

π -Acidity and π -basicity of *N*-heterocyclic carbene ligands. A computational assessment

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Received 31 October 2005; received in revised form 12 January 2006; accepted 13 January 2006

Available online 23 February 2006

Abstract

In this contribution we report on a systematic analysis of the bond between transition metals and *N*-heterocyclic carbene (NHC) ligands. We compare the σ and π -contributions in a series of complexes in which the formal d-electron count ranges from d^0 to d^{10} . Our results confirm the currently accepted idea that NHC are not pure σ -donors. In the series of complexes examined here π -contribution is 10% at least. Moreover, remarkable metal-to-ligand backdonation occurs also for d^0 complexes, and many systems present a substantial ligand-to-metal π donation.

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Keywords: *N*-Heterocyclic ligands; Carbene ligands; Transition metal complexes; DFT calculations

1. Introduction

Now, almost 15 years after Arduengo and co-workers have isolated a stable cyclic diamino carbene in the form of an imidazol-2-ylidene derivative [1] and have brought to conclusion Wanzlick's quest for stable carbenes actively pursued during the 1960s [2], *N*-heterocyclic carbenes (NHC) are emerging as a new class of versatile ancillary ligands in transition metal (TM) chemistry. The successful use of NHCs introduced a new and powerful concept in catalysis [3–5], since these compounds represent a valid alternative to the widely used phosphine ligands. Organometallic complexes containing NHC ligands are effectively used in ruthenium catalyzed olefin metathesis [6–10], iridium-catalyzed hydrogenation and hydrogen transfer [11–13], platinum catalyzed hydrosilylation [14], and palladium

catalyzed C–C coupling reactions [15–18], to name important, representative examples.

Although NHC ligands are acquiring a widespread usage, our understanding of the bonding of NHC ligands to transition metals is still limited, and constitutes a topic of ongoing research activity. The seminal theoretical studies of *N*-heterocyclic carbenes that appeared five years after Arduengo's initial report dealt with the issues of charge distributions and aromaticity [19,20], and supported the general picture of bonding properties of the NHC ligand that evolved during the first years of TM–NHC chemistry. Imidazol-2-ylidene was first suggested to bind to a transition metal center through σ -donation only [21], a notion that was further corroborated by calculations on TM complexes of the type $\text{CIM} \leftarrow \text{NHC}$, $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ [22]. However, a significant amount of π -interaction between group 11 metals and NHC ligands was recently proposed on the basis of structural data [23,24]. This proposal was further supported in theoretical calculations and the π -back-bonding interactions for a diaminocarbene model compound was estimated to contribute to approximately 15–30% of the complexes overall orbital interaction energy [25]. In a recent computational study, in which the bonding in

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CIM ← NHC complexes is reinvestigated [26], Frenking and co-workers estimate that the orbital interaction part of the bonding has about 20% π back-bonding, but they carry the bond analysis one step further. The authors state that the metal–carbene bonds are mainly held together by classical electrostatic attraction, which contributes at least to 65% of the binding interactions.

In view of the increasing importance of NHC ligands in catalysis, we decided to perform a systematic and comparative analysis of the [TM] ← NHC bond for a variety of complexes, in which the formal d-electron count for the transition metal ranges from d^0 -complexes over d^4 -, d^6 -, and d^8 -systems up to d^{10} -compounds. The emphasis will be on a qualitative assessment of the different σ - and π -contributions to the metal–carbene bond rather than on highly accurate, quantitative determination of bond energy values. The aspect of the nature of the π -bond is of special interest. Whereas the study of Frenking and co-workers on coinage metal carbene complexes reports a significant amount of π -back-bonding from the transition metal to the carbene ligand [26], a recent computational study of NHC binding in Ir(III) and Rh(III) complexes concludes that the electrophilic metal centers are stabilized by π -donation of the carbene ligands [27]. This suggests that NHC ligands display an ambivalent π -bonding character, and might function as a π -acid as well as a π -base. We set out to analyze the π -bond in TM ← NHC in detail, and to identify criteria for the TM fragment that take direct influence on the π -bond character.

Density-functional theory (DFT) in combination with suitable bond analysis schemes constitutes the method of choice when establishment of trends in chemical bonding is sought, and we will present a concise account of our theoretical approach before discussing our findings in detail.

2. Computational methodology

2.1. General procedure

Gradient-corrected density-functional calculations were based on the local density approximation with Slater exchange [28] and treatment of correlation according to Vosko et al. [29]. Gradient corrections for exchange and correlation were those proposed by Becke [30] and Perdew [31], respectively. All calculations have been performed with the Amsterdam Density Functional suite of programs, ADF version 2004.01 [32–35]. The valence electrons of transition metal atoms were described with ADF basis set V (triple- ζ STO plus two polarization functions), and hydrogen was treated with ADF basis set III (double- ζ STO plus one polarization function). For remaining atoms ADF basis set IV (triple- ζ STO plus one polarization function) was chosen. Electrons of the core shells have been treated within the frozen core approximation. Relativistic effects have been incorporated based on the zero-order regular approximation [36,37]. All geometries have been optimized with a C_s symmetry constraint.

2.2. Bond analysis

We analyze the bonding energy in [TM] ← NHC complexes according to the general energy decomposition scheme for the study of metal–ligand interactions as devised by Ziegler [38]. Here, we consider the interaction of two fragments [TM] and NHC, respectively, which both possess the local equilibrium geometry of the final molecule, and which both have an electronic structure suitable for bond formation. The energy associated with this process is referred to as the bond snapping energy, BE_{snap} [39]. Although the bond snapping energy, BE_{snap} , does not always correlate with bond dissociation enthalpies, since reorganization and relaxation of the fragments are not taken into account, the bond snapping energy, BE_{snap} , is closely related to bond enthalpy terms, which in turn provide a good approximation to bond strength values [40].

The bond snapping energy, BE_{snap} , can be decomposed into two main components, namely steric interaction ΔE^0 and the orbital interaction ΔE_{int} :

$$BE_{\text{snap}} = -[\Delta E^0 + \Delta E_{\text{int}}] \quad (1)$$

The steric interaction term ΔE^0 can further be split into an electrostatic interaction term ΔE_{elstat} and a Pauli repulsion term ΔE^{Pauli} , which is directly related to the two-orbital three or four electron interactions between occupied orbitals on both interacting fragments:

$$\Delta E^0 = \Delta E_{\text{elstat}} + \Delta E^{\text{Pauli}} \quad (2)$$

whereas ΔE_{elstat} constitutes a stabilizing contribution to BE_{snap} , ΔE^{Pauli} constitutes a destabilizing contribution, and it is the relative size of electrostatic interaction and Pauli repulsion that determines the overall character of the steric interaction term. The important contribution of electrostatic interaction for chemical bonding becomes evident in cases where ΔE^0 represents an attractive, rather than a repulsive interaction, and other partitioning schemes have been suggested to more clearly emphasize the relative importance of ΔE_{elstat} [26,41]. However, we shall adapt the partitioning scheme as outlined in Eq. (1).

The total orbital interaction energy ΔE_{int} can further be broken down into contributions from the orbital interactions within the various irreducible representations Γ of the overall symmetry group of the system [42]:

$$\Delta E_{\text{int}} = \sum_{\Gamma} \Delta E_{\text{int}}^{\Gamma} \quad (3)$$

All the molecules studied in the present work possess C_s symmetry, where the NHC ligands are located in the $\sigma(xy)$ mirror plane of the molecule. Therefore, A' contributions to the orbital interaction energy are associated with σ -bonding, whereas A'' contributions are related to π -bonding.

In order to differentiate between these two interactions, the bond decomposition analysis has been extended by performing additional constrained space orbital variation (CSOV) calculations [43]. According to ideas presented

by Bagus and Illas, a suitable division of the variational space makes it possible to judge the importance of various contributions to a chemical bond [44]. In particular, in order to assess the contribution of π -backdonation, the bond decomposition analysis was performed by again considering the interaction of a [TM] fragment and an NHC ligand, but now excluding the set of virtual a'' orbitals on the [TM] fragment from the variational space. This partitioning closely follows the procedure prescribed by Bagus and Illas [44]. As pointed out before, the orbital interaction energy can be decomposed into contributions that transfer according to irreducible representations of the underlying point group of the molecular system. The A'' contribution of the orbital interaction energy is now associated solely with interunit [TM] to NHC a'' donation, or π -backdonation. We refer to this orbital interaction as $\Delta E_{\text{int}}^{\pi}(\text{M} \rightarrow \text{C})$. Similarly, the amount of π -donation, $\Delta E_{\text{int}}^{\pi}(\text{M} \leftarrow \text{C})$, is determined in calculations explicitly excluding all virtual a'' orbitals of the NHC ligand from the variational space. These two individual contributions sum up to the non-synergic π -bond interaction $\Delta E_{\text{int}}^{\text{n.s.},-\pi}$.

$$\Delta E_{\text{int}}^{\text{n.s.},-\pi} = \Delta E_{\text{int}}^{\pi}(\text{M} \rightarrow \text{C}) + \Delta E_{\text{int}}^{\pi}(\text{M} \leftarrow \text{C}) \quad (4)$$

The synergic contribution to the π -bonding energy can then be determined from the difference between $\Delta E_{\text{int}}^{\text{n.s.},-\pi}$ and $\Delta E_{\text{int}}^{\text{a''}}$. The type of constrained variational space approach employed in the present work has been used before to assess the bonding characteristics of thioether complexes and related compounds [45]. This work also provides a critical assessment of synergic and residual contributions to the orbital interaction energy arising from different choices of variational space partitioning. We refer the reader to the literature for a more in-depth discussion. A detailed breakdown of the various bond decomposition analyses employed in the present work can be found in the [supplementary material](#).

We want to re-emphasize the fact that the BE_{snap} values obtained in the present work represent only an approximation to bond enthalpy terms ΔH . Contributions from the preparation energy required to bring the corresponding fragments into a proper geometric and electronic configuration for bond formation, from zero point energy ZPE contributions, and from basis set superposition errors BSSE have not been considered. However, the analysis presented here allows for a qualitative comparison of the various σ and π contributions to the [TM] \leftarrow NHC bond. We refer the reader to the literature for a detailed discussion of the energy decomposition analysis employed in the present work [46].

3. Results and discussion

We have optimized the structures of 36 model [TM] \leftarrow NHC complexes, which are schematically depicted in Fig. 1. The set of complexes includes systems in which the formal d-electron count for the transition metal amounts to d^0 , d^4 , d^6 , d^8 , and d^{10} , and further includes neutral, cationic as well as anionic compounds.

Twenty two molecules out of the set of model compounds are based on the X-ray crystal structures of 22 real [TM] \leftarrow NHC complexes. All NHC ligands have been replaced by imidazolin-2-ylidene and phosphines were replaced by PH_3 . Ligand environments comprising two C=C double bonds that are bonded to the metal center have been replaced by two ethylene molecules. The geometry was adjusted such that all molecules possess C_s symmetry, the plane of the NHC ligand coinciding with the $\sigma(xy)$ mirror plane of the molecule. The list of these 22 compounds together with the reference for the related crystal structure reads as follows: **ag3** [47] **au1**⁺ [48], **au2** [49] **au3** [50] **au4** [50] **au5** [50] **au6** [50] **au7** [50], **cr1** [51], **cu3** [52], **fe1** [53], **hf2**⁻ [54], **mo2** [55], **ni1** [56], **ni2** [57], **os3** [58], **pd1** [59], **pt1** [14], **ru2** [60], **ti1**⁺ [61], **v1** [62], **w1** [63]. Before we will present the results of our bonding analysis, we shall validate the soundness of our set of model complexes in a brief comparison between optimized and experimental geometries.

3.1. Geometries

Since we are interested in the nature of the [TM] \leftarrow NHC bond, the [TM]– C_{NHC} bond length is a self-evident structural parameter on which to base a comparison between calculated and experimental values. In fact, the nature of the M–C bond in [TM]–NHC complexes has recently been analyzed based on structural results obtained from an extensive crystallographic database analysis [64].

A plot of calculated versus experimental [TM]– C_{NHC} bond lengths is displayed in Fig. 2. The data reveal a satisfying linear relationship, the regression line having a slope close to one and an R^2 value of 0.96. On average, the BP86 bond length is 2.3 pm shorter than the experimentally determined structural parameter. This good structural agreement indicates that, despite structural adjustment and simplification of the ligand framework, the analysis of the set of model compounds will provide meaningful and qualitative insights into the nature of the [TM] \leftarrow NHC bond.

The good agreement is even more commendable when we consider the fact that for some model systems the NHC ligand was rotated by up to 90° to achieve the desired C_s orientation. For example, the crystal structure for the $(\text{CO})_3\text{Cl}_2\text{OsNHC}$ complex **os3** displays a geometrical arrangement in which the NHC ligand is oriented perpendicular to the $\sigma(xy)$ mirror plane of the molecule. We performed additional calculations on complexes **fe3a**, **ru3a**, and **os3a**, in which the NHC ligand adopts an orientation as found for **os3**, Chart 1.

The [TM]– C_{NHC} bond lengths decrease slightly by less than 1 pm, and changes in total bond energies amount to -3 , -2 , and -1 kJ/mol, respectively. These results suggest that the rotation of the carbene ligand is essentially free, as has been reported before for Fischer-type carbenes [65], and again support the notion that our set of model systems is qualitatively valid.

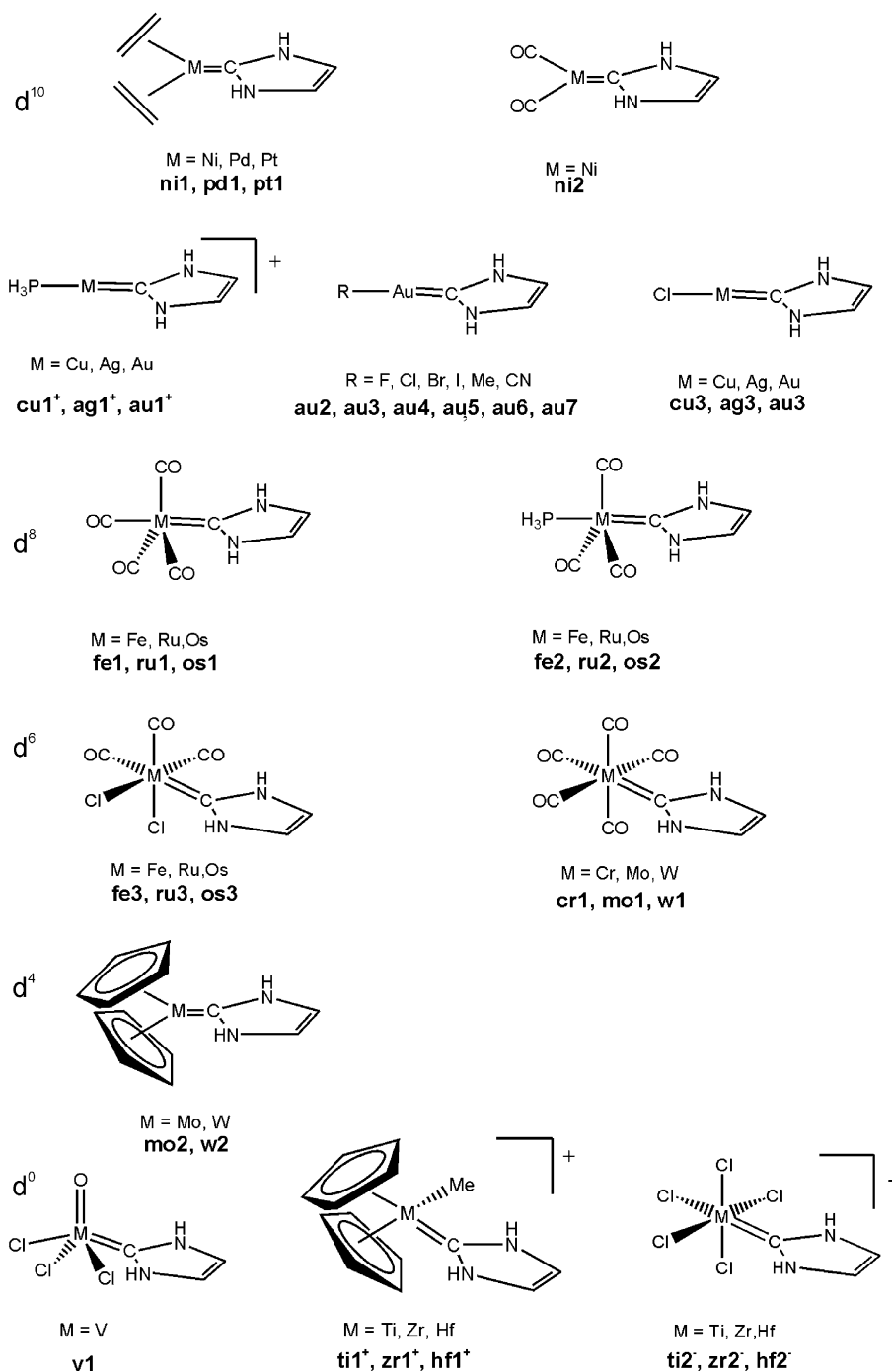


Fig. 1. Pictorial representation and numbering scheme for 36 model complexes.

3.2. Bond analysis

The results of the bond analysis according to Eq. (1) are presented in Fig. 3.

Values for the bond snapping energy BE_{snap} range over a large spectrum of about 300 kJ/mol from 409 kJ/mol for **au1⁺** to 111 kJ/mol for **ti2⁻**. However, the progression observed for the bond snapping energy BE_{snap} is paralleled neither in steric interaction ΔE^0 nor in orbital interaction ΔE_{int} . It appears that with the exception of cationic d^{10} systems, ΔE_{int} is by far the dominant bonding interaction, and

that the steric term is responsible for a fine-tuning of the relative bond strength of related systems, by providing either secondary attractive or secondary repulsive interactions. From closer inspection of Fig. 3, the following trends become evident: (i) Electrostatic interaction as attractive bonding force constitutes a most important factor for cationic systems. In such systems the steric interaction ΔE^0 is stabilizing, indicating that attractive electrostatic interaction outweighs Pauli repulsion. (ii) Systems with higher formal d electron count form stronger bonds. This observation mainly reflects trends observed in the orbital interaction

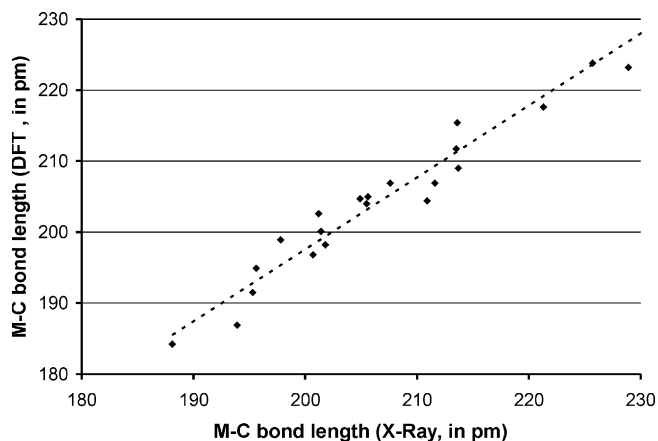


Fig. 2. Plot of calculated [TM]–C_{NHC} bond lengths for 22 model complexes vs. experimentally determined values of related compounds (linear regression: $y = 1.01x - 5.06$; $R^2 = 0.96$).

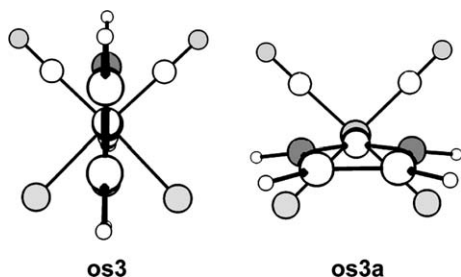


Chart 1.

term. (iii) Anionic systems form weaker bonds than cationic or neutral systems. Here, the steric interaction ΔE^0 contributes a fairly large destabilizing contribution, dominated by

Pauli repulsion. (iv) Ligands that deplete electron density at the transition metal center due to π -acceptance lead to a decrease in attractive orbital interaction ΔE_{int} and at the same time to a decrease in Pauli repulsion ΔE^{Pauli} . (v) Ligands that enhance electron density at the transition metal center due to secondary π -interaction lead to an increase attractive orbital interaction ΔE_{int} and at the same time to an increase in Pauli repulsion ΔE^{Pauli} . We will now analyze these five trends in more detail.

3.2.1. Ligand and charge influences

The series of gold complexes provides a good illustration of the ligand influences, and the bond analysis for the gold model compounds in terms of orbital interaction, ΔE_{int} , steric interaction, ΔE^0 , and bond snapping energy BE_{snap} is displayed in Fig. 4a. The cationic gold complex **au1**⁺ forms the strongest [TM]–NHC bond, which contains a strong bonding contribution from the steric term ΔE^0 due to a strong electrostatic interaction. When replacing the phosphine ligand by a fluoride anion, complex **au2**, the orbital interaction term changes only slightly, but the steric interaction only contributes half of additional stabilization, when compared to the cationic complex. With increasing atomic number for the chloride, bromide and iodide complexes **au3**, **au4**, and **au5**, we see that the orbital interaction terms remains approximately constant, but the influence of the Pauli repulsion term increases with increasing number of electrons. Thus, the stabilizing contribution of the steric interaction term decreases with increasing atomic number, and reaches a value of 0 kJ/mol for the iodide complex. Substituting a methyl group for a halogenide leads to a further increase in Pauli repulsion and decrease in orbital interaction. Thus, complex **au6** possesses a destabilizing steric

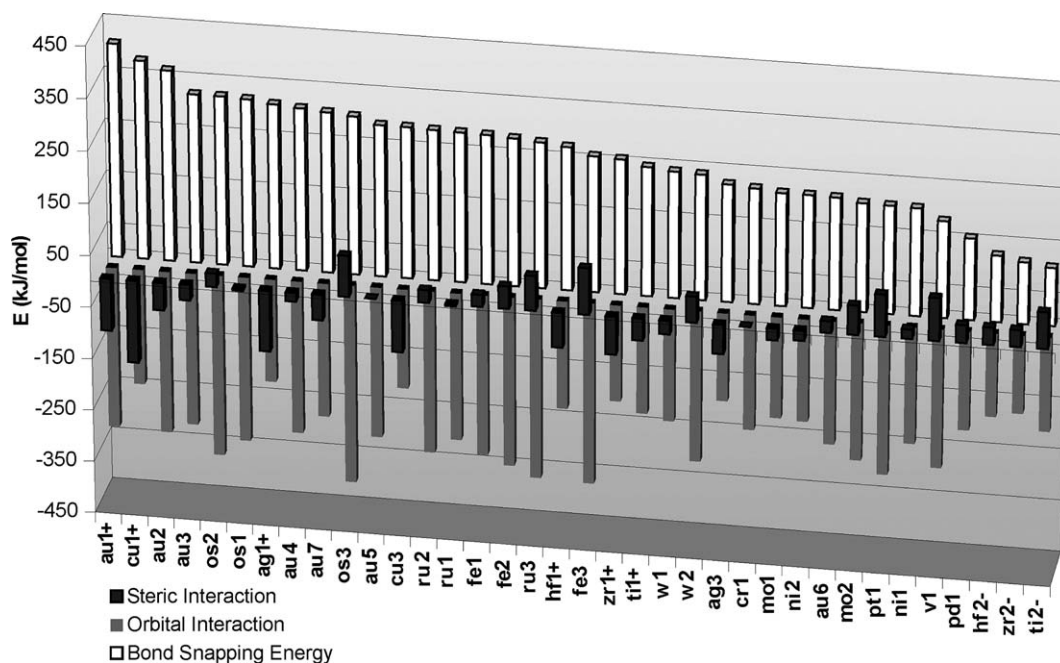


Fig. 3. Bond analysis for model [TM] ← NHC complexes in terms of bond snapping energy BE_{snap} , steric interaction ΔE^0 and orbital interaction ΔE_{int} .

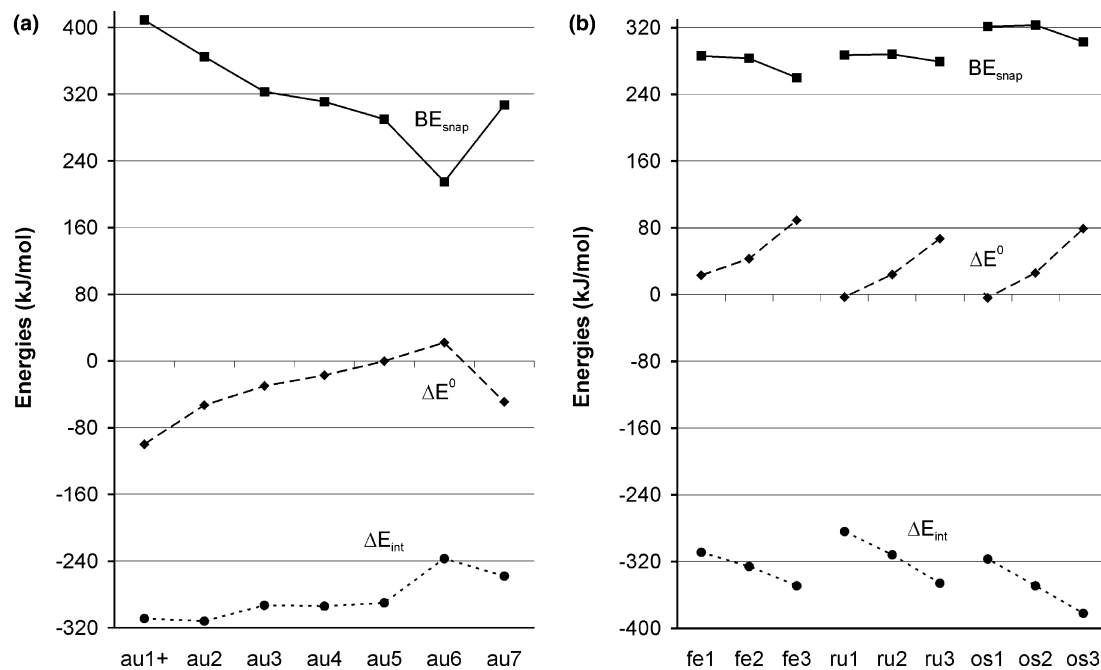


Fig. 4. Bond snapping energy BE_{snap} (solid line), steric interaction ΔE (dashed line) and orbital interaction ΔE_{int} (dotted line) for: (a) gold model compounds, and (b) group VIII model compounds.

interaction term. Replacing the methyl group by a cyanide ligand again renders the steric interaction term attractive, since due to back-bonding to the cyanide ligand, the electron density at the transition metal center is depleted. This causes both a decrease in Pauli repulsion as well as an increase in steric interaction. The orbital interaction terms are slightly stronger in **au7** when compared to **au6**, but still significantly smaller than found for the halogenide ligands. Overall, the bond snapping energy for the [TM]–NHC bond of the cyanide ligand metal fragment is comparable to that of the heavier halogenide ligand metal fragments.

The influence of ligands of the transition metal fragment is also evidenced in the series of model complexes with transition metals from the iron triad. The bond analysis for complexes **fe1**, **fe2**, **fe3**, **ru1**, **ru2**, **ru3**, **os1**, **os2**, and **os3** is shown in Fig. 4b. When replacing a π -accepting carbonyl group by a less π -acidic phosphine ligand, we see that the orbital interaction term ΔE_{int} increases and that the steric interaction, ΔE^0 becomes more destabilizing. This trend is continued when two π -accepting carbonyl ligands are substituted by two π -donating chloride ligands. Again, the argument to explain this trend employs depletion and enhancement of electron density, and more specifically, π -electron density at the transition metal center. The bond snapping energy BE_{snap} follows the trend $Os > Fe \approx Ru$. The trend found in the orbital interaction term interaction, ΔE_{int} , is $Os > Fe > Ru$, but the ruthenium and iron complexes display similar values for the bond snapping energy BE_{snap} .

The importance of charge of the transition metal fragment is best seen when analyzing the bonding for the group IV model complexes. The cationic systems **ti1**⁺, **zr1**⁺, and **hf1**⁺, although not showing an excessively strong orbital

interaction, do form moderately strong bonds of about 250 kJ/mol. This is mainly due to an attractive steric interaction term ΔE^0 . On the other hand, the anionic complexes **ti2**[−], **zr1**[−], and **hf2**[−], possess only a weak orbital interaction, and additional steric destabilization. They therefore have the lowest bond snapping energies of all the model complexes studied in this work.

The different trends we discussed so far already point to the importance of π -bonding interactions, and we will now discuss this aspect with respect to the NHC ligand.

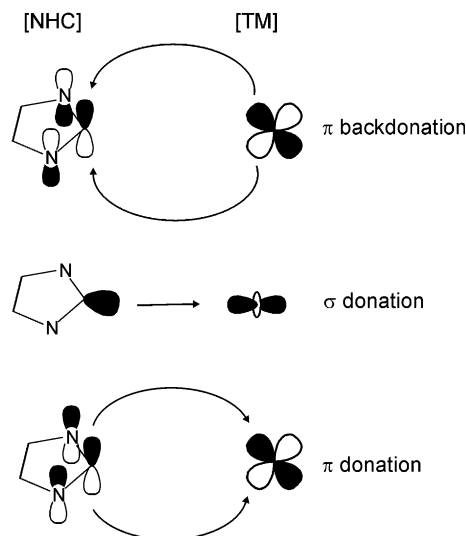


Chart 2.

3.2.2. σ and π Contributions

The relevant orbital interactions that dominate the [TM] ← NHC bond are schematically illustrated in Chart 2:

Besides σ donation, we do have two significant types of π -interactions, namely π donation as well as π backdonation. The importance of π interaction is shown in Fig. 5.

The plot of the π -contribution to the overall orbital interaction (Fig. 5, solid line), clearly indicates that for all of the complexes investigated in the present study, there exists at least a contribution of 10%. Even the NHC ligand in compound **ti1**⁺, which in a previous calculation has been described as a pure σ -donor [61], possesses a 17% π -bonding character.

Also shown in Fig. 5 is a plot of the π -contribution to the total bonding energy $-\text{BE}_{\text{snap}}$. This representation

takes into account the influence of the steric interaction term. Compounds that show a destabilizing ΔE^0 interaction (mainly the systems on the left side of Fig. 5) do have a higher π -contribution to the total bonding energy than to the orbital interaction term. This behavior is typical for neutral and anionic systems with low d-electron count. Similarly, compounds with attractive steric interaction (mainly the systems on the right side of Fig. 5) have a smaller π -contribution in terms of the total bonding energy.

It remains to assess the character and type of π -contribution to the [TM]–NHC bond. The question here relates to the relative importance of π -backdonation, and we shall address this issue in the last part of our discussion.

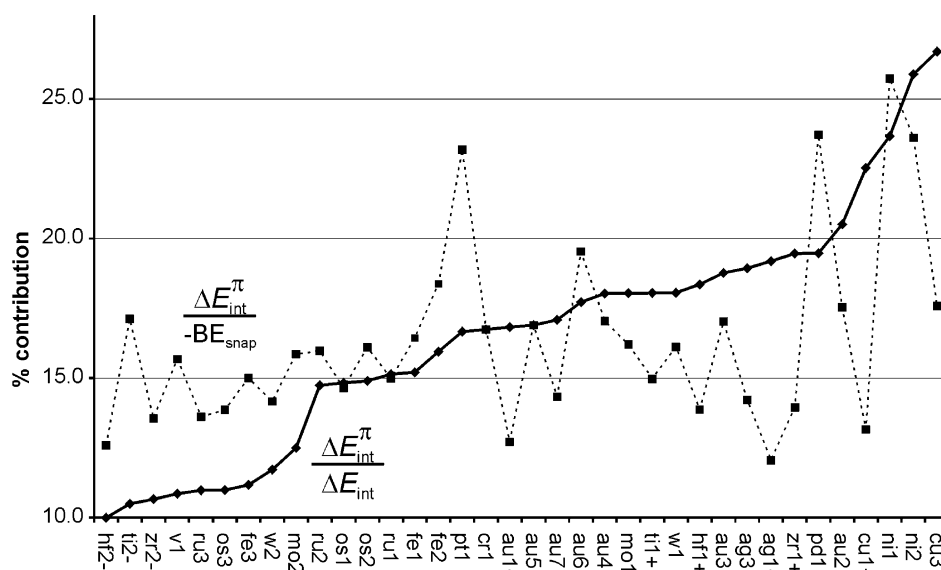


Fig. 5. π -Contribution $\Delta E_{\text{int}}^{\pi}$ (in %) to the orbital interaction energy ΔE_{int} (solid line) and to the total bonding energy $-\text{BE}_{\text{snap}}$ (dotted line).

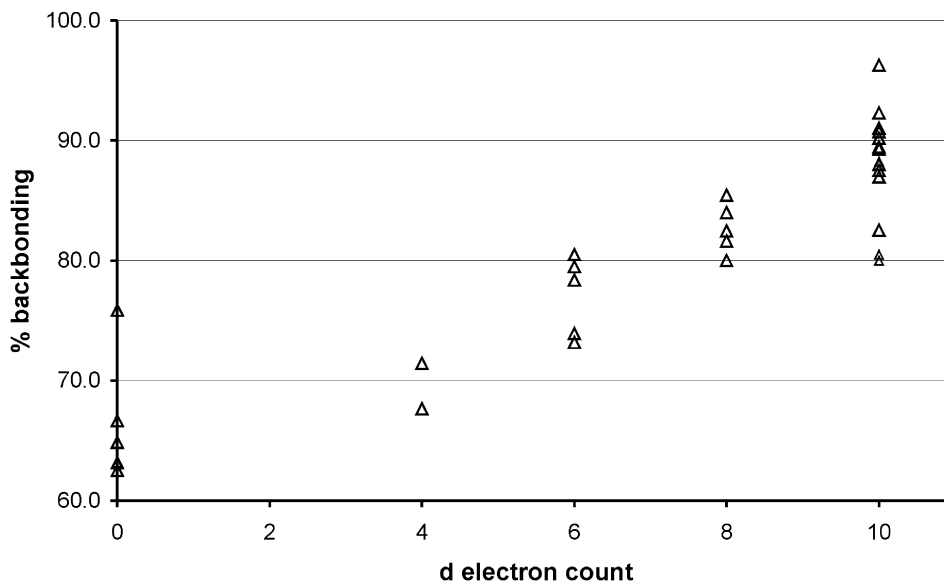


Fig. 6. Plot of π -back-bonding contribution (in %) to the non-synergic π -bond interaction $\Delta E_{\text{int}}^{\pi, -\pi}$ vs. formal d electron count. Detailed bonding analysis data can be found in Supporting material.

3.2.3. π Donation vs. π backdonation

Values for π -donation $\Delta E_{\text{int}}^{\pi}(\text{M} \leftarrow \text{C})$ have been obtained in an analysis run in which the unoccupied π -orbitals of the carbene ligand have been removed from the calculation. In the same way by removing unoccupied π -orbitals of the transition metal fragment a value for π -backdonation $\Delta E_{\text{int}}^{\pi}(\text{M} \rightarrow \text{C})$ is obtained. As mentioned before, these two contribution combine to the non-synergic π -bond interaction $\Delta E_{\text{int}}^{\text{n.s.}-\pi}$. Fig. 6 displays values of relative contribution of π -backdonation to the non-synergic π -bond interaction. These values are plotted against the formal d-electron number of the transition metal fragment.

We find that even the d^0 systems show a significant amount of π -backdonation around 65% of the total π -bonding contribution. This amount increases with increasing d-electron count and takes on values around 90% for d^{10} complexes. Whereas for systems with a low d electron count both π donation as well as π -backdonation constitute important contributions to the orbital interaction term, the NHC ligand in systems with a high d electron count is best described as a π -acid.

The back-bonding contribution for the d^0 complex **v1** is with 76% unusually high. The fact that this vanadium fragment contains a doubly bonded oxo group might provide a rationale for enhanced electron density at the transition metal center and thus for enhanced backdonation.

4. Conclusion

In line with previous papers, the results of our calculations on an extended set of TM complexes with NHC ligands suggest that the NHC ligand cannot be considered as a pure σ -donor. Even for d^0 systems, there exists a considerable amount of π -bonding. For system with a low d electron count, both π -donation as well as π -backdonation are of importance. For systems with a high d electron count, backdonation constitutes the major contribution to the π -interaction.

We hope that this work will contribute to and support studies such as the rational design of [TM]-NHC catalysts [66], or the development of new strategies to stabilize coordinatively unsaturated metal centers through the incorporation of NHC ligands [67].

Acknowledgements

We thank the MURST of Italy (Grant PRIN 2004) and the University of Salerno (Grant Medie Attrezzature di Ateneo 2002) for financial support.

Appendix A. Supplementary data

Optimized Geometries as well as detailed bonding analysis data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.026.

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