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Theoretical NMR spectroscopy of N-heterocyclic carbenes and their metal complexes

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Abstract. Recent theoretical analysis of the NMR properties of free N-heterocyclic carbenes (NHC) and Metal-NHC complexes has complemented experiments, allowing the establishment of structure/property relationships and the rationalization of otherwise surprising experimental results. In this review, the main conclusions from recent literature are discussed, with the aim to offer a vision of the potential of theoretical analyses of NMR properties.

Keywords. N-heterocyclic carbenes; density functional theory; nuclear magnetic resonance; π -acidity; σ -donicity; paramagnetic shielding.

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1. Introduction

The rational design of new catalytic systems requires detailed knowledge of the reaction pathways and intrinsic properties of catalysts in order to directly relate these properties with the catalytic behavior. From this point of view, computational techniques can provide a valuable contribution, since they allow for detailed characterizations of both. Modeling mechanistic pathways is now common and has broad applications in both metal and organo-based catalysis. On the other hand, achieving a good understanding of the fundamental features of catalysts to establish clear structure/property relationships with predictive power is definitely more challenging. The most used conceptual scheme in rationalizing catalysis is quantitatively correlating the catalyst behavior to steric and electronic properties of the catalyst components using ad hoc descriptors. Several descriptors have been proposed in the literature to quantify the steric properties of catalysts, and among the most popular are the Tolman cone angle [1], the sterimol parameters [2, 3], and the buried volume [4-6]. For modeling electronic properties, the situation is more complex, since influences of the electronic structure of the catalyst on the catalytic behavior can have different origins [7]. In this scenario, it is not surprising that the number of electronic descriptors capable of rationalizing catalytic behavior (such as nucleophilicity and electrophilicity indexes or the Tolman electronic parameter [1, 8, 9]) is large and that specific computational tools are capable of capturing different aspects of catalysts. Among the available computational tools, the theoretical analysis of NMR properties is extremely powerful due to the possibility of directly correlating theoretical calculations with experimental measurements. In addition, theoretical NMR analysis allows for the achievement of a thorough understanding of the origin of NMR chemical shifts, offering a unique perspective on the electronic structure of catalysts. One class of molecules that has been analyzed recently by this computational tool is N-heterocyclic carbenes, NHCs, which have a prominent role as ligands in metal-based catalysts, as well as organo-based catalysts.

NHCs are, without a doubt, the class of molecules that has attracted the most attention in the last twenty years, since the isolation and crystallographic characterization of the first stable NHC in 1991 [10]. The main reason for their success in catalysis is their superior or unique properties as ligands, offering an alternative to classic phosphines

[11]. NHCs have a very modular structure that allows for the fine tuning of their steric and electronic properties, see Chart 1. The electronic structure of NHCs can be tuned almost at will by changing the nature of the heterocyclic ring or its substituents, while the steric requirements can be strongly tuned by the nature of the N-substituents [8, 12-21].

Chart 1. Common 5-membered NHCs and the modular structure of NHCs.

In this review, we briefly describe insights provided by theoretical analysis of the NMR properties of NHCs. All the results that will be described in the next sections are based on density functional theory, DFT, as it is the main computational scheme for electronic structure calculations – we will thus refer to the computational tool as DFT-NMR. This review starts with a brief description of the electronic structure of NHCs and the metal-NHC bond, in section 2. This section reviews quite well established knowledge [14, 22-24]; however, we included it here to have a self-consistent contribution. Section 3 is devoted to introducing the most basic concepts needed to understand the remainder of the review. The discussion will not be exhaustive, as there are many excellent reviews on the subject, and we refer the interested reader to them [25-29]. Section 4 reports on the electronic structure properties of free NHCs from an NMR perspective, as the basis to understand the magnetic properties of metal-NHC complexes. Sections 5 and 6 are devoted to describing insights into the π and σ metal-NHC bonds through analysis of the NMR data of atoms bonded to the carbene C atom of NHC. Sections 7 and 8 are devoted to describing the impact of variations in the electronic and geometric features of the complexes on the magnetic response of the metal-NHC complex. Section 9 reports an extension of the analysis of the metal-NHC bond to the metal-alkylidene bond in order to show that the concepts introduced to rationalize the magnetic properties of metal-NHC complexes are general and have much broader applicability.

2. Electronic structure of NHCs and the metal-NHC bond

NHCs are usually described as classic σ -basic/ π^* -acidic ligands [14, 22] having the frontier molecular orbital (MO) pattern shown in Figure 1. The MO corresponding to the carbene lone pair usually is the highest occupied molecular orbital (HOMO) and confers σ -donicity behavior to the NHC [23, 24]. The pattern of the π MOs is more complex and depends on the nature of the backbone, see Figure 1, as well as on the presence of a 3rd N atom, as in triazoles, see again Figure 1. One of the lowest unoccupied molecular orbitals (LUMOs) usually corresponds to a π^* MO strongly localized on the carbene atom, see Figure 1, and confers π -acidity behavior to the NHC [12, 19, 30, 31]. Filled π MOs are usually lower in energy than the carbene lone pair and confer weak π -donicity character to the NHC [16].

Figure 1. Frontier molecular orbitals of typical NHC skeletons.

The interaction between an NHC and a metal center can be rationalized by considering the diagrams shown in Figure 2. The NHC donates electron density from the high-energy HOMO to an empty orbital on the metal (σ -donicity), see Figure 2a. At the same time, the NHC can accept electron density from the filled d orbitals of the metal (π -acidity) via a classic $d \rightarrow \pi^*$ back-donation scheme, see Figure 2b. Finally, for electron-deficient metals, the NHC can also donate electron density from its filled π orbitals to the empty d orbitals of the metal (π -basicity) via a $\pi \rightarrow d$ donation scheme, see Figure 2c.

Figure 2. Diagram illustrating: the $\sigma \rightarrow d$, $d \rightarrow \pi^*$ and $\pi \rightarrow d$ bonding interactions between an NHC and a transition metal, parts a-c, respectively.

3. Basic concepts for the theoretical rationalization of NMR data

Before discussing in detail how NMR-DFT can be used to shed light on NHC and Metal-NHC structures, we briefly recall the main features needed to understand the calculation of NMR properties via DFT (or any other electronic structure calculation scheme). The following discussion is not exhaustive, and we refer the interested reader to more detailed work in the field [25-29, 32, 33]. We start by recalling that the magnetic shielding tensor, σ , can be expressed as the second derivative of the energy of the

molecule, E , with respect to the magnetic moment of a nucleus, μ , and an external magnetic field, B , as in Eq. 1.

$$\sigma = \left(\frac{\partial^2 E}{\partial \mu \partial B} \right)_{\mu=B=0} \quad \text{Eq. 1}$$

The magnetic tensor σ is a non-symmetric 3×3 tensor, whose trace, $\sigma_{\text{iso}} = 1/3 (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, is the isotropic magnetic shielding of the nucleus. The chemical shift of a nucleus is then defined as $\delta_{\text{sample}} = \sigma_{\text{ref}} - \sigma_{\text{sample}}$, where σ_{ref} is the magnetic shielding constant of the reference and σ_{sample} is the magnetic shielding constant of the sample [34]. In addition to the chemical shift, NMR-DFT calculations allow for the decomposition of the total magnetic shielding, and thus the chemical shift, into paramagnetic and diamagnetic terms, $\sigma_{\text{iso}} = \sigma_{\text{d}} + \sigma_{\text{p}}$. The diamagnetic term of the shielding constant depends only on the unperturbed electron density in the ground state. We recall that the diamagnetic components in NHCs are positive and contribute to the shielding of the nucleus. In contrast, paramagnetic components in NHCs are negative and depend on both occupied-occupied and occupied-virtual couplings between molecular orbitals, induced by the external magnetic field. The paramagnetic term can be correlated to the ability of the external magnetic field to create a circulation of electrons through the molecules. The induced current density moves in a plane perpendicular to the external magnetic field, generating an induced magnetic field that adds to the external one, resulting in deshielding, or a downfield shift. Since transitions between occupied orbitals usually have a negligible impact on the variation of the chemical shielding of NHCs, attention is normally focused on transitions between occupied and virtual orbitals, which are the most relevant to explain variations in σ_{p} for NHCs. The two orbitals must be properly connected by symmetry, which means they have to overlap after a 90° rotation induced by the external magnetic field. In the case of NHCs, these two orbitals essentially correspond to the HOMO lone pair that can overlap, by a rotation of 90° around the y-axis, with the empty MO corresponding to the π^* orbital centered on the carbene C atom, see Figure 3. The deshielding is along the rotation axis, i.e., perpendicular to the plane defined by the two orbitals involved in the transition. Furthermore, it is inversely related to the energy gap between these two orbitals, and it is directly related to the overlap between the two orbitals after rotation [28, 35]. Thus, correlation of the

paramagnetic term to the molecular properties should focus on these two factors, which affect the paramagnetic shielding.

Figure 3. Schematic representation of the origin of the paramagnetic deshielding in NHCs.

4. Characterization of free NHCs

As reported in the Introduction, the isolation of stable and “bottable” NHCs [10] opened the route to a new research area, with applications in a wide range of organic [36-39] and metal-organic [11, 40, 41] reactions. Together with the explosion of works on the synthesis of many structurally different carbenes, significant effort has been dedicated to understanding and rationalizing the unique properties of these molecules [12, 30, 42, 43]. Initially, many attempts were dedicated to the characterization of free carbenes by using different experimental approaches [44-57]. Among the approaches, solid state NMR is one of the most successful techniques to obtain structural information on closed shell species, since in addition to the chemical shift, it allows for the proper characterization of the anisotropy of the magnetic shielding. However, along with experimental investigations, theoretical work has been highly useful for two main reasons: a) the possibility to analyze a wide number of different systems, preventing long and tedious experiments, and b) the ability of computational techniques to reach a detailed understanding and rationalization of the experimental results. Of course, before gaining any predictive power, computational approaches require a benchmark versus the experimental data.

During the 1980s, experimental measurements provided the chemical shifts of a series of free carbenes obtained from the deprotonation of the corresponding azolium salts with strong bases, offering an important source to test and refine computational protocols [58]. To this extent, the chemical shifts for this series of carbenes, see Chart 2, have been reproduced using a DFT approach. The possible theoretical protocols

essentially differ in the functional and the basis set used to obtain the molecular geometry and describe its electronic structure. DFT results at the B3LYP/6-31G* level [59, 60], which performs relatively well in the prediction of the chemical shifts of many organic molecules [61], are reported in Table 1 [62]. Comparison of the experimental and DFT isotropic magnetic shielding, σ_{iso} , and of the components of the magnetic shielding tensor, σ_{xx} , σ_{yy} and σ_{zz} , for **3** clearly indicates that DFT can predict ^{13}C solid state NMR properties of carbenes with an accuracy of a few ppm for the carbene C atom [63-65].

Chart 2. Schematic representation of the carbenes investigated by experimental and theoretical NMR analysis.

Table 1. Isotropic magnetic shielding, σ_{iso} , and magnetic shielding tensor components, σ_{ii} , for free carbenes from ref. [62]. $\sigma_{\text{iso}} = 1/3 (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.

	σ_{iso}	σ_{xx}	σ_{yy}	σ_{zz}
$:\text{CH}_2^{\text{b}}$	-1154.1	-284.8	-3377.7	200.3
$:\text{CF}_2^{\text{b}}$	-104.5	34.3	-387.7	39.9
1	-17.7	23.9	-240.0	162.9
2	-22.9	19.4	-209.5	121.2
3	-21.4	18.3	-200.5	117.9
	(-23.2) ^a	(9) ^a	(-184) ^a	(104) ^a
4^c	-41.2	6.4	-288.3	158.3

a) Experimental solid state NMR CP/MAS values [63]. b) $:\text{CH}_2$ = triplet ground state, $:\text{CF}_2$ = singlet ground state. c) The results reported on NHC **4** are novel and were calculated according to the protocol described in ref. [62].

An important advantage of computational approaches is the possibility to predict, without any ambiguity, the different components of the magnetic shielding tensor, defining the anisotropy of the shift and allowing the correlation between the components of the chemical magnetic tensor and the local molecular structure. In this context, it is worth recalling that only solid state NMR provides the three components of the magnetic shielding tensor, which are not available from solution NMR due to tumbling movements of the molecules in solution that average the magnetic shielding in different directions. Considering the classic Arduengo-type NHC, the three components of the magnetic shielding tensor are oriented as shown in Figure 4 [66].

Figure 4. Illustration of the three components of the chemical shielding tensor for **1**.

In good agreement with solid state experiments [63], calculations on the modeled carbenes showed that the σ_{xx} component, in the mean carbene plane along the carbene lone pair, was the smallest; the σ_{zz} component, perpendicular to the carbene plane along the empty p_z orbital, was the most shielded component; and the σ_{yy} component, perpendicular to the other two components and within the plane of the carbene, is the most deshielded. The three components show the trend $\sigma_{yy} > \sigma_{xx} > \sigma_{zz}$. It is worth noting that the relative values of the components of the magnetic shielding tensor strongly depend on the ground state multiplicity, with the carbene having a triplet ground state that is strongly deshielded relative to the carbene having a singlet ground state, compare $:\text{CH}_2$ and $:\text{CF}_2$ in Table 1. Focusing on the structure of NHCs **1-3**, it emerges that adding methyl groups at the N atoms in **1**, i.e., going from **1** to **2**, creates an almost stable σ_{xx} component and compensates for variations in the σ_{yy} and σ_{zz} components, with the overall change in σ_{iso} equal to only 5 ppm. Conversely, changing the substituents on the C=C backbone, i.e., going from **2** to **3**, has a marginal impact on the magnetic shielding tensor. On the other hand, changing the nature of the backbone,

compare **1** and **4** in Table 1, leads to the deshielding of σ_{iso} by 25 ppm due to the σ_{xx} and, principally, σ_{yy} components.

Table 2. Diamagnetic and paramagnetic components of the isotropic magnetic shielding components, σ_d and σ_p , and the paramagnetic component, $\sigma_{p,ii}$, of free carbenes from ref. [62].

	σ_d	σ_p	$\sigma_{p,xx}$	$\sigma_{p,yy}$	$\sigma_{p,zz}$
$:\text{CH}_2^{\text{a}}$	250.1	-1404.2	-531.9	-3633.0	-47.8
$:\text{CF}_2^{\text{a}}$	245.7	-350.2	-217.1	-648.8	-184.8
1	256.7	-278.1	-231.0	-507.2	-73.4
2	250.1	-1404.2	-237.5	-479.3	-118.4
3	245.7	-350.2	-240.2	-472.0	-122.1

a) $:\text{CH}_2$ = triplet ground state, $:\text{CF}_2$ = singlet ground state.

From the results reported in Table 2, it is clear that variations in the paramagnetic component, σ_p , between different carbenes are much larger than those in the diamagnetic component, σ_d . This indicates that the variation in the experimental chemical shift of different NHCs is mostly related to the diamagnetic contribution, correlated to the coupling between orbitals induced by the external magnetic field, whereas the impact of the diamagnetic term, which depends on the electron density of the ground state molecule, is negligible.

Thus, focusing on the paramagnetic contributions, the greatest term is $\sigma_{p,yy}$, which arises from an occupied-virtual $n-\pi^*$ transition from the orbital corresponding to the lone pair at the carbene center to one of the empty π^* molecular orbitals involving the p_z orbital at the carbene center [63, 67]. This transition strongly depends on the electronic structure of the molecule involved. For example, when the triplet ground state is the most stable and the singlet state is near in energy, as for $:\text{CH}_2$, electrons can easily move from the lone pair orbital to the orthogonal and empty π^* orbital (x and z directions in Figure 4, respectively) [68-70]. This transition creates a magnetic vector along the y direction and a significant σ_{yy} paramagnetic term. For molecules with the lone pair in a lower energy orbital, i.e., with a more stable singlet state and large singlet-triplet

splitting, as in :CF₂, the transition to promote the electrons from the lone pair orbital to the empty one requires more energy, and as a consequence, the paramagnetic σ_{yy} term decreases [71, 72]. The $\sigma_{p,yy}$ term is also strongly influenced by the π donation from the different substituents on the carbene. The significant π back-donation from the F atoms in :CF₂, compared to :CH₂, and from the methyl-substituted N atoms in **2**, compared to **1**, does not favor the transfer of additional electron density from the lone pair orbital to the π^* orbital, and the σ_{yy} term decreases. Therefore, the magnitude of the paramagnetic σ_{yy} term offers important details on both the energy gap between the lone pair occupied orbital and the empty π^* orbital on the carbene and on the amount of back-donation to the empty p_z orbital of the carbene C atom. Furthermore, the same concepts can be used to connect the more strongly deshielded σ_{yy} term in the saturated NHC to the lower energy gap between the lone pair orbital and the π^* orbital in **4**, relative to **5**, which is 4.64 and 5.47 eV at the B3LYP/6-31G* level, respectively.

The σ_{xx} paramagnetic term originates from transitions between molecular orbitals corresponding to the σ bonds between the carbene center and its substituents to the orthogonal π^* molecular orbital centered on the p_z orbital of the carbene atom. Due to the high stability of these σ bonds, the energy gap between these filled and empty molecular orbitals is large, which results in $\sigma_{p,xx}$ being smaller than $\sigma_{p,yy}$. In any case, the value of $\sigma_{p,xx}$ offers information about the electronegativity of the groups σ bonded to the carbene center. The more electronegative the groups, the smaller $\sigma_{p,xx}$. In fact, in :CF₂, the presence of fluorine atoms leads to a smaller $\sigma_{p,xx}$ than that of :CH₂.

Finally, the $\sigma_{p,zz}$ component originates from transitions between molecular orbitals corresponding to the lone pair on the carbene carbon atom and molecular orbitals corresponding to the σ bonds between the carbene center and its substituents. Since this transition (in contrast to the previous ones) is between two occupied orbitals, it leads to the smallest paramagnetic contribution. Again, the difference between the electronegativity of the carbene C atom and its substituents mainly influences $\sigma_{p,zz}$. The more electronegative the two groups bonded to the carbene, the less the two filled orbitals involved in the transition repel each other, which results in a larger $\sigma_{p,zz}$ term, compare :CF₂ and :CH₂ in Table 2. In conclusion, theoretical calculation of the ¹³C NMR

carbene carbon shieldings was revealed to be a powerful tool in the characterization of carbenes, providing meaningful insights into the electronic nature of these molecules.

5. Quantifying the π -acidity of NHCs

Having established the main features determining the NMR response of free NHCs, we turn our attention to using NMR techniques to shed light on the π -accepting capability of NHCs. This is a property of remarkable interest, since the bonding between NHCs and metals is considered to be a synergic contribution of $\sigma \rightarrow d$ donation from the NHC to the metal and $d \rightarrow \pi^*$ back-donation from the metal to the NHC, see Figure 2. To this end, selenourea and phosphinidene compounds, such as those in Figure 5, were synthesized and analyzed by ^{77}Se [73, 74] and ^{31}P [74, 75] NMR. These compounds can be considered to have two resonance structures, see Chart 3, where an increasing amount of $\text{Se} \rightarrow \text{NHC}$ or $\text{P} \rightarrow \text{NHC}$ back-donation deshields the Se or P center and moves the chemical shift downfield. Indeed, NMR experiments indicated that the ^{77}Se chemical shift in a set of 23 selenoureas covered a range of ca. 220 ppm, while the ^{31}P chemical shift in a set of 9 phosphinidenes covered a range of ca. 130 ppm [76].

Chart 3. Limit resonance structures and orbital representation of phosphinidene and selenourea compounds.

Figure 5. Selenourea and phosphinidene complexes.

The DFT-NMR magnetic shieldings correlate to the experimental chemical shifts with remarkable accuracy, $R^2 = 0.94$ and $R^2 = 0.99$, for selenoureas and phosphinidenes, see Figure 6, and thus were used to rationalize these results [76].

Figure 6. Calculated Se and P chemical shieldings versus experimental ^{77}Se and ^{31}P chemical shifts of carbene-Se/P adducts. Adapted from ref. [76].

As reported in the previous section, the theoretical magnetic shielding can be easily decomposed into paramagnetic and diamagnetic contributions. The analysis performed for the Se-NHC complexes revealed the main variable to be the σ_p term, covering a range of almost 270 ppm, see Table 3, whereas the σ_d term varies by only 3 ppm. This clearly indicates that the diamagnetic term, depending on the overall electron density in the ground state of the molecule, does not have a major effect on variations in the chemical shift between related compounds. Rather, variations in the chemical shift are principally due to transitions between occupied and virtual molecular orbitals.

Table 3. DFT isotropic magnetic shielding and diamagnetic and paramagnetic components of the isotropic magnetic shielding of Se (ppm) for the 23 carbene-Se compounds in Figure 5. Data taken from ref. [76].

	σ_{iso}	σ_d	σ_p
5	1617.0	3003.6	-1386.6
6	1608.0	3003.5	-1395.5
7	1618.6	3003.9	-1385.3
8	1535.6	3003.6	-1468.0
9	1531.1	3003.6	-1472.5
10	1521.4	3003.5	-1482.1
11	1349.6	3003.6	-1654.0

12	1441.9	3003.8	-1561.9
13	1435.9	3003.3	-1567.4
14	1427.2	3003.3	-1576.1
15	1427.6	3003.2	-1575.6
16	1439.2	3005.6	-1566.4
17	1442.9	3005.4	-1562.5
18	1462.6	3003.3	-1540.7
19	1347.4	3004.0	-1656.6
20	1354.9	3002.9	-1648.0
21	1443.6	3003.9	-1560.3
22	1347.3	3003.5	-1656.2
23	1360.6	3003.1	-1642.5
24	1498.3	3003.3	-1505.0
25	1508.4	3003.6	-1495.2
26	1472.8	3003.4	-1530.6
27	1441.8	3003.5	-1561.7

At this point, we focused our attention on the paramagnetic contribution, specifically on the paramagnetic tensor. The three components $\sigma_{p,xx}$, $\sigma_{p,yy}$, and $\sigma_{p,zz}$ of the paramagnetic tensor revealed that a small change is observed in the $\sigma_{p,xx}$ term and the largest change is in the $\sigma_{p,yy}$ term. Analysis of the transitions most contributing to the $\sigma_{p,yy}$ term indicated that they essentially correspond to a transition from the occupied p_z orbital on Se to the Se-NHC σ^* orbital, which is weakly affected by the structure of the NHC. In contrast, the $\sigma_{p,xx}$ term, aligned along the Se-NHC bond, is determined by the transition between the occupied p_y orbital on Se and the unoccupied orbital corresponding to the π^* Se-NHC bond, see Chart 4, and it strictly depends on the NHC involved.

Chart 4. Orbitals influencing paramagnetic shielding in selenoureas and phosphinidenes.

For some systems, the Se-NHC π^* bond is localized in a single molecular orbital, see Figure 7a for **12**, while for other systems, the π^* orbital is a combination of more than one virtual molecular orbital, see Figure 7b for **7**. All these virtual orbitals contribute to the transition, increasing the $\sigma_{p,yy}$ term.

Figure 7. Se-NHC π^* orbitals for a) **12** and b) **7**. Ref. [76] - Published by The Royal Society of Chemistry.

Since the paramagnetic shielding is directly related to the energy gap between the molecular orbitals involved in the transition, the calculated isotropic magnetic shielding was plotted versus the energy gap between the filled and virtual orbitals that mainly contribute to the transition. Despite a single outlying transition (the one contributing more to the diamagnetic shielding), a good linear correlation was observed, see Figure

8, confirming that the origin of the variation in magnetic shielding, σ_{iso} , is indeed connected to the variation in energy of the π^* Se-NHC bond.

Figure 8. Calculated Se NMR shielding versus the filled-virtual orbital energy gap for 23 carbene-Se compounds. Adapted from ref. [76].

This analysis offered an explanation for the reported trend in the chemical shift of Se. Further bond energy decomposition analysis led to a plot between the magnetic shielding and the orbital energy contribution to the σ ($\sigma \rightarrow d$ donation from NHC to Se) and π ($d \rightarrow \pi^*$ back-donation from Se to NHC) bonds, E_σ and E_π , respectively. In the decomposition of the isotropic magnetic shielding into diamagnetic and paramagnetic terms, the E_σ term is consistently substantially stable and independent of the specific NHC and chemical shift, whereas the E_π term gives a quite good correlation if the systems are properly grouped according to the NHC structure, see Figure 9.

Figure 9. Calculated Se NMR shielding versus the orbital energy contribution, E_π , for the Se-carbene compounds. Black diamonds represent imidazole and imidazoline

NHCs, green filled diamonds represent triazoles, and red diamonds represent cyclic (alkyl)(amino)carbenes. Adapted from ref. [76].

Similar conclusions were obtained when phosphinidene compounds were considered. For the Se compounds, the large change in the paramagnetic term, see Table 4, was ascribed to the transition between the lone pair on phosphorus and the orbital corresponding to the π^* NHC-P bond and was mainly localized on the carbene.

Table 4. DFT isotropic magnetic shielding and diamagnetic and paramagnetic components of the isotropic magnetic shielding of Se (ppm) for the 11 carbene-PPh compounds in Figure 5. Data taken from ref. [76].

	σ_{iso}	σ_{d}	σ_{p}
28	430.2	965.3	-535.1
29	424.0	965.5	-541.5
30	408.3	966.1	-557.8
31	402.1	964.8	-562.7
32	389.6	964.3	-574.7
33	387.3	964.6	-577.3
34	383.1	964.5	-581.4
35	359.7	963.7	-604
36	337.1	963.9	-626.8
37	335.3	964.6	-629.3
38	321.5	964.3	-642.8

In this case, the bond energy decomposition analysis also showed a good correlation between the magnetic shielding on the P atom and the orbital energy contribution, E_{π} , see Figure 10.

Figure 10. Calculated ^{31}P NMR shielding versus the orbital energy contribution, E_{π} , for the carbene-PPh compounds. Adapted from ref. [76].

In conclusion, the DFT-NMR analysis provided full support to the hypothesis that variations in the ^{77}Se chemical shift of selenoureas and ^{31}P chemical shift of phosphinidenes are reliable measures to quantify the π accepting capability of carbenes. The more downfield the chemical shift, the stronger the π -acidity of the NHC.

6. Comparing σ -donicity in metal-NHC bonds

DFT-NMR was also used to extract information on the σ -donicity power of NHCs in Metal-NHC complexes via analysis of the $J_{\text{M-C}}$ spin-spin coupling constant between the metal center and the carbene NHC atom. This analysis was performed on the NHC-Pt(dmso) Cl_2 complexes in Chart 5 [77].

Chart 5. Schematic representation of NHC-Pt(dmso) Cl_2 complexes, dmso = dimethylsulfoxide.

The experimental ^{195}Pt NMR chemical shift of the unsaturated complex, **39**, is 1017.0 ppm, which is 25.2 ppm downfield relative to the saturated complex, **40**, which has a

chemical shift of 991.8 ppm. Furthermore, the $J_{\text{Pt-C}}$ coupling constant is 1472 Hz in complex **39**, while it is 114 Hz lower in complex **40** at 1358 Hz.

The upfield shift of the ^{195}Pt resonance of complex **40** is consistent with the knowledge that replacing a harder ligand (the unsaturated NHC of **39**) with a softer ligand (the saturated NHC of **40**) causes an upfield shift and suggests that saturated carbenes transfer more electron density to the metal center than unsaturated analogues [78]. However, the smaller $J_{\text{Pt-C}}$ coupling constant for complex **40** was in apparent contradiction with this conclusion, since the coupling constant between two nuclei is directly related to the electron density present in the molecular orbital corresponding to the σ -bond, and thus the $J_{\text{Pt-C}}$ coupling constant of **40** should be larger than that of **39**. DFT-NMR calculations were used to clarify this point. The DFT magnetic shielding of the ^{195}Pt atom is 4912 and 4931 ppm for **39** and **40**, and the $J_{\text{Pt-C}}$ coupling constants are 1600 and 1458 Hz for **39** and **40**, which again reproduces the experimental upfield shift and the lower coupling constant of **40**. Analysis of the magnetic shielding indicated that the main variation in the ^{195}Pt resonance between the two complexes was due to the paramagnetic term, which is again in line with the concept that a softer ligand results in an upfield shift [78].

Focusing on the $J_{\text{Pt-C}}$ spin-spin coupling constant, the higher measured and calculated value for complex **39** suggests stronger σ character for the Pt-NHC bond in **39** relative to **40**. Analysis of the electron density difference map between the two complexes in the plane containing the Pt-NHC bond and perpendicular to the NHC mean plane, indicates increased electron density around the carbene atom along the Pt-C bond (see the red curves emerging from the carbene C atom along the Pt-NHC bond in Figure 11), confirming that the saturated NHC, **40**, is a slightly better σ donor than the unsaturated NHC, **39**. However, the same plot indicates increased electron density along the Pt-Cl and Pt-dmsO bonds in **40**, suggesting a more polarized Pt-NHC bond in **40**. This polarization of the σ density on the Pt atom away from the NHC and towards the Pt-S and Pt-Cl bonds is related to the reduced $J_{\text{Pt-C}}$ coupling constant in complex **40**. Incidentally, the same electron density difference map also indicates reduced electron density in the d orbitals of Pt (see the blue curves around Pt in Figure 11), suggesting increased back-donation from the d orbitals on Pt to the unsaturated NHC, **39**.

Figure 11. Electron density difference map, $\Delta\rho^{40-39} = \rho^{40} - \rho^{39}$, between complexes **39** and **40**. Red curves and blue curves refer to $\Delta\rho^{40-39} > 0$ and < 0 , respectively. Reprinted with permission from ref. [77] Copyright (2007) American Chemical Society.

A similar analysis has been reported for group 13 metal-NHC complexes, **41** and **42** in Chart 6 [79].

Chart 6. Schematic representation of NHC-AlMe₃ complexes.

DFT-NMR analysis was performed for both the carbene atom of the NHC and the hydrogen atoms of the -CH₃ group. Focusing on ¹³C NMR, the magnetic shielding was calculated to be -3.9 and -24.3 ppm for **41** and **42**, respectively, with the paramagnetic term σ_p varying by almost 21 ppm downfield from **41** to **42**. As reported above, the carbene magnetic shielding in NHC ligands correlates with transitions between the filled σ orbital corresponding to the M-NHC bond (HOMO) and the empty π orbital of the carbene (LUMO). The HOMO orbital is higher in energy in **42** than in **41**, leading to a reduced HOMO-LUMO energy gap by almost 0.2 eV for **42**. The consequent stronger magnetic coupling causes a downfield shift for **42** with respect to **41**. Moving to the ¹H NMR analysis of the Me groups on Al, the upfield shift of **42** is ascribed to reduced π back-donation [Al] $\rightarrow$ NHC (π^*) that results from a smaller π orbital overlap. As a result,

the electron density is pushed towards the other ligands on the Al center, i.e., the methyl groups, leading to an upfield shift of the H atoms.

7. Electronic properties and NMR response of metal-NHC complexes

DFT-NMR calculations have been applied to also characterize Metal-NHC complexes used in catalysis. In detail, new NHC-Ag-carboxylate complexes active in the synthesis of oxazolines via intramolecular addition of O-H bonds to alkynes have been reported recently, see Chart 7 [80, 81]. In contrast to Cu and Au, only a few Ag-NHC complexes have been experimentally investigated, due to the easier 'decomposition' reaction of ligand exchange yielding a bis-ligated complex [82]. In addition to the synthesis and catalytic application of these new compounds, a detailed spectroscopic analysis evidenced an unexpected trend in the NMR resonance of the carbene carbon atom in these complexes [83].

Chart 7. Synthesis of oxazolines via intramolecular addition of O-H bonds to alkynes promoted by NHC-silver complexes.

Specifically, the chemical shift of carbene in a series of related complexes indicated that complex **44**, with an unsaturated NHC, resonates slightly upfield, ca. 184.5 ppm, relative to complex **43**, presenting the analogous saturated NHC, which resonates ca. 207.9 ppm, while the adamantyl-substituted unsaturated complex, **45**, resonates further

upfield at 173.5 ppm. Based on standard concepts using the overall electron density around a given atom to assess its NMR response, this trend would suggest a clear increase in NHC to Ag σ -donation in the order SIPr > IPr > IAd, with the more donating SIPr resulting in a more deshielded carbene resonating downfield. However, the variations in the chemical shifts contradict the accepted knowledge that saturated NHC ligands are not better donors compared to their unsaturated analogues [84]. DFT-NMR calculations were used to shed light on the origin of this peculiar behavior via comparison of complexes **43-45**.

The very good correlation between the experimental and calculated chemical shift, see Figure 12, and the similar good correlation between the paramagnetic contribution and the HOMO–LUMO gap, $R^2 = 0.98$, confirmed that for these transition metal complexes, DFT-NMR analysis is able to describe the electronic structure of these systems and thus can be used for a deeper understanding of the origin of the changes in chemical shifts.

Figure 12. Calculated versus experimental ^{13}C NMR chemical shifts for selected NHC-Ag-COOCH₃ adducts. Adapted from ref. [83].

Decomposition of the isotropic magnetic shielding into diamagnetic and paramagnetic components revealed that the diamagnetic component of the three complexes differ from each other by less than 1 ppm, i.e., 243.9, 244.0, and 243.0 ppm for **43**, **44** and **45**, respectively, suggesting an overall equal amount of electron density around the carbene atom in the three complexes and indicating that concepts based on the atomic charge at the nucleus cannot rationalize the NMR response of NHCs. Indeed, also in

this case, all the changes in the magnetic shielding can be ascribed to the paramagnetic term that covers a range of almost 26 ppm and is -264.2, -247.4 and -236.3 ppm for **43**, **44** and **45**, respectively. To rationalize these data, the orbitals involved in the transition responsible for the paramagnetic shielding were again analyzed, revealing significant contributions to transitions from a set of six occupied orbitals having a strong Ag-NHC σ -bond component to a set of four virtual orbitals having a strong Ag-NHC π^* -bond component, which were mainly localized on the NHC moiety. Summing the contributions from the mentioned orbitals, the experimental trend is replicated, i.e., the carbene ^{13}C NMR signals for **44** and **45** are shifted upfield with respect to **43**. The complexity of the transitions contributing to the paramagnetic shielding necessitated further analysis of the free NHCs. The decreasing HOMO-LUMO energy gap, 4.66, 4.58 and 4.38 eV for the free NHC of **45**, **44** and **43**, correlates with an increased magnetic coupling between these orbitals, resulting in increased paramagnetic deshielding and a downfield shift of the carbene resonances.

8. Geometric properties and NMR response of metal-NHC complexes

The cases reported in the previous sections showed that the observed NMR chemical shifts of carbenes and metal-carbene complexes can be largely ascribed to variations in the paramagnetic component of the chemical shielding tensor, with the energy gap between the orbitals involved in the transition playing a major role in determining the specific chemical shift of single NHCs. In other words, the NMR response was connected to the specific electronic structure of the different NHCs. Nevertheless, the rationalization of the upfield shift of the NMR signal of the carbene carbon atom in a series of “tilted” Metal-NHC complexes, which are complexes where the metal-NHC bond is not aligned along the bisector of the N-C-N angle, showed that geometrical effects can also have a strong influence on the NMR response of carbenes [85]. This work started from the synthesis of $[\text{NHC-Ir}]^+$ systems, see Chart 8, showing an interaction between the metal and one of the substituents on the nitrogen atoms of the NHC, with an unexpected upfield shift of the ^{13}C NMR carbenic signal with respect to the corresponding neutral complex.

Chart 8. Schematic representation of linear and tilted NHC-Ir complexes.

Before rationalizing the specific case shown in Chart 8, the capability of the selected computational tool to capture the upfield shift due to the tilting of the Metal-NHC bond was tested. To this end, a dataset composed of 12 monodentate (i.e., linear) and chelated (i.e., tilted) Metal-NHC complexes with detailed NMR characterizations, systems **46-57** in Chart 9 [85-88], plus the free NHC ligand **58** and corresponding protonated structure **59** was assembled. Analysis of the systems shown in Chart 9 indicates that the upfield shift of the cationic tilted system in Chart 8 relative to the parent neutral complex cannot be related to the formation of a positive charge in the complex, since a similar shift is observed when comparing the chemical shift of **48** and **49**.

Chart 9. Schematic representation of linear and tilted Metal-NHC complexes.

As usual, the first test was correlating the DFT magnetic shielding of the carbenic C atom with the experimental chemical shifts, see Figure 13 [85]. The excellent correlation between the experimental and calculated values validated once more the computational protocol and the following analysis, which was performed on a model Se-NHC complex, see Figure 14. This system was selected because the Se-NHC bond was revealed to be a good mimic of the NHC-M bond, see the previous sections. Moreover, the size and simplicity of this model allowed for a clearer electronic analysis.

Figure 13. Calculated magnetic shielding versus the experimental ^{13}C chemical shift of the carbene atom in the complexes in Chart 9. Adapted from ref. [85].

The Se-NHC model has been optimized and, as expected, a linear geometry was obtained. Next, to mimic the tilting of the M-NHC bond of the complexes in Chart 8, the system was forced to tilt around the Se-NHC bond by 10° , 20° and 30° . The calculated magnetic shielding of the carbene C atom moved upfield upon increasing the tilting, see Figure 14, consistent with the experimental behavior of the $[\text{NHC-Ir}]^+$ systems **52** and **54**, confirming the tilting as the source of the shift in the ^{13}C NMR signal.

Figure 14. DFT magnetic shielding versus the tilt angle of the Se-NHC bond. Adapted from ref. [85].

At this point, the magnetic shielding was again decomposed into diamagnetic and paramagnetic components, and once again, the diamagnetic term was almost constant, while the paramagnetic term varied with tilting by almost 7 ppm. Attention was thus

focused on the energy of the molecular orbitals involved in the main transition affecting the σ_p term, which is the transition from the molecular orbital corresponding to the Se-NHC σ bond, with energy $E(\sigma)$, to the molecular orbital corresponding to the Se-NHC π^* bond, with energy $E(\pi^*)$.

Figure 15. $E(\pi^*)$ (black diamonds at top) and $E(\sigma)$ (red diamonds at bottom) plotted versus the tilt angle (θ).

The trend in the energy of these two orbitals versus the tilting angle θ is reported in Figure 15, and it indicates that $E(\sigma)$ increases by 0.54 eV, while $E(\pi^*)$ decreases by 0.24 eV when the tilting angle increases from 0° to 30° . As a consequence, the energy gap between them decreases by 0.78 eV from 0° to 30° . As stated before, a small energy gap should increase the magnetic coupling between the two orbitals involved in the transition, leading to a downfield shift, which is at odds with the experimental observations and theoretical predictions for the model system. However, the paramagnetic term is connected not only to the energy gap between the two orbitals

involved in the transition but also to the proper overlap of these orbitals after the rotation induced by the external magnetic field, see Figure 16.

Figure 16. Schematic representation of the magnetic $\sigma \rightarrow \pi^*$ coupling.

In the linear geometry, the Se-NHC σ bond is mainly composed of the s and p_x orbitals on the Se atom and the carbene C atom. This leads to an optimal overlap and a strong magnetic coupling with the π^* molecular orbital after rotation of the σ -bonding molecular orbital induced by the external magnetic field. On the contrary, when the Metal-NHC bond is bent, the molecular orbital on Se involved in the Se-NHC σ bond shows a different composition, with a contribution of 26% from p_x , 13% from s and 5% from p_y with respect to a contribution of 39% from p_x and 14% from s in the linear geometry, see Figure 17. After rotation induced by the magnetic field, the p_y component does not have the right symmetry to overlap with the empty π^* molecular orbital, which results in reduced overlap. The overall result is a weaker magnetic coupling on moving from the linear to the bent geometry, leading to an upfield shift of the signal.

Figure 17. Schematic representation of the MOs corresponding to the σ and π^* Se-NHC bonds. Adapted from ref. [85].

In conclusion, this analysis clearly showed that the NMR properties of NHC complexes depend not only on the energy gap between molecular orbitals involved in the transition, as typically occurs when different NHCs are considered, but also on the specific geometrical features when a single NHC is considered.

9. Extension to the metal-alkylidene bond

Recently, an accurate DFT-NMR analysis on the characterization of olefin metathesis catalysts based on well-defined d^0 group 6 and 7 transition metal-alkylidene complexes has been reported [89]. Despite these complexes not presenting an NHC ligand, the elegant DFT-NMR analysis that was performed is highly consistent with the analysis of the Metal-NHC bonds presented so far, and thus we believe they are worth including in this review.

Experimental ^{13}C solid state NMR analysis of these complexes, see Chart 10, revealed a surprising downfield chemical shift of the alkylidene carbon signal, i.e., between 200 and 300 ppm, see Table 5 [90].

Chart 10. Schematic representation of group 6 and 7 transition metal-alkylidene complexes active in olefin metathesis.

This result was surprising since these chemical shift values are usually observed for carbocations, while alkylidenes are nucleophilic groups. DFT-NMR calculations were used to shed light on the origin of the downfield chemical shift. The systems calculated as models of the experimental complexes are reported in Chart 11 as **60-64**.

Chart 11. Schematic representation of ethylene and group 6 and 7 transition metal-alkylidene complexes investigated by DFT-NMR.

Table 5. Calculated and experimental ^{13}C NMR chemical shifts of ethylidene in the systems in Chart 11. Data taken from ref. [90].

	δ_{iso} (Exp.)	δ_{iso} (DFT)
$\text{CH}_2=\text{CH}_2$	126	131
60	245	227
61	247	245

62	279	284
63	255	251
64	285	295

Ethylene was considered as a reference molecule since both alkylidene and ethylene bear sp^2 carbons. Also, for these systems, the calculated chemical shifts reproduced well the experimental trend and the downfield shift with respect to ethylene carbons, with $R^2 = 0.97$ between the experimental and DFT δ_{iso} , see Table 5. Both the experimental and theoretical data showed that the most shielded component of the magnetic shielding tensor in ethylene is the σ_{yy} term, oriented orthogonal to the molecular plane containing the C=C bond (blue volume in Figure 18). This term is remarkably reduced in the metal-alkylidene complexes. In contrast, in the metal-alkylidene complexes, there is a strong σ_{zz} deshielding term in the molecular plane containing the M=C bond (orange volume in Figure 18). This deshielding term is strongly reduced in ethylene.

Figure 18. Isosurfaces representing the calculated shielding tensors in the metal-alkylidene complexes. Reprinted with permission from ref. [90]. Copyright (2016) American Chemical Society.

This indicated that the presence of the metal leads to a deshielding of the carbon center with respect to ethylene, mainly due to the component in the alkylidene plane. To establish a connection between the NMR chemical shifts and the electronic structure at the carbene carbon, the classical decomposition of the chemical shielding into diamagnetic and paramagnetic terms was performed. Once again, the diamagnetic contribution is substantially independent of the specific metal-alkylidene system considered and no more than 20 ppm different from the value in ethylene. This once again indicated that the paramagnetic term is responsible for the 200-300 ppm downfield shift of the metal-alkylidene systems. Analysis of the molecular orbitals involved in the transitions mostly affecting the paramagnetic term showed that in ethylene, the largest influence is given by the transition, induced by the external magnetic field, from the molecular orbital corresponding to the C-C σ bond to the molecular orbital corresponding to the π^* C-C bond, see Figure 19a.

Figure 19. Schematic representation of the magnetic $\sigma \rightarrow \pi^*$ coupling for (a) ethylene and (b) a generic metal-alkylidene complex.

The situation is quite similar in the metal-alkylidene complexes, with the caveat that the transition is from the molecular orbital corresponding to the M-C σ bond to the molecular orbital corresponding to the π^* M-C bond, see Figure 19b. Considering that a stronger deshielding effect is directly related to a smaller energy gap between the two orbitals involved in the transition, the downfield shift of the metal-alkylidene resonance is easily explained by considering the relative energy of the two orbitals involved in the transition in both ethylene and the metal-alkylidene complexes. In fact, the energy gap between the M-C σ and π^* orbitals is smaller than the energy gap between the C-C σ and π^* orbitals in ethylene.

10. Perspective

In this review, we presented the potential of theoretical analyses of NMR properties of NHCs and Metal-NHC complexes to complement experiments. The exemplary cases discussed showed that modern DFT-based NMR techniques can be applied on quite large systems and can reproduce experiments with remarkable accuracy. In addition, the theoretical background at the heart of computational NMR spectroscopy allows for the decomposition of the experimental magnetic shielding and chemical shift values into diamagnetic and paramagnetic components, with these components correlating to the electronic structure of the species under investigation. This possibility allows one to easily rationalize otherwise unexpected trends observed in experiments. We hope that the overview presented in this work will stimulate more extensive applications of theoretical methods in the analysis of NMR properties of NHCs and Metal-NHC compounds.

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- The chemical shift of N-heterocyclic carbenes metal complexes is rationalized
- The paramagnetic shielding is responsible for variations in the chemical shift
- Transitions to virtual π orbitals on the carbene contribute to the paramagnetic shielding