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Theoretical Analysis of Bonding in N-Heterocyclic Carbene−Rhodium Complexes

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The natural orbitals for chemical valence and the Ziegler−Rauk bond energy decomposition analysis were used to describe the donor/acceptor character of the N-heterocyclic carbenes (NHC)−metal bond in two groups of square-planar rhodium(I) complexes: (NHC)RhCl(cod) (**1-X**; cod = 1,5-cyclooctadiene) and (NHC)RhCl$(CO)_2$ (**2-X**), with a group X = H, Cl, NO_2, or CN located on the NHC ligand. The results show that the NHC−metal bond consists of the components originating from donation (σ symmetry) and back-donation (two contributions of the π symmetry, out-of-plane and in-plane, accompanied by one σ-back-bonding component). The charge-flow measures from NOCV indicate that the total back-bonding contribution is of comparable importance to donation. The out-of-plane π component contributes to ca. 50% of the total back-bonding charge-flow. The energy measures from the Ziegler−Rauk analysis show that the total back-bonding energy corresponds to ca. 40% of the orbital interaction energy. The ligand trans to NHC (CO or cod) strongly affects the back-bonding component; for the complexes **1-X**, the back-donation is substantially enhanced compared to **2-X**. The back-bonding component increases with an increase in the π-withdrawing ability of X for both, **1-X** and **2-X**. However, this effect is relatively small. Back-bonding components of the two bonds involving the metal are strongly coupled; an increase in NHC−Rh leads to a decrease in Rh−olefin/CO(trans). The changes in the back-bonding are too small to be followed by the trends in bond energies, which are finally determined by the electrostatic and Pauli repulsion energy.

Introduction

Since the discovery in the 1960s[1−3] and first isolation of stable N-heterocyclic carbenes (NHC) in the early 1990s,[4] these ligands have been extensively investigated,[5−13] mainly due to their ability to enhance the catalytic activity of transition metals upon complexation. Numerous examples of the NHC-based transition-metal complexes can act as catalysts[7−12] for a great variety of organic reactions such as Heck and Suzuki couplings, polymerizations, transfer hydrogenations, hydroformylations, and arylation reactions.

Despite their significance in organometallic catalysis and a great number of research on the NHC-based transition-metal complexes, there still exist controversies concerning bonding in these systems,[13] especially in the context of the donor/acceptor properties of the NHC ligands and, in particular, importance of π-back-bonding.[14−29] These ligands are

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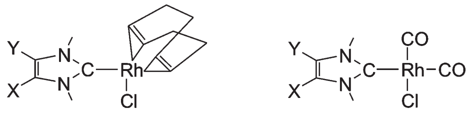
usually considered to be strong σ donors with negligible acceptor ability. Recently, on the basis of crystallographic and spectroscopic (^{1}H NMR and IR) analysis of various NHC−rhodium(I) complexes, it has been demonstrated that the acceptor properties of NHC ligands are "not only non-negligible, but tunable" in context of the π-acidity change of the substituents on the N-heterocyclic carbenes.[28]

The main goal of the present theoretical study, inspired by the aforementioned experimental account published by Bielawski et al.,[28] is a description of the bond formed between the N-heterocyclic carbene and the transition metal in the NHC−Rh(I) complexes, with a particular emphasis on back-bonding. Thus, the donor/acceptor properties of substituted imidazol-2-ylidene ligands for two groups of Rh(I) chloride complexes **1-X** and **2-X** (Scheme 1) will be characterized; a coupling between NHC and the ligand in the trans position (an olefin or CO) will also be investigated.

During the past few decades, many theoretical methods have been used[30−49] to address the "classical" Dewar−Chatt−Duncanson model[50,51] of donation/back-bonding in transition-metal systems. A list of the most popular methods and techniques includes charge decomposition analysis,[31−34] constrained space orbital variation (CSOV),[35,36] interaction-energy partitioning schemes,[37−39] and natural bond orbitals.[40] One of the most recently proposed[41−45] approaches is based on analysis of the natural orbitals for chemical valence (NOCV). A main advantage of NOCV is that they allow for a direct separation of the contributions to the deformation density (differential density) from the ligand → metal and the metal → ligand electron transfer processes. NOCV have been successfully applied in an assessment of the donor−acceptor properties of typical ligands in transition-metal complexes.

Scheme 1. Complexes Studied in the Present Work



X, Y = H, Cl, CN, NO$_2$
X = NO$_2$, Y = H

1-X **2-X**

It has been shown that NOCV measures of donation/back-bonding are in qualitative agreement with other theoretical methods.[41] NOCV have also been used in a description of bonding in conjugated molecules.[44] In the present work, this set of natural orbitals will be employed together with the Ziegler−Rauk energy decomposition analysis.[38,39]

Computational Details and the Model Systems

The optimized structures of the transition-metal complexes containing N-heterocyclic carbenes studied in the present work are shown in Figure 1. Following the experimental work,[28] we have considered two groups of square-planar rhodium(I) chloride complexes: (NHC)RhCl(cod) (**1-X**; Figure 1a) and (NHC)RhCl(CO)$_2$ (**2-X**, Figure 1b), where cod = 1,5-cyclooctadiene and NHC = 1,3-dimethyl-imidazol-2-ylidenes substituted with functional groups of varying electron-withdrawing character (4,5-dihydro, 4,5-dichloro, 4-nitro, 4,5-dinitro, and 4,5-dicyano; X = H, Cl, NO$_2$, CN). We would like to emphasize at this point that the monosubstituted NHC ligand was considered in the case of X = NO$_2$ in the experimental account by Bielawski et al.[28] Nevertheless, it would be consistent to use the bis-substituted system (X, Y = NO$_2$) for this ligand as well, in order to facilitate a discussion on the influence of different substituents, X. Therefore, in the present work, we have investigated both monosubstituted (with X = NO$_2$, Y = H) and bis-substituted systems (with X, Y = NO$_2$). However, to avoid confusion, we use the labeling scheme from ref 28, with **1-NO$_2$** corresponding to the monosubstituted complex. Its bis-substituted analogue, not studied experimentally, will be labeled here as **1-NO$_2$′**.

All of the results were obtained from the DFT calculations based on the Becke−Perdew exchange-correlation functional,[52−54] using the Amsterdam Density Functional (ADF) program.[55−59] A standard double-ζ STO basis with one set of polarization functions was used for main-group elements (H, C, N, O, Cl), while a standard triple-ζ STO basis set was employed for a transition metal (Rh). The 1s electrons of C, N, and O, as well as the 1s−2p electrons of Cl and 1s−3d electrons of Rh were treated as a frozen core. Auxiliary s, p, d, f, and g STO functions, centered on all nuclei, were used to fit the electron density and obtain an accurate Coulomb potential in each SCF cycle. Relativistic effects were considered using the first-order scalar relativistic correction.[60−62] The ADF program (version 2004.01) was used in the

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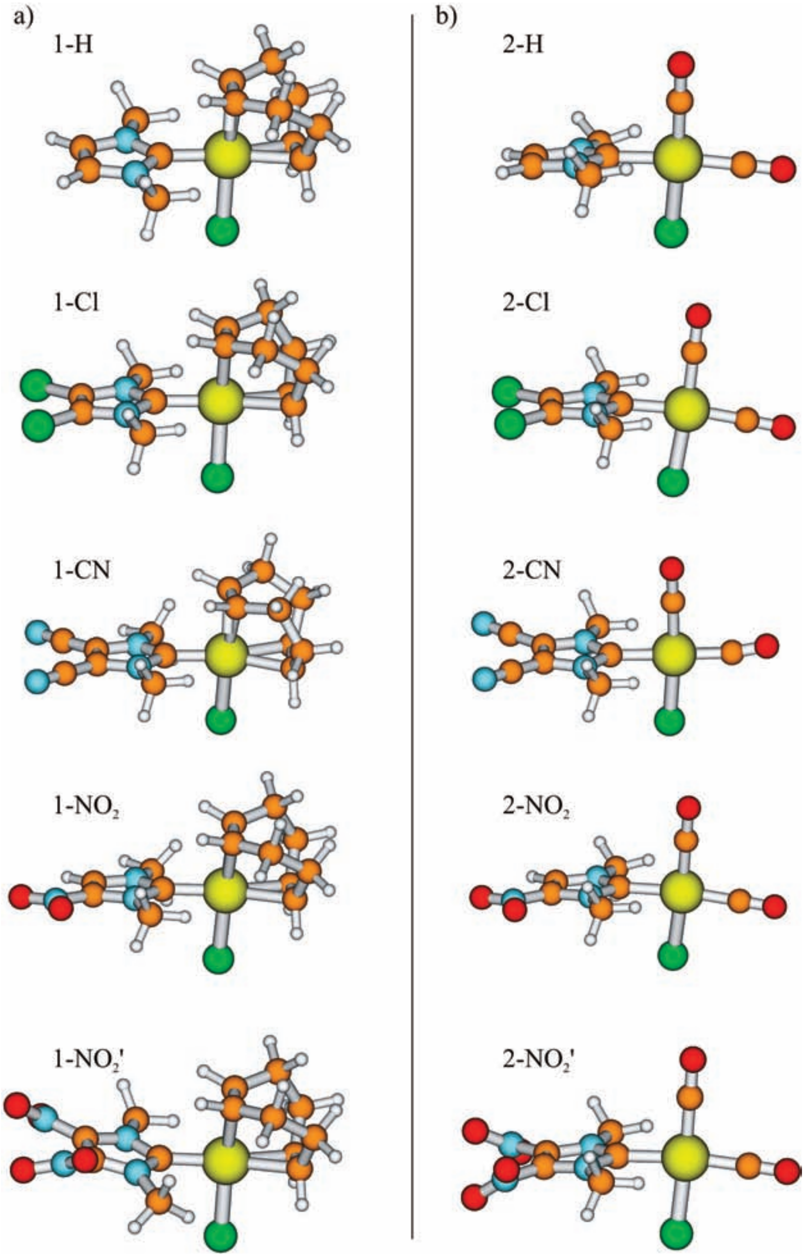

Figure 1. Optimized geometries of the molecular systems investigated in the present work **1-X** (panel a) and **2-X** (panel b).

geometry optimization and in the analysis of the electronic structure, while the NMR program[63] implemented in the ADF 2006.01 package was used in the calculations of NMR chemical shifts.

The bonding in **1-X** and **2-X** was described using the analysis of NOCV[41−45] and the Ziegler−Rauk bond-energy decomposition scheme.[38,39] The former approach provides contributions to the deformation density (differential density), $\Delta\rho$, due to the ligand → metal donation and the metal → ligand back-bonding, while the latter allows for a separation of the electrostatic, Pauli repulsion and the orbital interaction terms in the bond energy.

NOCV have been defined[41] as the eigenvectors of the chemical valence operator

$$\hat{V}\varphi_i = v_i\varphi_i \quad i = 1, ..., n \tag{1}$$

with the valence operator of the Nalewajski−Mrozek theory of valence and bond-order indices given in matrix form as[64]

$$\mathbf{V} = \frac{1}{2}\Delta\mathbf{P} \tag{2}$$

where $\Delta\mathbf{P} = \mathbf{P} - \mathbf{P}^0$ corresponds to the difference between the density matrices (*charge-and-bond-order* matrices) of a molecule, **P**, and promolecule, $\mathbf{P}^0$. As a reference state, one can use the *atomic* promolecule, that is, the set of noninteracting atoms placed in the same positions as in the molecule. In such a case, formation of the molecule from atoms is described. Alternatively, the *fragment-based* promolecule can be used, allowing for a description of bonding between the larger molecular fragments.

In the present work, NOCV have been determined in a *two-fragment resolution,* considering the bond between one ligand and the fragment containing the transition metal and the

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remaining ligands. NOCV have been evaluated for two partitionings: (L_1)—RhCl(L_2) and (L_1)RhCl—(L_2), where L_1 = (NHC ligand) and L_2 = cod, CO (trans to L_1). The former partitioning is used to characterize the bond between the NHC ligand and RhCl(cod)/RhCl(CO)$_2$. The latter allows for a description of the bond between (NHC)RhCl and the olefin ligand (in **1-X**) or between (NHC)RhCl(CO) and the carbonyl trans to NHC (in **2-X**).

One of the features of NOCV is that they can be grouped in pairs of complementary orbitals characterized by eigenvalues of opposite sign and the same absolute value

$$\hat{V}\varphi_{-k} = -v_k\varphi_{-k}, \hat{V}\varphi_k = v_k\varphi_k, k = 1, ..., n/2 \qquad (3)$$

Using eq 3, the deformation density (differential density), $\Delta\rho = \rho(\text{complex}) - \rho(\text{fragments})$, can be written in terms of the NOCV pairs as

$$\Delta\rho(r) = \sum_{k=1}^{n/2} v_k[-\varphi^2_{-k}(r) + \varphi^2_k(r)] \equiv \sum_{k=1}^{n/2} \Delta\rho_k(r) \qquad (4)$$

In eq 4 an eigenvalue ν_k corresponds to the fraction of electron density that is transferred from the φ_{-k} orbital to the φ_k orbital, when the molecule is formed from the fragments. Thus, a complementary pair of NOCV defines a channel for electron charge transfer between the molecular fragments. The total charge transferred in this channel is

$$\Delta q_k = v_k \qquad (5)$$

It should be pointed out that only a few pairs of the orbitals contribute to the bonding; a large majority of eigenvalues ν_k are practically equal to zero. Thus, there exist only a few nonvanishing $\Delta\rho_k$ components.

It has been found for other transition-metal complexes that, among the $\Delta\rho_k$ contributions, it is often possible to recognize components with negative sign on one fragment (i.e., an outflow of charge density from it) and the positive on the other fragment (i.e., an accumulation of charge density). Thus, in such a case, NOCV led to a separation of the charge-transfer channels corresponding to donation/back-donation, and the respective eigenvalue, ν_k, provides a quantitative measure of the donor/acceptor ability of the two fragments in the complex. It has been shown[41] that NOCV eigenvalues are in qualitative agreement with other measures of the donation/back-donation processes. It should be pointed out, however, that in general one should not rely solely on the eigenvalues; an inspection of the NOCV shapes, and especially their $\Delta\rho$ contributions, is always necessary to make sure that the donation/back-donation channels are separated, that is, which orbitals correspond to donation and which to back-bonding and so forth.

In the Ziegler−Rauk bond-energy decomposition analysis,[38,39] the overall bonding energy is decomposed as

$$\begin{aligned}\Delta E_\text{b} &= \Delta E_\text{geom} + \Delta E_\text{tot} \\ &= \Delta E_\text{geom} + [E_\text{el} + \Delta E_\text{Pauli} + \Delta E_\text{orb}] \qquad (6)\end{aligned}$$

where ΔE_geom is a geometry distortion term, comprising the contributions from both considered fragments, and ΔE_tot is the total interaction energy of distorted fragments. The latter can be further decomposed into the orbital interaction term, ΔE_orb; the electrostatic interaction, ΔE_el; and the Pauli repulsion, $\Delta E_\text{Pauli.}$

Results and Discussion

We will start the discussion with a description of the bond between the NHC ligand and the rhodium-containing fragment in **1-X** and **2-X**. In order to quantitatively characterize the contributions originating from the ligand → metal donation and metal → ligand back-donation using the NOCV eigenvalues, it is first required to identify a character of each pair of natural orbitals, k, on the basis of the contours of the corresponding deformation density contributions, $\Delta\rho_k$ (eq 4). For all of the systems studied in the present work, there exist four pairs of NOCV with non-negligible contribution to the NHC−Rh bond ($|\nu_k| > 0.1$). Figure 2 presents examples of $\Delta\rho_k$ contours determined from those pairs for the **1-NO$_2$** (panel a) and **2-NO$_2$** (panel b) complexes.

Figure 2 clearly demonstrates that one pair of NOCV describes a transfer of electron density from NHC to rhodium (σ donation). The other NOCV pairs describe a density transfer in the opposite direction, that is, from rhodium to the NHC ligand (back-bonding); two of them correspond to π back-donation and one to σ back-donation.

Using the NOCV eigenvalues as a measure of the corresponding charge-flows, we can characterize the donor/acceptor properties of N-heterocyclic carbenes. For clarity, we will

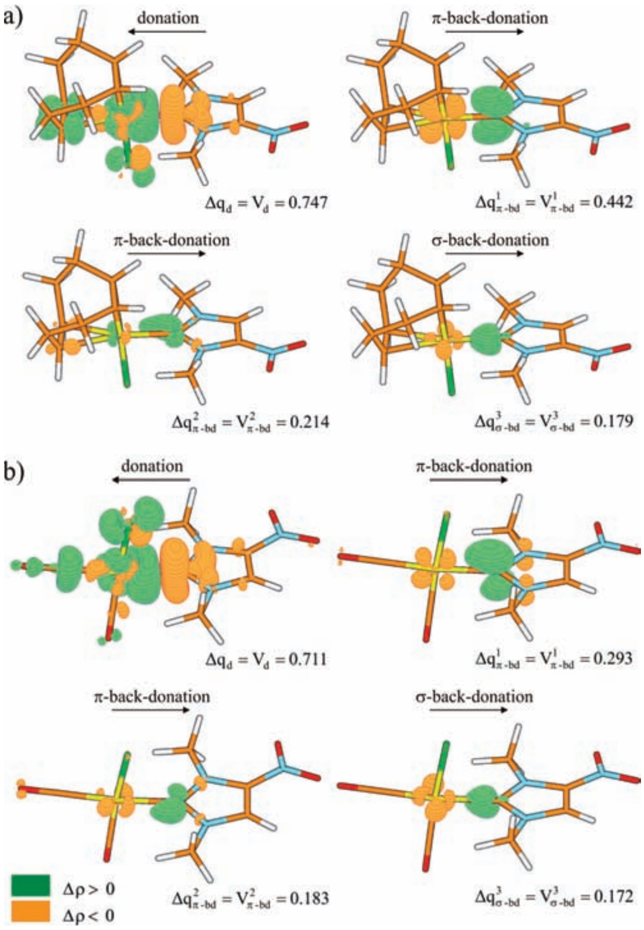

Figure 2. The NOCV contributions to the deformation density $\Delta\rho$ describing the bond between the NHC ligand and rhodium-containing fragment for **1-NO$_2$** (panel a) and **2-NO$_2$** (panel b). The contour value is $\Delta\rho(r) = 0.003$ au.

Table 1. The NOCV Eigenvalues Characterizing NHC Ligand → Metal Donation, Δq_{d}, and the Metal → Ligand Back-Bonding, $\Delta q^1_{\pi\text{-bd}}$, $\Delta q^2_{\pi\text{-bd}}$, $\Delta q^3_{\sigma\text{-bd}}$ (see Figure 2)

complex[a]	Δq_{d}	$\Delta q^1_{\pi\text{-bd}}$	$\Delta q^2_{\pi\text{-bd}}$	$\Delta q^3_{\sigma\text{-bd}}$
1-H	0.750	0.351	0.194	0.190
1-Cl	0.742	0.365	0.211	0.201
1-NO$_2$	0.747	0.442	0.214	0.179
1-CN	0.732	0.424	0.232	0.200
1-NO$_2$′	0.726	0.465	0.231	0.302
2-H	0.721	0.266	0.173	0.163
2-Cl	0.719	0.267	0.180	0.178
2-NO$_2$	0.711	0.293	0.183	0.172
2-CN	0.702	0.279	0.194	0.186
2-NO$_2$′	0.703	0.300	0.192	0.187

[a] See Scheme 1 and Figure 1.

use the following convention for NOCV-pair labeling: the symmetry and the direction of charge-transfer will be marked in the subscript, using "d", "π-bd", and "σ-bd" for the NOCV pairs contributing to donation, π back-donation, and σ back-donation, respectively. Further, the numbers in the superscript will be used for the NOCV pairs of the same symmetry/charge-transfer direction if more than one exist. Thus, the four contributions in each panel of Figure 2 are characterized by the eigenvalues labeled by V_{d}, $V^1_{\pi\text{-bd}}$, $V^2_{\pi\text{-bd}}$, and $V^3_{\sigma\text{-bd}}$.

Let us first discuss the NOCV eigenvalues for **1-NO$_2$**. For this complex, the charge-transfer due to the ligand → metal donation is described by $\Delta q_{\mathrm{d}} = V_{\mathrm{d}} = 0.75$. The two components corresponding to π back-bonding are characterized by $\Delta q^1_{\pi\text{-bd}} = V^1_{\pi\text{-bd}} = 0.44$ and $\Delta q^2_{\pi\text{-bd}} = V^2_{\pi\text{-bd}} = 0.21$. The eigenvalue for the last contribution, describing the charge-transfer due to σ back-bonding, is $\Delta q^3_{\sigma\text{-bd}} = V^3_{\sigma\text{-bd}} = 0.18$. Thus, it is clearly seen that the σ-donation component is visibly larger than each of the back-donation contributions. However, none of them is negligible. Consequently, the total acceptor ability of the NHC ligand in **1-NO$_2$**, measured by the sum of all eigenvalues, $\Delta q_{\mathrm{bd}} = \Delta q^1_{\pi\text{-bd}} + \Delta q^2_{\pi\text{-bd}} + \Delta q^3_{\sigma\text{-bd}} = V^1_{\pi\text{-bd}} + V^2_{\pi\text{-bd}} + V^3_{\sigma\text{-bd}} = 0.84$, not only is non-negligible but appears to be even larger than its donor capability, $\Delta q_{\mathrm{d}} = V_{\mathrm{d}} = 0.75$. However, it is important to emphasize that there is no simple relationship between the amount of the donation/back-bonding charge-transfer values and the corresponding bond-energy components. It will be shown later in this article, on the basis of the Ziegler–Rauk bond-energy analysis, that the total back-bonding contribution corresponds to ca. 40% of the orbital interaction energy.

All of the contributions participating in the NHC–Rh bond in **2-NO$_2$** are decreased compared to **1-NO$_2$**, with the largest effect for $\Delta q^1_{\pi\text{-bd}} = V^1_{\pi\text{-bd}}$ (changed by 0.15). As a result, the relative importance of the total acceptor ability is visibly lowered, $\Delta q_{\mathrm{bd}} = \Delta q^1_{\pi\text{-bd}} + \Delta q^2_{\pi\text{-bd}} + \Delta q^3_{\sigma\text{-bd}} = V^1_{\pi\text{-bd}} + V^2_{\pi\text{-bd}} + V^3_{\sigma\text{-bd}} = 0.65$ (compared to $\Delta q_{\mathrm{d}} = V_{\mathrm{d}} = 0.71$).

For the other complexes investigated in the present study, the $\Delta\rho$ contributions look qualitatively similar: in each case, there exist a pair of NOCV corresponding to the NHC ligand → rhodium σ donation and three pairs of NOCV describing rhodium → NHC ligand back-donation. Therefore, we will not show those contours. The corresponding eigenvalues for all of the systems are listed in Table 1.

Two main effects emerge from the data of Table 1: (i) a relatively small variation in the corresponding eigenvalues for different X's, for both **1-X** and **2-X**, (ii) a visible decrease in all of the eigenvalues describing bonding in **2-X** compared to that in **1-X**. Indeed, for the **1-X** systems considered, values of the donor/acceptor abilities of the NHC ligands range from 0.73 to 0.75 for Δq_d, 0.35 to 0.47 for $\Delta q^1_{\pi\text{-bd}}$, 0.19 to 0.23 for $\Delta q^2_{\pi\text{-bd}}$, and 0.18 to 0.30 for $\Delta q^3_{\sigma\text{-bd}}$, while for the **2-X** systems, the corresponding values are lower (Δq_{d}, 0.70– 0.72; $\Delta q^1_{\pi\text{-bd}}$, 0.27–0.30; $\Delta q^2_{\pi\text{-bd}}$, 0.17–0.19; $\Delta q^3_{\sigma\text{-bd}}$, 0.16–0.19). Again, the largest decrease is observed in $\Delta q^1_{\pi\text{-bd}}$ for all X groups.

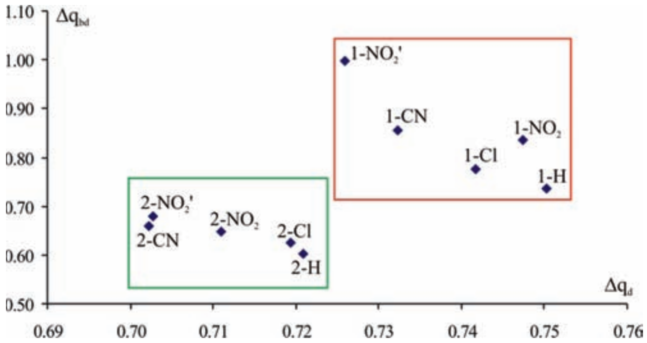

Figure 3. Two-dimensional map of the donor–acceptor properties measured by Δq_{d} and Δq_{bd} in the complexes **1-X** and **2-X**, containing different NHC ligands, X.

In order to facilitate a comparison of the donor/acceptor abilities for different X substituents in both groups of compounds, **1-X** and **2-X**, in Figure 3, the values of Δq_{d}, and $\Delta q_{\mathrm{bd}} = \Delta q^1_{\pi\text{-bd}} + \Delta q^2_{\pi\text{-bd}} + \Delta q^3_{\sigma\text{-bd}}$ are presented in the form of a two-dimensional map. It can be seen from the figure that both considered groups of complexes, **1-X** and **2-X**, occupy distinct parts of the map. Thus, substituted N-heterocyclic carbenes bound to the rhodium chloride complexes containing two carbon monoxide ligands demonstrate lower values of both Δq_{d} and Δq_{bd} in comparison to the corresponding systems with the olefin ligand. However, a more significant increase is demonstrated by Δq_{bd} values (from 0.60–0.68 to 0.74–1.00 for **2-X** and **1-X**, respectively), while the change of Δq_{d} is quite modest (from 0.70–0.72 to 0.73–0.75). Hence, the overall acceptor character of the NHC ligands measured by NOCV eigenvalues in **1-X** complexes is stronger than their donor character, except for X = H, for which they are practically equal.

Let us now discuss the donor/acceptor properties of the NHC ligands with different X's. The results presented in Table 1 show that a variation in X has a minor influence on the donor ability of the NHC ligand. Namely, for **1-X**, a charge transfer measured by the Δq_{d} value varies between 0.73 (for **1-NO$_2$′**) and 0.75 (for **1-H**). Similarly, for **2-X**, the value of Δq_{d} changes between 0.70 (for **2-NO$_2$′** and **2-CN**) and 0.72 (for **2-H**).

As far as an influence of X on the overall back-donation ability is concerned, a variation in the Δq_{bd} value is larger than in Δq_{d}. Namely, an increase in the Δq_{bd} values can be noticed in the following sequence: H < Cl < NO$_2$ (mono) < CN < NO$_2$ (bis); for **1-X** and **2-X**, the corresponding values are 0.74 < 0.78 < 0.84 < 0.86 < 1.00 and 0.60 < 0.63 < 0.65 < 0.66 < 0.68, respectively. Here "NO$_2$ (mono)" corresponds to **1-NO$_2$** and **2-NO$_2$**, while "NO$_2$ (bis)" corresponds to **1-NO$_2$′** and **2-NO$_2$′**. Thus, the increase in the Δq_{bd} values that characterize the ligand acceptor properties is correlated with an increase in the

π-withdrawing character of the substituents X on the imidazole ring.

In summary, the results of the NOCV analysis show that back-donation is an important part of the interaction between the NHC ligand and the metal. In order to visualize the effect of the ligand structure, in Figure 4, the values of Δq_{bd} are displayed for all of the systems studied in the present work. It can be concluded that back-bonding can be influenced to some extent by both the substituent X and, primarily, by modification of the ligands attached to the metal. Thus, our theoretical predictions based on *direct* measures of donation/back-donation qualitatively confirm the experimental conclusions[28] drawn from the *indirect*, spectroscopic (IR, NMR), and structural indicators of back-bonding.

Here, it is especially worth emphasizing that not only do direct experimental measures of back-bonding not exist but, furthermore, the conclusions about the NHC−metal bonding are in a large part based on the characteristics of other bonds/ligands in the system, such as IR stretching frequencies of −CO and −CN, ^{1}H NMR chemical shifts of the olefin protons, or selected bond lengths. Therefore, it is desired to perform, in addition, a theoretical analysis of the "coupled" bond, that is, the bond between the metal and the ligand in the trans position to NHC, Rh−cod and Rh−CO(trans) in **1-X** and **2-X**, respectively.

Let us first discuss the metal → olefin back-donation in **1-X** complexes. Figure 5a shows the only NOCV contribution to $\Delta\rho$ that describes π back-bonding to the C=C bond trans to the NHC ligand. Here, the **1-NO$_2$** complex is used as an example; for the other systems, such a contribution is qualitatively similar. It is worth emphasizing that the changes in the back-bonding part of $\Delta\rho$ are localized in the vicinity of the bond between the metal and one of the C=C bonds (trans to NHC) without participation of the other C=C bond of cyclooctadiene.

The corresponding NOCV eigenvalues providing a quantitative measure of the considered back-donation process are collected in Table 2. These numbers are summarized together with the calculated and experimental[28] values of ^{1}H NMR chemical shifts of the protons on the olefin trans to the N-heterocyclic carbene ligand, which have been used by Bielawski et al.[28] as indirect measure of back-bonding.

As it can be seen from the data presented in Table 2, the agreement of the calculated chemical shifts with experimental data is very good. Although all theoretical values are systematically overestimated by ca. 0.06 ppm, the changes in the chemical shifts for different complexes are almost perfectly reproduced. It has been conjectured from experimental data[28] that an increase in the chemical shifts of the olefin protons corresponds to a decrease in the metal → olefin back-bonding and, thus, to an increase in the metal → NHC ligand back-bonding. Further, it has been shown that the direction of these changes corresponds to the change in the π-withdrawing character of the substituent on NHC. This is indeed reflected by the calculated $\Delta q_{\pi\text{-bd}}$, decreasing in the sequence H > Cl > NO$_2$ (mono) > CN > NO$_2$ (bis) from 0.62 to 0.58. However, it should be pointed out that the changes in chemical shifts as well as the changes in the NOCV eigenvalues are rather subtle.

Similar conclusions can be drawn for the Rh−CO bond trans to the NHC ligand in **2-X**. The example contours of the NOCV contributions to $\Delta\rho$ describing back-bonding in **2-NO$_2$** are shown in Figure 5b. In the case of carbonyl complexes, **2-X**, there are three back-donation components: two major contributions describe π back-bonding, and the last one, of minor importance, has σ symmetry. Similarly to Figure 5a, the changes in the back-bonding part of $\Delta\rho$ are localized in the vicinity of the bond between the metal and

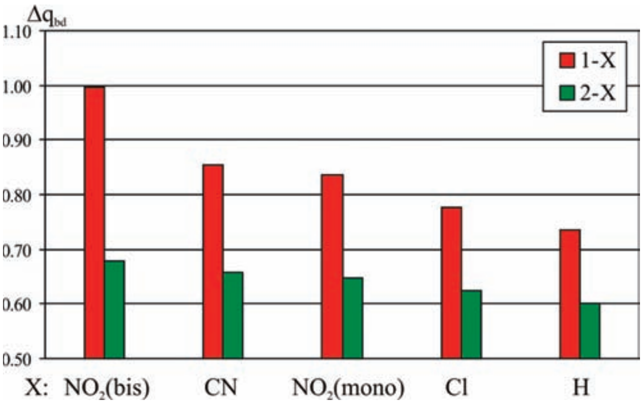

Figure 4. Comparison of the back-bonding components in the complexes **1-X** and **2-X**, containing different NHC ligands, X.

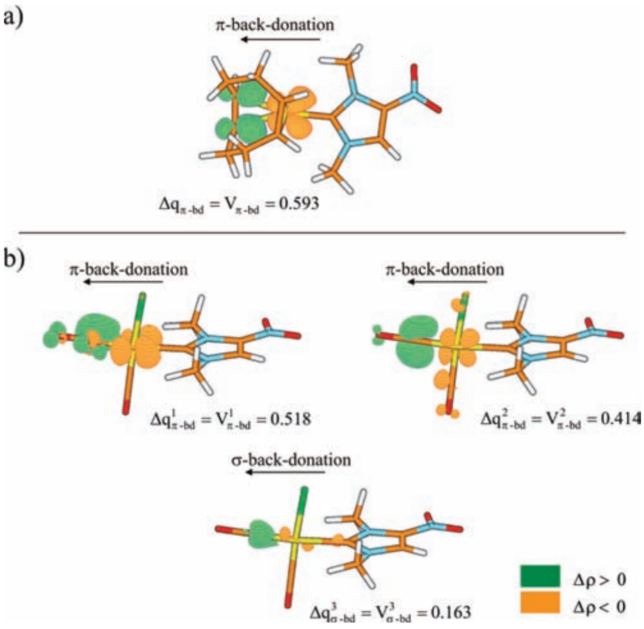

Figure 5. The NOCV back-donation contributions to the deformation density $\Delta\rho$ describing the bond between the metal and cod in **1-NO$_2$** (panel a) or metal and the CO ligand (trans to NHC) in **2-NO$_2$** (panel b). The contour value is $\Delta\rho(r) = 0.003$ au.

Table 2. The Back-Donation Measures for the Metal−Olefin Bond in the **1-X** Systems Obtained from ^{1}H NMR Spectroscopy and NOCV Analysis

	δ (=CH)[b]		
complex [a]	exptl[c]	calcd	$\Delta q_{\pi\text{-bd}}$[d]
1-H	5.00	5.06	0.616
1-Cl	5.03	5.09	0.610
1-NO$_2$	5.12	5.18	0.593
1-CN	5.17	5.22	0.592
1-NO$_2$′		5.32	0.583

[a] See Scheme 1 and Figure 1. [b] ^{1}H NMR chemical shift of the olefin protons, in ppm. [c] Experimental values from ref 28. [d] NOCV eigenvalue corresponding to the metal → olefin π-back-bonding (see Figure 5a).

one of the CO ligands (trans to NHC) practically without participation of the other carbonyl.

The NOCV eigenvalues for all of the **2-X** complexes are listed in Table 3, together with the experimental[28] CO stretching frequencies, providing an indirect estimation of the back-donation effects. In this case, it has been suggested[28] that an increase in ν_{CO} correlates with a decrease in the metal → CO back-donation and, thus, an increase in the metal → NHC back-donation due to an increase in the π-withdrawing ability of the substituents on NHC ligands. Table 3 shows that, among two contributions of the π symmetry, $\Delta q^2_{\pi\text{-bd}}$ are almost constant for **2-H**, **2-Cl**, **2-NO₂**, and **2-NO₂′**; thus, the changes in $\Delta q^1_{\pi\text{-bd}}$ are responsible for the experimental trend in ν_{CO}. The only exception, the **2-CN** complex, demonstrates the best back-donation ability (increase in both $\Delta q^1_{\pi\text{-bd}}$ and $\Delta q^2_{\pi\text{-bd}}$); this surprising result may be caused by the deformation of geometry, noticeable in Figure 1. Thus, it may be concluded that the influence of the NHC substituents on the bond between the metal and the ligand in the trans position is reflected by shifts in the experimental CO stretching frequencies as well as by changes in the NOCV charge-flow measure ($\Delta q^1_{\pi\text{-bd}}$). However, both effects are hardly detectible.

In order to illustrate the "coupling" between the two metal−ligand bonds trans to each other, Figure 6 presents the relationship between the corresponding overall Δq_{bd} measures, that is, for the NHC ligand and cod/CO in **1-X**/**2-X**. It is clearly seen from the figure that the substituents on NHC do influence its back-donation ability, and they have almost no effect on the back-bonding in the trans position. Figure 6 also shows that the ligand in the trans position has a strong influence on the metal → NHC back-donation: the higher Δq_{bd} values of the trans ligand correspond to the lower Δq_{bd} values obtained for the NHC ligand. Consequently, two groups of complexes considered in the present work, **1-X** and **2-X**, form two separated sets of points in Figure 6. This supports the interpretation of experimental results[28] suggesting that it is possible to modify the back-donation component of the metal−NHC bond by changing the trans ligand.

It has been shown previously that NOCV measures of donation/back-bonding are in qualitative agreement with other theoretical methods.[41] However, it is informative to analyze in addition the partial charge on the NHC ligand obtained from population analysis. It should be emphasized at this point that different population analysis schemes used in the literature lead to different *absolute* values of the charges. Therefore, *only the trend* (not the actual values) can be interpreted *as a qualitative indicator* of the changes in the electron density distribution in a family of complexes. In Table 4, we present the values of the partial charge on the NHC ligand obtained from the Mulliken,[65] Hirshfeld,[66] and Voronoi[67] population analyses implemented in the ADF program. The results demonstrate that similar trends can be observed from all of the methods. In particular, (i) the NHC charge for **1-X** is lower ("more negative") than for **2-X**; this is consistent with higher back-bonding for **1-X**. (ii) The NHC charge decreases on going from **1-H/2-H** to **1-NO₂′/2-NO₂′**; this corresponds to the observed increase in the back-bonding contribution. Thus, the population analysis results qualitatively support our interpretation based on NOCV analysis.

Table 3. The Back-Donation Measures for the Metal−CO (trans to NHC) Bond in the **2-X** Systems Obtained from IR Spectroscopy and NOCV Analysis

complex[a]	ν_{CO}[b]	$\Delta q^1_{\pi\text{-bd}}$[c]	$\Delta q^2_{\pi\text{-bd}}$[c]	$\Delta q^3_{\sigma\text{-bd}}$[c]
2-H	2087, 2004	0.531	0.417	0.163
2-Cl	2091, 2010	0.526	0.417	0.162
2-NO₂	2094, 2012	0.518	0.414	0.163
2-CN	2099, 2017	0.525	0.433	0.165
2-NO₂′		0.517	0.409	0.179

[a] See Scheme 1 and Figure 1. [b] Experimental CO stretching frequencies, from ref 28, in cm^{-1}. [c] NOCV eigenvalues corresponding to the metal → CO back-bonding (see Figure 5b).

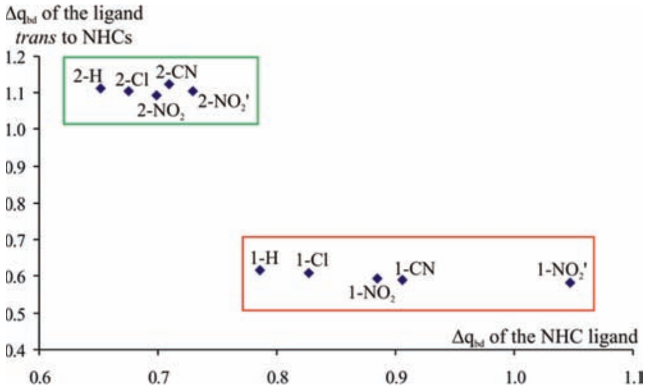

Figure 6. Relationship between the back-bonding contributions in the cod/CO−rhodium and the rhodium−NHC bonds for **1-X**/**2-X**, from the NOCV eigenvalues.

Table 4. The Mulliken, Hirshfeld, and Voronoi Population Analysis Results Concerning Partial Charge on the NHC Ligand for the Analyzed Complexes

	partial charge on NHC		
complex[a]	Mulliken	Hirshfeld	Voronoi
1-H	0.049	0.280	0.298
1-Cl	0.029	0.248	0.268
1-NO₂	−0.035	0.201	0.228
1-CN	−0.060	0.179	0.206
1-NO₂′	−0.096	0.145	0.155
2-H	0.166	0.316	0.374
2-Cl	0.155	0.297	0.354
2-NO₂	0.126	0.271	0.330
2-CN	0.113	0.263	0.315
2-NO₂′	0.104	0.243	0.303

[a] See Scheme 1 and Figure 1.

Finally, let us discuss the NHC−metal bond energies in the analyzed systems **1-X** and **2-X**. Table 5 lists the calculated bond energies and their components determined from the Ziegler−Rauk energy decomposition analysis (eq 6). We will start with the orbital interaction part of the total bonding energy, ΔE_{orb}, as it is directly linked to the charge-flow between the two fragments forming a bond (donation and back-donation). The results show that the orbital interaction between NHC and rhodium is stronger in **1-X** than in **2-X**, by 3.1−8.4 kcal/mol. This appears as a result of an increase in both components, donation and back-bonding (see Figure 2 and Table 1), in **1-X** systems compared to **2-X**.

It should be emphasized that, within the Ziegler−Rauk bond-energy analysis, it is possible to extract the components of the orbital interaction energy corresponding to donation and back-bonding. Such values can be obtained from the

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(65) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
(66) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.
(67) Fonseca Guerra, C.; Handgraaf, J.-W.; Baerends, E. J.; Bickelhaupt, F. M. *J. Comput. Chem.* **2004**, *25*, 189.

Table 5. The Bond-Energy Components [kcal/mol] According to the Ziegler−Rauk Energy Decomposition Scheme (eq 6)

complex[a]	ΔE_{orb}	ΔE_{el}	$\Delta E_{\mathrm{Pauli}}$	ΔE_{el} + $\Delta E_{\mathrm{Pauli}}$	ΔE_{tot}	ΔE_{geom}	ΔE_{b}
1-H	−74.72	−172.77	192.04	19.27	−55.45	7.05	−48.40
1-Cl	−74.37	−165.48	187.32	21.85	−52.52	6.91	−45.61
1-NO$_2$	−77.94	−176.04	199.16	23.12	−54.82	8.53	−46.29
1-CN	−77.08	−168.09	193.12	25.03	−52.05	7.78	−44.27
1-NO$_2$′	−79.18	−166.29	193.92	27.63	−51.55	9.58	−41.97
2-H	−71.60	−159.51	165.36	5.85	−65.74	6.83	−58.91
2-Cl	−70.85	−150.86	160.38	9.52	−61.34	6.30	−55.04
2-NO$_2$	−71.44	−155.89	166.55	10.66	−60.78	6.39	−54.39
2-CN	−68.69	−143.56	157.84	14.29	−54.40	4.29	−50.11
2-NO$_2$′	−70.83	−147.13	161.73	14.60	−56.23	5.94	−50.29

[a] See Scheme 1 and Figure 1.

Table 6. The Orbital Interaction Energies [kcal/mol] Corresponding to Donation, $\Delta E_{\mathrm{orb(d)}}$, and Back-Donation, $\Delta E_{\mathrm{orb(bd)}}$ from the Ziegler−Rauk Analysis within CSOV-like Approach

complex[a]	$\Delta E_{\mathrm{orb(d)}}$	$\Delta E_{\mathrm{orb(bd)}}$
1-H	−48.88	−29.56
1-CN	−46.64	−34.29
2-H	−48.33	−26.40
2-CN	−44.78	−27.66

[a] See Scheme 1 and Figure 1

CSOV-like[35,36] technique combined with the bond-energy analysis. Namely, in such an approach, two separate calculations are required in which (i) the virtual orbitals on the NHC ligand are removed from the basis, in order to characterize the NHC ligand → metal donation, and (ii) the virtual orbitals on the metal fragment are removed from the basis, in order to describe independently the metal → NHC ligand back-bonding. We have performed such an analysis for the systems exhibiting the largest/smallest donation/back-bonding charge-transfer values (among the systems studied experimentally), that is, **1-H** and **1-CN** and **2-H** and **2-CN**. The results are presented in Table 6. The donation/back-bonding energy components confirm general conclusions drawn from our NOCV analysis. Namely, (i) back-bonding energy is an important part (ca. 40%) of the orbital interaction energy: the back-bonding energy varies between −26.4 and −34.3 kcal/mol, while the donation contribution changes between −44.8 and −48.9 kcal/mol. (ii) A variation of the ligand/substituent affects both components, donation and back-bonding. (iii) The ligand in the trans position to NHC visibly affects the back-bonding component with minor influence on the donation contribution: the back-bonding energy changes by 3.2 kcal/mol (from −29.6 in **1-H** to −26.4 in **2-H**) and by 6.6 kcal/mol (from −34.3 in **1-CN** to −27.7 in **2-CN**). (iv) The substituent X has an influence on the back-bonding component of the orbital-interaction energy: for **1-H** and **1-CN** (**2-H** and **2-CN**), the back-bonding energy is −29.6 and −34.3 kcal/mol (−26.4 and −27.7 kcal/mol), respectively.

However, when both components of the orbital interaction energy are summed up, no systematic trend is observed in the orbital interaction energy for different substituents on the NHC ligand; the orbital interaction energy order is NO$_2$ (bis) < NO$_2$ (mono) < CN < H < Cl in the Rh−cod complexes, **1-X**, while it is different in the carbonyl systems, **2-X**: H < NO$_2$ (mono) < Cl < NO$_2$ (bis) < CN (see Table 5).

Furthermore, when all of the other components (electrostatic, Pauli repulsion) are considered, the total interaction energy ΔE_{tot} (see Table 5) is more stabilizing for **2-X** (changing between −54.4 and −65.7 kcal/mol) than for **1-X** (changing between −51.6 and −55.6 kcal/mol). Comparing the system with different X's, ΔE_{tot} changes in the order H < NO$_2$ (mono) < Cl < CN < NO$_2$ (bis) for **1-X**, while for **2-X**, it is H < Cl < NO$_2$ (mono) < NO$_2$ (bis) < CN. Thus, the preferences observed in the orbital interaction energy (following the back-bonding charge-transfer) are not reflected in the total bonding energy, due to the dominating electrostatic and Pauli repulsion terms. Finally, the variations in the geometry distortion term, ΔE_{geom}, that should be included in overall bond dissociation energy are less pronounced (changing between 6.9 and 9.6 in **1-X** and between 4.3 and 6.8 kcal/mol in **2-X**), and consequently the trends in ΔE_{b} are the same as in ΔE_{tot}.

It can therefore be concluded that the differences in back-bonding (in **1-X** compared to **2-X**, and within **1-X**/**2-X** for different X's) are too small to determine the trends in the overall bonding energy.

Concluding Remarks

In the present work, the NOCV and the Ziegler−Rauk bond energy decomposition analysis were used to describe the donor/acceptor character of the bond between the NHC ligand and the transition metal in two groups of square-planar rhodium(I) complexes with chloride and olefin/CO: (NHC)RhCl(cod) (**1-X**) and (NHC)RhCl(CO)$_2$ (**2-X**). A series of NHC ligands with substituents X = H, Cl, NO$_2$, CN, was investigated.

The following major conclusions can be drawn from the results of this study:

1. The NHC−metal bond consists of the components originating from the ligand → metal donation and metal → ligand back-donation. There is one NOCV contribution of the σ symmetry describing donation and three NOCV back-bonding components: two of the π-symmetry (out-of-plane and in-plane) and one σ-back-bonding component. The results indicate that the total back-bonding contribution is of comparable importance as donation.
2. The charge-flow measures, derived from NOCV, indicate that total back-bonding is roughly similar to, or even exceeding, donation. The out-of-plane π component contributes to ca. 50% of the total back-bonding charge-flow.
3. The energy measures, based on the Ziegler−Rauk analysis, show that the total back-bonding energy corresponds to ca. 40% of the orbital interaction energy.
4. The ligand in the trans position to NHC strongly affects the back-bonding component with minor influence on the donation contribution. Thus, for the olefin complexes, **1-X**, the back-donation is substantially enhanced compared to the carbonyl complexes, **2-X**.
5. The back-bonding component of the NHC−metal bond increases with an increase in the π-withdrawing ability of X for both **1-X** and **2-X**. However, the effect is relatively small.
6. The back-bonding components of the two bonds involving metal, NHC−Rh and Rh−olefin/CO(trans), are strongly coupled. An increase in NHC−Rh leads to a decrease in Rh−olefin/CO(trans), and vice versa.

7. Comparing **1-X** and **2-X**, the change in the Rh−NHC orbital interaction energy follows a difference in the metal → NHC back-bonding.
8. Comparing the systems with different X's, the effect observed in back-bonding (point 4) appears to be too small to be followed by the orbital interaction component.
9. The final trends in the total NHC−metal bond energy are determined by the electrostatic and Pauli repulsion components, inverting the preference observed from back-bonding: both ΔE_{tot} and ΔE_{b} are more stabilizing (more negative values) in **2-X** than in **1-X**.

Thus, the results of the present study provide direct measures of donation and back-bonding from theoretical calculations and show that back-bonding is not negligible in the systems studied. Similar conclusions have been drawn recently by Radius and Bickelhaupt[29] for the nickel complexes, for which it was found that the π back-bonding accounts for up to 43% of the total interaction energy.

Theoretical results presented here confirm interpretation of the experimental results presented by Bielawski et al.[28] Namely, back-bonding can be controlled by substituents on the NHC ligand as well as by a choice of the ligand in the trans position. In addition to NOCV measures, the respective bond energies and their components were determined from DFT computations. They lead to the conclusion that the effect observed for back-bonding is not sufficient to be followed by bond-energies.