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Review

Stereoelectronic parameters associated with N-heterocyclic carbene (NHC) ligands: A quest for understanding

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Contents

Abstract

The latest advances in N-heterocyclic carbene-based organometallic chemistry have drawn increasing attention to this class of ancillary ligands as an attractive alternative to tertiary phosphines. Studies focusing on the fundamental steric and electronic factors characterizing this family of compounds are therefore essential for the rationalization of the activity observed for such organometallic complexes in metal-mediated organic transformations. This knowledge is also of fundamental importance in catalyst design efforts. This review intends to provide a comprehensive overview of the progress in this area.

Keywords: N-Heterocyclic carbenes; Transition metals; Metal–ligand bond; Stereoelectronic; Catalysis

1. Introduction

Carbenes are electron-deficient two-coordinate carbon compounds that have two non-bonding electrons on that carbon. In the ground state, the two unshared electrons may be either in the same orbital with antiparallel spins (singlet state), or in two different orbitals with parallel spins (triplet state).

The quest for a stable carbene was long considered an unreasonable target, until Wanzlick showed that the stability of carbenes could be dramatically increased by vicinal amino substituents [1]. However, no isolation of a ‘monomeric’ carbene was achieved at that time. In 1964, Fischer reported the first stable transition metal complexes bearing carbene ligands [2]. The so-called Fischer-carbene complexes were characterized as having a electrophilic carbenic carbon. Ten years later, Schrock isolated a different type of carbenic complex in which the polarization of the metal-carbon bond is inverted and the carbenic carbon was nucleophilic [3].

Between these two groundbreaking discoveries, Wanzlick [4] and Öfele [5] reported independently the first (NHC)-transition metal complexes. In 1988, Bertrand and co-workers succeeded in isolating the first stable carbene [6]. Unfortunately, the

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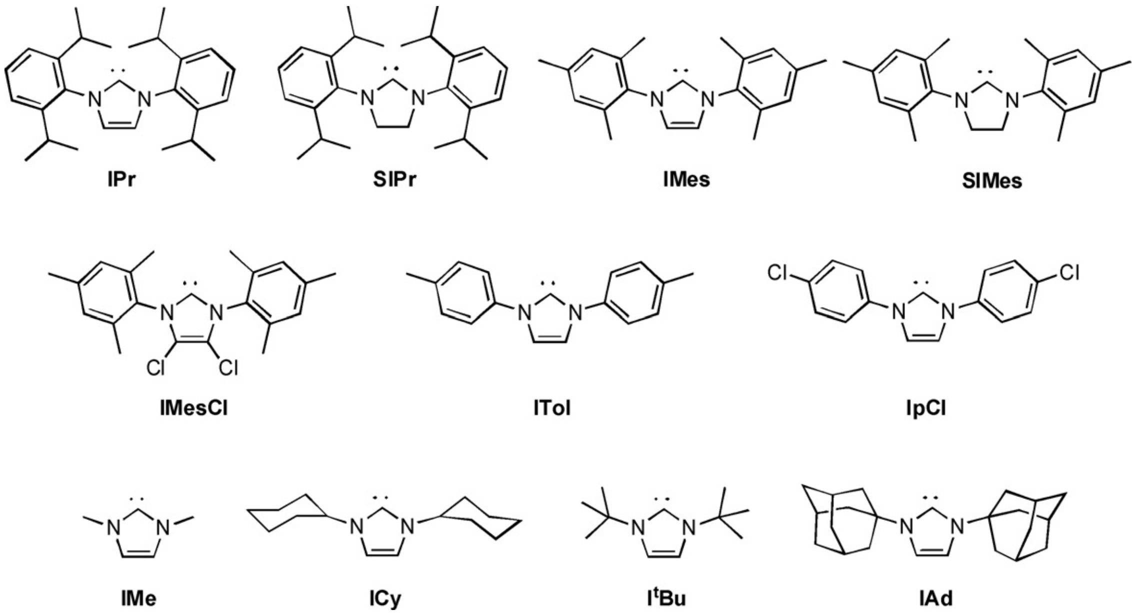


Fig. 1. Structures of N-heterocyclic carbene ligands.

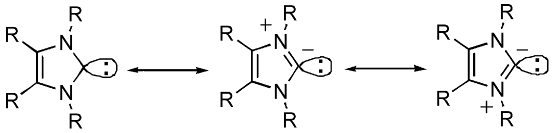
reported (phosphino)(silyl)carbene did not show any ability as a ligand for transition metals. The isolation of a free imidazol-2-ylidene by Arduengo et al. in 1991 provided access to numerous transition metal carbene complexes by simple complexation of a stable carbene [7]. The dogma that carbenes were only transient species disappeared and a new and exciting field of research unfolded for synthetic chemists.

The unexpected stability of the N-heterocyclic carbenes (NHCs) has prompted several groups to carry out studies in order to better understand these unusual species. The nature and strength of the (NHC)–metal bond are key information to rational catalyst design. Studies aimed at quantifying phosphine steric and electronic effects have had a major impact on the development of new and improved ligands for catalysis [8].

First considered as simple phosphine mimics [9], there is increasing experimental evidence that (NHC)–metal catalysts surpass their phosphine-based counterparts in both activity and scope [10]. Despite the existence of several families of stable carbenes, only the five-membered cyclic diamino carbenes have found numerous applications so far. Even if exceptions have been reported [11], free acyclic carbenes including diamino carbenes [12] are far more fragile than these NHCs and are poorer ligands, so far, for transition metal complexes [13]. Although some representative examples will be presented, their discussion will not be exhaustive. Structures for the most commonly employed carbene ligands are shown in Fig. 1.

2. Electronic structure of NHCs: the aromaticity question

To date, all theoretical and experimental evidence indicates that, in order to form a stable carbene, the carbenic carbon needs to be bonded to strong π-donor atoms [14]. However, the remarkable stability of the first isolated carbene, IAd, was totally unexpected at the time. Ab initio studies led Dixon and Arduengo to postulate that p(π)–p(π) delocalization is not extensive and that the bonding in these ligands should be considered carbenic since ylidic resonance structures are not dominant contributors (Eq. (1)) [15]. Similar conclusions have been reached using diverse techniques [16]: the unexpected stability of free NHC would arise mainly from substantial σ-charge transfer from the carbenic carbon to the more electronegative neighboring nitrogen atoms. Therefore, π-donation would only play a minor role.

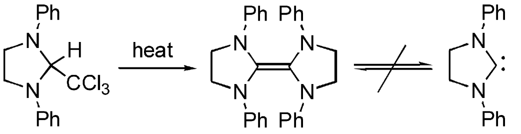


(1)

Additional steric protection from the N-substituents may enhance the stability of the carbenes and it might compensate for less electronic stabilization, but it is not a decisive factor since sterically less demanding substituents also lead to isolable carbenes [17].

However, it has been argued that the dominant factor stabilizing the carbenes is the donation from the nitrogen lone pairs into the formally empty p(π) orbital of the carbene carbon atom [18]. These authors also showed that the method of density mapping employed by Arduengo was not suitable for analyzing electron delocalization. Related theoretical and experimental reports have also suggested that there is a cyclic electron stabilization, conferring the imidazol-2-ylidenes a certain aromatic character [19]. This aromaticity would be appreciably smaller than in 'standard' systems such as benzene or imidazolium salts but still significant from magnetic and thermodynamic perspectives. At this point, it is important to note that there is no direct way to correlate the degree of conjugation with the resulting thermodynamic stabilization [20].

Intuitively, the essential stabilizing role of the C=C bond in imidazol-2-ylidenes has been evoked for a long time. Wanzlick's pioneer work on saturated carbenes, where only the corresponding dimers could be isolated [21], seemed to also point in this direction (Eq. (2)). The classical explanation invoking a thermodynamic stabilization of the carbenes via cyclic 6π-electron delocalization had to be reviewed after the isolation of the first imidazolin-2-ylidenes in 1995 (Eq. (3)) [22]. It was then clear that such a delocalization would only be an additional stabilizing factor, and that the electron donation of the nitrogen atoms would be necessary and sufficient for stabilizing the free carbene. Arduengo alternatively suggested a kinetic stabilization provided by the double bond which was stated as critical for achieving an electron repulsion strong enough to prevent any electrophilic reactivity of the carbene [16c].



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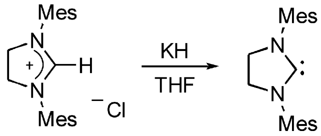

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3. Thermodynamics of the (NHC)–metal bond: electronic and steric factors

3.1. Electronic factors

Chemical computations often provide good approximations for bond strength values, but the experimental determination by thermodynamic means results in unquestionable values.

A major breakthrough in the importance of NHCs in metal-catalyzed reactions came from the preparation of NHC–ruthenium complexes. These highly thermally stable catalysts **C** [23] and **D** [24] (Fig. 2) have allowed the preparation of functionalized carbocycles and heterocycles from the corresponding acyclic diene precursors that were unattainable using Schrock's [25] or Grubbs' [26] catalysts **A** and **B**.

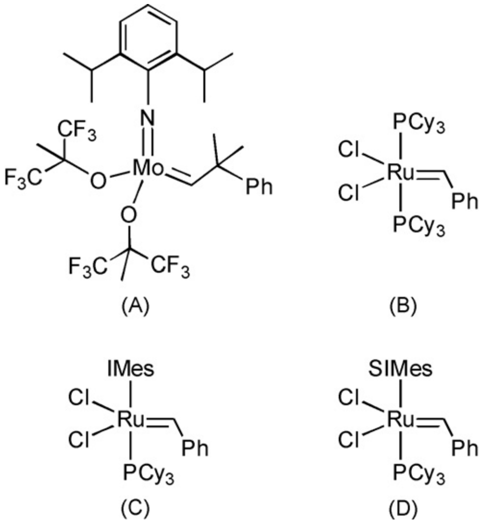


Fig. 2. Pre-catalysts for olefin metathesis.

Table 1
Enthalpies of ligand substitution and relative reaction enthalpies (kcal/mol)

$$[Cp^*RuCl]_4 + 4L \xrightarrow[30\ ^{\circ}C]{THF} 4Cp^*Ru(L)Cl$$

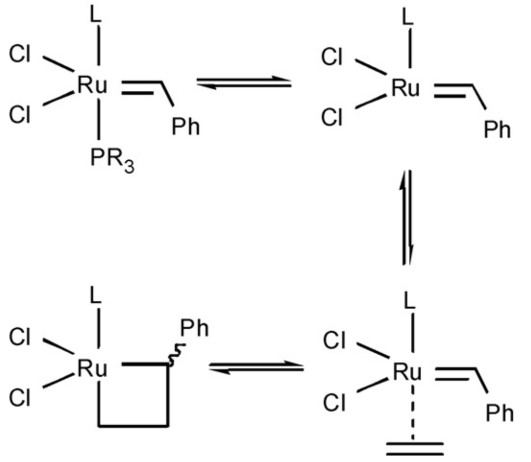
L	$-^2H_{rxn}$	Relative BDE
ICy	85.0 (0.2)	21.2
ITol	75.3 (0.4)	18.8
IpCl	74.3 (0.3)	18.6
IAd	27.4 (0.4)	6.8
IMesCl	48.5 (0.4)	12.1
IMes	62.6 (0.2)	15.6
PCy_3	41.9 (0.2)	10.5
P^iPr_3	37.4 (0.3)	9.4

The $Cp^*Ru(L)Cl$ system ($Cp^* = \eta^5$-C_5Me_5) has been used as model for quantifying ligand effects in ruthenium-based olefin metathesis [27]. The measurement of reaction enthalpies of $[Cp^*RuCl]_4$ [28] with different sterically demanding two electron donors allowed for the establishment of a relative scale of bond dissociation energy (BDE). Enthalpy values were determined by anaerobic solution calorimetry, reacting 4 equiv of each carbene with 1 equiv reaction enthalpies could be converted to BDE values by simply dividing by 4 (the number of bonds formed in the course of the reaction) [29]. As shown in Table 1, NHCs behave as better donors than the best donor phosphine ligands with the exception of IAd. The origin of the low BDE in this case is in the steric effect of the adamantyl groups on the imidazole, which hinder the carbene lone pair overlap with metal orbitals.

The higher catalytic activity of **D** over **C** in alkene metathesis has been attributed to a greater donor ability of saturated carbenes, with no supporting quantitative evidence. Calorimetric studies showed that contrary to expectation, differences in reaction enthalpies between IMes and SIMes (as well as IPr and SIPr) were of only 1 kcal/mol [30]. These data suggest that small differences in the donor capacities of NHC ligands might be responsible for significant enhancements in catalytic activity but subtle steric factor differences may also play an important role.

In the widely accepted mechanism for the ruthenium-catalyzed olefin metathesis [31], dissociation of a phosphine is followed by the formation of an olefin π complex that evolves to the metalacycle intermediate (Scheme 1). Unlike what was first believed, the NHC ligand does not promote phosphine dissociation. Recent theoretical studies [32] have shown that the strong steric pressure due to the NHC destabilizes a phosphine and olefin free intermediate, thus slowing the catalyst initiation. However, this ligand promotes olefin coordination, lowers the activation barrier and stabilizes the metalacycle intermediate, which explains the overall reaction acceleration experimentally observed with **C** and **D**.

It has also been suggested that the higher catalytic activity of ruthenium complexes bearing saturated carbenes might be due to the increased basicity of the ligand [23b]. However, there are only a few reports in the literature dealing with the experimental pK_b [33] of imidazo-2-ylidenes [34]. Recent theoretical calculations have allowed for a classification of a number of car-



Scheme 1. Partial proposed mechanism for the olefin metathesis.

bene according to their basicity (Fig. 3) [35]. This study showed that electron delocalization is not key in determining basicity. The most influential factors would be the substitution on the backbone and mainly the NCN bond angle.

These results support the experimental suggestion that the bis(diisopropylaminocarbene) [36] is probably the most basic carbene ligand known to date [37]. Moreover, the very basic phosphine P^{t}Bu$_3$ is still 10 pK_b units less basic than the least basic carbene [38]. However, it should be taken into account that no studies on the basicity of late generation phosphines, that have shown enhanced catalytic activities, have been reported to date [39].

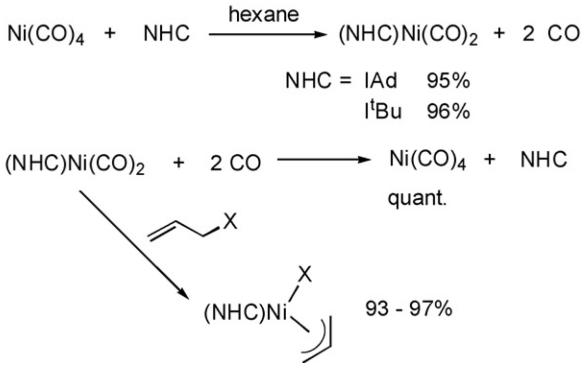
Another empirical approach to the understanding of these ligands is based on the study of the carbonyl stretching frequencies of NHC-containing carbonyl transition metal complexes. To date, all reports point to the fact that NHCs are more electron-donating than phosphines [40]. Notably, the substitution reactions involving Ni(CO)$_4$ and NHC ligands have been studied to some extent [41]. When reacted with this nickel precursor, most carbene ligands form the saturated (NHC)Ni(CO)$_3$ complexes (Scheme 2) [42]. Direct comparison of the electronic properties of NHCs with phosphines [43] could be done measuring the carbonyl stretching frequencies of these complexes. These data clearly showed that NHCs are better σ-donor than even the very basic phosphine, P^{t}Bu$_3$. Of note, IR data have also suggested that abnormal C5-bound NHCs would be substantially stronger electron–donor than normal C2-bound carbenes [44].

$$\mathrm{Ni(CO)_4} + \mathrm{L} \xrightarrow[\text{hexane}]{\text{THF or}} \mathrm{(L)Ni(CO)_3} + \mathrm{CO}$$

Ligand	Yield (%)	υ_{CO} (A$_1$)^a	υ_{CO} (E)^a
IPr	86	2051.5	1970.0
SIPr	84	2052.2	1971.3
IMes	95	2050.7	1969.8
SIMes	91	2051.5	1970.6
ICy	88	2049.6	1964.6
P^{t}Bu$_3$		2056.1	1971
PPh$_3$		2068.9	1990

^{a} In cm^{-1}, mesured in CH$_2$Cl$_2$

Scheme 2. Preparation and IR values of (NHC)Ni(CO)$_3$ complexes.



Scheme 3. Preparation and reactivity of (NHC)Ni(CO)$_2$ complexes.

These results suggest notably that the saturated NHC ligands would be slightly less electrodonating than their unsaturated analogues and that alkyl-substituted NHCs are only marginally more electron-donating than their aryl-substituted counterparts, which contradicts again the accepted dogma.

Under the reaction conditions depicted in Scheme 2, more hindered NHCs such as IAd and I^{t}Bu led to the formation of extremely rare [45] tricoordinated carbonyl complexes (Scheme 3). Due to the unsaturated nature of these complexes, both the NHC or the carbonyl ligands could be displaced depending on the reaction conditions.

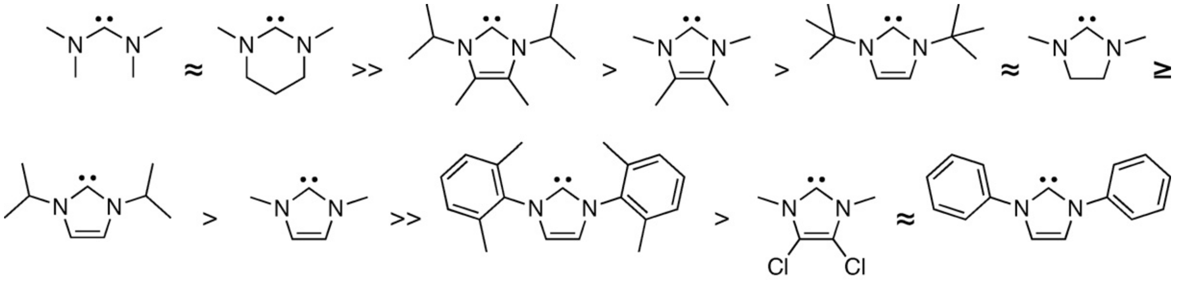


Fig. 3. Classification of carbenes according to their theoretical pK_b values.

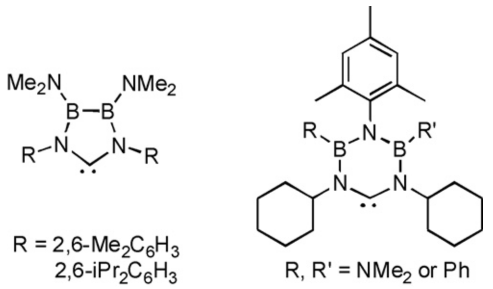


Fig. 4. Boron-substituted carbenes.

Stable NHCs with a diboron backbone [46] and six-membered ring carbenes derivatives of borazines have recently been reported (Fig. 4) [47]. Variation of the boron substituents would notably allow tuning the electronic properties without changing the steric demands and therefore might permit a better understanding of the factors governing the catalytic activity of organometallic complexes.

3.2. Steric factors

It is clear that the overall availability of the carbene lone pair is dependent of a combination of steric and electronic properties of the ligand in a given coordination environment [48]. Crystallographic studies on the Cp*Ru(L)Cl complexes did not lead to a straightforward correlation between the enthalpy of reaction and the bond length [27]. This is due to the existence of significant reorganization energies in this system, a phenomenon previously observed in a rhodium-based system [49]. In general, from structural studies one can only conclude that bulkiness of the groups bound to the nitrogen atoms of the NHC ligands and more importantly, the short metal–carbon distances in these complexes, increase the steric congestion around the metal center when compared to tertiary phosphines.

In order to quantify the steric requirements of these ligands, a new model was designed: the percent of the volume occupied by ligand atoms in a sphere centered on the metal (%V_{Bur}, see Fig. 5). This model allows for a more realistic comparison with other ligands, particularly tertiary phosphines. The model also takes into account the high asymmetry of these ligands.

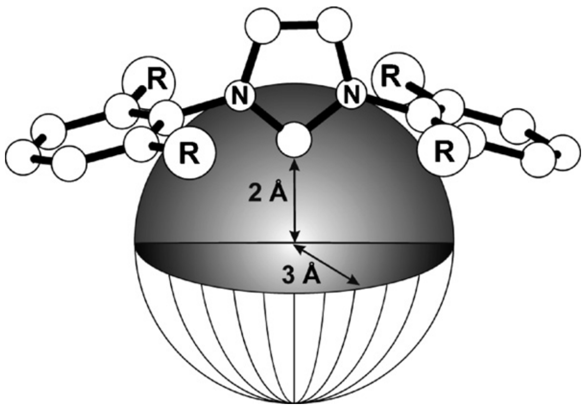


Fig. 5. Representation of the sphere dimensions for steric parameter determination (%V_{Bur}) of NHC ligands (figure was reproduced from Ref. [10g]).

Table 2
CO and ligand BDE and %V_{bur} values for (L)Ni(CO)$_2$ and (L)Ni(CO)$_3$ complexes (kcal/mol)

Ligand	BDE of CO in (L)Ni(CO)$_3$	BDE of L in (L)Ni(CO)$_3$	BDE of L in (L)Ni(CO)$_2$	%V_{bur}
I^{t}Bu	13.3	24.0	44.3	37
IAd	7.6	20.4	46.5	37
IMes	28.3	41.1	46.5	26
SIMes	26.8	40.2	47.2	27
IPr	26.7	38.5	45.4	29
SIPr	25.6	38.0	46.1	30
ICy	27.0	39.6	46.3	23
PPh$_3$	30.4	26.7	30.0	22
P^{t}Bu$_3$	27.4	28.0	34.3	30

For Cp*Ru(L)Cl complexes the experimental (and theoretical) BDEs plotted versus %V_{Bur} resulted in a linear correlation, which indicates that in this system the BDEs are essentially controlled by the steric requirements of the ligand [30].

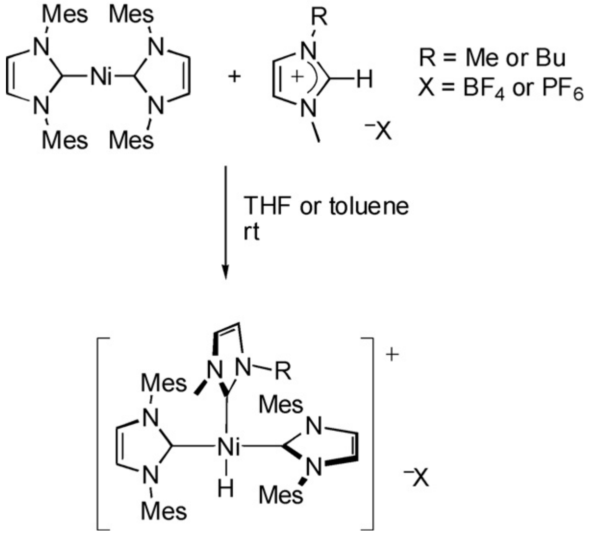
As mentioned before, only small electronic differences were experimentally observed in (NHC)Ni(CO)$_x$ complexes [42]. Theoretical calculations reinforced this observation, indicating that any difference between NHC ligands is steric in nature (Table 2). In fact, the larger values of %V_{Bur} I^{t}Bu and IAd ligands relative to IMes, SIMes, IPr, SIPr and ICy ligands were in qualitative agreement with the different calculated BDEs. Moreover, calculation of %V_{Bur} of PR$_3$ systems allowed for a direct comparison between the two ligand families showing that interestingly, the two most sterically demanding carbenes are bulkier than P^{t}Bu$_3$.

3.3. Influence of both factors in catalysis and stabilization effects

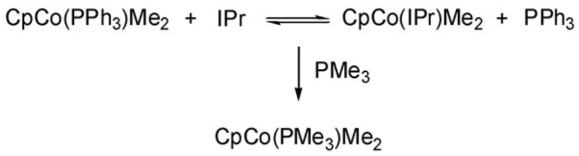
The right combination of electronic and steric factors characterizing NHCs has been key to rationalize the stabilization of otherwise highly reactive species. Triscarbene-nickel–hydride complexes are a representative example [50]. Prepared by oxidative addition of electron-rich (NHC)$_2$Ni complexes into the C2–H bond of imidazolium salts (Scheme 4), these first reported (NHC)nickel–hydrides turn out to be surprisingly stable in solution, in the solid state and even in air. The stabilization of these hydrides was explained by the directional distribution of the steric bulk and the electronic properties of carbene ligands. The ‘steric factor’ has also been evoked in the study of other nickel(0) complexes and their catalytic activity in the C–C and C–F activation reactions [51].

Structural and catalytic studies on (NHC)Pd(R-allyl)Cl complexes showed a striking difference of activity in aryl amination reactions between the IPr-containing complex and the SIPr analogue, the latter being up to 60 times faster in catalysis than the former [52]. This variation in reactivity was associated with the increased hindrance associated to the SIPr ligand, rather than its electronic donation ability.

Nevertheless, an excessive steric pressure around the metal center can render labile the NHC–metal bond. Relief of this pressure would be a significant driving force leading to lig-



Scheme 4. Preparation of $(NHC)_3$Ni-hydride complexes.



$CpCo(PPh_3)Me_2$ + IPr ⇌ $CpCo(IPr)Me_2$ + PPh_3 ; $\xrightarrow{PMe_3}$ $CpCo(PMe_3)Me_2$

Scheme 5. Phosphine–carbene exchange reactions in cobalt complexes.

and dissociation. For instance, the reaction of a (PPh_3)-bearing cobalt complex with free IPr did not led to a displacement of the phosphine by the NHC, as expected [53]. On the contrary, the reaction reached an equilibrium that allowed for the collection of thermodynamic data for the interchange of phosphine and carbene ligands (Scheme 5). Furthermore, addition of a less demanding phosphine to the reaction mixture led to the total displacement of the carbene ligand.

Another example with direct implications in catalysis is an analog of Wilkinson's catalyst, $(PPh_3)_3RhCl$, in which one of the phosphines had been replaced by an IMes ligand [54]. This complex underwent cleavage of the Rh–carbene bond when treated with triphenylphosphine in hot dichloroethane to yield quantitatively Wilkinson's catalyst (Scheme 6) [55]. The corresponding carbene salt and a dimer formed from a double S_N2 reaction between the solvent and two molecules of the carbene were also formed during this reaction. Catalytic studies showed that the NHC complex is less active than the Wilkinson catalyst in hydrogenation reactions. Remarkably, no displacement was observed from a less congested (NHC)–rhodium complex, even under harsher reaction conditions.

This work illustrates the need of carefully interpreting the catalytic results. During the reaction, loss of the carbene and formation of new species with greater catalytic activity can lead to incorrect assumptions regarding the activity of the original carbene-ligated complex [56].

4. Nature of the (NHC)–metal bond

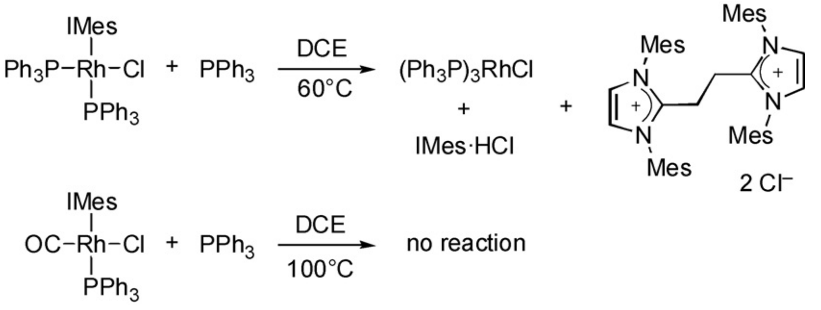
For decades it has been accepted that divalent carbon species: CR^1R^2 exhibit σ-donor and π-acceptor properties upon binding to transition metals. The coordination of conventional carbenes depends mainly on π back-bonding since they are weak σ-donor, but early studies suggested that the π-acceptor ability of NHCs, lying between those of nitriles and pyridine, was negligible [57]. However, more recent results point to a more flexible behavior of NHCs where back-donation might importantly contribute to the stabilization of the metal center [58].

4.1. NHC ligands as pure σ-donors

The potential of NHCs to bind metal centers incapable of π back-donation has long been used as an empirical evidence of their pure σ-donor character. NHC-bearing complexes of main group elements and rare earth metals can be viewed as donor adducts, just like ammonia and ether complexes [59]. Magnesium [60], boron [61], aluminum [62], gallium [63], thallium [64], or silicon [65] as well as ytterbium and samarium [66] form stable adducts with NHCs.

The complexation chemistry of the heavier members of group 2 was first reported by Arduengo [67]. A number of mono carbene metallocene adducts derived from Mg, Ca, Sr and Ba were carefully studied by NMR and crystallography techniques. It was found that the nature of the carbene-metal bond ranges from somewhat covalent for magnesium to rather ionic for barium.

Later, Arnold and co-workers reported the synthesis of metal complexes bearing bidentate amido-NHC ligands [68]. These lithium, magnesium and uranium complexes showed significant distortion of the metal–carbene bond that did not translate in a



Scheme 6. Reactivity of (NHC)–rhodium complexes in chlorinated solvents.

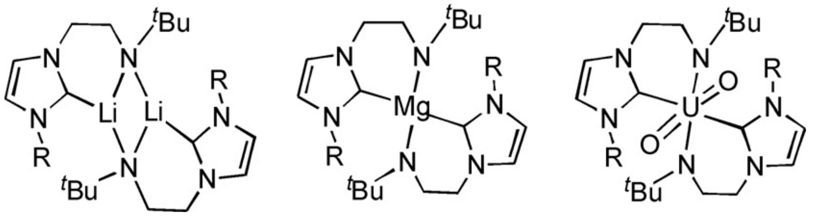
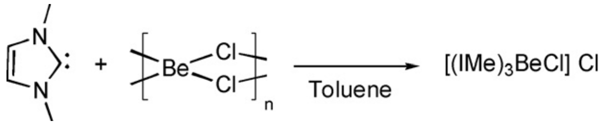


Fig. 6. Amido NHC complexes.



Scheme 7. Synthesis of a (NHC)–Be complex.

decrease of this bond strength. This fact indicates that bonding is predominantly electrostatic in nature (Fig. 6).

The beryllium case deserves to be highlighted since Be^{2+} is one of the hardest Lewis acids known [69]. Treatment of beryllium chloride with IMe led to the formation of a tris-carbenic ionic complex (Scheme 7) [70]. Introduction of four ligands proved impossible even when a large excess of ligand was employed.

Theoretical analysis of the bonding situation in beryllium carbene complexes showed that the population of the p(π) orbital of the carbenic carbon is the key factor in the isolation of carbene complexes [71]. Since no back-donation would be possible in the case of beryllium, π-donation from the substituents of the carbene, enhanced by the coordination to a pure acceptor metal, would explain the stability of this complex.

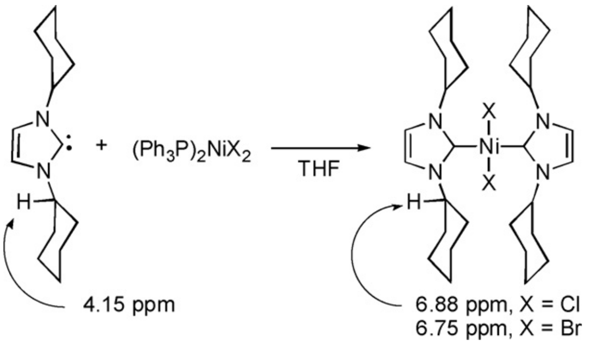
Strong electron donation from the nitrogen atoms to the carbene–metal bond has also been suggested in transition metal complexes. For example, in bis(NHC)nickel(II) complexes, the NMR signal corresponding to the α-CH proton at the cyclohexyl ring (Scheme 8) shifted more than 2 ppm when compared to the free carbene [72]. This effect could also be explained by the anisotropy of the imidazolium ring, though.

A number of experimental and/or theoretical studies have also suggested that π-back donation is negligible in NHC-transition metal bonding [73].

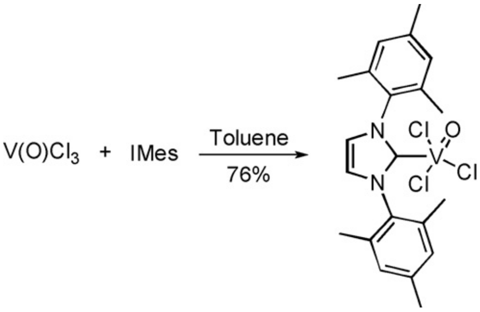
4.2. Importance of the π interaction in NHC-bearing complexes

The simplified picture of NHC as mere σ-donors is now obsolete and several reports have suggested that empty π, π* orbitals on the NHC ring can contribute to the NHC–metal bond [74]. Already in 1975, the existence of π back-bonding in ruthenium(II) complexes bearing a carbon-bound xanthine was reported [75]. Similar interactions were reported to allow for the isolation of a vanadium(V) trichloro-oxo NHC complex (Scheme 9) [76]. In this first report concerning NHC as stabilizing ligands of high oxidation state transition metal complexes, unexpectedly short distances were observed between the *cis* chlorine atoms and the carbonic carbon (2.849 and 2.887 Å, respectively). The strong interaction between chlorine lone pair electron density and the formally vacant p(π)-orbital of the carbenic carbon was illustrated by DFT calculations and it can be considered as a form of back-donation in which the electron density comes from the chlorine ligands rather than the metal center [77]. Similarly, Shukla et al. found that there is an electron-density transfer from the ancillary chloride ligands to the p(π) orbital of the carbenic carbon of the $TiCl_2(NMe_2)_2$ adduct with IMes [78].

Non-negligible π-interaction between group 11 metals and NHC ligands had also been previously postulated [79], but it was Meyer and co-workers who showed their existence by computational analysis [80]. First reported with silver, copper and gold complexes bearing tripodal polycarbene ligands ($TIME^{Me}$, see Fig. 7) were also subjected to DFT calculations. An overall σ donation from the ligand to the metal, in accordance with the well-known strong Lewis basicity of NHCs, was established. Nevertheless the π back-bonding interactions were estimated to contribute to 15–30% of the complexes overall orbital interaction energies, which can hardly be considered as negligible.



Scheme 8. Preparation of nickel(II) carbene complexes.



Scheme 9. Synthesis of a (NHC)–vanadium(V) complex.

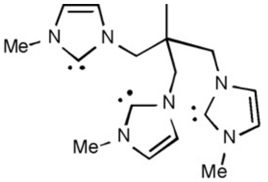
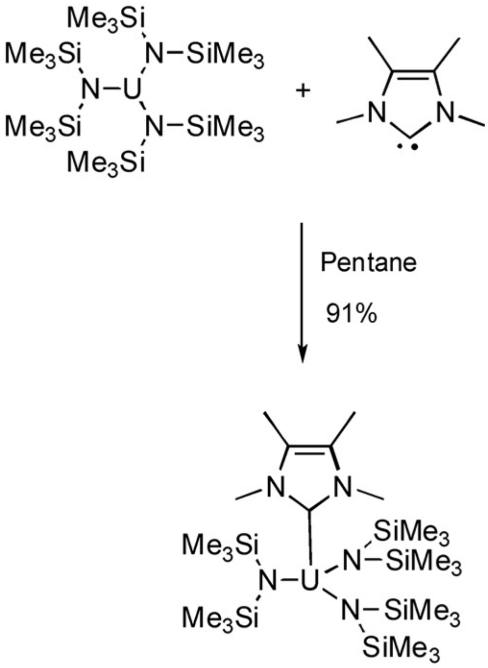


Fig. 7. Structure of 1,1,1-tris[3-methyl(imidazol-2-ylidene)methyl]ethane (TIME^{Me}).

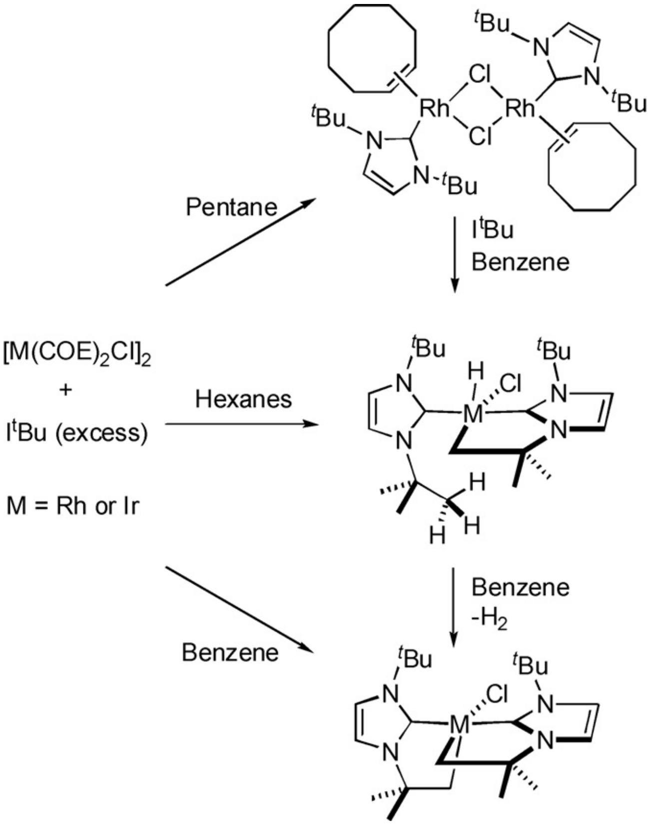


Scheme 10. Synthesis of a (NHC)–uranium(III) complex.

Similar conclusions were drawn from EDA calculations (EDA = energy decomposition analysis) on group 11 complexes with NHC ligands [81]. In fact, calculated data suggested that the π back-donation in these complexes is not substantially smaller than in classic Fischer carbene complexes bearing two π donor groups [82].

In comparison to transition metals or lanthanides, only few examples of NHC–actinide metal complexes have been reported so far [83]. Computational analysis of low-valent uranium complexes coordinated to N-heterocyclic carbene ligands (Scheme 10) revealed that the stabilization of the electron-rich uranium center was achieved due to the π-accepting character of NHCs [84].

Recently, a new aspect in the bonding interaction of NHC with metal center was revealed by the study of the interaction of the bulky and very basic I^{t}Bu with $[M(COE)_2Cl]_2$ (M = Rh or Ir) [85]. These solvent-dependent reactions (solubility of the product dictated the outcome of the reaction) led to the first characterization for both the immediate precursor and the product of a C–H activation process (Scheme 11).

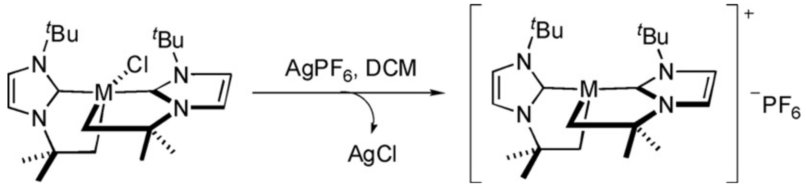


Scheme 11. Reactivity of I^{t}Bu with $[M(COE)]_2Cl]_2$ (M = Rh or Ir).

Abstraction of the chlorine atom in these dicyclometalated complexes led to the isolation and characterization of the corresponding 14-electron complexes (Scheme 12). Remarkably, no agostic interactions, nor formation of metal–ligand adducts with σ-donor ligands such as THF or acetone, were observed in these cationic complexes.

Molecular orbital analysis of these 'bare' complexes indicated that the ability of NHC ligands to act as π electron donors is essential in understanding the unusual stability of these complexes. These are again examples of stabilizing effects afforded by NHC coordination.

This bonding ability had not been considered before and it might have important implications in catalysis. Notably, it could play an important role in explaining the higher thermal stabil-



Scheme 12. Synthesis of 'bare' 14-electron complexes.

ity of NHC-based systems when compared to phosphine-based complexes.

5. Final remarks

Fifteen years have passed since the isolation of the first NHC. In spite of the true revolution that these ligands have brought to metal-catalyzed reactions, we are still far from entirely understanding the factors governing their reactivity. We are confident that further experimental exploration as well as improved computational methods will continue to highlight the unique features associated with these very versatile ligands.

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