

An Electronic Rationale for Observed Initiation Rates in Ruthenium-Mediated Olefin Metathesis: Charge Donation in Phosphine and N-Heterocyclic Carbene Ligands

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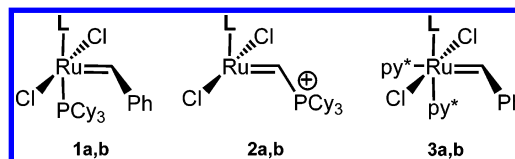
The emergence of N-heterocyclic carbenes (NHC) as an effective class of ligands in organometallic chemistry has revolutionized the field of homogeneous catalysis.¹ These ligands have been shown to modulate reactivity in a number of catalytic systems with generally positive effects on activity.² A well-known example is that of the classic Grubbs olefin metathesis catalysts of the form $\text{Cl}_2\text{L}(\text{PR}_3)\text{Ru}=\text{CHR}$ (see Chart 1). The parent bisphosphine precatalyst, that is, the first-generation Grubbs catalyst³ (**1a**, $\text{L} = \text{PCy}_3$), is generally less active than the equivalent second-generation catalyst^{4,5} (**1b**, $\text{L} = \text{H}_2\text{IMes}$) where one of the phosphine ligands has been replaced with an NHC ligand. It was originally thought that initiation (i.e., phosphine dissociation) of **1b** would be faster than in **1a** because of stronger σ -donation from the NHC ligand relative to PCy_3 .^{4,6} However, kinetic data have shown that, although **1b** is an overall more active catalyst,^{4,7} it is a poorer initiator by 2 orders of magnitude⁸ for reasons that have remained elusive. In this study, we report the first experimentally verifiable rationale for the differences in initiation rates between these two precatalysts, on the basis of unexpected electronic differences between PR_3 and NHC ligation in these and related complexes.

The ability to experimentally determine the effect of a specific ligand on a catalytic center is challenging because of the numerous factors involved. Our approach to this problem focuses on the use of element-specific X-ray spectroscopies in conjunction with electronic structure calculations to probe bonding, quantify electronic contributions to reactivity, and determine the influence of specific catalyst modifications. To address the paradox of the observed kinetic differences between **1a** and **1b**, our initial efforts have focused on determining the electronic effect of PR_3 and NHC ligation on the metal center itself. We have thus used Ru K-edge X-ray absorption spectroscopy (XAS) to probe the nature of the metal center as a function of its ligand environment in these important ruthenium-carbene species.

In the near-edge region of the Ru K-edge XAS spectrum, two important features of relevance to ligand effects on the metal center are expected. First, pre-edge features due to discrete transitions to low-lying valence states such as $\text{Ru } 4d \leftarrow 1s$ transitions are observed.¹⁰ Second, an intense edge jump feature corresponding to electric dipole allowed ionization of a Ru $1s$ electron (i.e., $\text{Ru } \infty \leftarrow 1s$) dominates the spectrum.¹¹ Importantly, the energy of this metal $1s$ ionization (IE_{1s}), which corresponds to the rising edge of the spectrum, is sensitive to the overall isotropic charge distribution at the metal center, that is, it is a good measure of the charge at the Ru center (q_{Ru}).^{11–13} Therefore, IE_{1s} is a useful probe of the overall donor properties of the ligands surrounding the metal center.^{13,14}

Figure 1 shows the Ru K-edge XAS near-edge spectra for **1a** and **1b**. The data were fit with a cumulative Gaussian/Lorentzian edge jump and a single Voigt pre-edge feature. The overall features of the spectra are quite similar, as would be expected owing to

Chart 1. Ruthenium Carbene Species Investigated in This Study Where $\text{L} = \text{PCy}_3$ (a) or $\text{L} = \text{H}_2\text{IMes}$ (b)⁹



their structural similarities near the metal center; however, a distinct difference emerges upon fitting the edge jump: IE_{1s} for **1b** is higher than that for **1a** by 0.8 eV (see Table 1). Analysis of second derivatives of the edge data (inset, Figure 1) confirms the shift to higher energy in **1b**. These data suggest that the charge on the metal ion is larger (more positive) for the NHC-bound complex than for the analogous bisphosphine complex. The observed energy difference is smaller than that which has been observed in oxidation state changes (~ 2 eV)¹⁵ but greater than the experimental error.¹⁶ This result implies, at least to a first approximation, that H_2IMes is donating less electron density to the metal than PCy_3 , which is contrary to the generally accepted behavior of these ligands.

To explore this effect more closely, we compared IE_{1s} for two related classes of metathesis-active Ru carbenes: the four-coordinate Piers phosphonium complexes¹⁷ (**2a,b**) and the six-coordinate bis-(3-bromopyridine) species¹⁸ (**3a,b**). In each case, ΔIE_{1s} is positive (see Supporting Information, S5–6; Table 1), although the magnitude of the change varies with coordination number (see Sup-

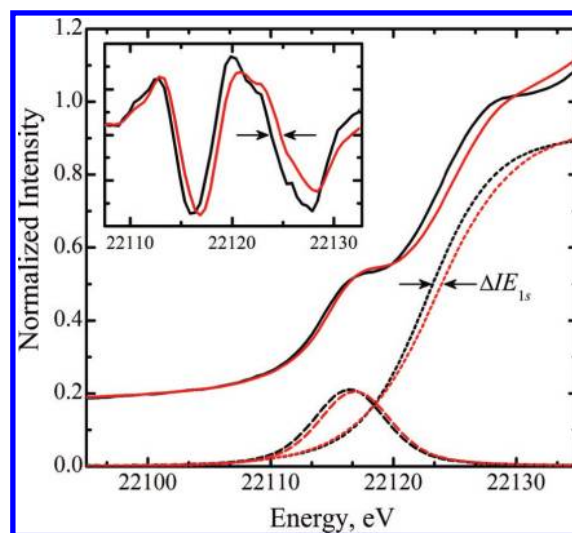


Figure 1. Near-edge Ru K-edge XAS spectra for **1a** ($\text{L} = \text{PCy}_3$, black) and **1b** ($\text{L} = \text{H}_2\text{IMes}$, red). Fits to the Ru $4d \leftarrow 1s$ pre-edge feature and the Ru $1s$ ionization edge are also shown as dashed lines with the same color-coding (raw data are offset for clarity). Inset: Second derivative plots of the data in the edge region. Arrows are used to indicate the differences in the edge jump positions (IE_{1s}) between the two complexes.

Table 1. Experimental Ionization Energies (in Electron-Volts, eV) and DFT-Calculated Ruthenium Charges (Mik = Mulliken, MDC = Multipole Derived Charges Including Quadrupole Contributions)

| | IE _{1s} | ΔIE _{1s} ^a | <i>q</i> _{Ru} ^{Mik} | Δ <i>q</i> _{Ru} ^{Mik} | <i>q</i> _{Ru} ^{MDC} | Δ <i>q</i> _{Ru} ^{MDC} |
|-----------|------------------|--------------------------------|---------------------------------------|---|---------------------------------------|---|
| 1a | 22122.7 | +0.8 | 0.36 | +0.27 | 1.35 | +0.26 |
| 1b | 22123.5 | | 0.63 | | 1.61 | |
| 2a | 22122.7 | +1.0 | 0.54 | +0.31 | 1.79 | +0.35 |
| 2b | 22123.7 | | 0.85 | | 2.14 | |
| 3a | 22122.9 | +0.4 | 0.83 | +0.24 | 1.62 | +0.21 |
| 3b | 22123.3 | | 1.07 | | 1.83 | |

^a Differences defined as $\Delta X = X^b - X^a$

porting Information, S13). We note that ΔIE_{1s} decreases with increasing coordination number, which implies that the other ligands mediate the effect through charge redistribution. The trend is maintained over an even larger series of similar complexes, with an average ΔIE_{1s} of +0.5 eV (**4a,b**–**7a,b**, see Supporting Information, S4–S10). In every case, the result is the same: the metal center is *more positively charged* with NHC ligation.

The Ru 4d←1s pre-edge features are also expected to shift to higher energy in response to changes in *q*_{Ru}.¹² This is clearly observed in **1a,b** (+0.4 eV, see Figure 1) and **2a,b** (+0.5 eV).^{10,19} Similarly, the energy of electric dipole allowed Ru 4d←2p transitions in the Ru L_{2,3}-edge XAS spectra show an analogous positive energy shift (see Supporting Information, S12).^{20,21} Both of these results are consistent with the assertion that the metal center has less electron density for the NHC-bound complexes than for the bisphosphine species, which should play an important role in defining their relative reactivities.

Density functional calculations²² have been used to evaluate whether these unexpected results are also observed theoretically and to explore the provenance of the differences in charge donation. As shown in Table 1, the charge at the Ru center is consistently more positive (Δ*q*_{Ru} > 0) in the complexes where L = H₂IMes, in accordance with the experimental data. A Mulliken population analysis of the calculated electron density distribution indicates that the electron occupancies of the Ru 4d and 5p orbitals experience the greatest changes in charge distribution between **1a** (7.06e[−], 0.47e[−]) and **1b** (6.94e[−], 0.34e[−]), confirming that these differences primarily reflect anisotropic covalent interactions with the valence Ru 4d orbitals.²³

An orbital analysis of the Kohn–Sham orbitals in **1a,b** reveals specific differences in bonding, which determine the differences in ligand donor/acceptor interactions between these complexes. In general, the effect of changing L from PCy₃ to H₂IMes results in only a minor perturbation of the overall bonding in the molecule. For instance, the overall ligand field changes very little (see Figure 2), with just a slight impact on the total bonding. This is consistent with the only minor changes observed in the entire near-edge region of the Ru K-edge spectra¹⁰ (see Supporting Information, S11) as well as a very small effect on Cl 3p donation into the Ru 4d orbitals as measured by Cl K-edge XAS.²⁰ The differences in Ru–L bonding, however, indicate that replacing a phosphine ligand with an NHC ligand alters the electron distribution at the metal center through two distinct mechanisms: σ-donation and π-backbonding.

Electron delocalization through σ-donor interactions from the ligands acts to increase electron density at a metal center. In these complexes, the composition of the two empty 4d_{σ*} orbitals reflects the nature of the σ-donor character of the ligands. A Mulliken decomposition of these orbitals indicates that the calculated charge donation from the conserved PCy₃ ligand is almost identical in both complexes. However, charge donation from L differs substantially depending on its identity: it is greater for PCy₃ in **1a** (0.36e[−]) than for the NHC ring in **1b** (0.20e[−]). The most important contributions

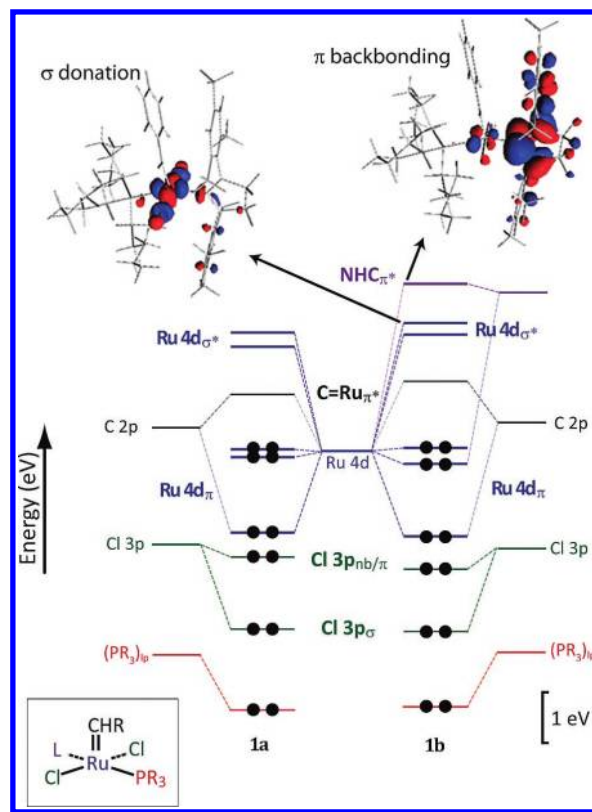


Figure 2. Simplified representation of the valence electronic structure for **1a** (left) and **1b** (right). MOs are color coded by fragment orbitals as shown in the structure at the bottom left. Only important contributors to bonding are included; filled alkylidene and NHC-based orbitals are significantly deeper in energy and not shown in this diagram. A complete listing of valence MOs are given as Supporting Information (S21–S22). Relevant MOs for **1b** discussed in the text are also shown: the dominant Ru–NHC σ-donor interaction is seen in the highest-lying Ru 4d_{σ*} orbital (213A, 0.03e[−]/Å³) whereas π-backbonding to the NHC ligand is seen in MO 219A (0.05e[−]/Å³).

to σ-donation are illustrated in the molecular orbital (MO) diagrams shown in Figure 2. Contrary to σ-donation, π-backbonding will act to remove electron density from the metal center; therefore, it is expected that increasing π-acceptor character will decrease electron density at the metal center. The orbital analysis indicates negligible π-contributions to Ru–PCy₃ bonding in both **1a** and **1b**.²⁴ By contrast, a noticeable π interaction is observed between the metal center and the H₂IMes ligand in **1b** (see Figure 2). The interaction represented by the Ru–NHC π* orbital accounts for a 0.1e[−] shift in electron density from the Ru center to the ligand. This simple orbital analysis, which focuses solely on the major contributions to differences in charge delocalization, accounts for essentially all of the calculated Δ*q*_{Ru} (see Table 1): 0.16e[−] through a decrease in σ-donation and an additional 0.1e[−] due to π-backbonding.

The nature of the ligand properties of phosphine and NHC ligands and their differences have been explored experimentally by others,^{25,26} although these have generally focused on σ-donation as the predominant contributor to bonding. The potential for π-acceptor character of NHC ligands has recently received more scrutiny.²⁷ Theoretical studies have explored these issues as well as electrostatic stabilization and their respective contributions to metal–ligand bonding.^{28–31} A major conclusion of recent theoretical work is that the strength of M–PR₃ and M–NHC bonds are dominated by electrostatic as opposed to covalent contributions. Furthermore, these studies indicate that the covalent contributions to bond energies are generally larger for phosphine ligands³⁰ (35–44%) than for NHC ligands³¹ (22–32%). Although it is difficult to compare

such findings directly with charge delocalization, these results suggest that stronger M–L bonding when L = NHC does not necessarily imply greater charge donation from that ligand. Given these results and our experimental and computational findings, it seems most reasonable to suggest that NHC ligands are poorer charge donors than phosphine ligands even though they form stronger bonds.²⁶

The fact that there is greater charge delocalization in the first-generation precatalyst and that NHC ligation results in a more electron-deficient metal center, should have important implications regarding the relative reactivity of **1a** and **1b**. We propose that our results provide a compelling rationale for the experimentally observed initiation rates in these precatalysts: the rate of phosphine dissociation is slower in **1b** due to the increased electron-deficiency of the metal center relative to **1a**. Interestingly, similar relative rates of dissociation between phosphine and NHC ligands have recently been observed in Rh(I) complexes.³² We are currently exploring whether this conclusion may be extended to other systems of importance in olefin metathesis and beyond.

The details of charge delocalization in these systems are still a major consideration, especially since the nature of the π -interactions should be highly dependent on the metal center.²⁹ It seems particularly important to provide experimental measures of bonding contributions as a way of complementing and validating theoretical investigations in these areas. For this reason, and especially given the predominance of these ligands in homogeneous catalysis, our ongoing efforts focus on spectroscopic characterization of the specific nature of covalent contributions to bonding in phosphines and N-heterocyclic carbenes.

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Supporting Information Available: Experimental details (S1–S3), Ru K-edge XAS spectra and fit parameters (S4–S11), Ru L_{2,3}-edge XAS spectra (S12), plot of Δq vs ΔE_{1s} (S13), computational details including input files (S14–S20), breakdown of valence Kohn–Sham orbitals (S21–S22), and supplementary references (S23). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (22) ADF 2005.01 calculations were performed using a TZP basis set with the VWN-BP86 functional. Details are given as Supporting Information.
- (23) Differences in the Ru 5s occupancy (+0.04) account for the remainder of the overall charge differential on the metal centre.
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