Review

Steric and electronic effects in the bonding of N-heterocyclic ligands to transition metals

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Abstract

N-heterocyclic (NHC) ligands constitute a new class of ligands that is going to commonly be used in organometallic chemistry. Nevertheless, detailed understanding of the bonding properties of these ligands to transition metals is scarce. In particular, a clear separation between steric and electronic effects is missing. Only in recent years combined experimental and computational studies on this topic have been performed. Here we review some advances in the field. We thus present a quantification of steric effects on the bond dissociation energy of various NHC-ligands from transition metals in complexes as Cp*Ru(NHC)Cl and Ni(CO)$_3$(NHC). We further compare the steric requirements of various NHC ligands with the steric requirements of some phosphines. In the second part, we examine the different bonding modes that can contribute to the NHC–metal bond. We will review examples of metal-to-NHC back-donation ($\sigma \rightarrow d^*$) as well as of ligand-to-metal-to-NHC back-donation ($\pi \rightarrow d$).
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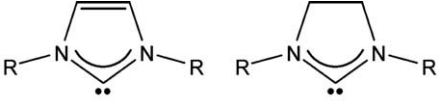
Contents

1. Introduction

N-heterocyclic (NHC) ligands are emerging as a new class of versatile ancillary ligands in organometallic chemistry, and they often are a valid alternative to the widely used phosphine ligands. Organometallic complexes containing NHC ligands are effectively used in ruthenium catalyzed olefin metathesis [1–7], iridium-catalyzed hydrogenation and hydrogen transfer [8–10], platinum catalyzed hydrosilylation [11], and palladium catalyzed C–C coupling reactions [12–15]. The most widely used NHCs of this class are represented in Chart 1.

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R		
4-Me-Phenyl	ITol	SITol
Mesityl	IMes	SIMes
2,6-diisopropylphenyl	I*i*Pr	SI*i*Pr
Cyclohexyl	ICy	SICy
tert-butyl	I*t*Bu	SI*t*Bu
Adamantyl	IAd	SIAd

Chart 1.

Although NHC ligands are acquiring a widespread usage, they are by far less well characterized than the phosphine ligands that they often replace. Pioneering studies by Tolman [16] evidenced that the bonding of phosphines to transition metals can be well rationalized in terms of steric and electronic effects. Concepts as the Tolman cone angle are widely used, and a large number of phosphines is now classified in terms of these concepts. The profound understanding and quantification of the basic factors that control the binding properties of phosphines certainly contributed to the development of new and better performing phosphines.

Conversely, our understanding of the bonding of NHC ligands to transition metals is still limited, and a factorization and quantification of electronic and steric effects in the binding of NHC to transition metals is scarce. Some spectroscopic studies have revealed the close relationship of NHCs and phosphine ligands [17,18], while some structural studies [19] suggested that NHC ligands could be considered almost pure σ-donors [19,20]. In the case of the NHC ligands shown in Chart 1, surprising differences in catalytic activities of the corresponding metal catalysts have already been observed, but could not be rationalized or explained experimentally. To fill this gap a series of studies have been recently published, in which attempts were undertaken to separate and quantify steric and electronic contributions to the NHC–metal bonding [21–26].

The saturated NHC ligands SIMes and SI*i*Pr were compared with their unsaturated analogues IMes and I*i*Pr in terms of both steric bulk and electron donor ability in the Cp*Ru(L)Cl complexes, L = NHC or PR₃ [23]. The data demonstrated that SIMes is a better donor ligand than its unsaturated analogue in this system. Moreover, the Cp*Ru(L)Cl system was proven to be a good model for the ruthenium based olefin metathesis system in terms of quantifying ligand effects and properties. In a different study, substitution reactions involving Ni(CO)₄ and some NHC ligands of Chart 1. were investigated [25,27]. Most of the ligands give rise to saturated complexes of general composition Ni(CO)₃(NHC). The electronic properties of these NHCs were compared to tertiary phosphine ligands, PR₃. The most bulky NHC ligands IAd and I*t*Bu led to the isolation of three-coor-

dinate and unsaturated Ni(CO)₂(NHC) complexes. These unsaturated complexes allowed to determine NHC–metal bond dissociation energies for this class of ligands and enabled the establishment of a method for the direct comparison of steric requirements of the NHC and phosphine ligand classes [25,27]. Finally, in another study the characterization of the 16e complex IrCl(I*t*Bu′)₂ and of the 14e complex [Ir(I*t*Bu′)₂]⁺[PF₆]⁻, both shown in Scheme 1, indicated that the former complex is stabilized by an agostic interaction between the C–H bond of one of the free *t*-Bu groups and the metal, whereas the latter complex is neither stabilized by agostic interactions nor by coordinating solvent molecules. Analysis of these systems suggested that the π-electron donor ability of NHCs is crucial in understanding the remarkable stability as well as the lack of agostic interactions in [Ir(I*t*Bu′)₂]⁺[PF₆]⁻ [26].

All these investigations were performed with a synergic experimental and theoretical approach, and here we review the main conclusions we obtained on the basis of combined QM/MM calculations [28–30].

2. Factorizing steric and electronic effects in NHC–metal bonding

Table 1 reports the bond dissociation energies (BDE) of NHC, PR₃ and CO calculated for a series of Ru and Ni complexes. Comparison with the available experimental data indicates that the calculated values reasonably reproduce the experimental data, both for the Ru and the Ni based complexes. This validates the computational approach we used, and the theoretical values we discuss in the following.

Weakest NHC-bonds (around 10–20 kcal/mol) are observed in the Cp*Ru(NHC)Cl complexes. In the saturated Ni(CO)₃(NHC) the BDE is in the 20–40 kcal/mol range, while in the unsaturated Ni(CO)₂(NHC) the BDE is approximately 40–45 kcal/mol. Comparison between the BDE of PR₃ and NHC indicates that NHC ligands usually coordinate better than both phosphines or CO. The finding that the BDE we calculated for the NHC ligands are remarkably higher that those of the PR₃ ligands is in agreement with the common assumption that

[IrCl(I*t*Bu′)₂]   [Ir(I*t*Bu′)₂]⁺[PF₆]⁻
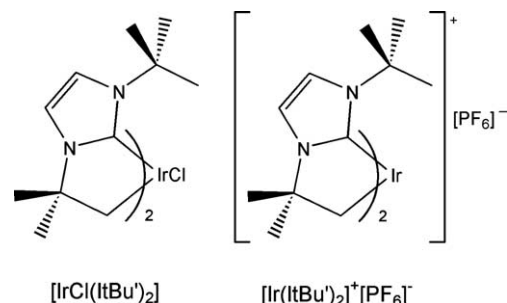
Scheme 1.

Table 1
Bond dissociation energies, BDE, in a series of Ru and Ni complexes

Entry	Complex	BDE of	BDE (experimental)	BDE (theoretical)
1	Cp*Ru(ITol)Cl	ITol	18.8[a]	26.2
2	Cp*Ru(SITol)Cl	SITol	–	27.5
3	Cp*Ru(IMes)Cl	IMes	15.6[a]	19.2
4	Cp*Ru(SIMes)Cl	SIMes	16.8[a]	19.2
5	Cp*Ru(IiPr)Cl	IiPr	11.1[a]	11.6
6	Cp*Ru(SIiPr)Cl	SIiPr	12.1[a]	10.9
7	Cp*Ru(IAd)Cl	IAd		1.8
8	Cp*Ru(PCy$_3$)Cl	PCy$_3$	10.5[a]	
9	Ni(CO)$_2$IMes	IMes		46.5
10	Ni(CO)$_2$SIMes	SIMes		47.2
11	Ni(CO)$_2$IAd	IAd	43[b]	46.5
12	Ni(CO)$_2$ItBu	ItBu	39[b]	44.3
13	Ni(CO)$_2$PPh$_3$	PPh$_3$		30.0
14	Ni(CO)$_3$IMes	IMes		41.1
15	Ni(CO)$_3$SIMes	SIMes		40.2
16	Ni(CO)$_3$IAd	IAd		20.4
17	Ni(CO)$_3$ItBu	ItBu		24.0
18	Ni(CO)$_3$PPh$_3$	PPh$_3$		26.7
19	Ni(CO)$_3$IMes	CO		28.3 (27.2)[c]
20	Ni(CO)$_3$SIMes	CO		26.8 (26.4)[c]
21	Ni(CO)$_3$IAd	CO		7.6 (14.1)[c]
22	Ni(CO)$_3$ItBu	CO		13.3 (15.6)[c]
23	Ni(CO)$_3$PPh$_3$	CO		30.4

BDE in kcal/mol.
[a] Taken from [23].
[b] Taken from [25].
[c] Calculated with a QM/MM approach, see [25].

NHC ligands bind more tightly than phosphines to transition metals. Within a single class, comparison between NHC with different steric and electronic properties allows to factorize between these effects.

First, in all the systems the difference between the BDE of saturated and unsaturated NHC ligands like IMes and SIMes (entries 3 and 4, 9 and 10, 14 and 15), IiPr and SIiPr (entries 5 and 6) and ITol and SITol (entries 1 and 2) is very small and amounts to about 1 kcal/mol. The small differences in BDE are in agreement with the available experimental values. Moreover, for the less bulky Cp*Ru(NHC)Cl NHC = ITol and SI-Tol complexes, the saturated SITol ligand is predicted to bind more strongly than the unsaturated ITol ligand by 1.3 kcal/mol, whereas for the bulkier IiPr and SIiPr based complexes, the saturated SIiPr ligand binds less strongly than the unsaturated IiPr ligand by 0.7 kcal/mol. Similar behavior is presented by the Ni(CO)$_3$-(NHC) complexes (NHC = IMes and SIMes, entries 14 and 15). The relative stability of the saturated and unsaturated complexes we calculated is affected by the bulkiness of the NHC ligands because shorter Mt–C distances (roughly 0.01–0.02 Å) are predicted for the saturated complexes. This enhances steric effects. Considering that our computational approach underestimates the differences in the relative BDE by roughly

1–2 kcal/mol (compare the relative experimental and theoretical BDE for the IMes and SIMes systems, entries 3 and 4, as well as for the IiPr and SIiPr systems, entries 5 and 6), it is reasonable to estimate that in the absence of steric effects saturated NHC ligands are better donors than the corresponding unsaturated NHC ligands by roughly 2–3 kcal/mol.

Second, the BDE are clearly dependent on the steric properties of the NHC-ligands in the crowded Cp*Ru-(NHC)Cl and Ni(CO)$_3$(NHC) complexes. In the former class, the BDE of the NHC ligands is remarkably dependent on the bulkiness of the substituents in the *ortho* position of the aromatic rings of the NHC ligand. In fact, BDEs are higher in the complexes without substituents in the *ortho* postions (NHC = ITol and SITol, entries 1 and 2), they decrease of about 7–8 kcal/mol in the complexes with Me substituents (NHC = IMes and SIMes, entries 3 and 4) and further decrease by another 7–8 kcal/mol in the complexes with ^{i}Pr substituents (NHC = IiPr and SIiPr, entries 5 and 6). In the second class, the stability of the complexes is dramatically dependent on the bulkiness of the groups bound to the N atoms of the NHC ligands. In fact, with the less bulky IMes and SIMes based ligands the saturated Ni(CO)$_3$-(NHC) complexes are stable, whereas with the bulky IAd and ItBu based ligands the 18e Ni(CO)$_3$(NHC)

complexes are so much destabilized that the 16e Ni-$(CO)_2$(NHC) complexes are formed.

In order to quantify the steric factors characterizing these ligands, we measured the amount of volume of a sphere centered on the metal, buried by overlap with atoms of the various NHC ligands, $\%V_{Bur}$. The volume of this sphere would represent the space around the metal atom that must be shared by the different ligands upon coordination. Of course, the bulkier a specific ligand, the larger the amount of the sphere that will be occupied by the ligand, i.e. greater $\%V_{Bur}$. To have an aseptic estimate of the bulkiness of the various ligands, we examined the DFT optimized geometries of the free ligands, and positioned the putative metal atom at 2.00 Å from the coordinating C or P atom (for NHC and PCy_3 ligands, respectively) in the Ru complexes, and at 2.28 Å in the Ni complexes. A graphical representation of this geometrical analysis is reported in Fig. 1. Test calculations suggested that 3 Å is a reasonable radius for the sphere centered on the metal. Incidentally, 3 Å is roughly the distance between the N atoms and the putative metal atom. Clearly, different values for the radius of this sphere would results in different values of $\%V_{Bur}$. A compilation of $\%V_{Bur}$ values is presented in Table 2.

While it is common to characterize the steric demand of PR_3 ligands using the Tolman cone angle, in the case of NHC ligands we prefer to use the $\%V_{Bur}$ molecular descriptor. In fact, NHC ligands are usually highly asymmetric, and steric demand in the direction of the N–R bonds can be very different from steric demand in the direction perpendicular to the imidazolyl ring plane.

Since the value of $\%V_{Bur}$ depends on the NHC–metal distance, in Table 2 we report the $\%V_{Bur}$ of all ligands, calculated at two values of the NHC–metal distance. Of course, all the $\%V_{Bur}$ calculated at NHC–metal = 2.28 Å are smaller, by roughly 5%, than the corresponding values calculated at NHC–metal = 2.00 Å.

For the Cp*Ru(NHC)Cl complexes, the experimental BDE reported in Table 1 are plotted versus the $\%V_{Bur}$ of Table 2, and the resulting plot is presented in Fig. 2. The data show a linear correlation between both the experi-
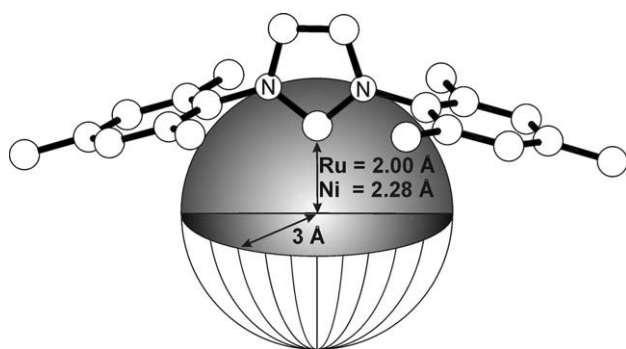
Table 2
Steric Parameter $\%V_{Bur}$ calculated for selected L = NHC and PR_3 ligands

Ligand	$\%V_{Bur}$	
	M–L (2.00 Å)	M–L (2.28 Å)
ITol	23	19
SITol	25	20
IMes	26	20
SIMes	27	21
IiPr	29	22
SIiPr	30	23
IAd	37	32
ItBu	37	32
PPh_3	27	22
PCy_3	32	26

mental and theoretical BDEs and the $\%V_{Bur}$, which suggests that the BDEs are essentially controlled by the steric requirements of the ligands, and that $\%V_{Bur}$, although a very simple and intuitive descriptor of molecular properties, is able to capture the different steric requirements of the different ligands. The higher slope for the line fitting the theoretical values indicates that the combined QM/MM approach overestimates steric effects.

Regarding the Ni-based complexes, we first calculated the BDE of CO in the Ni$(CO)_3$(NHC) systems with a combined QM/MM approach (reported in parenthesis in Table 1). Within this approach unsaturated and saturated NHC ligands, as well as ligands with aromatic or alkyl groups share the same QM part, and different behavior can be ascribed to their different steric properties (see [25]). The BDE reported in Table 1 indicate that the QM/MM approach substantially replicates the full QM calculations. This indicates that any difference between NHC ligands is steric in nature. It remains to see whether it is possible to use a molecular descriptor to rationalize this behavior. The different steric factors
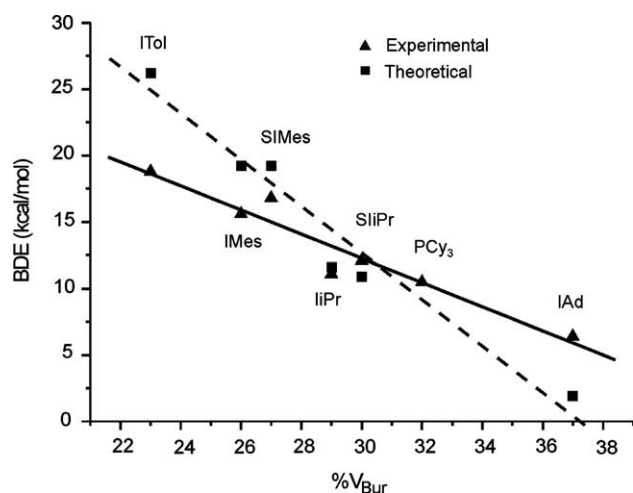

Fig. 1. Schematic representation of the sphere dimensions used for determination of the steric parameter $\%V_{Bur}$.

Fig. 2. Experimental and theoretical BDE (kcal/mol) vs steric parameter ($\%V_{Bur}$) in the Cp*Ru(L)Cl systems.

characterizing these ligands were quantified once more using the $\%V_{Bur}$ of Table 2. The quite larger values of $\%V_{Bur}$ of the I*t*Bu, SI*t*Bu and IAd ligands, relative to the IMes, SIMes, I*i*Pr, SI*i*Pr and ICy ligands is in fact in qualitative agreement with the different BDEs we calculated for the two groups of NHC ligands.

Geometrical inspection of the calculated structures of Ni(CO)$_2$(I*t*Bu) and Ni(CO)$_3$(I*t*Bu) supports the previous conclusions. The Ni(CO)$_3$(I*t*Bu) complex of Fig. 3 presents several shorter distances between the *t*-Bu group and the CO molecules, relative to Ni(CO)$_2$(I*t*Bu) complex. These strong steric interactions in Ni(CO)$_3$(I*t*Bu) result in the severe distortion of one of the Ni–C–O angles from the ideal value of 180°, to assumes a value of 169.4°. Differently, the Ni(CO)$_3$(I*i*Pr) of Fig. 3 is characterized by very few short distances between the NHC ligand and the CO molecules, which explains its stability.

Comparing NHC and PR$_3$ Ni-based systems, the BDE of the CO in the PR$_3$ systems and in the less bulky NHC systems is similar, which suggests a high stability of the PR$_3$-based tricarbonyl systems. Calculation of the $\%V_{Bur}$ of the PR$_3$ systems allows for the direct comparison of the steric requirements of the NHC and phosphine ligand families. The calculated values for $\%V_{Bur}$ show that sterically, the very bulky phosphine ligand P^{t}Bu$_3$ is best compared to I*i*Pr and SI*i*Pr, whereas PPh$_3$ has a similar $\%V_{Bur}$ to the one found for ICy. The most bulky NHC ligands, namely I*t*Bu, SI*t*Bu and IAd, are all significantly more bulky than P^{t}Bu$_3$, a fact that can lead to different behavior in reactivity and catalysis of metals incorporating these ligands [31].

3. Nature of the NHC–metal bond

In this final section we discuss the σ and π bonding properties of NHC ligands. The molecular orbitals of the NHC five-membered ring that are involved in bonding to the metal are shown in Fig. 5(a). We use the saturated imidazolyl ring to simplify the analysis. In fact, only three π atomic orbitals are needed to describe the molecular orbital (MO) interactions with d orbitals of the metal. Extension to the more common unsaturated imidazolyl ring is straightforward.
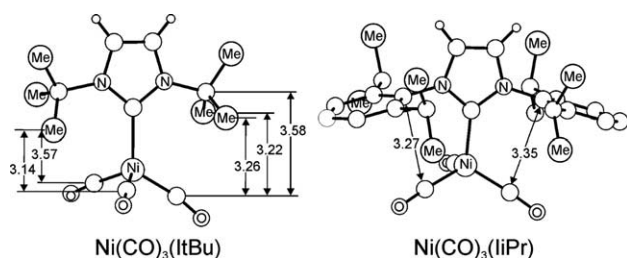
NHC ligands were initially considered to be almost pure σ-donors, through σ → d donation as shown in Fig. 5(b). The σ molecular orbital of the NHC involved in this donation is of course MO3. However, this simplified picture is changing rapidly, and it has been suggested that NHC ligands are not simple σ donors, since filled and empty π, π* orbitals on the NHC ring can contribute to the NHC–metal bond. Meyer et al. [21,22] nicely evidenced that NHC can accept electron density from electron rich group 11 metal atoms, through a d → π* back-donation scheme, as shown in simplified fashion in Fig. 5(c).

We contributed to further broaden the conceptual ideas of bonding ability of NHC ligands through a molecular orbital analysis of the electron poor group 9 [Ir(I*t*Bu′)$_2$]PF$_6$ complex of Fig. 4. This system is characterized by an octahedral geometry with two vacant coordination positions at the Ir atom. The two vacant coordination position are *trans* localized relative to the two σ Ir–CH$_2$ bonds. Although C–H bonds of the *t*-Bu groups are in proximity of the vacant coordination positions, there is no evidence for strong agostic interactions. These findings are in agreement with the X-ray structure of the same systems.

Molecular orbital analysis of complex [Ir(I*t*Bu′)$_2$]PF$_6$ indicated a remarkable donation of electron density from the filled π MOX orbital of the NHC ligands to empty d orbitals of the Ir atom through a π → d donation scheme, as shown in Fig. 5(d). This analysis indicated that the ability of NHC ligands to act as π-electron donors can rationalize the unusual stability of the 14e complex [Ir(I*t*Bu′)$_2$]PF$_6$. Moreover, the electron deficiency on the metal in complex [Ir(I*t*Bu′)$_2$]PF$_6$ is better alleviated by donation from π orbitals of the NHC ligand than by donation from σ orbital of the C–H bond of the *t*-Bu groups. This explains the absence of agostic interactions in IrCl(I*t*Bu′)$_2$. Stabilization of this kind might have important implications in catalysis, where
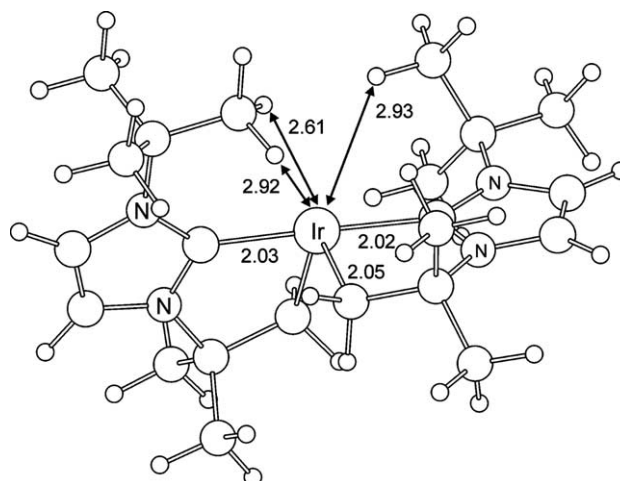

Fig. 3. Short distances, in Å, in the QM/MM geometries of the saturated Ni(CO)$_3$I*t*Bu and Ni(CO)$_3$I*i*Pr complexes.

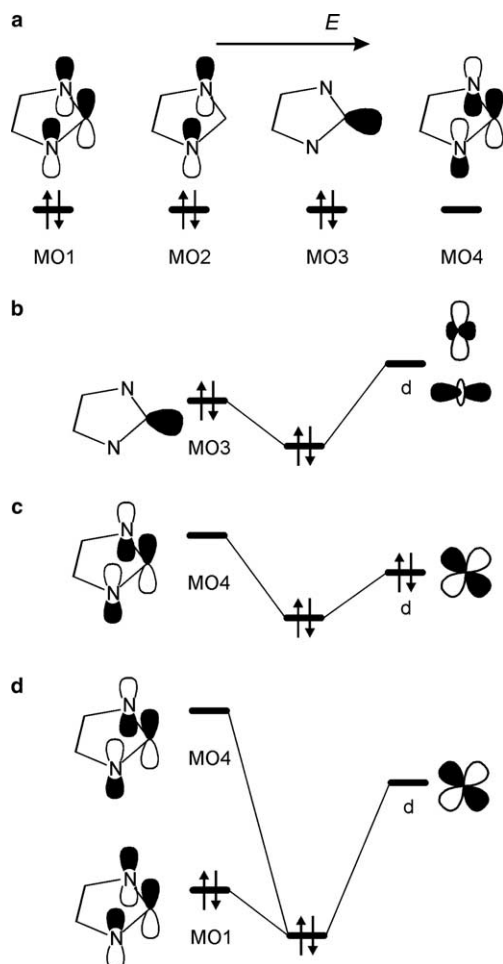Fig. 4. QM/MM geometry of the [Ir(I*t*Bu′)$_2$]$^+$ system. Distances, in Å.

Fig. 5. Schematic representation of the most important NHC molecular orbitals (MO) involved in the NHC–metal bonding (a). Schematic representation of the NHC-to-metal $\sigma \rightarrow d$ donation (b), of the metal-to-NHC $d \rightarrow \pi^*$ donation (c), and of the NHC $\rightarrow$ metal $\pi \rightarrow d$ donation (d).

late transition metal–NHC compounds often display higher thermal stability when compared to analogous phosphine systems.

4. Conclusions

In this brief review we reported on the steric and electronic contributions to the NHC–metal bonding. Steric effects play a fundamental role in determing the BDE of the NHC–metal bond. In some instances steric effects can be so strong to alter completely the stability of complexes, as in the $Ni(CO)_3(NHC)$ systems. To quantify the steric bulkiness of NHC ligands we introduced the $\%V_{Bur}$ molecular descriptor, and we gave an estimate of this descriptor for a series of NHC ligands and we compared it to the $\%V_{Bur}$ calculated for some typical phosphines. The calculated values for $\%V_{Bur}$ show that sterically, the very bulky phosphine ligand P^tBu_3 is best compared to IiPr and SIiPr NHC-ligands, whereas PPh$_3$ is best compared to ICy. The most bulky NHC ligands, namely ItBu, SItBu and IAd, are all significantly more bulky than P^tBu_3.

Electronic effects are as important as steric effects. The common knowledge that NHC ligands should be considered as simple σ donors is being replaced by the idea that NHC ligands are electronically much more flexible. Both filled and empty π, π^* orbitals on the NHC ring can be deeply involved in the bonding to the metal. They can contribute to stabilize electron rich metals through a $d \rightarrow \pi^*$ back-donation scheme, but they are so flexible that can also stabilize electron deficient metals through a $\pi \rightarrow d$ donation scheme.

We believe that the large variability in terms of steric and electronic properties of NHC ligands explains their rapid introduction in organometallic chemistry, and that they potentially are much more tunable than phosphines. Of course, it would be very useful to arrive to a quantification and classification of different NHC ligands similar to that obtained for phosphines.

5. Technical details

For the V_{Bur} calculations we used a program developed by us. V_{Bur} is calculated through a numerical evaluation of the volume of a sphere of radius R, centered on the metal atom, which is occupied by atoms of the ligands. In the V_{Bur} calculation H atoms are not considered. This allows the method to be applied also to X-ray structures. The following Van der Waals radii were assigned to main group atoms (Csp^2, 1.76 Å; Csp^3, 1.87 Å; Nsp^2, 1.65 Å; P, 1.90 Å).

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