comparison of experimental vs. calculated ^{13}C chemical shifts for the complexes at Figure 7 containing the $=\text{CHR}$ motif, using tetramethylsilane (TMS) as reference: $\delta = \sigma_{\text{ref}} - \sigma$.

As it was also observed for the Ru-PCy_3 and Ru-NHC bonds, the main term contributing to the $\sigma(^{13}\text{C})$ of ylidene C in the Ru=ylidene bond is due to the paramagnetic term, σ_p , spanning in 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 orbitals (MO) transitions, Figure 9 rationalizes the most

important of them for a simple $[\text{Ru}(=\text{CH}_2)(\text{NHC})(\text{PMe}_3)][\text{Cl}]_2$ model, being $\text{NHC} = 2,3\text{-dihydro-1H-imidazole}$. As can be seen, optimization under the constraint of C_s symmetry, with the NHC ring lying in the σ_{XY} plane, indicates that for this system, $\sigma(^{13}\text{C}) = -113.9$ ppm and $\sigma_p(^{13}\text{C}) = -364.5$ ppm. Paramagnetic shielding tensors reveal that the main contributions for $\sigma_p(^{13}\text{C})$ come from MOs transitions projected along the OX (occupied) and OY (virtual) axes, with a shielding answer along the OZ axis: $\sigma_{p,\text{ZZ}}(^{13}\text{C}) = -711.8$ ppm. This corresponds with the transition between the occupied $\sigma_{\text{Ru=C}}$ bond to the empty $\pi^*_{\text{Ru=C}}$ bond, contributing with a total of -69.4 ppm and an energy gap, $\Delta\epsilon$, of 6.0 eV. In addition, a smaller but also notorious contribution comes from a transition from the filled $\pi_{\parallel\text{Ru=C}}$ bond to the virtual $\sigma^*_{\text{Ru=C}}$ bond, participating with -14.5 ppm and an energy gap of 5.0 eV.

Figure 9. Most significant MO transitions explaining σ_p for the simplest $[\text{Ru}(=\text{CH}_2)(\text{NHC})(\text{PMe}_3)]\text{Cl}_2$ model, being NHC = 2,3-dihydro-1*H*-imidazole.

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 $\sigma_{p,xx}({}^{13}\text{C}) = -315.0$ ppm. In this case, $\pi_{\perp} \text{Ru}=\text{C} \text{ bond} \rightarrow \pi_{\parallel}^* \text{Ru}=\text{C} \text{ bond}$ transition is showed as the main one explaining $\sigma_{p,xx}({}^{13}\text{C})$, contributing with -10.3 ppm and an energy gap of 7.8 eV. Finally, the very low value of $\sigma_{p,yy}({}^{13}\text{C}) = -66.6$ ppm, suggests practically no participation of MOs projected along the OX and OZ axes.

Focusing on the main $\sigma \text{Ru}=\text{C} \text{ bond} \rightarrow \pi_{\parallel}^* \text{Ru}=\text{C} \text{ bond}$ transition for the set of 17 Ru adducts showed 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 transition and the calculated ${}^{13}\text{C}$ magnetic shielding. This reveals the dominant role that they play exhibiting that the smaller $\Delta\epsilon$, the stronger coupling (deshielded) and *vice versa*. Interestingly, similar adducts that only differentiate by the presence of two PCy₃ ligands (first-generation) or one PCy₃ and one NHC ligand (second-generation) present close values of both $\Delta\epsilon$ and $\sigma({}^{13}\text{C})$, showing that there is a minor influence of such ligands in the NMR response of the ylidene C atom.⁶⁷ In addition to this, ${}^{13}\text{C}$ magnetic shieldings can be grouped based on the nature of the alkylidene group, thus ylidene C atoms directly attached to aromatic C atoms are less shielded than those in which this is bounded to a chalcogen atom such as O or S, and these are less shielded than those directly bounded to a N atom, such as the carbazole and pyrrolidone derivatives. The energy of the empty MOs of the $\pi_{\parallel}^* \text{Ru}=\text{C} \text{ bond}$ range 1.68 eV over the 21 adducts studied, while the occupied MOs of the $\sigma \text{Ru}=\text{C} \text{ bond}$ 0.83 eV, thus a larger range of energy is spanned by the virtual ones. Finally, excluding both first- and second-generation $[\text{Ru}]=\text{CH}_2$ and **PCy₃-a** complexes, a good correlation ($R^2 = 0.78$) can be seen in Figure 10.

Figure 10. Comparison of energy gap, $\Delta\epsilon$, vs. the calculated ${}^{13}\text{C}$ magnetic shielding, $\sigma({}^{13}\text{C})$, for the MOs involved in the $\sigma \text{Ru}=\text{C} \text{ bond} \rightarrow \pi_{\parallel}^* \text{Ru}=\text{C} \text{ bond}$ transition. Points in red are excluded from the regression analysis.

Supporting these observations, EDA analysis also shed light onto the nature of the $\text{Ru}=\text{ylidene}$ bond and its relationship with $\sigma({}^{13}\text{C})$. For the considered 21 ruthenium adducts, rigidly fragmented into the $[\text{Ru}(\text{NHC})_x(\text{PCy}_3)_{2-x}]\text{Cl}_2$ ($x = 0, 1$) and the CHR moieties (including $[\text{Ru}]=\text{CH}_2$ and $[\text{Ru}]=\text{PhInd}$ complexes), it can be seen that the stronger coupling (low field), the stronger bond and *vice versa*, being $[\text{Ru}(\text{NHC})_x(\text{PCy}_3)_{2-x}]\text{Cl}_2$ ($x = 0, 1$) moieties as triplet multiplicity fragments in all cases, while for CHR ones singlet vs. triplet stability depends on the fragment. This relationship also exhibits a good correlation ($R^2 = 0.89$, excluding $[\text{Ru}]=\text{CH}_2$ and $[\text{Ru}]=\text{PhInd}$ adducts), with shielding grouped by alkylidenes and exhibiting a minor influence of the PCy₃ and NHC ligands (see Figure 11).

Figure 11. Comparison of the binding energy, ΔE_{bind} , vs. the calculated ${}^{13}\text{C}$ magnetic shielding, $\sigma({}^{13}\text{C})$, of the $[\text{Ru}]$ and $=\text{CHR}$ ylidene fragments. Points in red are excluded from the regression analysis.

Previously described by us, calculated $\text{Ru}-\text{PCy}_3$ and $\text{Ru}-\text{NHC}$ bond lengths were found as good indicators of the corresponding bond strengths. For the case of the $\text{Ru}=\text{ylidene}$ bond, it is observed that calculated $\text{Ru}=\text{C}$ distances also correlate with calculated ${}^{13}\text{C}$ magnetic shielding, observing 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 (**PCy₃-PhInd** and **IMes-PhInd**) excluded from this correlation (see Figure 12); or for those cases in which the ylidene C atom is bounded with another heteroatom (O, S, N) or for the two [Ru]=CH₂ complexes (**PCy₃-CH₂** and **IMes-CH₂**), a very good correlation is also obtained ($R^2 = 0.97$). Based on these two groups, it is seen that lower field means stronger and shorter Ru=C bonds. However, it is worth mentioning that for a given Ru=C distance, $\sigma(^{13}\text{C})$ for Ru=C–C motif is more deshielded than for the case of Ru=C–X (X = O, S, N).

Figure 12. Comparison of the calculated ^{13}C magnetic shielding, $\sigma(^{13}\text{C})$, vs. $R(\text{Ru}=\text{C})$ 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 when it is bounded with a different heteroatom (red). Points in violet are excluded from the regression analysis.

Once elucidated the basis about the connectivity between the NMR shielding of the ylidene C atom with the orbital, bonding, and structural properties of the $\text{Ry}=\text{ylidene}$ bond in the $[\text{Ru}(\text{CHR})(\text{NHC})_x(\text{PCy}_3)_{2-x}][\text{Cl}]_2$ ($x = 0, 1$) 16e species, 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 the 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 $\text{C}(\alpha)$, and the two $\text{C}'(\alpha)$ and $\text{C}'(\beta)$ from C_2H_4 .

Scheme 2. General Mechanism for the Formation of the Metallacycle Compound from the 16e Species.

Contrary to what have been recently observed by Gordon *et al.*³⁹ in some transition metal olefin metathesis catalysts, 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 in 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 it 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 bounded to $\text{C}(\alpha)$. However, surprising information can be extracted from Figure 13b, in which with exception of some complexes such as **PCy₃-CH₂**, **IMes-CH₂**, **PCy₃-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 $\sigma(^{13}\text{C})$ in the 16e species. But does this relationship mean the capacity of $\text{C}'(\beta)$ to retain the information from the pre-catalyst? Additional comparison between $\sigma(^{13}\text{C}'(\beta))$ and $\sigma(^{13}\text{C})$ in the isolated $\text{C}'(\beta)\text{H}_2=\text{C}(\alpha)\text{HR}$ alkenes demonstrates that this correlation does not come from the entering olefin, which points to validate our hypothesis.

Figure 13. (a) Comparison of calculated ^{13}C magnetic shielding for $\text{C}(\alpha)$ in metallacycle and the carbene C in the 16e species. Groups of points are clustered by colors. (b) Comparison of calculated ^{13}C magnetic shielding for $\text{C}'(\beta)$ in metallacycle and the carbene C in the 16e species. Points in red are excluded from the regression analysis.

In this sense, the very low window of $\sigma(^{13}\text{C}'(\beta))$ (*ca.* 20 ppm) as well as the big number of MOs transitions contributing to $\sigma_p(^{13}\text{C}'(\beta))$ does not allow to establish a clear correlation as did in Figure 10 between $\Delta\varepsilon$ and $\sigma(^{13}\text{C}'(\beta))$. However, it seems that

the nature of this shielding covers σ C–H bond to π^* C–H bond transitions mainly involving C(α) and C'(β) atoms with p orbitals from X at C'(β)–C(α)–X playing some role in the up or downfield shielding of σ [$^{13}\text{C}'(\beta)$].

CONCLUSIONS

In summary, using DFT calculations we have investigated the electronic nature of the Ru–PCy₃ and the Ru–NHC bonds, probing a possible mode of communication between the PCy₃ and the NHC ligands for a set of 20 [Ru(=CH₂)(NHC)-(PCy₃)]Cl₂ adducts. Phosphorous NMR shielding derived from calculations correlated well ($R^2 = 0.87$) with the calculated R(Ru–P) bond lengths. The latter was strongly correlated ($R^2 = 0.86$) with the calculated PCy₃ 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(Ru–NHC) bond lengths and NHC ligand dissociation energies.

Bond Energy Decomposition Analysis (EDA) indicated a strong correlation ($R^2 = 0.93$) between σ and π orbital interaction energies for Ru–PCy₃ bond, while a poor correlation ($R^2 = 0.23$) for Ru–NHC bond was seen. Additionally, we observed an excellent correlation ($R^2 = 0.91$) between π orbital interaction energies of the Ru–PCy₃ and the Ru–NHC bonds, suggesting that both ligands communicate through π -bonding, *i.e.*, a stronger Ru–NHC π -bond means a weaker Ru–PCy₃ π -bond and *vice versa*. Furthermore, π orbital interaction energies of PCy₃ ligand were found to be strongly correlated to ΔE_{PCy_3} ($R^2 = 0.82$), as well as to the R(Ru–P) bond lengths ($R^2 = 0.95$). These observations indeed reflect the importance of Ru to PCy₃ backdonation, which in turn regulated by the π -accepting ability of NHCs, in determining lability of PCy₃ ligand for the 20 studied ruthenium adducts.

Furthermore, for the set of 17 [Ru(=CHR)(NHC)_{*x*}(PCy₃)_{2–*x*}][Cl]₂ first- ($x = 0$) and second-generation ($x = 1$) complexes, our DFT findings hypothesize that changes occurring in the ^{13}C NMR shielding of the Ru=ylidene bond are mainly due to $\sigma(\text{Ru}=\text{C}) \rightarrow \pi^*(\text{Ru}=\text{C})$ molecular orbitals (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(Ru=C) bond lengths.

Finally, novel preliminary results showed by us also hypothesizes 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 $\sigma(^{13}\text{C})$ in the 16e species, although it surprisingly does not with the $^{13}\text{C}(\alpha)$ NMR shielding, being C(α) the former carbene C form the ylidene moiety.

CONFLICTS OF INTEREST

The authors declare no competing financial interests.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: XXX.

Extended Computational data ([PDF](#))

Cartesian coordinates ([XYZ](#))

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REFERENCES

1. Arduengo, A. J.; Harlow, R. L.; Kline, M. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.
2. (a) Díez-González, S.; Nolan, S. P. Stereoelectronic Parameters Associated with N-Heterocyclic Carbene (NHC) Ligands: A Quest for Understanding. *Coord. Chem. Rev.* **2007**, *251*, 874-883. (b) Samojłowicz, C.; Bieniek, M.; Grela, K. Ruthenium-Based Olefin Metathesis Catalysts Bearing N-Heterocyclic Carbene Ligands. *Chem. Rev.* **2009**, *109*, 3708-3742. (c) Mercks, L.; Albrecht, M. Beyond Catalysis: N-Heterocyclic Carbene Complexes as Components for Medicinal, Luminescent, and Functional Materials Applications. *Chem. Soc. Rev.* **2010**, *39*, 1903-1912. (d) Janssen-Müller, D.; Schlepphorst, C.; Glorius, F. Privileged Chiral N-Heterocyclic Carbene Ligands for Asymmetric Transition-Metal Catalysis. *Chem. Soc. Rev.* **2017**, *46*, 4845-4854. (e) Peris, E. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* **2018**, *118*, 9988-10031.
3. (a) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. Understanding the M(NHC) (NHC=N-Heterocyclic Carbene) Bond. *Coord. Chem. Rev.* **2009**, *253*, 687-703. (b) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. Erratum: Understanding the M(NHC) (NHC=N-Heterocyclic Carbene) Bond. *Coord. Chem. Rev.* **2009**, *253*, 2784-2784. (c) Rouen, M.; Queval, P.; Borré, E.; Falivene, L.; Poater, A.; Berthod, M.; Hugues, F.; Cavallo, L.; Baslé, O.; Olivier-Bourbigou, H.; Mauduit, M. Selective Metathesis of α -Olefins from Bio-Sourced Fischer–Tropsch Feeds. *ACS Catal.* **2016**, *6*, 7970-7976. (d) Gimferrer, M.; Salvador, P.; Poater, A. Computational Monitoring of Oxidation States in Olefin Metathesis. *Organometallics* **2019**, *38*, 4585-4592. (e) Poater, A.; Falivene, L.; Urbina-Blanco, C. A.; Manzini, S.; Nolan, S. P.; Cavallo, L. How Does the Addition of Steric Hindrance to a typical N-heterocyclic Carbene Ligand Affect Catalytic Activity in Olefin Metathesis? *Dalton Trans.* **2013**, *42*, 7433-7439. (f) Manzini, S.; Urbina-Blanco, C. A.; Nelson, D. J.; Poater, A.; Lebl, T.; Meiries, S.; Slawin, A. M. Z.; Falivene, L.; Cavallo, L.; Nolan, S. P. Evaluation of an Olefin Metathesis Pre-Catalyst with a Bulky and Electron-Rich N-Heterocyclic Carbene. *J. Organomet. Chem.* **2015**, *780*, 43-48.
4. (a) Marion, N.; Díez-González, S.; Nolan, S. P. N-Heterocyclic Carbenes as Organocatalysts. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988-3000. (b) Biju, A. T.; Kuhl, N.; Glorius, F. Extending

- NHC-Catalysis: Coupling Aldehydes with Unconventional Reaction Partners. *Acc. Chem. Res.* **2011**, *44*, 1182-1195.
5. (a) Hahn, F. E.; Jahnke, M. C. Heterocyclic Carbenes: Synthesis and Coordination Chemistry. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172. (b) Raubenheimer, H. G.; Cronje, S. Carbene Complexes of Gold: Preparation, Medical Application and Bonding. *Chem. Soc. Rev.* **2008**, *37*, 1998-2011. (c) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* **2009**, *109*, 3612-3676. (d) Nolan, S. P. The Development and Catalytic Uses of N-Heterocyclic Carbene Gold Complexes. *Acc. Chem. Res.* **2011**, *44*, 91-100. (e) Bellemin-Laponnaz, S.; Dagorne, S. Group 1 and 2 and Early Transition Metal Complexes Bearing N-Heterocyclic Carbene Ligands: Coordination Chemistry, Reactivity, and Applications. *Chem. Rev.* **2014**, *114*, 8747-8774. (f) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485. (g) Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; Inoue, S. NHCs in Main Group Chemistry. *Chem. Rev.* **2018**, *118*, 9678-9842. (h) Krehl, S.; Geißler, D.; Hauke, S.; Kunz, O.; Staudte, L.; Schmidt, B. The Catalytic Performance of Ru-NHC Alkylidene Complexes: PCy₃ Versus Pyridine as the Dissociating Ligand. *Beilstein J. Org. Chem.* **2010**, *6*, 1188-1198.
 6. Grubbs, R. H. Olefin-Metathesis Catalysts for the Preparation of Molecules and Materials (Nobel Lecture). *Angew. Chem. Int. Ed.* **2006**, *45*, 3760-3765.
 7. Chauvin, Y. Olefin Metathesis: The Early Days (Nobel Lecture). *Angew. Chem. Int. Ed.* **2006**, *45*, 3740-3747.
 8. Schrock, R. R. Multiple Metal–Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture). *Angew. Chem. Int. Ed.* **2006**, *45*, 3748-3759.
 9. Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. Reactions of Ruthenium Carbenes of the Type (PPh₃)₂(X)₂Ru:CH:CH:CPh₂ (X = Cl and CF₃COO) with Strained Acyclic Olefins and Functionalized Olefins. *J. Am. Chem. Soc.* **1995**, *117*, 5503-5511.
 10. (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. Olefin Metathesis-Active Ruthenium Complexes Bearing a Nucleophilic Carbene Ligand. *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678. (b) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. Synthesis and Activity of a New Generation of Ruthenium-Based Olefin Metathesis Catalysts Coordinated with 1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene Ligands. *Org. Lett.* **1999**, *1*, 953-956. (c) Weskamp, T.; Kohl, F. J.; Heringer, W.; Gleich, D.; Herrmann, W. A. Highly Active Ruthenium Catalysts for Olefin Metathesis: The Synergy of N-Heterocyclic Carbenes and Coordinatively Labile Ligands. *Angew. Chem. Int. Ed.* **1999**, *38*, 2416-2419. (d) Poater, A.; Cavallo, L. A Comprehensive Study of Olefin Metathesis Catalyzed by Ru-based Catalysts. *Beilstein J. Org. Chem.* **2015**, *11*, 1767-1780. (e) Poater, A.; Ragone, F.; Correa, A.; Cavallo, L. Comparison of Different Ruthenium–Alkylidene Bonds in the Activation Step with N-Heterocyclic Carbene Ru-Catalysts for Olefins Metathesis. *Dalton Trans.* **2011**, *40*, 11066-11069. (f) Bielawski, C. W.; Grubbs, R. H. Highly Efficient Ring-Opening Metathesis Polymerization (ROMP) Using New Ruthenium Catalysts Containing N-Heterocyclic Carbene Ligands. *Angew. Chem. Int. Ed.* **2000**, *39*, 2903-2906.
 11. Nelson, D. J.; Nolan, S. P. Quantifying and understanding the electronic properties of N-heterocyclic carbenes. *Chem. Soc. Rev.* **2013**, *42*, 6723-6753.
 12. Tolman, C. A. Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. *Chem. Rev.* **1977**, *77*, 313-348.
 13. (a) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. SambVca: A Web Application for the Calculation of the Buried Volume of N-Heterocyclic Carbene Ligands. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759-1766. (b) Clavier, H.; Nolan, S. P. Percent Buried Volume for Phosphine and N-Heterocyclic Carbene Ligands: Steric Properties in Organometallic Chemistry. *Chem. Commun.* **2010**, *46*, 841-861.
 14. Setiawan, D.; Kalescky, R.; Kraka, E.; Cremer, D. Direct Measure of Metal–Ligand Bonding Replacing the Tolman Electronic Parameter. *Inorg. Chem.* **2016**, *55*, 2332-2344.
 15. (a) Falivene, L.; Credendino, R.; Poater, A.; Petta, A.; Serra, L.; Oliva, R.; Scarano, V.; Cavallo, L. SambVca 2. A Web Tool for Analyzing Catalytic Pockets with Topographic Steric Maps. *Organometallics* **2016**, *35*, 2286-2293. (b) Falivene, L.; Cao, Z.; Petta, A.; Serra, L.; Poater, A.; Oliva, R.; Scarano, V.; Cavallo, L. Towards the Online Computer-Aided Design of Catalytic Pockets. *Nat. Chem.* **2019**, *11*, 872-879.
 16. (a) Huynh, H. V. Electronic Properties of N-Heterocyclic Carbenes and Their Experimental Determination. *Chem. Rev.* **2018**, *118*, 9457-9492. (b) Veenboer, R. M. P.; Azofra, L. M.; Gasperini, D.; Collado, A.; Cordes, D. B.; Slawin, A. M. Z.; Cavallo, L.; Nolan, S. P. Regression Analysis of Properties of [Au(IPr)(CHR₂)] Complexes. *Dalton Trans.* **2019**, *48*, 7693-7703.
 17. (a) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. Structural Diversity in Pyridine-N-Functionalized Carbene Copper(I) Complexes. *Organometallics* **2001**, *20*, 2027-2031. (b) Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. π -Acidity and π -Basicity of N-Heterocyclic Carbene Ligands. A Computational Assessment. *J. Organomet. Chem.* **2006**, *691*, 4350-4358. (c) Andrada, D. M.; Holzmann, N.; Hamadi, T.; Frenking, G. Direct Estimate of the Internal π -Donation to the Carbene Centre Within N-heterocyclic Carbenes and Related Molecules. *Beilstein J. Org. Chem.* **2015**, *11*, 2727-2736.
 18. Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. Steric and Electronic Properties of N-Heterocyclic Carbenes (NHC): A Detailed Study on Their Interaction with Ni(CO)₄. *J. Am. Chem. Soc.* **2005**, *127*, 2485-2495.
 19. (a) Nitsch, J.; Wolters, L. P.; Fonseca Guerra, C.; Bickelhaupt, F. M.; Steffen, A. Enhanced π -Back-Donation as a Way to Higher Coordination Numbers in d¹⁰ [M(NHC)_n] Complexes: A DFT Study. *Chem. Eur. J.* **2017**, *23*, 614-622. (b) Khranov, D. M.; Lynch, V. M.; Bielawski, C. W. N-Heterocyclic Carbene–Transition Metal Complexes: Spectroscopic and Crystallographic Analyses of π -Back-Bonding Interactions. *Organometallics* **2007**, *26*, 6042-6049. (c) Sanderson, M. D.; Kamplain, J. W.; Bielawski, C. W. Quinone-annulated N-Heterocyclic Carbene–Transition-Metal Complexes: Observation of π -Backbonding Using FT-IR Spectroscopy and Cyclic Voltammetry. *J. Am. Chem. Soc.* **2007**, *129*, 16514-16515.
 20. Vummaleti, S. V. C.; Nelson, D. J.; Poater, A.; Gómez-Suárez, A.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P.; Cavallo, L. What Can NMR Spectroscopy of Selenoureas and Phosphinidenes Teach Us About the π -Accepting Abilities of N-Heterocyclic Carbenes? *Chem. Sci.* **2015**, *6*, 1895-1904.
 21. Fantasia, S.; Petersen, J. L.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. Electronic Properties of N-Heterocyclic Carbene (NHC) Ligands: Synthetic, Structural, and Spectroscopic Studies of (NHC)Platinum(II) Complexes. *Organometallics* **2007**, *26*, 5880-5889.
 22. Back, O.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G. ³¹P NMR Chemical Shifts of Carbene–Phosphinidene Adducts as an Indicator of the π -Accepting Properties of Carbenes. *Angew. Chem. Int. Ed.* **2013**, *52*, 2939-2943.

23. Liske, A.; Verlinden, K.; Buhl, H.; Schaper, K.; Ganter, C. Determining the π -Acceptor Properties of N-Heterocyclic Carbenes by Measuring the ^{77}Se NMR Chemical Shifts of Their Selenium Adducts. *Organometallics* **2013**, *32*, 5269-5272.
24. Dutta, S.; Maity, B.; Thirumalai, D.; Koley, D. Computational Investigation of Carbene-Phosphinidenes: Correlation between ^{31}P Chemical Shifts and Bonding Features to Estimate the π -Backdonation of Carbenes. *Inorg. Chem.* **2018**, *57*, 3993-4008.
25. (a) Nelson, D. J.; Collado, A.; Manzini, S.; Meiries, S.; Slawin, A. M. Z.; Cordes, D. B.; Nolan, S. P. Methoxy-Functionalized N-Heterocyclic Carbenes. *Organometallics* **2014**, *33*, 2048-2058. (b) Nelson, D. J.; Nahra, F.; Patrick, S. R.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P. Exploring the Coordination of Cyclic Selenoureas to Gold(I). *Organometallics* **2014**, *33*, 3640-3645.
26. (a) Marchione, D.; Belpassi, L.; Bistoni, G.; Macchioni, A.; Tarantelli, F.; Zuccaccia, D. The Chemical Bond in Gold(I) Complexes with N-Heterocyclic Carbenes. *Organometallics* **2014**, *33*, 4200-4208. (b) Gaggioli, C. A.; Bistoni, G.; Ciancaleoni, G.; Tarantelli, F.; Belpassi, L.; Belanzoni, P. Modulating the Bonding Properties of N-Heterocyclic Carbenes (NHCs): A Systematic Charge-Displacement Analysis. *Chem. Eur. J.* **2017**, *23*, 7558-7569. (c) Gregori, L.; Sorbelli, D.; Belpassi, L.; Tarantelli, F.; Belanzoni, P. Alkyne Activation with Gold(III) Complexes: A Quantitative Assessment of the Ligand Effect by Charge-Displacement Analysis. *Inorg. Chem.* **2019**, *58*, 3115-3129.
27. Ciancaleoni, G.; Scafuri, N.; Bistoni, G.; Macchioni, A.; Tarantelli, F.; Zuccaccia, D.; Belpassi, L. When the Tolman Electronic Parameter Fails: A Comparative DFT and Charge Displacement Study of $[(\text{L})\text{Ni}(\text{CO})_3]^{0/-}$ and $[(\text{L})\text{Au}(\text{CO})]^{0/+}$. *Inorg. Chem.* **2014**, *53*, 9907-9916.
28. Azofra, L. M.; Veenboer, R. M. P.; Falivene, L.; Vummaleti, S. V. C.; Poater, A.; Nolan, S. P.; Cavallo, L. Quantifying Electronic Similarities Between NHC-Gold(I) Complexes and Their Isolobal Imidazolium Precursors. *Phys. Chem. Chem. Phys.* **2019**, *21*, 15615-15622.
29. (a) Becke, A. D. Density-functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098-3100. (b) Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. *Phys. Rev. B* **1986**, *33*, 8822-8824.
30. Van Lenthe, E.; Baerends, E. J. Optimized Slater-Type Basis Sets for the Elements 1-118. *J. Comput. Chem.* **2003**, *24*, 1142-1156.
31. (a) Becke, A. D. A multicenter numerical integration scheme for polyatomic molecules. *J. Chem. Phys.* **1988**, *88*, 2547-2553. (b) Franchini, M.; Philipsen, P. H. T.; Visscher, L. The Becke Fuzzy Cells Integration Scheme in the Amsterdam Density Functional Program Suite. *J. Comput. Chem.* **2013**, *34*, 1819-1827.
32. (a) Lenthe, E. v.; Baerends, E. J.; Snijders, J. G. Relativistic Regular Two-Component Hamiltonians. *J. Chem. Phys.* **1993**, *99*, 4597-4610. (b) Lenthe, E. v.; Baerends, E. J.; Snijders, J. G. Relativistic Total Energy Using Regular Approximations. *J. Chem. Phys.* **1994**, *101*, 9783-9792. (c) Lenthe, E. v.; Ehlers, A.; Baerends, E.-J. Geometry Optimizations in the Zero Order Regular Approximation for Relativistic Effects. *J. Chem. Phys.* **1999**, *110*, 8943-8953.
33. (a) Schreckenbach, G.; Ziegler, T. Calculation of NMR Shielding Tensors Using Gauge-Including Atomic Orbitals and Modern Density Functional Theory. *J. Phys. Chem.* **1995**, *99*, 606-611. (b) Schreckenbach, G.; Ziegler, T. The Calculation of NMR Shielding Tensors Based on Density Functional Theory and the Frozen-Core Approximation. *Int. J. Quantum Chem.* **1996**, *60*, 753-766. (c) Schreckenbach, G.; Ziegler, T. Calculation of NMR Shielding Tensors Based on Density Functional Theory and a Scalar Relativistic Pauli-type Hamiltonian. The Application to Transition Metal Complexes. *Int. J. Quantum Chem.* **1997**, *61*, 899-918.
34. Mitoraj, M. P.; Michalak, A.; Ziegler, T. A Combined Charge and Energy Decomposition Scheme for Bond Analysis. *J. Chem. Theory Comput.* **2009**, *5*, 962-975.
35. Gaggioli, C. A.; Belpassi, L.; Tarantelli, F.; Harvey, J. N.; Belanzoni, P. Spin-Forbidden Reactions: Adiabatic Transition States Using Spin-Orbit Coupled Density Functional Theory. *Chem. Eur. J.* **2018**, *24*, 5006-5015.
36. (a) Minenkov, Y.; Occhipinti, G.; Jensen, V. R. Metal-Phosphine Bond Strengths of the Transition Metals: A Challenge for DFT. *J. Phys. Chem. A* **2009**, *113*, 11833-11844. (b) Lummiss, J. A. M.; Higman, C. S.; Fyson, D. L.; McDonald, R.; Fogg, D. E. The Divergent Effects of Strong NHC Donation in Catalysis. *Chem. Sci.* **2015**, *6*, 6739-6746.
37. Minenkov, Y.; Occhipinti, G.; Heyndrickx, W.; Jensen, V. R. The Nature of the Barrier to Phosphane Dissociation from Grubbs Olefin Metathesis Catalysts. *Eur. J. Inorg. Chem.* **2012**, *2012*, 1507-1516.
38. Falivene, L.; Cavallo, L. Theoretical NMR Spectroscopy of N-Heterocyclic Carbenes and Their Metal Complexes. *Coord. Chem. Rev.* **2017**, *344*, 101-114.
39. (a) Gordon, C. P.; Culver, D. B.; Conley, M. P.; Eisenstein, O.; Andersen, R. A.; Copéret, C. π -Bond Character in Metal-Alkyl Compounds for C-H Activation: How, When, and Why? *J. Am. Chem. Soc.* **2019**, *141*, 648-656. (b) Gordon, C. P.; Yamamoto, K.; Liao, W.-C.; Allouche, F.; Andersen, R. A.; Copéret, C.; Raynaud, C.; Eisenstein, O. Metathesis Activity Encoded in the Metallocyclobutane Carbon-13 NMR Chemical Shift Tensors. *ACS Central Sci.* **2017**, *3*, 759-768.

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