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How Important Is Backbonding in Metal Complexes Containing N-Heterocyclic Carbenes? Structural and NBO Analysis

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DFT calculations have been used to analyze the degree of metal-to-ligand backbonding in a range of model transition metal complexes of N-heterocyclic carbenes. Two new methods of analysis have been introduced for this purpose. The first is structural and involves comparing the variation of the C–N bond length and N–C–N angle in complexes in which σ-donation is dominant (e.g. complexes with BF_3) and others in which backbonding might be expected. The second uses the perturbative natural bonding orbital (NBO) method. Both methods lead to the firm conclusion that backbonding is significant in these compounds – as large or even larger than in the corresponding phosphane complexes. This is partly due to the very strong σ-donor nature of the ligand, which makes typical metal acceptor centers very electron-rich and hence very apt to undergo backbonding.

Introduction

Pioneering work by Öfele[1] and Wanzlick[2] led to the report of the first metal complexes containing an N-heterocyclic carbene (NHC). More than two decades later, Arduengo and co-workers[3] isolated the first stable free cyclic diaminocarbene [1,3-bis(1-adamantyl)imidazol-2-ylidene]. Since then, the impact of NHCs and the related diaminocarbenes in organometallic chemistry has been unquestionable.[4–8] They[9] have been used in several metal-based catalysts for a large variety of reactions such as hydrogenations,[10,11] hydrosilylations,[12,13] olefin metathesis,[14–17] and C–C coupling reactions.[18–22] The large number of applications is due in part to the fact that complexes of these ligands are kinetically robust towards decomposition reactions.[7]

Another factor, however, is that NHC ligands are generally recognized to be stronger donor ligands than phosphanes.[14,23–27] As a result, replacement of phosphanes by NHCs has broadened and improved the catalytic activity of some metal complexes. One of the best known examples is the second-generation Grubbs catalyst, derived from the first-generation system by substitution of one PCy_3 ligand by an NHC, which leads to a more effective and versatile catalyst.[16,17] Another successful example is the palladium complex $(NHC)Pd(PR_3)I_2$, which is frequently used in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions. The replacement of one of the phosphane ligands by one NHC ligand combines the stability and the activity provided by the bis(carbene) and bis(phosphane) complexes, respectively.[19,20]

In organometallic chemistry, carbenes are commonly classified as being either of Fischer- or Schrock-type, which are associated with different substitution patterns and chemical behavior. Complexes of Fischer carbenes are more common when the metal atom is in a low oxidation state. The carbene carbon atom bears π-donor substituents such as alkoxy or dialkylamino, leading to a singlet ground state for the isolated carbene. For complexes of these species, the metal–carbon bond can be well described as involving a donor–acceptor relationship, with σ-donation from the carbene to an empty orbital on the metal atom and π-backbonding from the metal atom to the carbene. The bond description is thereby similar to the Dewar–Chatt–Duncanson model used to describe the chemical bond between a metal atom and an olefin.[28,29] Complexes of Schrock carbenes tend to involve metal atoms with a high oxidation state, and the chemical bonding is better described as a covalent interaction between two triplet fragments. Complexes of Fischer carbenes frequently display a reactivity involving the electrophilic character of the carbene carbon atom, whereas complexes of Schrock carbenes often involve nucleophilic behavior of the carbene carbon atom. The popular new class of diaminocarbenes is sometimes considered to be a subclass of Fischer carbenes, because they are singlets and have π-donor substituents. However, these carbenes are also sometimes taken to form a completely new class of "persistent" carbenes,[30,31] due to their significant stability towards reactions such as dimer formation.[32]

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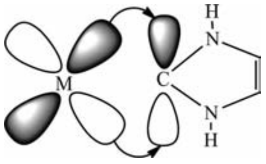
Classically, NHC ligands are well known to be strong σ-donor ligands, with the extent of backbonding due to their π-acceptor character being less well established.[31,33] It must be pointed out that backbonding can only occur if there are occupied d orbitals on the metal atom of appropriate symmetry for interaction with the formally vacant p orbital of the carbene (Scheme 1). In principle, this requirement leads to a significantly anisotropic character to the backbonding, whereas for ligands such as phosphanes, there are two acceptor orbitals, hence d-electron donation is more isotropic, as it can occur with fewer constraints on the relative orientation of the metal fragment and the ligand.[34–36]



Scheme 1. π-Backbonding between the d orbitals of the metal complex and the p orbital of the diaminocarbene.

Nevertheless, over recent years, the π-acceptor ability of NHCs has received considerable attention with several experimental and theoretical studies aimed at characterizing it, which have found it to be appreciable in several cases. This characterization is of considerable importance as the strength of this interaction can have a significant tuning effect on the reactivity of metal complexes.

The IR stretching frequency of CO coligands is one parameter that has been used as an indication of the relative σ-donor/π-acceptor character of the NHCs.[25,26,33,37] This is a natural choice for comparison, given the extensive experience available, e.g. for vibrational frequencies in phosphane complexes of tricarbonylnickel, which give rise to the Tolman electronic parameter (TEP) to measure the electron donor/acceptor character of phosphanes.[38,39] For example, this approach was used for a variety of *fac*-$[Mo(CO)_3L_3]$ complexes, which led to the conclusion that the backbonding ability of NHCs lies between that of nitriles and pyridine and is thereby essentially insignificant.[33] According to the computed TEP for $LNi(CO)_3$ and $LRhCl(CO)_2$, the NHC ligands were significantly stronger σ-donors than phosphanes.[23,40–42]

Another experimental approach is to add a reporter group to the NHC ligand, which has properties that would be expected to vary depending on the extent of backbonding. For example, some Rh^I and Ag^I complexes have been prepared, which bear an NHC imidazolylidene ligand with a fused *p*-quinone moiety in the 4- and 5-positions of the ring. The two carbonyl groups of the quinine are formally conjugated to the vacant p-orbital of the carbene atom. This carbonyl stretching frequency can be studied in the parent complex and electrochemically reduced derivatives. The authors suggested that the frequency shifts observed provide unambiguous evidence for a significant π-backbonding contribution.[43,44] The latter analysis was also extended to diaminocarbene[3]ferrocenophanes and their transition metal complexes.[45] In another report, the NMR resonances of the H atoms in the 4- and 5-positions of an NHC were compared in the free ligand and several metal complexes. An upfield shift was obtained for some Ni^0 and Pt^0 complexes, with a downfield shift for Ag^I and Cu^I complexes. These shifts were interpreted in terms of a loss of electron density upon complexation, which is compensated for, in the case of the nickel and platinum complexes, by backbonding and a resulting increase of the electron density on the diaminocarbene ring.[46] For some $M(CN_2R_2C_2H_2)_2$ ($M = Pd^0, Pt^0$) complexes, photoelectron spectroscopy combined with DFT calculations have been used to assess the π-orbital energies in the free and bound ligands.[47] In this case, the conclusion was that minimal π-backbonding occurred in the complexes, as the bands corresponding to the carbene π-orbitals were practically unperturbed upon complexation. As a final example, *K*-edge X-ray absorption spectroscopy has been used to evaluate the electronic density of the ruthenium center in first- and second-generation Grubbs precatalysts. The analysis suggested that the metal atom has lower electron density in the second-generation NHC complex than in the tricyclohexylphosphane (PCy_3) derivative. This was rationalized though a charge flow analysis based on DFT calculations, which provided information concerning the σ-donor and π*-acceptor character of the ligands based on the charge flow from the highest $4d_{\sigma*}$ Ru orbital to the Ru–L π* orbital. This analysis suggested that the NHC ligand in these complexes is less σ-donating and more π-accepting than PCy_3[48] – an almost diametrically opposite conclusion to the usual picture of bonding for these two classes of ligands.

As well as the experimental and mixed experimental/computational work, many purely computational studies have also addressed this matter. With calculations, there is always a concern about how well the theoretical model reproduces the physical reality, depending on the size of the model (full ligands or models, presence or absence of solvent, etc.) and on the level of theory used. To compensate for this potential weakness, it is possible to use various methods to decompose the overall bonding interaction into terms of different origin, thereby providing, in principle, a breakdown that can pinpoint the precise level of metal–ligand backbonding.

Most of the theoretical studies have used the extended transition state (ETS) method[49] for bonding analysis and, broadly speaking, have thereby suggested that NHC ligands can be significant π-acceptors. In one study of a series of coinage metal complexes in the +1 oxidation state [XAg(NHC), X = F–I: as well as ClM(NHC) and $M(NHC)_2^+$, M = Cu, Ag, Au], the backbonding contribution was found to be not substantially smaller than that in corresponding complexes of classical Fischer carbenes such as $(CO)_5W–C(OH)_2$.[50,51] A similar analysis was used for $Rh_2(O_2CH)_4L$ (L = CH_2 and imidazol-2-ylidene), and the contribution of backbonding to the overall bond energy was found to be 54.2 and 10.6 kcal/mol, respectively,[52] which indicates a significant degree of backbonding. Similar analysis was performed with other Rh complexes: (NHC)RhCl(cod)(X) (cod = 1,5-cyclooctadiene) and (NHC)RhCl$(CO)_2(X_2)$ (X = H, Cl, NO_2, or CN located on the NHC ligand)[53] and for group 10 transition metals.[54] Meyer and co-workers analyzed the π-backbonding for diaminocarbene ligands attached to Cu^I, Ag^I, Au^I, and Pd^{II} by molecular orbital (MO) analysis and the ETS procedure.[55,56] They reported that the π-backbonding contribution to the overall orbital interaction energy was as much as 15–30%.[56] Analogous studies for other metal complexes, such as [Cp(NHC)Ir=CH_2] and $[Cp(NHC)Fe(CO)_2]^+$, reported π-backbonding contributions to the overall orbital interaction term for NHC binding of 20 and 15%, respectively.[57,58] Other reports have described the π-acidity of NHC ligands by showing that the NHC ligands may enhance the Lewis basicity of the metal reactants.[59]

In a recent study of a series of 36 complexes between transition metals and NHCs, Jacobsen and co-workers used a related energy decomposition analysis, the constrained space orbital variation (CSOV) method, to differentiate between the σ- and π-contributions.[60,61] They reported π-contributions of at least 10% of the overall bond energy for all the complexes. In this work the π-contribution was also subdivided into contributions from π-backdonation by the metal atom and π-donation from the ligand to the metal atom. This analysis showed that for a low d-electron count on the metal atom, the latter term can be significant. In a similar vein, Nolan and Cavallo suggested that the π-donating character of NHC ligands contributes to the stability of 14 electron complexes of Rh^{III} and Ir^{III} based on the MO analysis of DFT calculations.[62,63]

Other computational studies do not rely on energy decomposition analyses, but instead involve the theoretical prediction of experimental observables that are expected to correlate with the ligand properties. As well as the work mentioned above for computation of the TEP,[23] CO vibrational frequencies have also been computed for a set of $Cr(CO)_5L$ complexes. As well as investigating the carbonyl vibration frequencies, the force constant for the C–O bond lying *trans* to L was also obtained. Based on these parameters and structural ones such as the Cr–L, Cr–CO_{trans}, and C–O_{trans} bond lengths, the authors argued that backbonding was negligible for the NHC ligands, by comparison to the pattern obtained with other types of carbenes.[64]

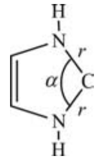
In a study aimed at rationalizing the activity of various $LL'Cl_2RuCH_2$ Grubbs-type catalysts for olefin metathesis, a quantitative structure–activity relationship (QSAR) model was constructed to relate the calculated properties for different ligands to various key energies involved in the catalytic cycle. In this study, one of the descriptors used was the amount of π-electron density transferred from the metal atom to the ligand in the 14-electron LCl_2RuCH_2 fragment based on NBO analysis. Unexpectedly, electron backdonation to the NHC ligands was found to be larger than for all phosphanes except PF_3, with ca. 0.15 electrons transferred to the ligand, vs. only 0.07 for PPh_3 and 0.09 for pyridine.[65] This property was also found to have a significant impact on the metathesis activity predicted by the QSAR model, which in turn agreed quite well with experimental observations.

Although the experimental and computational data available in the literature sheds light on several aspects of the bonding between metals and NHCs, the topic is still not fully understood, and using new theoretical tools in order to refine the theoretical picture can be valuable. Thus, we report new DFT calculations and structural and NBO analyses[66–69] on a variety of metal complexes and suggest that these new analyses provide valuable new insight into the extent of π-backbonding in different environments. We compare the outcome of these analyses to the methods mentioned above, which have been described in the literature. The NBO method, especially second-order perturbative analysis, has been successfully applied to some interesting chemical systems including transition metal complexes,[66] as it can provide an estimate of the strength of secondary bonding interactions, which act as small corrections to the overall bonding picture. This work is complementary to the development of the knowledge base of the ligand[70] and the NBO second-order perturbative energy analysis of metal–ligand backbonding towards YX_3 (Y = P, N, C, Si; X = H, F, Me, Ph, OMe) ligands as well as pyridine and bipyridine.[71] In addition, the knowledge base of the ligand has been extended to carbyne ligands, which allows characterization of different types of carbenes by using a set of properly selected descriptors.[72]

Results and Discussion

We started by analyzing the changes in structure that occur upon binding a reference NHC to a range of metals and other acceptors. Chemical structures arise as a result of a combination of electronic and steric effects, and it has long been known that their detailed analysis can provide a valuable insight into bonding patterns.[73] Small changes in structure were found to be remarkably useful diagnostics for backbonding in metal–phosphane complexes, based both on experimental and computed structures.[74] One-electron oxidation at the metal center of a range of metal–phosphane complexes led to an increase in the M–P bond length. This unexpected change, together with analysis of the change in electron density (finite difference Fukui function), suggests that π-backbonding from the metal atom to the P–R σ*-antibonding orbitals plays a role even in complexes of simple alkyl- and arylphosphanes.[74,75] Structural analysis has been used previously to investigate backbonding in metal complexes of diaminocarbenes. For example, an increase in the C–N bond length of the NHCs upon binding to Au^I centers was suggested to be due to non-negligible backbonding.[76] In various bis(carbene)Pt and -Ni complexes, extended C–N bonds were found together with short M–C distances. However, as shown below, C–N bond lengths alone are not a good diagnostic for backbonding, and a more careful analysis is needed. This analysis is facilitated by considering the response of the σ-donor highest occupied molecular orbitals (HOMO) and π-acceptor lowest unoccupied molecular orbitals (LUMO) of an NHC to changes in its structure.

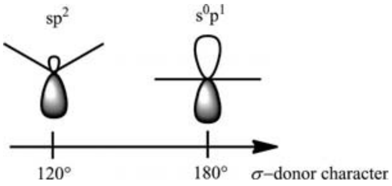
For the parent diaminocarbene, by means of two one-dimensional scans we have independently varied the C–N bond length *r* and the N–C–N angle *α* (Scheme 2) from their equilibrium values, and optimized the other degrees of freedom, thereby computing the B3LYP LUMO and HOMO energies as a function of *r* and *α*.



Scheme 2. Structural parameters of the diaminocarbene (NHC) analyzed in this section: N–C–N angle (*α*) and C–N distance (*r*).

The distance *r* is found to have a linear relationship with the energy of the LUMO, with a correlation coefficient R^2 of 0.9999, for *r* values between 1.410 and 1.450 Å. The linear correlation is of the form $E_{\text{LUMO}} = -0.306r + 0.480$, which shows that the LUMO energy decreases significantly upon extension of the bond. This is expected, as bond lengthening leads to less effective donation of the π-lone pairs on the two nitrogen atoms into the empty p-orbital on the carbon atom. Note that the LUMO and LUMO+1 exchange character near *r* = 1.40 Å, with the π-acceptor orbital on the carbene carbon atom that we discuss as the LUMO for larger values of *r* and the LUMO+1 for smaller values of *r*.

Shorter C–N bonds in a given complex are expected to be due, all other things being equal, to a higher electron demand on the carbon atom and thereby to a greater degree of N→C lone pair donation. In contrast, the HOMO energy is found to vary linearly with the α angle for values between 99.9 and 107.0°. The linear correlation $E_{\text{HOMO}} = 0.0027\alpha - 0.472$ has a correlation coefficient R^2 of 0.9999. This link is slightly less obvious in nature, but it can be explained if one realizes that changes in α lead to changes in hybridization at the carbon atom, with the in-plane lone pair having essentially pure sp^2 character for *α* = 120°. For smaller (or larger) angles, the HOMO acquires greater (or smaller) s character and thereby decreases (or increases) in energy, which explains the positive nature of the correlation (Scheme 3).



Scheme 3. Increasing the N–C–N angle leads to an increase of the p character of the HOMO and hence an increase of the σ-donor character.

What is expected to happen to these orbital energies (and structural parameters) upon interaction with a σ-acceptor such as a metal center? Stronger σ-acceptors will lead to a rehybridization of the donor carbon atom and an increase in *α*. This is due to Bent's rule, which states that the central atom will tend to bond using a hybrid with higher p (or lower s) character in the presence of a more electronegative bonding partner.[77] In turn, the electron density on the donor carbon atom will decrease, which will lead to a smaller *r* value, due to enhanced lone pair donation from the nitrogen atoms. Hence, when bonding to σ-acceptor metal centers, simultaneous changes in *α* and *r* are expected, and on their own, these changes cannot be correlated to backbonding. Upon bonding to metal or other centers that backdonate significant electron density into the carbene acceptor orbital, one might expect that competition will arise between donation from the metal atom and from the nitrogen lone pairs. Hence donation from the latter will be smaller than otherwise expected. This will mean that the change in *α* will be larger than the change in *r*.

To probe this behavior, the value of the N–C–N angle *α* and the C–N bond length *r* were computed at the same level of theory for a range of species involving the parent NHC ligand and various acceptors. The latter included a set of centers expected to be dominantly σ-acceptors, namely H^+, BH_3, BF_3, $AlCl_3$, Na^+, NaCl, $CaCl_2$, $CaCl^+$, and $MgCl^+$. Free optimization of the corresponding complexes led, in some cases, to the motion of a group on the metal center to the carbene carbon atom. To avoid this, all species were restricted to C_s symmetry, with a plane of symmetry bisecting the N–C–N angle of the diaminocarbene. For these reference complexes, a reasonably good linear correlation ($R^2 = 0.965$) was found between the values obtained for *α* and *r*, with the latter decreasing as the former increases, as expected. As might also be expected, the values obtained for the free diaminocarbene (NHC) lie fairly close to the regression line (Figure 1). The correlation is not perfect, perhaps due to other bonding effects that arise in some of these metal centers. For example, the three C–B–H bond angles in the BH_3 adduct are not identical, with the B–H bond that is synperiplanar to the carbene p-orbital being slightly bent towards the carbene (C–B–H 107.5° vs. 107.6° for the other two bonds). This may be due to slight hyperconjugative backbonding to the carbene p-orbital. Such effects prevent the correlation being used in a quantitative way.

The optimized values of *α* and *r* obtained for a range of complexes of the same parent NHC to a range of metal environments typical of recent experimental applications of these ligands are also shown in Figure 1. As well as the metal complexes, two "complexes" are shown in which the imidazolidene carbene is coordinated to an oxygen or sulfur atom. These "complexes" correspond to urea and thiourea, respectively, and serve to represent what happens to *α* and *r* in situations where backbonding is strongly present. In the urea complex, the oxygen lone pair forms a double bond with carbon, and there is also double bond character in the thiourea. As can be seen in Figure 1, these two "com-

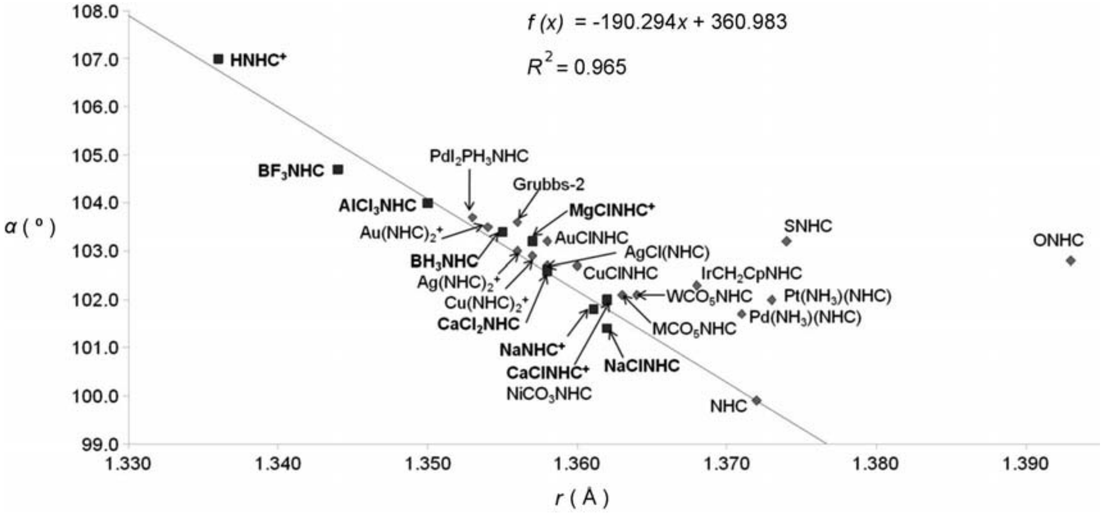


Figure 1. Values of the N–C–N angle *α* [°] and the C–N bond length *r* [Å] for a set of diaminocarbene complexes (grey diamonds). The heavy correlation line is a least-squares fit for the complexes with pure σ-acceptor centers (black squares, labels in bold): $HNHC^+$, BH_3NHC, BF_3NHC, $AlCl_3NHC$, $NaNHC^+$, NaClNHC, $CaCl_2NHC$, $CaClNHC^+$, and $MgClNHC^+$. The bare carbene NHC, as well as the "complexes" ONHC and SNHC have been added for reference. MCO_5NHC (M = Cr and Mo), $NiCO_3NHC$ and $CaClNHC^+$ are located at the same position.

plexes" deviate strongly from the linear correlation found in complexes of σ-acceptors, with the C–N bond length found to be much longer than one would expect based on the change in angle with respect to the free ligand. This is the type of deviation that would be expected to occur in the presence of backdonation, as stated above.

The positions corresponding to the metal complexes might therefore be expected to provide an indication of the strength of backbonding. Deviations above the line formed by the complexes with the σ-acceptors can be attributed to backbonding, and deviations below the line would not be expected to occur. This second prediction is indeed confirmed, with none of the species studied displaying a significant negative shift with respect to the line. In contrast, several complexes show positive shifts, much smaller in magnitude than found for the urea complex, as one would expect given that urea contains a formal C=O double bond. In fact, this method of analysis is quite a blunt instrument, as the σ-acceptor-only linear correlation is not perfectly linear. Hence only quite large deviations from the linear correlation, hence large backbonding interactions, can be ascribed to backbonding with confidence. It is therefore remarkable that some of the complexes discussed here deviate positively from the linear correlation. The variation in the magnitude of the shift with respect to the nature of the metal center is interesting and is discussed below separately for each type of complex.

The first group of complexes are coinage metal monocationic dicarbene complexes $M(NHC)_2^+$ (M = Cu, Ag, Au). The results shown correspond to computed geometrical parameters for D_{2d}-symmetric species. As found previously at the BP86/TZ2P level of theory, the D_{2d}-symmetric structures are slightly more stable than the corresponding D_{2h}-symmetric species ($\Delta E \leq 0.5$ kcal/mol).[51] Moreover, the D_{2h} species presented one imaginary frequency, although small in magnitude. Based on the results shown in Figure 1, the amount of backbonding in these cationic complexes is rather small, as they fall nearly on the correlation line found for nonbackbonding acceptor centers.

Next, we considered the three related M^I coinage metal complexes ClM(NHC) (M = Cu, Ag, Au). The silver species falls again on the correlation line, but there is a slight shift in both the copper and gold cases. This might be evidence for some weak backbonding, with a pattern within the series that is not trivial to account for.

The next interesting case is the Ni^0 species $Ni(CO)_3(NHC)$. Here, the metal atom is quite electron-poor due to the presence of three carbonyl groups, and again, despite the absence of a real or formal charge, the evidence for backbonding is weak – though it can be noted that this complex lies less far along the correlation line; so $Ni(CO)_3$ is apparently a weaker σ-acceptor than the coinage metal $M(NHC)^+$ fragments. In the tungsten complex $W(CO)_5(NHC)$, there is a small positive deviation, which may perhaps indicate more effective backbonding from 5d-orbitals than the more compact 3d-orbitals in the nickel species. A final example of a complex showing a small deviation is the Pd^{II} complex $PdI_2(PH_3)(NHC)$, which again indicates no notable backbonding interaction.

In contrast, the electron-rich Pd^0 and Pt^0 species $(H_3N)Pd(NHC)$ and $(H_3N)Pt(NHC)$ all show deviations from the correlation line that cannot easily be explained in any other way than by significant backbonding. These species involve a low oxidation state of the metal atom and a significantly electron-donating ancillary ligand such as ammonia. The present structural argument provides strong evidence for significant backbonding in these cases. Although no indication is given as to the energetic consequences of this backbonding, the use of structural arguments to simply establish that an interaction exists is valuable and common, e.g. for phosphanes.[75]

A final intriguing pair of examples are [(Cp)(NHC)-Ir=CH_2] and the model second-generation Grubbs catalyst [$(PH_3)(Cl)_2$(NHC)Ru=CH_2] (labeled Grubbs 2 in Figure 1). These are closer to complexes with significant experimental interest. In the first, the structural argument suggests a very significant π-backbonding contribution. This is supported by previous calculations using energy decomposition analysis, in which the π-backbonding contribution to the bond energy was estimated as 21.2 kcal/mol, i.e. 20% of the total orbital interaction energy.[57] The Grubbs 2 species has been suggested to display weak backbonding.[57,78] These compounds both involve metal centers with formal oxidation states higher than 0, which suggests that such high oxidation states do not preclude backbonding, providing that an electron-rich metal center is involved.

As already mentioned in the case of the iridium species, some of the complexes discussed here have been analyzed by other techniques. Frenking and co-workers have studied ClM(NHC) (M = Cu, Ag, Au) by charge decomposition analysis (CDA) in MP2/DZP calculations.[79] They reported a π-contribution much smaller than the σ-donation. In the case of the gold complex, the π-contribution was slightly more important, which was justified by relativistic effects. They also performed NBO calculations, which indicated an enhancement in the population of the p(π) orbital of the NHC carbon atom. They suggested that the increase was due to N→C donation based on the increase of the bond order in the C–N bond compared to that of the free carbene. From their point of view this N→C donation would explain the decrease of the C–N length in the metal complexes in comparison with the C–N distance in the free carbene. They used the decrease in the C–N bond length in the $HNHC^+$ complex as complementary proof. In our fragment analysis we have also seen a decrease of the C–N bond length in comparison with the free carbene for the $HNHC^+$ complex as well as for the different σ-acceptors and metal complexes (Figure 1).

NBO Analysis

The second part of our study attempts to provide a more quantitative assessment of the importance of backbonding, and for this we used NBO analysis as in previous work on phosphane complexes.[71] NBO analysis is based on a method for optimally transforming a given wavefunction into a localized form, corresponding to one-center (lone pair), two-center (bond), and three-center (delocalized bond over three atoms) terms. Deviations from the reference electronic structure, in terms of electron pair donation into vacant orbitals, can be used to assess the importance of weaker interactions. Here, NBO second-order perturbative energy analysis was used to compute the energy contribution of backbonding interactions (ΔE_{bb}) towards NHC ligands in most of the transition metal complexes involved in the structural study and for the CH_2 ligand in $W(CO)_5$-(CH_2) and $Cr(CO)_5(CH_2)$, which have been added for comparison. Recently, the nature of the transition metal–carbene bond in Grubbs olefin catalysts has also been studied by means of NBO calculations.[80]

The magnitude of the backbonding was determined by examining the interactions between filled donor Lewis-type NBOs and empty acceptor non-Lewis-type NBOs, which estimates their energetic importance by means of second-order perturbation theory. This method can be applied, because there are only relatively small deviations from the idealized Lewis structure for the NHC complexes. For each donor (*i*) and acceptor (*j*), the stabilization energy *E*(2) associated with delocalization $i \rightarrow j$ is estimated as

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon j - \varepsilon i}$$

where q_i is the donor orbital occupancy, εi and εj are the diagonal elements (orbital energies), and $F(i,j)$ is the off-diagonal NBO Fock matrix element.

In the calculations, it was necessary to specify the reference Lewis structure in order to obtain a constant reference and hence a meaningful comparison from one complex to another. The reference structure chosen was not usually the default one obtained by the program, but the amount of the electron density accounted for by the reference structure was always high. The *trans* pairs of ligands in linear, square-planar, and octahedral metal complexes have mostly been described as three-center four-electron bonds (ω-bonding). This reference electronic structure was also used to describe the π-bonding within the N–C–N array of atoms of the diaminocarbene ligand. The latter has already been described elsewhere as a three-center four-electron bond.[81] In the complexes containing halide groups *trans* to other ligands, it proved difficult to force the program to treat these bonds within the three-center four-electron bond formalism, and an ionic description was used instead. This means that the halide was treated as a nonbonded anionic species (e.g. Cl^-, Br^-, I^-) and the bonds *trans* to the halides were considered as single bonds. The necessary, if somewhat arbitrary, choice of a reference configuration, and the dependence of the second-order stabilization energies on the choice made, mean that the values obtained here cannot be considered to be exact measures of the strength of backbonding. Nevertheless, the consistent approach used in choosing the reference does mean that the results should be semiquantitatively reliable. For reference, we have also computed the energy of the fragments obtained from breaking the metal–NHC bond and hence obtained a calculated bond energy at the same level of theory. This provides some insight into the relative contribution of backbonding to the overall bond energy.

We started with $M(CO)_5CH_2$ (M = Cr, Mo, W). These complexes are experimentally not stable[82] but provide a useful reference for the behavior of Fischer carbenes. The CH_2 ground state is a triplet, with the experimentally reported value of the singlet–triplet splitting of 9.0 kcal/

mol.[83,84] This suggests the formation of two covalent bonds to an M^{II} center in the complex. Nevertheless, CH_2 can also be described as a neutral, singlet ligand. This choice was somewhat artificial for these complexes and led to a very large formal backbonding contribution to the bonding in terms of electron donation from a metal d-orbital to the empty p-orbital on the carbene. In $W(CO)_5(CH_2)$, the bond energy was decomposed by Ziegler and Frenking using the ETS procedure in DFT calculations. Ziegler reported a π-contribution of 52.8 kcal/mol (221 kJ/mol),[85] and a similar value (58.7 kcal/mol, 53.6% of the total orbital energy) was reported by Frenking.[86]

For $M(CO)_5(CH_2)$ (M = Cr, Mo, W), we found high backbonding contributions of 150.5, 219.7, and 511.7 kcal/mol, respectively. These large values are clearly beyond the perturbative regime for which this NBO analysis can be considered to be reliable, hence are of little quantitative value. This result can be rationalized by the poor description of the metal–CH_2 interaction as involving simple acceptor–donor bonding with a singlet carbene fragment. The interaction is better described as a double bond between the metal center and the CH_2 ligand.

Encouragingly, the results of the NBO analysis broadly follow those obtained based on the structural analysis. The coinage metal M^I complexes $M(NHC)_2^+$ and ClM(NHC) show small values for the backbonding interaction, in most cases of less than 10 kcal/mol. The largest value of 12.9 kcal/mol is obtained for AuCl(NHC), which also shows the largest structural deviation from the linear correlation. Although the values for these compounds are smaller than those for the other species, it is notable that the contribution is not zero. This is in line with previous theoretical analyses of the same compounds. The values shown in Table 1 are similar to those obtained for the ΔE_π contribution to bonding in energy decomposition analysis calculations carried out by Frenking and co-workers for the same species, which are also of the order of 10 kcal/mol or less.[51] In that study, the largest contribution was obtained for AuCl(NHC), with calculated ΔE_π backbonding values for the copper, silver, and gold chloride NHC complexes of –12.3, –7.3, and –13.2 kcal/mol, respectively.

Table 1 also includes the overall calculated charges on the NHC ligand. These are positive in all cases and mainly reflect the strong σ-donor character of the ligand. It is more difficult to detect a trend between the magnitude of the backbonding contribution and the calculated charge. For example, in AuCl(NHC), the charge on the NHC ligand is more positive than in the corresponding silver complex, yet the strength of the backbonding is computed to be larger. This suggests that the strength of the backbonding is sensitive and depends on the overall binding properties of the complex. All things being equal, it would appear that stronger σ-donation may lead to stronger backbonding.

For the tetrahedral $Ni(CO)_3(NHC)$ complex, the small backbonding contribution (3.9 kcal/mol) obtained from the NBO analysis is consistent with the low backbonding structural distortions found for this complex. In contrast, for the group 6 d^6-NHC complexes, $M(CO)_5(NHC)$, the calculated contribution for the backbonding is larger, especially for the tungsten complex, which also showed a noticeable deviation from the structural linear trend. Frenking et al. have calculated backbonding energies based on energy decomposition analysis for the same species of between 7 and 9 kcal/mol.[51] The backbonding in these complexes has also been studied by other groups by the CSOV method.[60,87] For $Cr(CO)_5(NHC)$, we obtained a similar result (8.8 kcal/mol); however, for the W complex we found a significantly higher value of 21.3 kcal/mol[59] and a slightly higher value for the Mo complex of 14.1 kcal/mol.

As found in the structural study, the largest backbonding components are found for the electron-rich species $(H_3N)M(NHC)$ (M = Pd, Pt). In these complexes, the σ-donating ammonia ligand raises the energy of the d-orbitals on the metal atom, making them even more strongly donating towards the NHC. For the platinum compound, the backbonding component of bonding obtained from the NBO perturbative analysis is found to be almost half of the total calculated bond energy, which indicates that diaminocarbene ligands really can accept very significant electron density from the metal center in very electron-rich species. These observations are consistent with previous experimental and computational work on some Pt^{II} complexes, for

Table 1. NBO overall charge of the NHC ligand, bond dissociation energy (BDE), and backbonding for the different complexes.

Complex	NBO charge	BDE [kcal/mol]	Backbonding [kcal/mol]	Contribution from backbonding in BDE [%]
$Cu(NHC)_2^+$	0.247	82.9	5.2	6.3
$Ag(NHC)_2^+$	0.275	74.4	4.4	5.9
$Au(NHC)_2^+$	0.340	92.7	9.0	9.7
$(AuNH_3NHC)^+$	0.411	110.4	10.0	9.1
CuClNHC	0.168	67.9	7.8	11.5
AgClNHC	0.205	58.3	6.1	10.5
AuClNHC	0.268	79.4	12.9	16.2
$NiCO_3NHC$	0.122	76.3	3.9	5.1
$CrCO_5NHC$	0.410	52.8	8.8	16.7
$MoCO_5NHC$	0.343	54.2	14.1	26.0
WCO_5NHC	0.318	59.4	21.3	35.9
$PtNH_3NHC$	0.252	81.2	31.5	38.8
$PdNH_3NHC$	0.229	58.6	17.9	30.5
$RuCl_2(PH_3)(CH_2)(NHC)$	0.410	57.4	10.2	19.0
PdI_2PH_3NHC	0.353	65.5	7.6	11.6

which NMR spectroscopy and an energy decomposition analysis (EDA) have suggested a large backbonding contribution.[88]

Finally, the computed values in the square-planar $PdI_2(PH_3)(NHC)$ complex and model Grubbs metathesis precatalyst are also much larger than zero, but more modest than for the Pd^0 and Pt^0 cases, as expected from the structural analysis. Attempts to calculate the backbonding contributions in $Ir(CH_2)Cp(NHC)$ were thwarted by the fact that it was not possible to select an appropriate Lewis reference structure to describe the metal–Cp bonding.

Overall, the calculated NBO values for the backbonding component for the NHC binding to metal centers were found to be remarkably similar in magnitude to those obtained previously[71] for phosphane ligands. Indeed, the results obtained for $Cr(CO)_5(L)$ and $Mo(CO)_5L$ suggest that the NHC ligand may be a better π-acceptor than simple phosphanes such as PH_3 or PPh_3, for which NBO contributions of much less than 10 kcal/mol were obtained vs. the value of 14.4 kcal/mol obtained here for $Mo(CO)_5(NHC)$. At first sight this rather counterintuitive result can perhaps be explained by considering that the NHC ligand is also a much stronger σ-donor, so the metal center is more electron-rich.

In the NBO formalism, the magnitude of the backbonding is due to the energy difference between the donor and acceptor orbitals and $F(i,j)$. This term is a resonance integral which measures the gain in energy by sharing electrons between orbitals i and j, which can roughly be interpreted as being due to the extent of the spatial overlap between these orbitals. These two values are collected in Table 2 and provide an interesting additional insight into the trends observed. The magnitude of the backbonding energy contribution [$E(2)$] is repeated in Table 2 for convenience.

Table 2. Total second-order perturbative interaction between metal d-orbitals and the three-center four-electron antibonding orbitals of the NHC (3C*) [$E(2)$], energy of the donor ($\varepsilon_{\text{donor}}$) and acceptor ($\varepsilon_{\text{acceptor}}$) orbitals, the energy difference ΔE, and the off-diagonal NBO Fock matrix element [$F(i,j)$]. All the values are in kcal/mol.

Complex	$E(2)$	$\varepsilon_{\text{donor}}$	$\varepsilon_{\text{acceptor}}$	ΔE	$F(i,j)$
$Cu(NHC)_2^+$	5.2	–252.5	–71.8	182.0	22.6
$Ag(NHC)_2^+$	4.4	–285.4	–69.2	213.4	22.6
$Au(NHC)_2^+$	9.0	–275.5	–75.5	200.8	30.7
$(AuNH_3NHC)^+$	10.0	–291.1	–88.8	200.8	32.6
CuClNHC	7.8	–166.0	–6.5	156.9	25.7
AgClNHC	6.1	–200.5	–7.0	194.5	25.1
AuClNHC	12.9	–191.9	–12.6	182.0	35.1
$NiCO_3NHC$	3.9	–148.4	11.6	163.2	17.6
$CrCO_5NHC$	8.8	–103.4	7.5	113.0	23.8
$MoCO_5NHC$	14.1	–90.3	7.2	100.4	28.9
WCO_5NHC	21.3	–79.0	3.5	81.6	33.3
$PtNH_3NHC$	31.5	–101.0	24.9	125.5	45.2
$PdNH_3NHC$	17.9	–100.4	39.9	138.1	36.4
$RuCl_2(PH_3)(CH_2)(NHC)$	10.2	–149.0	12.9	163.2	28.9
PdI_2PH_3NHC	7.6	–180.8	2.6	182.0	27.0

Analysis of the donor and acceptor orbital terms provides further insight into the respective properties of NHC and phosphane ligands. We discuss here only the data for $M(CO)_5(L)$ (M = Cr, Mo), for which previous results were reported by using NBO analysis for the PH_3 ligand. In the PH_3 complexes, backbonding is calculated by the NBO analysis to contribute only 4.4 and 8.7 kcal/mol, and this involves donation from two different d-orbitals into two different linear combinations of σ*-acceptor orbitals on the phosphane. The corresponding values for the NHC complexes are of 8.8 and 14.1 kcal/mol, respectively, which involve a single acceptor orbital on the NHC ligand. This is partly due to a higher-lying d-orbital in the NHC complexes (–104 kcal/mol vs. –120 kcal/mol for the Cr complexes, and –90 kcal/mol vs. –109 kcal/mol for Mo).[71] This reflects the strong σ-donor character of the NHC complex, which drives the d-orbitals higher in energy. However, a more important factor appears to be the much lower energy of the acceptor orbital, which is close to zero in both NHC complexes, yet is above 100 kcal/mol in the phosphane complexes.[71] If one accepts that the σ-donation is very strong, then the NHC has a formal positive charge, and the acceptor orbital will be reduced in energy compared to the free ligand. Finally, it appears that there is also better overlap between the acceptor and donor orbitals, with the off-diagonal matrix element equal to 24 and 29 kcal/mol, respectively, for the NHC complexes vs. 13 and 16 kcal/mol for the phosphane complexes.

The data in Table 2 enable many other trends relating to the strength of backbonding to be investigated. The charged $M(NHC)_2^+$ species (M = Cu, Ag, Au) involve less backbonding than the neutral MCl(NHC) analogues, due to a larger gap between the donor and acceptor orbitals. The M^0 Pd and Pt species have rather small ΔE values, hence large backbonding effects, which is also due to favorable overlap between the donor and acceptor orbitals. Periodic trends are also of interest: $AuNH_3NHC^+$ involves much less backbonding than its d^{10}-analogue $PtNH_3NHC$, which is expected given the higher oxidation state and the charge on the metal atom. First-, second-, and third-row transition metals lead to quite different backbonding magnitudes. In the two coinage metal series shown in Table 2, the orbital gap is largest for the silver compound, hence this has the weakest backbonding. The overlap matrix element is much larger for the gold species, probably due to relativistic effects, hence this has the largest backbonding. A different trend is found for $M(CO)_5(NHC)$ (M = Cr, Mo, W), where there is the complicating factor that the NHC ligand is competing with the much more strongly accepting carbonyl ligands. Here also, the overlap matrix element is greatest for the larger tungsten atom, but in this case, the chromium species shows the smallest backbonding, perhaps due to greater electron donation to the carbonyl ligands.

Comparing the results from the NBO analysis with those obtained from the structural study reveals that neither can be expected to yield a fully quantitative insight. For example, the NBO-derived backbonding in $W(CO)_5(NHC)$ (21.8 kcal/mol) is larger than that found for $Pd(NH_3)(NHC)$ (17.9 kcal/mol). Yet the deviation of the C–N bond length and N–C–N angle from the "donor-only" trend line is larger in the palladium compound. It is tempting to conclude that these contradictory results reveal the limitations of the structural analysis. Indeed, the main virtue of this approach, as stated above, is that it provides evidence for backbonding, which is independent of the need to decompose the total energy expression for the system into different contributions.

A recent study has also analyzed the backbonding in $Cl_4M(NHC)$ (M = Ti, Zr, Hf), $M(CO_5)(NHC)$ (M = Cr, Mo, W), $[(CO)_4M(L)]$ (M = Fe, Ru, Os), and ClM(NHC) (M = Cu, Ag, Au) by EDA. The π-contribution was found to be significant, which is in agreement with this work.[59] It was determined that the backdonation played a major role in the π-interactions with percentages increasing with the increasing number of electrons in the d-metal orbitals. A similar trend was found by Jacobsen and co-workers with the CSOV method.[60,61]

Conclusions

Through structural and NBO second-order perturbative energy analysis, the metal-to-diaminocarbene backbonding in metal complexes has been studied. The structural analysis was based on an observed linear trend between the computed N–C–N angle and the C–N bond length in a series of complexes between NHCs and a range of dominantly σ-acceptor centers. In other complexes, in which backbonding can occur, it is argued that increased backbonding will correlate with larger values of either the bond length or the angle compared to the linear trend based on orbital arguments. Indeed, for some of the more electron-rich metal complexes, significant deviations were observed, which provide unambiguous structural support for substantial backbonding interactions in NHC complexes. In principle, this analysis could be repeated by using experimental values of the structural parameters, e.g. from crystallographic databases, although the level of resolution needed to identify the smaller effects is probably higher than could be easily obtained, bearing in mind packing effects and other likely perturbations.

The second analysis performed provides quantitative insight into the contribution of bonding, which was chemically rationalized by the energy difference between localized donor orbitals on the metal atom and the acceptor π-orbitals on the NHC ligand and the overlap matrix element. This NBO perturbative analysis, which was previously shown to give chemically reasonable values for phosphane, amine, and other ligands,[71] requires careful selection of the reference configuration in order to give meaningful results.

The backbonding contribution calculated in this way was found to be significant, comparable or indeed larger than that obtained with phosphanes, in agreement with previous work by using other methods that also found significant M→NHC backbonding.[51–61,78,79,87,88] It also strongly depends on the metal, the ancillary ligands, and the geometric environment. Thus, for all the complexes studied, the backbonding takes values from 3.9 $[Ni(CO)_3(NHC)]$ to 31.5 kcal/mol $[Pt(NH_3)(NHC)]$, although most of the values are within the range 5–20 kcal/mol. For example, the second-generation Grubbs catalyst $RuCl_2(PH_3)(CH_2)(NHC)$ has a value of 10.9 kcal/mol. As found previously for phosphane complexes, third-row complexes have higher backbonding contributions than first- and second-row analogues, which is a reflection of the relativistic d-shell expansion.

In conclusion, both the structural analysis and the NBO calculations confirm that backbonding is quite strong in diaminocarbene complexes: in many cases, these ligands act not as pure σ-donors but also as π-acceptors to quite a significant degree. Our study also provides insight into the factors that can determine the strength of backbonding, such as the electron-rich character of the metal center, the nature of the ancillary ligands, and the energy difference and overlap between the donor (metal) and acceptor (carbene) orbitals.

Computational Details

All the calculations were carried out with the Gaussian 03 program package.[89] Full geometry optimization was carried out for all species by using the hybrid DFT B3LYP functional.[90–92] The standard 6-31G* basis set was used for all the main-group elements except for iodine, where the cc-VZP-PP core potential and associated basis set was used.[93] For the metals the Stuttgart pseudopotential and its associated basis set were employed.[94,95]

Second-order perturbative NBO analysis was used to estimate the metal–ligand backbonding contribution (ΔE_{bb}). The analysis was carried out on geometries reoptimized with the Jaguar program[96] also using the B3LYP functional. No significant structural changes were observed after the reoptimization. For the metal atoms and iodine, the Los Alamos relativistic pseudopotential was used to represent the core electrons [for metals, all but the valence *n*d and (*n* + 1)s and outer core *n*s and *n*p electrons]. Valence electrons were described with a triple-zeta contraction of the original double-zeta basis set (LACV3P). For the main elements the 6-31g* basis set was used.[97–99]

For the NBO perturbative analysis, the same correct reference configuration must be obtained for all species, so that perturbative corrections obtained for different complexes can be compared to one another. The reference configuration was specified manually, and the output checked to ensure that it had been correctly used. In some cases, it proved impossible to generate a reference configuration with the desired nature, hence for these systems analysis cannot be carried out. All filled metal d-orbitals were treated as occupied, lone-pair donor orbitals. For the simple carbene, CH_2, the empty valence orbital on the carbon atom was used as the acceptor orbital for the CH_2 ligand. For the diaminocarbene ligands, the specified reference configuration included a three-center four-electron π-interaction (or ω-bond)[100] within the N–C–N array. Two of corresponding π-orbitals are occupied, with the third, which is completely antibonding and largely located on the carbon atom, treated here as the acceptor orbital. The reported energy terms are a sum of all contributions arising between the donor and acceptor orbitals as specified here.

Supporting Information (see footnote on the first page of this article): Optimized geometries and NBO details for all species.

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