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Bonding of Imidazol-2-ylidene Ligands in Nickel Complexes

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The bonding of imidazol-2-ylidenes (H_2Im) in a series of nickel complexes with seemingly different complex fragment group electronegativities, i.e., [$Ni(H_2Im)_3$], [$Ni(H_2Im)_2$], [$Ni(H_2Im)(CO)$], [$Ni(H_2Im)(CO)_2$], and [$Ni(H_2Im)(CO)_3$], was analyzed. This series provides theoretical evidence that the bonding of imidazol-2-ylidene ligands to metal−complex fragments strongly depends on the nature of the ligand environment of the metal complex. An analysis of a series of isostructural complexes D_{2h}- and D_{2d}-$M(H_2Im)_2$ with different metals (M = Ni, Pd, Pt) reveals that the bonding also strongly depends on the metal used in the complex.

In the last 50 years, N-heterocyclic carbenes (NHCs; 1,3-diorganylimidazol-2-ylidenes: R_2Im) have evolved from intermediates whose existence could be demonstrated by kinetic and trapping studies in the 1960s[1] to stabilized forms currently being studied in many research groups.[2] Although Fischer- as well as Schrock-type complexes have been known for many decades and there were early reports on NHC complexes,[3] NHCs have come to occupy a central position in organometallic chemistry just recently. During the past decade there has been considerable interest in N-heterocyclic carbenes as spectator ligands in organometallic chemistry, particularly as alternatives to phosphine ligands in the field of homogeneous catalysis.[4] Despite the seemingly universal usage of these ligands, some questions regarding the bonding of NHCs to transition metals (TM) have still not been clarified.[5]

It is generally assumed that NHCs have bonding properties similar to electron-rich trialkylphosphanes (strong σ-donors with negligible π-accepting ability).[2,4] This belief arose mainly from theoretical studies of the electronic structure of NHCs, which assigned a strong N−C(carbene) π-donation as the main reason for the high kinetic stability of this class of compounds.[6] This interaction leads to a high occupancy of the formally unoccupied carbene carbon p(π) orbital, and there is thus no need for TM−NHC back-donation to stabilize the complex. A number of experimental and/or theoretical studies have also suggested that π-back-donation is negligible in TM−NHC bonding.[5,7] The simplified picture of NHC as mere σ-donors was then revised in several reports that suggested that unoccupied π^* orbitals on the NHC ring can contribute to the NHC−metal bond to various amounts.[5]

Here we provide theoretical evidence that the bonding of imidazol-2-ylidene ligands to metal−complex fragments strongly depends on the nature of the metal and the nature of the complex

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metal fragment for a given metal. Therefore, we analyzed the bonding of imidazol-2-ylidenes in nickel complexes with seemingly different complex fragment group electronegativities. We have also investigated, for selected examples, the role of the metal by including palladium and platinum complexes into our set of model systems. We have chosen Ni−NHC as compounds for the present study because a wealth of experimental data have been reported for this class of complexes over the past few years.[8–10] This provides a decent basis for comparing our computational results with experiment.

All calculations are based on ZORA-relativistic density functional theory (DFT)[11] and were carried out using the Amsterdam Density Functional (ADF) program.[12,13] The BLYP density functional was used,[14] in combination with a large uncontracted set of Slater-type orbitals (STOs) containing diffuse functions, designated as TZ2P. The bond energy was analyzed in terms of a quantitative decomposition of the bond energy into electrostatic attraction, Pauli repulsive orbital interaction, and bonding orbital interactions.[15] All complexes and complex fragments are closed-shell species with singlet spin states and have been treated with the spin-restricted formalism. The bonding orbital interactions were further decomposed into contributions from σ, π, and other symmetries using the extended transition state (ETS) scheme developed by Ziegler and Rauk.[15c–e] More details on the computational methods and the energy decomposition scheme are given in the Supporting Information.

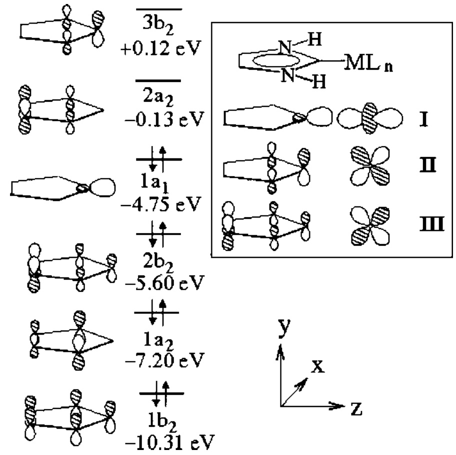

Figure 1. Main electronic features of the parent imidazol-2-ylidene (H_2Im) (left side) and likely important interactions between H_2Im and a transition metal complex fragment ML_n (right side).

For our purpose it is instructive to recall the main electronic features of the parent imidazol-2-ylidene (H_2Im) (Figure 1, left side). Shortly after the discovery of stable singlet carbenes by Arduengo et al.[16] a number of theoretical papers appeared that presented models for the bonding and structure in imidazol-2-ylidenes and diaminocarbenes in general.[6] Our quantitative MO analyses confirm that the electrons of imidazol-2-ylidene responsible for π-interaction with the formally unoccupied carbene carbon p_y orbital are embedded into a 6 π-electron aromatic system (see Figure 1, left side). Similarly to the well-known cyclopentadienide anion, the occupied orbitals of the π-system have no nodal plane (orbital $1b_2$ in C_{2v} symmetry, at −10.31 eV) or one nodal plane ($1a_2$, −7.20 eV; $2b_2$, 5.60 eV), whereas the unoccupied π orbitals ($2a_2$, −0.13 eV; $3b_2$, +0.12 eV) have two nodal planes. These pairs of orbitals are not degenerated due to the heteroatomic substitution of the aromatic ring. The orbital $3b_2$ is mainly centered on the carbene carbon atom (71.4% carbene carbon p_y) and is usually regarded as the carbene p_π orbital. Orbitals of a_2 symmetry have no contributions at the carbene carbon atom, whereas $1b_2$ and $2b_2$ have carbene carbon p_y contributions of 13.2% ($1b_2$) and 20.0% ($2b_2$), respectively. The HOMO of H_2Im is the orbital $1a_1$ at −4.75 eV, usually referred to as a carbene σ orbital, which contains 49.5% carbene carbon p_z and 33.5% carbene carbon s as main contributions. Within our level of theory we calculate an energy gap of 4.87 eV between $1a_1$ and $3b_2$.

Thus, to assess the M−C orbital interaction in TM−NHC complexes completely, three interactions might be of relevance (see Figure 1, right side): (a) σ-donation I from the NHC σ-donor orbital to a TM acceptor orbital, (b) π-back-donation II from a suitable occupied TM d orbital into the NHC carbon p_π orbital, and (c) delocalization of the NHC π-system into an unoccupied TM d orbital, i.e., π-donation III: The orbital $2b_2$ might be well suited for some degree of π-donation, since it contains a considerable amount of carbene carbon p_y and lies at energies (−5.60 eV) well suitable for ligand TM interaction. The orbital $1b_2$ seems to be too low in energy to play an important role in TM−NHC binding. As a comparison, the unoccupied 2π-

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acceptor orbitals of CO[17] lie energetically much lower (at −1.93 eV at our level of theory, containing approximately 76% C 2p) compared to H_2Im's $3b_2$, a strong indication that CO is indeed the much better π-acceptor ligand.

For an analysis of TM−NHC bonding with respect to the nature of the metal complex fragment it is coordinated to, we chose to perform calculations on models of known nickel complexes. Electron-rich NHC nickel complexes are among the first NHC metal compounds that have been synthesized starting from isolated N-heterocyclic carbenes.[8a] 2-Fold-coordinated, homoleptic complexes $[Ni(Mes_2Im)_2]$[8a] (Mes = 2,3,5-$Me_3C_6H_2$) and $[Ni(Dip_2Im)_2]$[8b] (Dip = 2,5-${}^iPr_2C_6H_3$) have been synthesized in the groups of Arduengo and Herrmann, respectively. Cloke et al. reported the synthesis of the alkyl-substituted $[Ni({}^tBu_2Im)_2]$ in approximately 10% yield via co-condensation reaction of nickel vapor and 1,3-di(*tert*-butyl)imidazol-2-ylidene.[8c] X-ray crystal structures of these complexes reveal that these compounds crystallize as (pseudo) D_{2d} symmetric molecules. We recently reported the X-ray crystal structure of $[Ni(Me_2Im)_3]$, a homoleptic 3-fold-coordinated complex, which essentially crystallizes in a D_3 symmetric structure.[10b] Similarly, as observed for the preparation of homoleptic nickel complexes, the outcome of the synthesis of NHC-stabilized nickel carbonyl complexes critically depends on the steric properties of the NHC ligand used. In the case of aryl-substituted NHCs such as Mes_2Im or Dip_2Im and others, tricarbonyl complexes of the type $[Ni(R_2Im)(CO)_3]$ are formed, which crystallize in a pseudo C_s-type structure.[9h] The most bulky NHC ligands ${}^tBu_2$Im and Ad_2Im (Ad = adamantyl), however, led to the formation of pseudo-C_{2v}-symmetric, 16-electron three-coordinate carbonyl nickel compounds $[Ni(R_2Im)(CO)_2]$.[9f,h]

This series of compounds is ideal for our purpose, because they allow a formal cleavage of the Ni−NHC bond under C_{2v} and/or C_s symmetry restrictions and thus a separation of σ- and π-interactions in these compounds. For simplicity and to avoid any influence from steric congestion, all calculations have been performed with hydrogen-substituted derivatives, i.e., H_2Im coordinated to the metal atom. An overview of the model complexes under investigation with calculated metal carbon distances of the calculated structures is given in Figure 2. All the compounds have been optimized without any symmetry constraints as well as under symmetry restrictions.

The experimentally observed trends in M−C bond lengths in complexes of the type $M(NHC)_2$ are well reproduced by our calculations. X-ray crystal structures of the nickel complexes reveal bond lengths of 1.827 and 1.830 Å for $Ni(Mes_2Im)_2$[8a] and 1.874 Å for $Ni({}^tBu_2Im)_2$.[8c] The platinum carbon distances were found to be 1.942 and 1.952 Å in the solid state structure of $Pt(Mes_2Im)_2$,[8a] and the palladium−carbon distances in three X-ray analyses on different palladium complexes $Pd(R_2Im)_2$are in a range between 1.990 and 2.084 Å.[8d–f] We calculate the shortest M−C distances for nickel complexes (e.g., 1.8461 Å for D_{2h}-$Ni(H_2Im)_2$) and the longest for the palladium complexes (e.g., 2.0260 Å for D_{2h}-$Pd(H_2Im)_2$). The optimized platinum carbon bond lengths are slightly reduced compared to the distances in the palladium complexes (e.g., 1.9973 Å for D_{2h}-$Pd(H_2Im)_2$). For $Ni(Me_2Im)_3$ we observed bond lengths in the range 1.860 to 1.888 Å,[10b] which is in good agreement with 1.882 Å found in the optimized structure for D_3-$Ni(Me_2Im)_3$.

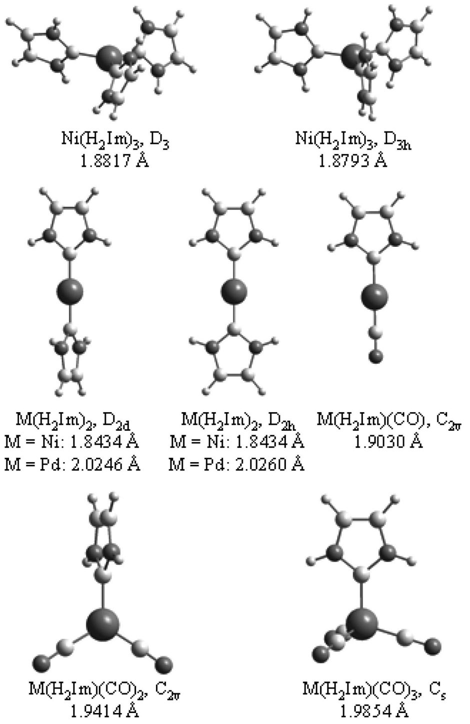

Figure 2. Model complexes under consideration.

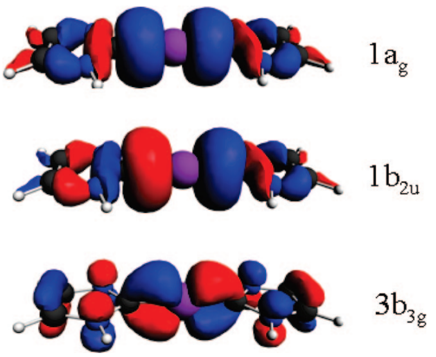

Figure 3. Important σ- and π-bonding orbitals of D_{2h}-$Ni(H_2Im)_2$.

For complexes of the type $[Ni(R_2Im)(CO)_3]$ and $[Ni(R_2Im)(CO)_3]$ Ni−$C_{carbene}$ distances in the range between 1.9528 and 1.971 Å have been observed in the X-ray structures,[9f,h] which is also well reproduced by our calculations.

A good starting point for the analysis on Ni−H_2Im bonding is D_{2h}-$Ni(H_2Im)_2$, which is actually a transition state for the twist of the ligands to give the global energy minimum D_{2d} symmetric molecule. This model is only 0.61 kcal/mol higher in energy compared to D_{2d}-$Ni(H_2Im)_2$. Three orbitals of this complex (Figure 3) are mainly responsible for Ni−NHC bonding. These are the σ-type orbitals $1a_g$ (in D_{2h} symmetry) and $1b_{2u}$, which represent the two σ-bonds in the molecule, and the π interaction $3b_{3g}$, representing a π-bond in the molecule.

The importance of nickel−carbon π-back-bonding in this type of complex was substantiated by the decomposition of the Ni−$C_{carbene}$ orbital interaction of the two fragments $Ni(H_2Im)$ and H_2Im in C_{2v} symmetry (see Table 1). Out of a total orbital interaction of −47.06 kcal/mol, −22.83 kcal/mol stem from interaction of a_1 symmetry (i.e., σ-contribution), −16.92 kcal/mol from interaction of b_2 symmetry (i.e., π-contribution), and −7.31 kcal/mol from interactions of a_2 and b_1 symmetry (i.e., interaction of nickel-centered orbitals

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Table 1. Metal−carbene Bond Energy Decomposition (in kcal/mol)[a]

	$Ni(H_2Im)_3$ $D_{3h}(C_{2v})$	$Ni(H_2Im)_2$ $D_{2h}(C_{2v})$	$Ni(H_2Im)_2$ $D_{2d}(C_{2v})$	$Pd(H_2Im)_2$ $D_{2d}(C_{2v})$	$Pt(H_2Im)_2$ $D_{2d}(C_{2v})$	$Ni(H_2Im)CO$ $C_{2v}(C_{2v})$	$Ni(H_2Im)(CO)_2$ $C_{2v}(C_{2v})$	$Ni(H_2Im)(CO)_3$ $C_s(C_s)$
Decomposition of Orbital Interactions[b]								
σ	−36.01	−22.83	−21.86	−23.44	−38.90	−20.63	−30.69	−39.32
π	−23.17	−16.92	−20.94	−11.92	−16.31	−10.71	−11.48	−7.03
other		−7.31	−5.75	−4.32	−6.68	−4.35	−3.02	
ΔE_{oi}	−64.65	−47.06	−48.55	−39.69	−61.89	−35.69	−44.83	−46.35
% π to ΔE_{oi}	36	36	43	30	26	30	26	15
Decomposition of Interaction Energy[c]								
ΔE_{oi}	−64.65	−47.06	−48.55	−39.69	−61.89	−35.69	−44.83	−46.35
ΔE_{Pauli}	171.19	136.84	137.81	136.52	197.41	103.31	123.88	123.92
ΔV_{elstat}	−143.36	−142.67	−143.46	−141.36	−195.33	−125.48	−125.38	−118.42
ΔE_{int}	−36.82	−52.89	−54.21	−44.52	−59.81	−57.86	−46.33	−40.85
Decomposition of Overall Bond Energy[d]								
ΔE_{int}	−36.82	−52.89	−54.21	−44.52	−59.81	−57.86	−46.33	−40.85
$\Delta E_{prep}(ML_n)$	+18.70	+2.35	+2.23	+1.01	4.57	+1.08	+7.01	+8.78
$\Delta E_{prep}(L)$	+0.46	+0.35	+0.39	+0.24	0.38	+0.36	+0.28	+0.33
ΔE	−17.66	−50.19	−51.59	−43.27	−54.86	−56.42	−39.04	−31.74

[a] Computed at ZORA-BLYP/TZ2P. [b] $\Delta E_{oi} = \Delta E_{oi}(\sigma) + \Delta E_{oi}(\pi) + \Delta E_{oi}(\text{other})$. [c] $\Delta E_{int} = \Delta E_{oi} + \Delta V_{elstat} + \Delta E_{Pauli}$. [d] $\Delta E = \Delta E_{int} + \Delta E_{prep}(ML_n) + \Delta E_{prep}(L)$.

with the σ-frame of the carbene). For this complex, π-bonding contributes as much as 36% to the net orbital interaction. This value even increases up to 43% for D_{2d}-$Ni(H_2Im)_2$, a model for the experimentally observed complexes $Ni(R_2Im)_2$. Note how important orbital interaction of the carbene carbon atom with the metal atom is in this case since it contributes −47.06 kcal/mol (D_{2h}-$Ni(H_2Im)_2$) and −48.55 kcal/mol (D_{2d}-$Ni(H_2Im)_2$), respectively, to the overall coordination-bond energy ΔE of −50.19 kcal/mol (D_{2h}-$Ni(H_2Im)_2$) and −51.59 kcal/mol (D_{2d}-$Ni(H_2Im)_2$). Without this contribution the complexes would be hardly bound at all.

The amount of π-back-bonding also critically depends on the nature of the metal atom involved in TM−NHC bonding: For Pd and Pt complexes of the type D_{2d}-$M(H_2Im)_2$ (M = Pd, Pt), we calculate 30% and 26% π-contribution to the total orbital interaction, strongly reduced as compared to 43% obtained for the corresponding nickel complex. Note that the trend of a steadily decreasing percentage of π-bonding along Ni, Pd, and Pt arises at first from an absolute decrease in π-bonding (from Ni to Pd) but thereafter from a more significant increase in σ- than in π-bonding (from Pd to Pt); see Table 1. The analysis of Table 1 leads to the conclusion that σ orbital interaction as well as electrostatic attraction terms is significantly larger for the platinum complex. We assume that this is related to the relative orbital energies of the interacting orbitals. Whereas the orbital energies of the NHC σ-donor orbital denoted as $1a_1$ in Figure 1 remain constant, the σ-acceptor orbitals decrease in energy going from Ni (−1.558 eV) and Pd (−1.592 eV) to Pt (−2.075 eV).

For the overall coordination-bond energy ΔE we recognized a trend typically observed for bonding energies within a group of metals, i.e., a minimum for the 4d metal palladium:[18] −51.59 kcal/mol (Ni), −43.27 kcal/mol (Pd), and −54.86 kcal/mol (Pt). The analyses of the present series of model systems show that the decrease in bonding interaction from the nickel to the palladium compound mainly originates from a reduced π-back-donation, whereas the strengthening from the palladium to the platinum compound is associated with a much more favorable σ orbital interaction for the heaviest congener. Note however also that it is especially the sharp increase of the electrostatic attraction from the palladium to the platinum complex that contributes to the concomitant increase in overall TM−NHC bond strength.

So far, we have established that π-contribution to carbene nickel bonding depends on the nature of the metal. Next, we systematically varied the nature of the nickel complex fragment ML_n attached to the H_2Im ligand to systematically investigate the influence of the groups characterized by different degrees of basicity of the complex fragment to Ni−NHC bonding. Starting out from seemingly electron-rich $Ni(H_2Im)_2$, one of the NHC ligands was replaced to give the (hypothetical) molecule $Ni(H_2Im)(CO)$, which optimizes in a structure with a linear $C_{carbene}$−Ni−C_{CO} axis. Analysis of the Ni−$C_{carbene}$ bond reveals a drop in π-contribution to 30% and an increased importance of electrostatic contributions to bonding. We attribute this decrease to the competition of the occupied d orbitals of the metal atom with the virtual orbitals of the NHC and CO ligand; that is, CO is a much better π-acceptor ligand compared to NHC and thus reduces π-character in the Ni−NHC bond. This trend is continued when increasingly more CO ligands are added to the nickel complex to give $Ni(H_2Im)(CO)_2$ (26%) and $Ni(H_2Im)(CO)_3$ (15%).

We have shown that for a proper description of the bonding of NHCs to transition metal atoms, π-interactions have to be considered. In the case of the electron-rich nickel complexes under consideration, π-interaction accounts for up to 43% of the total interaction energy. However, in the case of real systems the σ/π as well as other contributions to NHC metal bonding might be different than those obtained for the model complexes with hydrogen substituents. This is currently under investigation. The importance of back-bonding to the metal center critically depends on the nature of the metal (for d^{10} metals Ni > Pd > Pt) and the nature/electronic situation of the metal complex fragment. With increasing carbonyl content of our model complexes, π-contributions become less important. This is probably one reason for the picture of NHCs as more or less pure σ-donating ligands. Previous theoretical investigations have been mainly performed either on NHC-stabilized carbonyl complexes and/or on complexes of 4d and 5d metals, in which π-contributions are less important as compared to 3d metals. TM−NHC bonding has apparently more facets than commonly accepted, and the nature of TM−NHC bonds varies in detail from metal to metal and from metal complex fragment to metal complex fragment.

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(18) See, for example: (a) Ziegler, T.; Autschbach, J. *Chem. Rev.* **2005**, *105*, 695. (b) Li, J.; Ziegler, T. *Organometallics* **1996**, *15*, 3844. (c) Dapprich, S.; Frenking, G. *Angew. Chem., Int. Ed.* **1995**, *34*, 354.

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Supporting Information Available: Computational Details. This material is available free of charge via the Internet at http://pubs.acs.org.

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