How can bonding properties of N-heterocyclic carbenes (NHCs) be modulated? A quantitative analysis in [(NHC)AuCl] complexes

Carlo Alberto Gaggioli,[a] Giovanni Bistoni,[b] Gianluca Ciancaleoni,[c*] Francesco Tarantelli,[ad] Leonardo Belpassi,[d*] Paola Belanzoni[ad*]

a) *Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, I-06123, Perugia, Italy*

b) *Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34 – 36, 45470 Mülheim an der Ruhr, Germany*

c) *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Giuseppe Moruzzi 13, I-56124, Pisa, Italy*

d) *Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), c/o Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, via Elce di Sotto 8, I-06123, Perugia, Italy*

Abstract

In view of their intensive use as ligands in many reactions catalyzed by transition metal complexes, modulation of the N-heterocyclic carbenes (NHCs) bonding properties on a rational basis is highly desirable, which should enable optimization of current applications or even promote new functions. In this paper we provide a quantitative analysis of the chemical bond between the AuCl fragment and a series of 27 different NHCs in [(NHC)AuCl] complexes, whose electronic properties are modulated through a variation of the groups attached to the NHC nitrogen atoms or backbone, of the NHC unsaturation/size or of the heteroatom on the NHC ring. For evaluating the donation and back-donation components within the Dewar-Chatt-Duncanson (DCD) model in the NHCs-AuCl bond, we apply the Charge-Displacement (CD) analysis within the NOCV (Natural Orbitals for Chemical Valence) framework, a methodology that avoids the constraint of using symmetrized structures. We show that modulation of NHCs bonding properties requires substantial modification

in their structure, such as insertion of two ketone groups on the NHC backbone (which enhances the π back-donation bond component and introduces an effective electronic communication within the NHC ring) or replacement of a nitrogen atom in the ring with an sp^3 or sp^2 carbon atom (which increases and decreases the π back-donation bond component, respectively). We extend our investigation for a subset of 13 NHCs in [(NHC)PPh] and [(NHC)AuCl] molecular systems in relationship with their experimentally available ^{31}P NMR chemical shift values. The latter qualitatively correlate with the π acceptor properties of the NHC, but such a correlation is less reliable for strongly π acidic NHCs, demonstrating that caution should be used when experimental data are used as a tool for quantifying the electronic properties of carbenes.

Introduction

Since the seminal work by Arduengo et al. in 1991 about the synthesis of a stable imidazole-2-ylidene,[1] the use of N-heterocyclic carbenes (NHCs) in many fields of chemistry increased enormously. Of particular interest is nowadays their use as nucleophilic organocatalysts[2] and as ligands for transition metals[3] with applications in homogeneous and heterogeneous catalysis.[4]

The most used approach for analyzing a coordinate bond between a metal and a ligand is the Dewar-Chatt-Duncanson (DCD) model, which describes the bond formation in terms of σ donation and π back-donation components.[5] In the language of valence bond theory, a singlet NHC adopts an sp^2 hybrid structure on the divalent C atom with an sp^2 lone pair, which is responsible for σ donation to the metal, and an empty *p* orbital perpendicular to the NHC plane, which is available for π back-donation from the metal.[6]

Concerning the nature of bond between NHCs and transition metals, it was first postulated that carbenes were strong σ-donor with almost no π-accepting properties.[7] However, both computational and experimental studies have recently established the occurrence of a non-negligible π-back-donation from metal to NHCs.[8]

Among experimental methodologies for evaluating electronic properties of carbenes, the Tolman Electronic Parameter (TEP) is the most widely used. It is based on the measure, through the infra-red spectroscopy, of the A_1 CO stretching frequency in nickel complexes $[Ni(CO)_3(L)]$[9] or, alternatively, in $[MCl(CO)_2L]$ (M = Rh or Ir) complexes.[10] This method relies on the fact that the electron density donated from the ligand to the metal transfers also to the π* of the CO ligands, changing the A_1 stretching frequency of the latter according to the donor power of L. This methodology, however, does not allow deconvolution of the DCD components, because of the interplay between polarization and back-donation.[11]

For some specific carbenes, the amount of back-donation can be experimentally evaluated by analyzing its structural[12] or dynamic[13] properties, but generally the deconvolution of the DCD components of a coordinate bond yet remains a challenge.

The importance of the M → carbene π backbonation has been growing so fast in the last years to induce Fürstner et al. to synthesize different NHCs, with supposedly different π-acceptor abilities, and use a gold-catalyzed reaction to study the effect of the back-donation on the regioselectivity of the catalysis.[14] Despite their outstanding results, a theoretical methodology able to quantify the π-acceptor abilities of the different NHCs is needed to ascertain the M → NHC π back-donation role, since in many cases the relationship between a variation in the carbene structure and its effect on the DCD components of the M-C bond is not straightforward.

To assess the π acceptor ability of NHCs, Nolan[15] proposed the use of $J_{Pt\text{-}C}$ coupling constants in $[PtCl_2(DMSO)(NHC)]$ complexes, Ganter the ^{77}Se NMR spectroscopy of selenourea NHC=Se compounds,[16] and Roesky the ^{14}N NMR spectroscopy.[17]

Recently, Bertand et al. suggested that the ^{31}P NMR chemical shift of carbene-phosphinidene [(NHC)PPh] adducts is an indicator of the π accepting properties of the carbene,[18] taking advantage of the similarities between the M → C back-donation and the sharing of the phosphorous lone pair with the carbon of the carbene.[19] In this framework, the NMR δ of the phosphorous atom will be shielded to a different extent, depending on the π acidity of the carbene. Although this study

proposes an attractive method, the authors only infer, based on chemical intuition, that the changes in ^{31}P chemical shifts were due to changes in the NHC-PPh bond π back-donation component.

In a work by Cavallo et al.[20] it has been found that, both for NHC-Se and NHC-PPh bonds, the ^{77}Se and ^{31}P NMR chemical shift indeed well correlate with the extent of π-backbonding, evaluated in terms of orbital energies computed on symmetrized structures, confirming the experimental intuition of Bertrand. This exhaustive analysis suggests that similar relationship between P and/or Se and transition metal systems could be found, with the only difference that metals participate to π backbonding using their *d* orbitals.

An ideal tool to explore such interesting topics, namely the carbene structure/M-C bond relationship and the reliability of ^{31}P NMR to measure the π accepting properties of NHCs, is the charge-displacement (CD) analysis,[21] a computational methodology developed by our group. Up to now, the CD analysis has been applied to disentangle donation/back-donation effects on experimental observables,[11,12,13,22] including experimental reaction barriers.[23] A recent study by some of us[24] showed that the π M → NHC back-donation is highly tunable by changing the ancillary ligand (L) in $[(L)Au(NHC)]^n$ systems with fixed NHC.

In this contribution we first analyze the chemical bond between the NHCs and gold with the CD methodology in [(NHC)AuCl] complexes by considering a series of 29 NHCs, whose electronic properties are modulated through a variation of the groups attached to the nitrogen atoms or to the NHC backbone, of the backbone itself (*via* saturation of double bond or change of the ring size) or of the heteroatom on the NHC ring (by addition/removal of N atoms, or by N substitution with C or S atoms). The aim of this study is to investigate how NHC bonding properties can be modulated on a quantitative ground. In Figure 1 the sketch of the studied carbenes is shown.

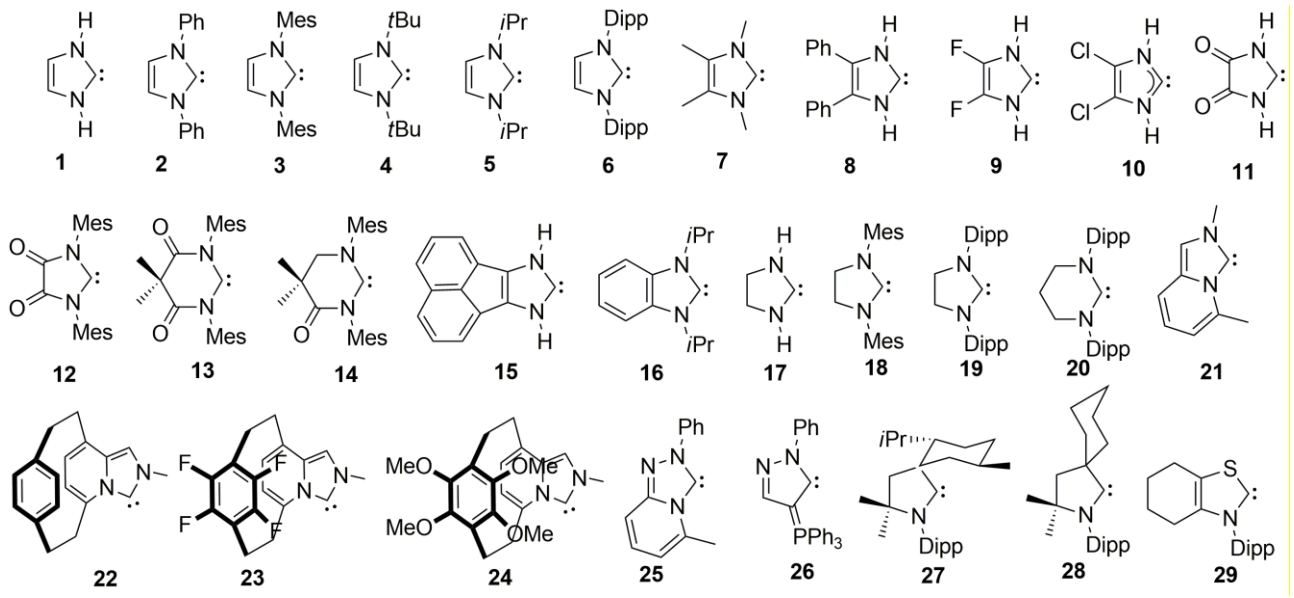


Figure 1: Sketch of the 29 analyzed NHCs (Mes = 1,3,5 – Trimethylbenzene, Dipp = 2,6 – Diisopropylphenyl).

We decided to use gold(I) as metal because in recent years gold (and its use with NHCs as ligands) revealed to be a promising metal in many organometallic and catalytic applications[25], so that the quantification of its DCD components when interacting with NHCs is key. In particular, we selected the AuCl fragment because both it is neutral (and therefore polarization contributions are minimized) and Cl^- is an electron rich ligand (which accepts almost no back-donation from gold), which should allow to maximize the Au → NHC back-donation.[13,24]

For evaluating the DCD components of the NHCs-AuCl bond, we use the CD analysis within the NOCV (Natural Orbitals for Chemical Valence) framework,[26] which avoids the constraint of using symmetrized structures, a restraint which would limitate too much the scope of the present analysis. For example, carbenes **22**-**24** and **26**-**27** cannot be symmetrized, while others, as **13** and **14**, can be symmetrized but the resulting geometry is quite high in energy, and only the NOCV methodology can be used in such cases.

Noteworthy, the NHCs used in the afore-mentioned Fürstner's paper[14] have been included in our list (carbenes **21**-**26**).

We then select a subset of 13 NHCs (wider than in previous works) for which the experimental ^{31}P NMR data of the corresponding [(NHC)PPh] compounds are available[18, 27] and we explore whether the correlation between the NHCs-PPh bonding characteristics and ^{31}P NMR chemical shifts is maintained and if such information can be transferred to the DCD components of NHCs-metal bonding, using as specific case [(NHC)AuCl] complexes (Figure 2).

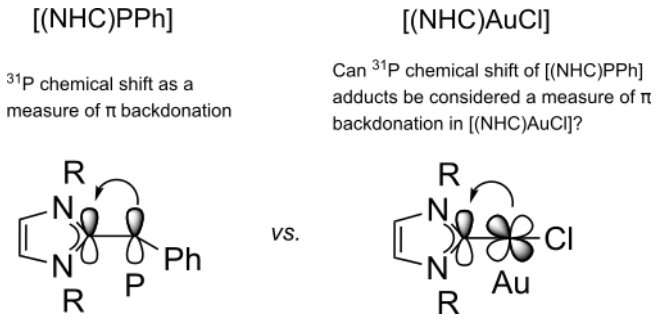


Figure 2: Schematic representation of the relationship between π back-donation bond component and ^{31}P NMR chemical shift in a) [(NHC)PPh] and b) [(NHC)AuCl] molecular systems.

Methodology

Computational Details

All geometry optimizations and electron densities used for the bond analysis (Charge-Displacement Function and Energy Decomposition Analysis) have been computed with the ADF package[28] (version 2012.01) at DFT level using TZ2P Slater-type basis sets, BP86 functional[29], frozen core approximation (1s for N, C, O and F, 2p for P, 4f for Au) and ZORA Hamiltonian [30] to account for relativistic effects.

Charge Displacement Function.

An efficient way to visualize thoroughly the rearrangement of the electron density taking place upon bond formation between two fragments is to use the Charge Displacement function (CD) approach[25], which allows to estimate the exact amount of electron charge that, upon the formation

of a bond, is displaced from a fragment to another. The CD analysis is today a well established and successful tool for chemical bond analysis in a wide variety of context; it has been successfully used, for example, to study the chemical bond between gold(I) and the noble gases [31] and bonds in organometallic chemistry.[22,32] Mathematically, the CD function is defined as:

$$\Delta q(z)=\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{z} \Delta\rho(x,y,z')\, dz' \qquad (1)$$

Here z' is the axis of interest, typically one joining the interacting species (in our work, the axes that passes through the NHCs carbon atom and gold) and Δρ(x,y,z') is defined as the electron density Δρ of the molecule minus the Δρ of the isolated noninteracting fragments placed at the same position as in the molecule. Thus Δq(z) measures, at each point of the z'axis, the number of electrons that, upon formation of the bond between the two fragments, moves across a plane perpendicular to the internuclear axis through the z point (defined as Charge Transfer, CT). A positive (negative) value of Δq(z) indicates electrons moving towards the decreasing (increasing) z'. Furthermore, by looking at the slope, one can immediately deduce regions of charge accumulation (positive slope) or charge depletion (negative slope). To have a numerical estimate of the CT, the value of the CD curve can be taken at some specific point between the fragments, namely define a plane separating them. This is of course arbitrary, but a reasonable model, which has been already used, is to take the CT value at the so-called isodensity boundary, i.e. the point along z' where the electron densities of the non interacting fragments become equal. All the CTs used in this work refer to the CT taken at the isodensity boundary.

If both the molecule and its constituting fragments can be classified in the same symmetry group, the electron density difference can be partitioned into additive symmetry components according to the following equations

$$\Delta\rho = \sum_{\Gamma} \Delta\rho_{\Gamma} \qquad (2)$$

where Γ labels the different irreducible representations of the (unique) symmetry point group of the molecule and its fragments. The overall CD function Δq (Eq. 1) is similarly decomposed in additive symmetry components (defined as in Eq. 1 for each $\Delta\rho_\Gamma$) which, for suitable cases when the symmetry components correspond unambiguously to DCD components, give a quantitative picture of donation and back-donation charges.

When the system under study and its fragments do not satisfy the symmetry requirements (as it happens for systems without symmetry), the above decomposition cannot be applied and the Natural Orbital for Chemical Valence theory (NOCV) scheme has to be used. In the NOCV framework, the charge rearrangement taking place upon formation of a molecule AB from fragments A and B is no longer the simple superposition of the densities of A and B at their molecular positions (isolated fragments as reference) but is rather obtained from the occupied orbitals of A and B suitably orthogonalized to each other and renormalized ("promolecule" as reference). The resulting density rearrangement Δρ' can be written in terms of NOCV pairs, i.e. the eigenfunctions $\varphi_{\pm k}$ of the so-called "valence operator" of Nalewajski and Mrozek valence theory[33], as follows

$$\Delta\rho' = \sum_k \Delta\rho'_k \qquad (3)$$

It is worth stressing here, however, that only a small subset of these NOCV pairs actually contributes to the overall charge rearrangement Δρ' because a large part of them presents eigenvalues close to zero. NOCV method has been applied with success for the characterization of transition metal compounds[34] and for disentangling donation and back-donation in the CD function of non-symmetric systems as for instance in M-ethyne (M=Au, Ni and W) coordination bonds.[22]

Energy Decomposition analysis.

To gain insights into NHC-AuCl and NHC-PPh bonds, we carried out the Energy Decomposition Analysis (EDA)[35] as implemented in the ADF package, since this method allows to decompose the NHC-AuCl and NHC-PPh bond energy into contributions associated with the orbital, Pauli and

electrostatic interactions. The interaction energy between two fragments is divided into three terms, as shown in eq. 4):

$$\Delta E_{int} = \Delta E_{elst} + \Delta E_{Pauli} + \Delta E_{oi} = \Delta E^0 + \Delta E_{oi} \qquad (4)$$

The ΔE_{elst} is the classical electrostatic interaction between the unperturbed charge distributions of the fragments at their final positions, giving rise to an overall density that is simply a superposition of fragment densities $\rho_A+\rho_B$. The Pauli repulsion (ΔE_{Pauli}) arises as the energy change associated with going from $\rho_A+\rho_B$ to the antisymmetrized and renormalized wavefunction, thus properly obeying the Pauli principle and it comprises the destabilizing interactions between the occupied orbitals and it is responsible for any steric repulsion. The last term, ΔE_{oi}, is the contribution arising from allowing the wavefunction to relax to the fully converged one, accounting for electron pair bonding, charge transfer and polarization. This term can be further decomposed into the contributions from the distinct irreducible representations Γ of the interacting systems, $\Delta E_{oi} = \sum_\Gamma \Delta E_{oi,\Gamma}$, which proves to be very informative in systems with a clear σ/π separation. The sum of the electrostatic interaction ΔE_{elst} and the Pauli repulsion ΔE_{Pauli} terms, ΔE^0, is usually called the steric interaction energy which can be considered as a measure of the "ionic" contribution to the bond.

Results and discussion

NHCs bonding properties in [(NHC)AuCl] complexes

We start our theoretical study by analyzing the NHC-AuCl bond in non-symmetrized [(NHC)AuCl] structures, using the NHC carbene **1** in Figure 1. The isodensity surfaces of $\Delta\rho$ maps for the total charge rearrangement and the first four NOCV components of $\Delta\rho$, together with the corresponding CD curves are shown in Figure 3. All the other NOCV contributions are very small or show zero

eigenvalue and do not deserve further analysis (see Table S1 in the Supporting Information and Methodology section).

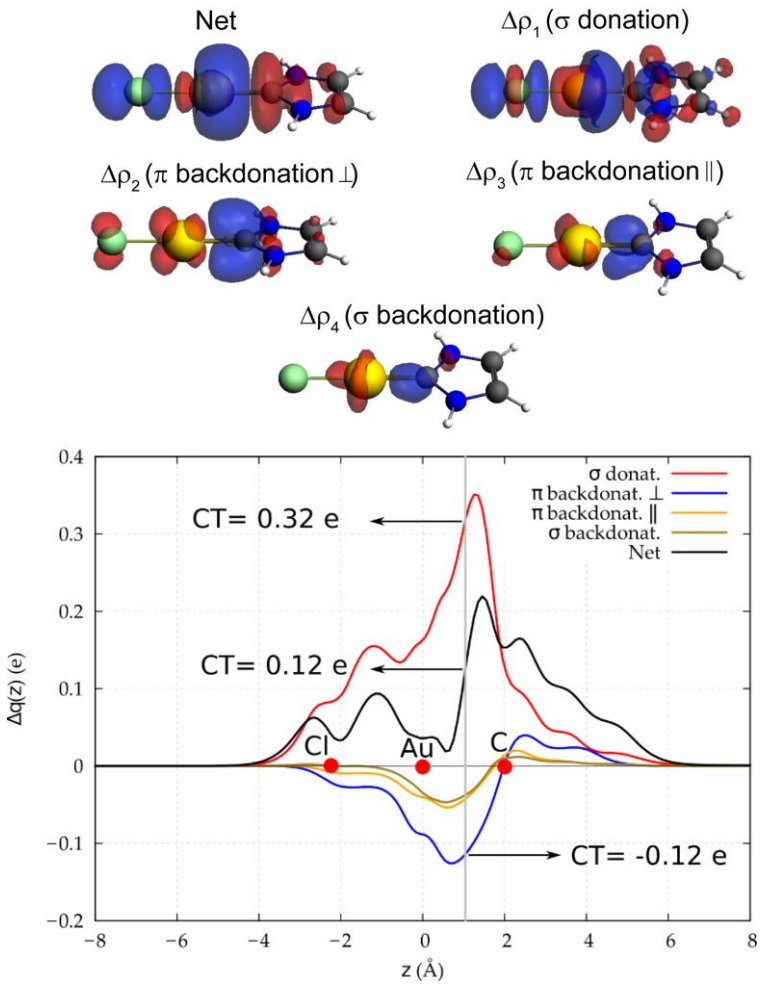


Figure 3: **1**-AuCl bond: top) Isodensity surfaces of the total Δρ, and the $\Delta\rho_1$, $\Delta\rho_2$, $\Delta\rho_3$ and $\Delta\rho_4$ NOCV components (isodensity value +/- 0.001 electrons $a.u.^{-3}$); red lobes correspond to region of depletion of electron density, while blue lobes correspond to region of accumulation; bottom) CD curves for the Δρ components. Red dots indicate the z position of the atomic nuclei (C represents the NHC carbon atom bonded to gold, $C_{carbene}$). A solid vertical line marks the boundary between the NHC **1** and the [AuCl] fragments.

Upon inspection of the total Δρ isodensity surfaces, we notice accumulations of electron density on the outer chlorine region, on the $C_{carbene}$-Au bond region, and on the Au-Cl region. A pronounced

depletion of charge is found on $C_{carbene}$ atom and on the Au-Cl bonding region close to Au. The examination of the first four NOCV Δρ components reveals that each of them can be physically ascribed to a distinct DCD bonding component. Indeed, the first Δρ component ($\Delta\rho_1$) shows a depletion near the carbon of NHC and accumulation on gold and chlorine atoms: this component clearly represents the σ donation from NHC to the metallic fragment. The second Δρ component ($\Delta\rho_2$) shows depletions on chlorine and on a *d* filled orbital of Au atom and accumulation on *p* empty orbital of the carbene carbon C_1: this component describes the π back-donation from Au to NHC perpendicular to the NHC plane ($\pi_\perp$). The third Δρ component ($\Delta\rho_3$) depicts small depletion on chlorine and higher depletion on a *d* filled orbital of Au atom and an increase of electron density on the carbene carbon in the plane of NHC; this component describes π back-donation from Au to NHC occurring on the NHC plane ($\pi_\parallel$). The fourth Δρ component ($\Delta\rho_4$) shows a depletion in the gold region and accumulation on Au-$C_{carbene}$ bond localized close to NHC; this component depicts a σ back-donation contribution. Noteworthy, in all of the NOCV contributions related to the back-donation ($\Delta\rho_2$, $\Delta\rho_3$ and $\Delta\rho_4$) the nitrogen and the carbon atoms on the back of the NHC (C_2 and C_3) show no modifications or small charge depletion, rather than an accumulation. The NOCV bond analysis in relationship with the DCD components has been already reported for [(**19**)AgX] compounds, where similar Δρ isodensity pictures as ours emerged.[36]

In Fig. 3 (bottom right), the corresponding CD curves are shown. The red one refers to σ donation, with a charge transfer (CT σ don) of 0.32 electrons. The $\pi_\perp$ back-donation has a CT (CT $\pi_\perp$ back) of -0.12 electrons; the minus sign signals the flux of charge from the left to the right (see Methodology section). The $\pi_\parallel$ back-donation and σ back-donation components have only small CTs (CT $\pi_\parallel$ back -0.04 electrons, CT σ back -0.04 electrons). The net CD curve (black line) shows a CT of 0.12 electrons from NHC to Au. We already reported the analysis of the **1**-AuCl bond using a C_{2v}-restrained geometry, using its C_{2v} irreducible representation contributions to decompose the DCD components, obtaining very similar results: the total CT resulted to be 0.11 (with C_{2v} symmetry

constraint) which closely compares to the 0.12 e calculated here (without symmetry constraints), indicating a very small influence of the symmetry for this system. The σ donation resulted to be 0.24 e (A_1 symmetry), while in the NOCV scenario we are able to decompose such a contribution into two: a proper σ donation of 0.32 e and a σ back-donation of -0.04 e. The sum of these two contributions is 0.28 e, which is quite close to 0.24 e. The π back-donation was split in two also using the symmetry, giving -0.10 (B_1 symmetry, perpendicular to the NHC plane) and -0.03 e (B_2 symmetry, in the NHC plane), while using the NOCVs the corresponding contributions are -0.12 and -0.04 e, respectively. From this comparison, it can be inferred that the two methodologies are consistent and give very similar results, despite the differences between them, which basically are the different starting geometries and the different reference system used in CD analysis in C_{2v} symmetry (isolated fragments) and within the NOCV framework ("promolecule").[37]

It is interesting to analyze in detail the CD curves not only at the isoboundary, but throughout the entire molecule region. As noted above for the Δρ functions, also the curves representing the back-donation contributions change sign from Au-$C_{carbene}$ bond region (negative) to the NHC nitrogen or C_2/C_3 atom region (positive), likely suggesting the co-existence of two contributions in each curve: a proper Au → $C_{carbene}$ σ or π back-donation, and a polarization of the NHC electronic density in the direction of the positive gold. This implies that the back-donation contribution does not extend to the C_2/C_3 atoms, or, if it does, it is anyway smaller than the polarization contribution. In other words, the electronic communication between the N-$C_{carbene}$-N and the C_2=C_3 moieties is very poor (low "aromaticity").[38]

The NOCV methodology has been applied to all the carbenes in Figure 1, and in all cases the Au-$C_{carbene}$ bond can be described within the same framework (σ donation, σ back-donation, $\pi_\perp$ back-donation and $\pi_\parallel$ back-donation). The CTs data are reported in Table 1.

Table 1. CD-NOCV bond analysis results (in electrons) for the NHC-AuCl bond using the 27 NHCs listed in Figure 1.

NHC	CT σ don	CT $\pi_{\perp}$ back	CT $\pi_{\parallel}$ back	CTπ_{total} back	CT σ back	CT_{Net}
1	0.32	-0.12	-0.04	-0.16	-0.04	0.12
2	0.32	-0.12	-0.04	-0.16	-0.04	0.09
3	0.33	-0.11	-0.04	-0.15	-0.04	0.09
4	0.32	-0.09	-0.04	-0.13	-0.04	0.12
5	0.33	-0.09	-0.04	-0.13	-0.04	0.15
6	0.33	-0.11	-0.04	-0.15	-0.04	0.06
7	0.32	-0.09	-0.04	-0.13	-0.04	0.15
8	0.32	-0.12	-0.04	-0.16	-0.04	0.14
9	0.32	-0.12	-0.05	-0.17	-0.04	0.11
10	0.32	-0.12	-0.05	-0.17	-0.04	0.11
11	0.33	**-0.26**	-0.04	-0.30	-0.03	-0.01
12	0.34	-0.25	-0.04	-0.29	-0.04	-0.02
13	0.33	-0.20	-0.04	-0.24	-0.04	0.00
14	0.34	-0.16	-0.04	-0.20	-0.04	0.03
15	0.33	-0.12	-0.05	-0.17	-0.04	0.13
16	0.33	-0.11	-0.04	-0.15	-0.04	0.13
17	0.33	-0.13	-0.04	-0.17	-0.04	0.12
18	0.34	-0.12	-0.04	-0.16	-0.04	0.08
19	0.34	-0.12	-0.04	-0.16	-0.04	0.05
20	0.34	-0.11	-0.04	-0.15	-0.04	0.04
21	0.32	-0.09	-0.04	-0.13	-0.04	0.13
22	0.32	-0.09	-0.04	-0.13	-0.04	0.13
23	0.32	-0.09	-0.04	-0.13	-0.04	0.12
24	0.32	-0.09	-0.04	-0.13	-0.04	0.14

25	0.31	-0.11	-0.04	-0.15	-0.04	0.09
26	0.34	-0.09	-0.05	-0.14	-0.03	0.09
27	0.35	-0.16	-0.04	-0.20	-0.04	0.04
28	0.35	-0.16	-0.04	-0.20	-0.04	0.07
29	0.33	-0.14	-0.05	-0.19	-0.04	0.07

In Table 1 we collected the NHCs organized on the basis of the modulations we performed on the structure. From entry **1** to **12**, we changed either the groups attached to the nitrogen atoms (from **1** to **6**) or the groups of the NHC backbone. From entry **13** to **20** we changed the backbone of the NHCs, both by saturating the double bond (**17-19**) or by modifying the size of the ring (**13**, **14** and **20**). From entry **21** to **26** we studied some of the carbenes used in the work by Fürstner et. al.[14] (see Introduction), in order to quantitatively assess their electronic properties and explore the correlation between the DCD components of the Au-$C_{carbene}$ bond and the catalytic properties of the complexes. Finally, from entry **25** to **29** we modified the heteroatoms, by adding (**25**) or removing (**27** and **28**) nitrogen atoms, by replacing one nitrogen atom with a carbon (both sp^3 as for **27** and **28** or sp^2 as for **26**) or a sulfur (**29**).

We should note here that in Table 1 the CT σ don and CT $\pi_{\perp}$ back values provide the best comparative description of the NHCs-AuCl bond characteristics, since both CT $\pi_{\parallel}$ back and CT σ back values do remain constant along the series and the total CT values (CT_{Net}) might contain contributions which cannot be purely ascribed to σ donation/ π back-donation DCD components of the NHC-AuCl bond.

For entries **1** to **6**, we can see that replacing H atoms on the nitrogens with phenyl, mesityl or 2,6-diisopropylphenyl groups does not change the bonding properties, whereas replacing them with tert-butyl, isopropyl or methyl groups slightly reduces the $\pi_{\perp}$ back-donation component (from -0.12 e in

entry **1** to -0.09 e in entries **4**,**5** and **7**). This can be easily expected since alkyl groups are electron-donating groups and make $C_{carbene}$ less prone to receive the electronic density from gold.[39,40]

Changing the groups on the NHC backbone, namely inserting methyl or phenyl groups (entries **7** and **8**) have no sizeable effect on the Au-$C_{carbene}$ bond, corroborating the poor communication between the N-$C_{carbene}$-N and C_2=C_3 sides of the carbene. Remarkably, even electron withdrawing groups like F or Cl in NHC backbone positions (entries **9** and **10**, respectively), do not change at all the bonding properties. Indeed, looking at the CD curve representing the $\pi_\perp$ back-donation for the **9**-AuCl bond (Figure 4), we note the same general shape observed for **1**-AuCl: the electronic flux for the $\pi_\perp$ back-donation is negative (direction Au → NHC) only until the $C_{carbene}$ position is reached and the NHC → Au polarization is still dominant in the NHC region, despite the large electronegativity of fluorine atoms. The fluorine atoms do not show any variation of electronic density upon the Au – NHC bond formation.

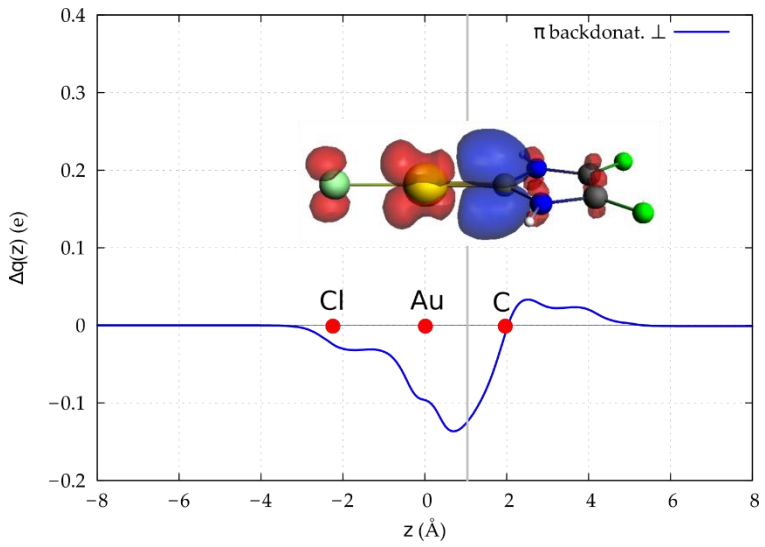
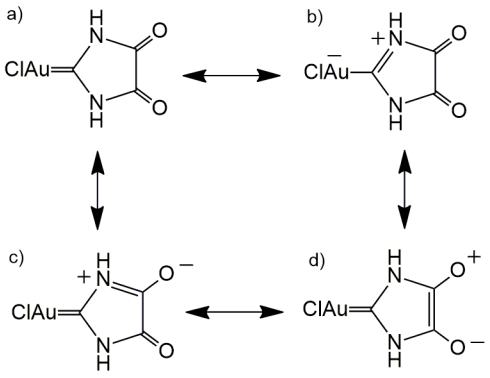


Figure 4. Isodensity surface and CD curve of the Δρ component of **9**-AuCl bond representing the $\pi_\perp$ back-donation. Red dots indicate the z position of the atomic nuclei (C represents the NHC carbon atom bonded to gold, $C_{carbene}$). A solid vertical line marks the boundary between the NHC **9** and the [AuCl] fragments.

However, NHC **9** and **10** may have still an effect in catalysis, where other factors than Au-C bond components can be important, like for instance the counterion position,[41] which can be influenced by the presence of an electron withdrawing group on the NHC backbone.[42]

Concerning the NHC with two oxygen atoms on the backbone (entry **11**), we can see that the σ donation and $\pi_{\parallel}$ back-donation values are very similar to those of all of the considered NHCs, while a huge increase in $\pi_{\perp}$ back-donation is calculated, varying from -0.12 for carbene **1** to -0.26 electrons for carbene **11**. Correspondingly, the net charge donation is decreased to an even negative value (-0.01 electrons), suggesting that actually NHC **11** is accepting electron density from [AuCl]. This result can be easily rationalized in terms of the high ability of oxygen to accept π charge through mesomeric effect (Figure 5, top, structure c). In this case, and unlike the other NHCs, the two sides of the NHC (that are the NCN moiety and the backbone) show an effective electronic communication, as observed from the π back-donation CD curve (Figure 5, bottom), which is negative throughout the whole NHC region. The NHC → Au polarization is likely present also in this case, but it does not overcome the back-donation.



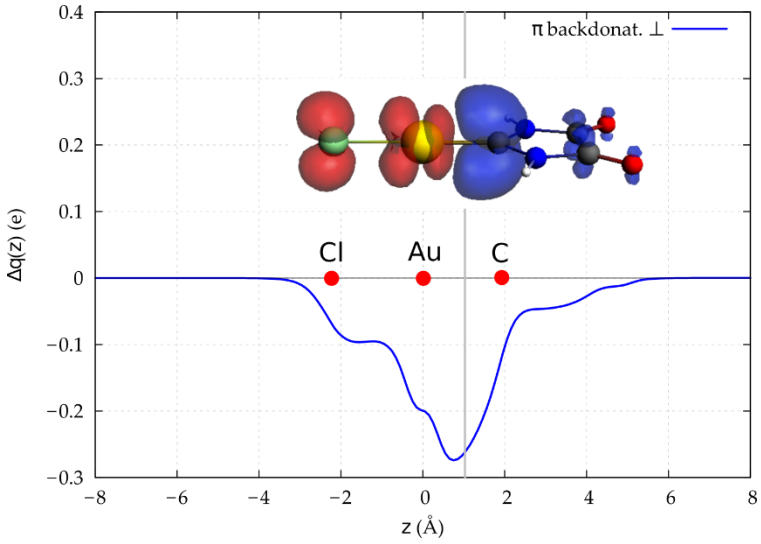


Figure 5. Top) Relevant resonance structures for the complex [(**11**)AuCl]. Bottom) Isodensity surface and CD curve of the Δρ component of **11**-AuCl bond representing the $\pi_{\perp}$ back-donation. Red dots indicate the z position of the atomic nuclei (C represents the NHC carbon atom bonded to gold, $C_{carbene}$). A solid vertical line marks the boundary between **11** and the [AuCl] fragments.

Our results, either the visual inspection of the Δρ or the analysis of the CD curve in the ketone region (Figure 5), do not support the importance of the structure d shown in the Figure 5, which leads us to say that also the NHC 11 does not show a complete "ring aromaticity".

Regarding this, it is interesting here to analyze the series **12-14**, in order to compare what happens modifying the ring size and inserting a methylene moiety between the two ketone groups,[43] which prevent any "ring aromaticity". [(**12**)AuCl] is essentially similar to [(**11**)AuCl], being the only difference the group on the nitrogen, and indeed the Au-$C_{carbene}$ bond properties are essentially the same for the two systems. On the other hand, the $\pi_{\perp}$ back-donation component of the **13**-AuCl bond is slightly reduced with respect to that of **12**-AuCl (-0.20 instead of -0.26, respectively), even if it is still much larger than in the case of NHCs without oxygen substituents (between -0.09 and -0.13, see Table 1). The difference between carbenes **12** and **13** can be ascribed likely to the absence of ring planarity in **13**, which makes the electronic communication less effective. Substituting a ketone

group with a methylene unit (carbene **14**), the $\pi_{\perp}$ back-donation component of the NHC-AuCl bond becomes intermediate between those of **13**-AuCl and of the oxygen-free NHCs.

This indicates that in the cases of **11** and **12** there is not a real "aromaticity" because the ring is only partially involved in the electronic mobility.

Entries **15** to **20** represent changes in the NHC backbone unsaturation, showing almost no variations with respect to the corresponding NHC bearing the same corresponding groups on nitrogen atoms. In all the cases the σ donation is slightly higher for saturated rings (0.1 e, compare entries **1** and **17**, **3** and **18** and **6** and **19**), in agreement with the literature.[15]

Entries **21-26** in Table 1 refer to some of the carbenes reported in the work by Fürstner et al.[14] as previously mentioned. The authors claimed that the observed regioselectivity in gold-catalyzed cycloaddition of eneallene was achieved through modulation of the π accepting properties of the different NHCs. For example, carbenes **21** and **22**, which differ only by the presence on **22** of a cyclophane, showed opposite regioselectivity (100:0 and 0:100), but our NOCV-CD analysis indicates that they have exactly the same bond contributions in terms of σ donation and π back-donation.

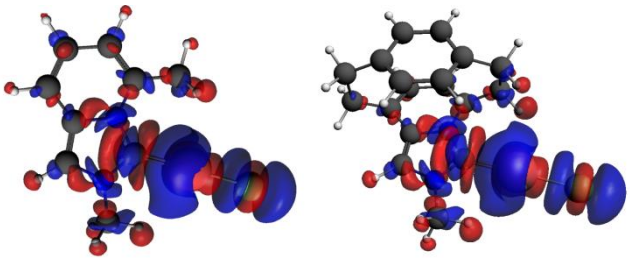


Figure 6. Isodensity surfaces of the Δρ for **21**-AuCl (left) and **22**-AuCl (right) bonds.

Indeed, comparing the isodensity surfaces of Δρ maps for the total charge rearrangement for **21**-AuCl and **22**-AuCl (Figure 6), they appear very similar and, importantly, the cyclophane of **22** does not show any depletion/accumulation of charge upon the complex formation. This justifies the fact that the presence of the cyclophane moiety does not influence the bond properties. Furthermore, we

find that such electronic properties do not change neither by varying the cyclophane substituents (fluorine atoms, **23,** or methoxy groups, **24**), confirming once again that the cyclophane is not able to modulate the Au–NHC bond.

On the other hand, the carbene **25**, which bears an additional nitrogen atom in the NHC backbone, has been reported to give a regioselectivity that is similar to those of **22** (85:15 instead of 100:0, respectively) but the NOCV-CD analysis in this case points out a slightly larger Au → $C_{carbene}$ back-donation (-0.11 instead of -0.09 e). Finally, in the NHC **26**, a nitrogen has been substituted with an sp^2 carbon, and experimentally it gives the same regioselectivity as that of **22** and opposite to that of **21**, but according to our calculations, the $\pi_\perp$ back-donation value for **26** is the same as those for **21** and **22** (-0.09 e). On the other hand, the Au ← $C_{carbene}$ σ donation is slightly enhanced (0.34 vs. 0.32 e, respectively).

On the basis of these results, we suggest that the structural variations did not lead to the desired modulation of NHCs electronic properties and therefore, the different regioselectivities in gold-catalyzed cycloaddition of eneallene studied in ref. 14 are likely to be ascribed to other effects.

Finally, we modified the carbene structure by varying the heteroatom. As noted above, addition of a nitrogen atom in the NHC structure does not change the electronic properties (entry **25**). On the contrary, the substitution of a NHC nitrogen atom with an sp^3 carbon atom (entries **27-28**) has a sizable effect both in the $\pi_\perp$ back-donation and in the σ donation. The $\pi_\perp$ back-donation component increases since the sp^3 carbon cannot obviously donate π charge on the carbene carbon, which in turn will accept more π charge from the metal, but it has a higher σ electron-donating inductive effect with respect to the nitrogen. For entry **29**, we can see that substitution of a nitrogen atom with a sulphur produces a slightly larger $\pi_\perp$ back-donation than that calculated for entry **1**.

In summary, from our detailed NHC-AuCl bond analysis, considering a large set of different NHCs, we conclude that modulation of bonding properties of NHCs requires substantial variations in their structure. Both insertion of two oxygen atoms on the NHC backbone (which enhances the $\pi_\perp$ back-donation component and introduces an electronic communication between the N-$C_{carbene}$-N and

C_2=C_3 sides of the ligand) and variation of the heteroatom in the ring, namely replacement of a nitrogen atom with an sp^3 or sp^2 carbon atom (which increases and decreases the $\pi_\perp$ back-donation component, respectively) substantially modify the NHC bonding properties, which is expected to have an impact on the catalytic activity.

Quantitative comparison of the NHC π acceptor abilities in [(NHC)PPh] and [(NHC)AuCl] systems

In this section, we aim at combining charge displacement analysis and NMR study to quantitatively compare the π acceptor properties of NHCs in [(NHC)PPh] and [(NHC)AuCl] complexes.

It is already known from the work of Nolan and Cavallo[20] that within a subset of 11 NHCs (as those shown in Figure 7 but without NHCs **12** and **13**) the DFT-computed NMR shielding of phosphorus well correlate with the experimental ^{31}P NMR chemical shift, with the energy gap between the full lone pair orbital on P and the empty π* orbital corresponding to the P–NHC bond (E_π) and reasonably well with the Hirshfeld charge on the phosphorus atom.[20] It is important to note here that the inclusion of symmetry is mandatory for NHC-PPh bond analysis in terms of σ donation and π back-donation components, since in order to prepare the PPh fragment for chemical bond with NHC, we need to doubly occupy the *p* orbital of the phosphorous atom perpendicular to NHC plane and to empty the *p* orbital of the phosphorous atom on this plane. For this reason, the geometries of all of the [(NHC)PPh] adducts have been optimized under C_s symmetry constraint, with the symmetry plane lying on the plane defined by the N-$C_{carbene}$-N atoms of NHC. In C_s symmetry, the σ donation and total π back-donation NHC-PPh bond components can be associated to the A' and A" irreducible representations, respectively. This will limit our study to the subset of carbenes for which not only the experimental value of ^{31}P NMR chemical shift is available,[18] but also for which the corresponding [(NHC)PPh] adduct can be constrained under the C_s symmetry.

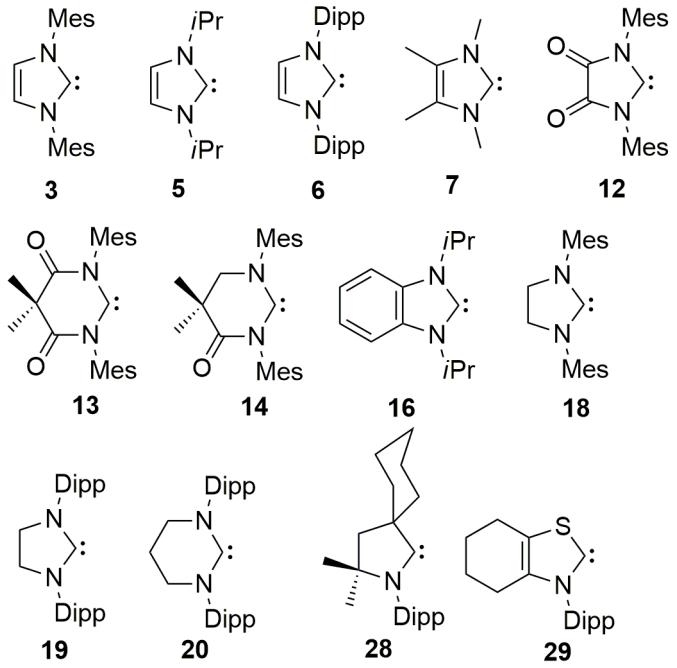


Figure 7: Schematic representation of the 13 carbenes selected for this section.

The results of the EDA and CD analysis of the NHC-PPh bond for all of the 11 NHCs are shown in Table 2 (complete EDA results available in the Supporting Information, Table S2). The EDA analysis has been performed considering neutral NHC and PPh as fragments.

Table 2. Experimental ^{31}P NMR chemical shifts (δ, in ppm), EDA (ΔE, in kcal/mol) and CD (CT, in electrons) analysis results for the NHCs-PPh bond.

NHC	δ	$\Delta E_{A'}$	$\Delta E_{A''}$	$CT_{A'}$	$CT_{A''}$	CT_{Net}
3	-23.0	-168.9	-37.0	0.48	-0.43	0.05
5	-61.2	-175.8	-29.4	0.46	-0.38	0.09
6	-18.9	-168.5	-38.2	0.48	-0.45	0.03
7	-53.5	-175.4	-28.8	0.46	-0.37	0.09
12	78.6	-173.1	-66.6	0.55	-0.71	-0.16
13	83.0	-172.7	-62.0	0.56	-0.68	-0.12
14	39.7	-172.0	-49.6	0.52	-0.57	-0.04

16	-34.6	-179.9	-34.9	0.48	-0.45	0.03
18	-10.4	-172.1	-40.8	0.50	-0.47	0.03
19	-10.2	-172.2	-41.8	0.50	-0.48	0.02
20	14.8	-171.0	-38.6	0.49	-0.45	0.04
28	68.9	-190.8	-50.9	0.53	-0.56	-0.04
29	57.0	-174.2	-45.7	0.49	-0.53	-0.05

From Table 2 we can see that the A' component of CTs varies from 0.46 e for carbenes **5** and **7** to 0.56 e for carbene **13**, whereas the A' orbital energy component ($\Delta E_{A'}$) varies from -168.5 to -190.8 kcal/mol for carbenes **6** and **28**, respectively. For the A" component the CTs variation range is 0.34 e, with carbene **12** being the most π acceptor ligand. Correspondingly, $\Delta E_{A"}$ varies from -28.8 to -66.6 kcal/mol, with carbene **12** showing the largest value, in agreement with its strongest π acceptor properties. Indeed, from EDA and CD analysis results we find that $\Delta E_{A"}$ nicely correlates with $CT_{A"}$ ($r^2 = 0.9879$, Figure S3, Supporting Information).

To be consistent in our NHC π acceptor property transferability study from [(NHC)PPh] to [(NHC)AuCl] complexes we re-analyzed the NHC-AuCl bond in C_s symmetrized geometries, using the NHCs shown in Figure 7.

Analogously, the results of the EDA (which has been performed considering neutral NHC and AuCl as fragments) and CD analysis of the NHC-AuCl bond for all of the 13 carbenes are shown in Table 3 (complete EDA results available in Table S3, Supporting Information).

Table 3: EDA and CD analysis results for the NHCs-AuCl bond. All energies are in kcal/mol and all CTs are in electrons.

NHC	$\Delta E_{A'}$	$\Delta E_{A"}$	$CT_{A'}$	$CT_{A"}$	CT_{Net}
3	-60.7	-14.2	0.20	-0.12	0.08

5	-60.6	-12.4	0.21	-0.08	0.12
6	-60.9	-14.5	0.18	-0.13	0.05
7	-59.9	-12.2	0.21	-0.08	0.13
12	-60.4	-22.7	0.23	-0.25	-0.02
13	-61.1	-20.4	0.21	-0.22	-0.01
14	-61.7	-16.6	0.20	-0.17	0.02
16	-60.6	-13.6	0.21	-0.10	0.11
18	-61.6	-14.6	0.20	-0.13	0.07
19	-61.8	-15.0	0.19	-0.15	0.04
20	-62.7	-14.3	0.18	-0.15	0.03
28	-63.3	-17.6	0.23	-0.17	0.05
29	-61.2	-16.1	0.21	-0.14	0.06

We should remind here that the CT_{Net}, $CT_{A'}$ (σ donation) and $CT_{A''}$ (π back-donation) values in Table 3 are not identical to the corresponding values in Table 1, as expected, but, as discussed above for the [(**1**)AuCl] complex, results from the NOCV-CD and the symmetry-based CD methodologies are similar.

From Table 3 we can see that the A' component of CTs varies from 0.18 e for carbene **6** to 0.23 e for carbenes **12** and **28**. For the A'' component, the CT variation range is 0.17 e, with carbene **12** being the most π acceptor ligand. Correspondingly, $\Delta E_{A'}$ spans a range of 3.4 kcal/mol, with carbene **24** showing the largest value (-63.3 kcal/mol) in agreement with its largest σ donating ability. For $\Delta E_{A''}$, the orbital energy varies from -12.2 to -22.7 kcal/mol, for carbenes **7** and **12**, respectively, the latter showing again the largest value, in agreement with its strongest π acceptor properties. Analogously to the NHC-PPh bond, from EDA and CD analysis results in Table 3, $\Delta E_{A''}$ correlates reasonably well with $CT_{A''}$, with a correlation coefficients R^2 of 0.9705 (Figure S4,

Supporting Information). The system [(**20**)AuCl] lies out of the trend, but for this system the C_s constraint leads to a particularly tense configuration.

Importantly, the values of $CT_{A"}$ for the two systems linearly correlate each other (r^2 = 0.961, see Figure 8), even if some scattering is present, with NHCs **16** and **20** being the most outliers.

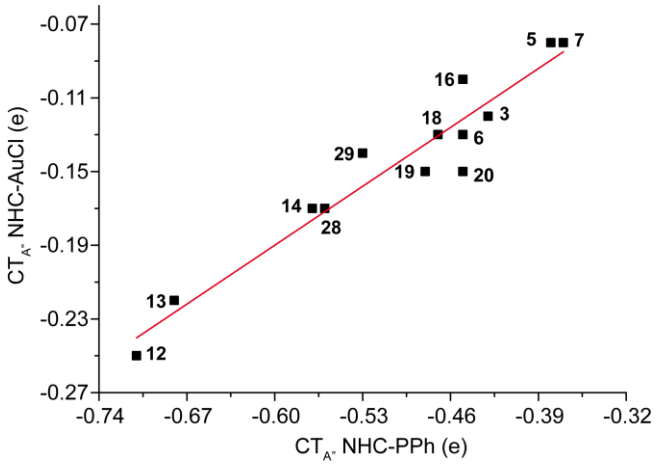


Figure 8. Correlation plot of $CT_{A"}$ for [(NHC)PPh] and [(NHC)AuCl] systems.

According to such a correlation, any information obtained on the nature of the NHC-PPh bond can be transferred to the nature of the NHC-AuCl bond with a precision of about ± 0.04 e.

We can now analyze in the Figure 9 the correlation between the experimental NMR chemical shift (δ) of the ^{31}P nucleus in [(NHC)PPh] systems, and the $CT_{A"}$ component of the bond, for both [(NHC)PPh] and [(NHC)AuCl] systems. As said in the Introduction, such a parameter well correlates with $\Delta E_{A"}$,[20] at least for a subset of the carbenes here studied.

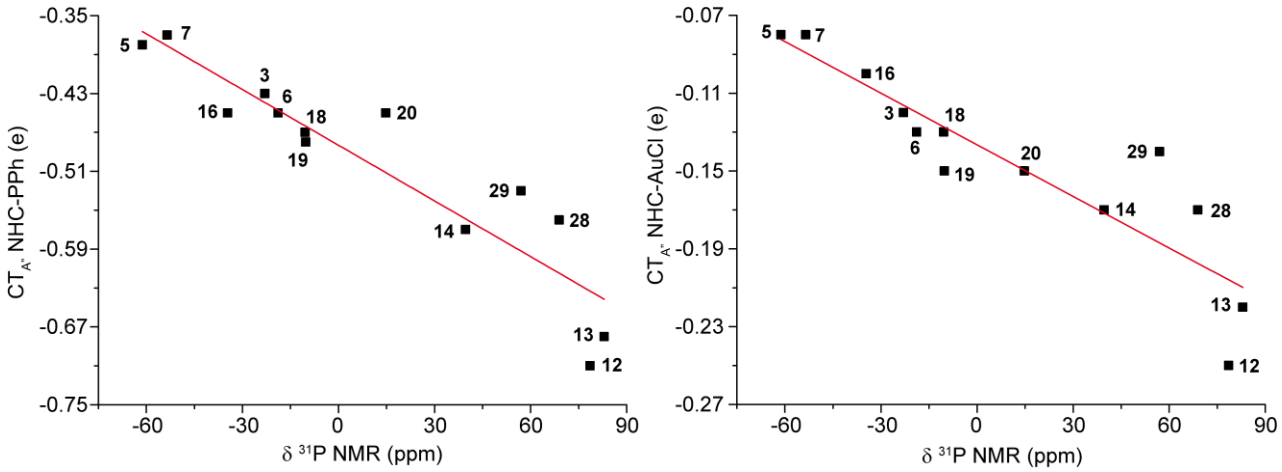


Figure 9: Correlation plot of experimental ^{31}P NMR chemical shifts vs. $CT_{A''}$ of the left) NHC-PPh bond on the basis of the values given in Table 2 and right) NHC-AuCl bond on the basis of the values given in Table 3.

Such correlations hold from the qualitative point of view, with r^2 = 0.8341 and 0.9170 for [(NHC)PPh] and [(NHC)AuCl] systems, respectively, but fail under the quantitative one, giving a precision in the estimation of CT of ± 0.08 e. The correlation parameter for the [(NHC)PPh] system is essentially the same using $\Delta E_{A''}$ (0.8489), but it is much worse for [(NHC)AuCl] systems (0.7864, see Figure S5, Supporting Information).

Interestingly, the data are less scattered in the negative region of the chemical shield (NHC with a low π acidity), whereas the correlation is practically lost for carbenes with an enhanced π acceptor ability, as **12**, **13** and **28**. Indeed, all of them show similar values of δ ^{31}P NMR (78.6, 83.0 and 68.9 ppm, respectively) and very different values of $CT_{A''}$ for the NHC-PPh bond (0.71, 0.68 and 0.56 e, respectively). Since the latter well correlates with the $CT_{A''}$ for the NHC-AuCl bond, also in the case of the metal the correlation is better at negative values of δ and worse in the positive region.

Evidently, other factors than the π acceptor properties of the carbene are important for the NMR chemical shielding. In particular, this ^{31}P NMR chemical shift/NHC π acceptor ability mismatching may be due to the large variation that the inclusion of oxygen atoms on the carbene backbone induces on the dipole moment of the complex. We actually checked that the calculated dipole

moment of **12** is greatly reduced (-3.0 Debye) compared to those of the other NHC (with dipole moments in the range 1.3-4.0 Debye) (see Table S4 in the Supporting Information).

Conclusions

N-Heterocyclic Carbenes (NHCs) represent nowadays a very important class of molecules used in many fields of chemistry, such as organocatalysis, organometallics and as ligands for catalytic processes. The great variability of the carbene structure allows the fine tuning of the chemical bond components in organometallic chemistry, namely σ donation and π back-donation. However, the complete rational control of these properties, based on a quantitative ground, is still a challenge, both experimentally and computationally. In this work, we used an innovative methodology, the Charge-Displacement CD within the NOCV approach, to quantify the electronic properties of carbenes. For this purpose, we used the AuCl fragment as a probe. We analyzed the NHC-AuCl bond for a large set of 29 NHCs, with different structures. We found that, contrary to the common belief, the modulation of the electronic properties of NHCs requires strong changes in their structure. Substitution of groups on nitrogen atoms or NHC backbone, modification of the backbone insaturation or insertion of cyclophane rings only marginally change the bonding properties of NHCs. Instead, the inclusion of two oxygen atoms on the NHC backbone sensibly increases the π back-donation component of the NHC-AuCl bond. Another way for deeply modifying the electronic properties of NHCs is to change the heteroatom. For example, replacing a nitrogen atom with an sp^3 carbon, namely considering a CAAC, produces an increase in the π back-donation and a decrease in the σ donation ability of NHC. Substitution of a nitrogen atom with an sp^2 carbon atom, instead, causes a decrease of the π back-donation bond component.

We also addressed the NHC π acceptor properties and ^{31}P NMR chemical shift relationship issue. selecting a subset of 13 NHCs for which experimental the ^{31}P NMR data are available in [(NHC)PPh] adducts. We analyzed the chemical bond in these [(NHC)PPh] adducts, since, as it has been suggested by Bertrand et al.,[18] their ^{31}P NMR chemical shift should be related to the π acceptor

properties of the NHCs. We supported the qualitative correlation between π back-donation NHC-PPh bond component and ^{31}P NMR (found also previously[20]) and we also demonstrated that the information on the chemical bond obtained for [(NHC)PPh] adducts can be qualitatively transferred to [(NHC)AuCl] complexes. Despite that, the attempt to generalize the NHC π acceptor properties and ^{31}P NMR chemical shift relationship, by extending the carbene already studied in the literature[20] through inclusion of others with stressed π back-donation component, failed, since data are much more scattered for these systems. All these findings lead us to conclude that the ^{31}P NMR can be indeed indicative of the NHC π acceptor ability when carbenes of similar structure are compared, and probably only in a limited range of π back-donation. Caution should be used when NMR data are used as a general tool for quantifying π accepting properties of carbenes.

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[39] It can be noted that carbenes **1**, **2** and **6** show similar values for all the components, but different values of CT_{Net}. This can be explained by the fact that the sum of all the other components, other than those described here, can be important. In the case of **1** and **2**, small charge rearrangements can be noted on the group bound to N (Figure S1, Supporting Information).

[40] It is important to underline that the correlation between the back-donation and the Au-$C_{carbene}$ bond distance is quite poor, see Figure S2, Supporting Information.

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