The Measure of All Rings—N-Heterocyclic Carbenes

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Quantification and variation of characteristic properties of different ligand classes is an exciting and rewarding research field. N-Heterocyclic carbenes (NHCs) are of special interest since their electron richness and structure provide a unique class of ligands and organocatalysts. Consequently, they have found widespread application as ligands in transition-metal catalysis and organometallic chemistry, and as organocatalysts in their own right. Herein we provide an overview on physicochemical data (electronics, sterics, bond strength) of NHCs that are essential for the design, application, and mechanistic understanding of NHCs in catalysis.

1. Introduction

For a long time, carbenes, divalent species with an electron sextet, were considered to be very reactive and short lived molecules that could not be isolated. Thus, the first report of a stable (phosphino)carbene,[1] and, moreover, the first unequivocal isolation of an N-heterocyclic carbene (NHC; Figure 1), and its crystal structure analysis by Arduengo et al. in 1991 caused a lot of excitement.[2] Remarkably, in the absence of oxygen and moisture, this 1,3-diadamantyl substituted imidazol-2-ylidene (IAd) was found to be stable at room temperature and to melt at 240 °C without decomposition. Soon thereafter, many other NHCs were reported, with TPT (1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene) being even commercially available in free form.[3]

The unusual stability of NHCs is in part a result of shielding by sterically demanding substituents on the ring. However, much more important is the electronic stabilization by mesomeric interaction of the lone pairs of electrons on the nitrogen atoms with the empty p orbital of the sp^2 hybridized carbene. This latter feature, the importance of resonance structures like **2b** (Scheme 1), also nicely explains why NHCs are electron-rich nucleophilic species, whereas other carbenes
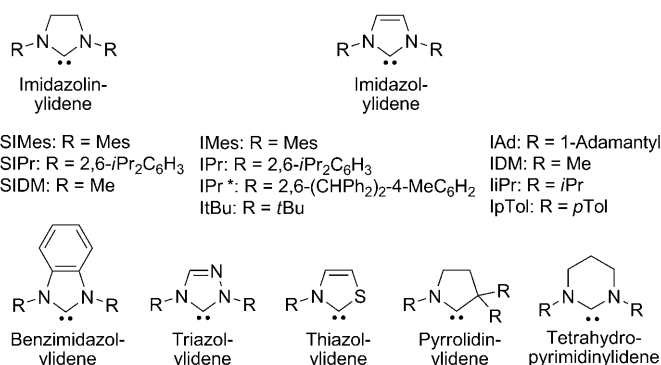

Figure 1. Some of the most frequently encountered NHCs and their nomenclature.[2f]

are generally found to be electrophilic. Nevertheless, the significance of the carbene resonance structure **2a** is clearly supported by a structural comparison of imidazolin-2-ylidenes **2** with their corresponding imidazolium salts **1** (Scheme 1): the C2—N bonds are longer and the N-C-N angle is smaller in the carbene than in the imidazolium salt. Both findings indicate an increased σ-bond character in **2** and thereby highlight the importance of **2a**.[4]

However, even though NHCs are stable and isolable in many cases, it is important to note that they must still be considered as sensitive species. Whereas monoaminocarbenes do split hydrogen and ammonia at low temperature, diaminocarbenes only react with O$_2$ and H$_2$ in the presence of a

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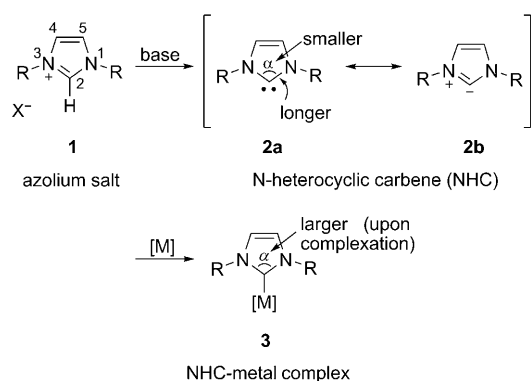
Scheme 1. Structural comparison of azolium salts, NHCs, and NHC-metal complexes.

suitable catalyst. Both classes of carbenes are very sensitive to moisture (H_2O) and other electrophiles.[5,6]

In the last two decades, NHCs have become ubiquitous ligands in organometallic chemistry and organocatalysts in their own right. It should not be forgotten, however, that the first metal complexes of NHCs were already reported by Wanzlick and Schönherr[7] and by Öfele[8] in 1968. Moreover, applications of thiazolylidenes in umpolung organocatalysis—although not well understood at that time—were reported as early as 1943.[9,10] Since these early days, thiazolylidenes and related NHCs have been employed as organocatalysts in numerous interesting reactions.[11]

In 1995, Herrmann et al. reported on the first application of NHCs as ligands in transition-metal catalysis.[12] Their article "*Metal Complexes of N-Heterocyclic Carbenes—A New Structural Principle for Catalysts in Homogeneous Catalysis*" was the starting point for an enormous number of publications on catalytic applications of NHCs in reactions such as ruthenium-catalyzed metathesis or transition metal catalyzed cross-coupling reactions.[13] The facile access to structurally diverse NHCs and their characteristic properties make them very attractive ligands and catalysts.[13] Namely, many NHCs are especially electron donating and sterically demanding, and the resulting metal–carbene bonds are often found to be very stable. The ability to quantify these three distinct properties as well as to vary and to maximize them, is extremely desirable to allow the design, selection, and

utilization of tailor-made NHC ligands and catalysts for a given application. Herein, we provide an overview on the physicochemical data of NHCs (electronics, sterics, bond strength), data that is essential for the design, application, and mechanistic understanding of NHCs in catalysis.

2. Generation of Free NHCs

Several methods allow the formation of free NHCs, with deprotonation of an azolium salt precursor being by far the most common one (Scheme 2a).[14] The advantages of this method are the ready availability and stability of the precursor azolium salts and the rather mild deprotonation conditions. However, to separate the free NHC from the
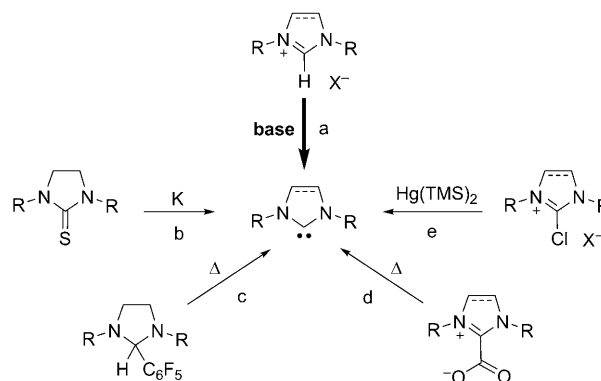
Scheme 2. Most important methods for the formation of free NHCs. TMS = trimethylsilyl.

protonated base is often not trivial and, consequently, in many cases not done. Naturally, the knowledge of the corresponding pK_a values is very helpful and also provides insight into the basicity of the free NHC. Alder et al. determined the pK_a value of the conjugate acid of an imidazol-2-ylidene to be around 24 in DMSO.[15] Since 2004 there have been some more detailed reports on pK_a values of azolium salts, but the database is still quite small. The pK_a value of the 2-position of imidazolium salts ranges from 16 to 23 (in DMSO; Table 1, entries 4, 6–9). Other than the influence of the N-substituents, the type of heterocycle has to be considered. In DMSO, the

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Frank Glorius *was educated in chemistry at the Universität Hannover, Stanford University (Prof. Paul A. Wender), Max-Planck-Institut für Kohlenforschung and Universität Basel (Prof. Andreas Pfaltz), and Harvard University (Prof. David A. Evans). He began his independent research career at the Max-Planck-Institut für Kohlenforschung (Mentor: Prof. Alois Fürstner) in 2001 and was appointed Associate Prof. at the Philipps-Universität Marburg in 2004. Since 2007 he has been a Full Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster. His research program focuses on the development of new concepts for catalysis and their implementation in organic synthesis.*

Table 1: pK_a values of some azolium salts.

Entry	Azolium cation	pK_a in DMSO
1		(33.0 in H_2O, 4-position)[16a]
2		27.9[16b]
3		27.1[16b]
4		23.2[16c]
5		22.3[16b]
6		22.0,[16c] 21.1[16b] (23.0 in H_2O)[16d]
7		(21.6 in H_2O)[16d]
8		19.7[16c]
9		16.1[16b]
10		14.5[16b] (19.5 in H_2O)[16d]

acidity strongly increases from the tetrahydropyrimidinium salt (Table 1, entry 3) to imidazolinium and imidazolium salts (Table 1, entries 4–9) to the thiazolium salt (Table 1, entry 10). The 4-position of azolium salts is significantly less acidic, with its deprotonation resulting in the formation of abnormal and generally more electron-rich (see below) NHCs (Table 1, entry 1).

Besides the deprotonation of azolium salts, some additional, less commonly applied methods for the formation of free NHCs exist (Scheme 2), and they might have attractive features, such as a simpler purification or a slow in situ formation of the NHC:[17]

- Desulfurization of thioureas with molten potassium in boiling THF (Scheme 2 b). An attractive feature of this method is the insolubility of the by-product (potassium sulfide) in THF.[18]
- Vacuum pyrolysis under removal of (volatile) by-products like MeOH, $CHCl_3$, CHF_3, or C_6F_5H has been used for the formation of imidazolinylidenes and thiazolylidenes (Scheme 2 c).[19] For example, vacuum pyrolysis was used to prepare the stable carbene TPT.[3]
- The use of NHC–CO_2 or NHC–metal (Sn^{II}, Mg^{II}, Zn^{II}) adducts for the in situ formation of NHCs (Scheme 2 d). These compounds were skillfully exploited as delayed

action catalysts for polyurethane synthesis, an area of great industrial relevance.[20]

- Treatment of chloro amidinium and azolium salts with bis(trimethylsilyl)mercury, providing elemental Hg, TMSCl, and the metal-free carbene (Scheme 2 e).[21] These 2-chloro azolium species can also be utilized for the formation of metal–NHC complexes by oxidative addition to the C−Cl bond.[22]

In characterizing NHCs, the ^{13}C NMR chemical shift of the carbene carbon atom is quite diagnostic (Figure 2).[23] For most NHCs, this signal can be found in the range between $\delta = 200$ and 330 ppm, where few other functional groups
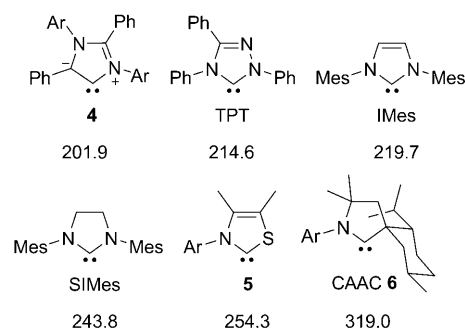
Figure 2. ^{13}C chemical shifts (in ppm) for some prominent NHCs; Ar = 2,6-diisopropylphenyl.

appear (Table 2). Imidazolylidenes exhibit ^{13}C NMR resonances for the carbene at $\delta = 210$–220 ppm, whereas saturated imidazolinylidenes and acyclic diaminocarbenes display downfield-shifted resonances at around $\delta = 235$–260 ppm. The substitution of one nitrogen atom for a sulfur or carbon atom in the corresponding thiazolylidenes or cyclic (alkyl)-(amino)carbenes (CAAC)[24] results in significantly downfield-shifted resonances (Figure 2). In addition, a trend was noticed between these ^{13}C NMR shifts of different classes of NHC and the N-C-N angle: the larger the chemical shift, the larger the N-C-N angle.[23b] Upon complexation of the nucleophilic NHCs with main-group elements or transition metals, the carbene carbon atom is substantially shielded, providing a sensitive probe for the formation of the adduct (Table 2, entries 14–32).

3. Electronic Character of NHCs

One of the most characteristic features of NHCs is their extraordinary electron richness. Several distinctly different methods[26] allow the quantification of electron-donor properties of ligands (Figure 3), that is, the ability to measure the effect a ligand exhibits upon the electronic nature of a metal complex.

The arguably most recent method utilizes the ^{13}C chemical shift of the carbene carbon atom in palladium(II)-benzimidazolylidene complexes as a probe for the measurement of the donor strength of the additional NHC ligand of interest.

Table 2: ^{13}C Chemical shifts and N-C-N bond angle for free NHCs and their transition-metal complexes.

Entry	Ligand/complex	δ [ppm]	N-C-N [°]	Lit.	Entry	Ligand/complex	δ [ppm]	N-C-N [°]	Lit.
1	abnormal NHC **4**	201.9[a]	101.0	[25a]	17	[(IMes)CuCl]	178.7[c]	–	[25j]
2	IAd	211.4[a]	102.2	[1a]	18	[(IMes)Ir(cod)Cl]	180.9[c]	103.1	[25k]
3	ItBu	213.2[a]	102.3	[25b]	19	[(IMes)Rh(cod)Cl]	183.5[c]	103.5	[25l]
4	TPT	214.6[b]	100.1	[3]	20	[(IMes)AgCl]	185.0[c]	–	[25m]
5	IDM	215.2[a]	–	[25c]	21	[(IMes)Pd(allyl)Cl]	185.7[b]	103.8	[25n]
6	IMes	219.7[a]	101.4	[25c]	22	[(IMes)Ni(allyl)Cl]	186.2[b]	–	[25o]
7	IPr	220.6[b]	101.4	[25d]	23	[(IMes)₂Pd]	186.2[b]	101.8, 102.0	[25p]
8	IPrCl	220.6[b]	101.2	[25d]	24	[(IMes)₂Ni]	193.2[b]	101.5, 102.5	[25q]
9	SIMes	243.8[a]	104.7	[25e]	25	[(SIMes)AuBr₃]	172.3[c]	112.9	[25h]
10	SIPr	244.0[a]	–	[25d]	26	[(SIMes)AuCl]	195.0[c]	109.3	[25i]
11	*N,N′*-Dimesityltetrahydropyrimidinylidene	244.9[b]	114.7	[25f]	27	[(SIMes)AuBr]	198.1[c]	–	[25h]
12	**5**	254.3[a]	104.2	[25g]	28	[(SIMes)CuCl]	202.8[c]	–	[25r]
13	CAAC **6**	319.0[a]	106.5	[24a]	29	[(SIMes)Ir(cod)Cl]	207.4[c]	107.1	[25k]
14	[(IMes)AuBr₃]	144.4[c]	106.9	[25h]	30	[(SIMes)AgCl]	207.5[c]	108.5	[25m]
15	[(IMes)AuCl]	173.4[c]	107.0	[25i]	31	[(SMes)Pd(allyl)Cl]	211.5[c]	107.9	[25n]
16	[(IMes)AuBr]	176.7[c]	–	[25h]	32	[(SIMes)Rh(cod)Cl]	212.0[c]	–	[25s]

[a] In [D₈]THF. [b] In [D₆]benzene. [c] In [D]chloroform.
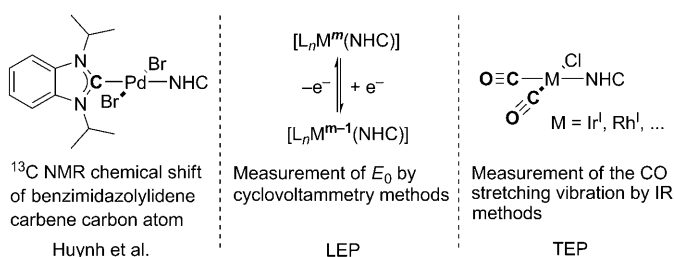
Figure 3. Comparison of different methods for the determination of the donor strength of NHC ligands.

By using this method, Huynh et al. analyzed ten different NHC ligands by the formation of the corresponding hetero-bis(carbene)/Pd^{II} complexes and their ^{13}C NMR spectra (Figure 3).[27]

Another useful method, developed by Lever et al., is based on the electrochemical E_0 value for various redox couples in series of Ru^{III}/Ru^{II} complexes containing the ligands of interest (Figure 3, middle). The data are deconvoluted into Lever electronic parameters (LEP) for individual ligands.[28] However, whereas this data can nicely be correlated with the one of the other classes of ligands, the LEP has not been determined for many NHC ligands, probably in part because of the requirement for less common electrochemical devices.[29]

One established method for measuring the electron-donor ability of ligands is the synthesis of [Ni(CO)₃(L)]. This method makes use of the fact that electron density from a ligand can not only be passed on to the metal, but also on to the π* orbital of CO ligands. Thus, the frequency A₁ of [Ni(CO)₃(L)] complexes is a direct probe to quantify the level of electron donation of the ligand. The lower the stretching frequency of CO, the more strong the σ-donating ability of the NHC ligand. This frequency is known as Tolman's electronic parameter (TEP; Figure 3, right),[30] and was developed by Tolman building upon the pioneering work by Strohmeier et al.[31] as well as Bigorgne et al.[32]

For the investigation of NHC ligands, these Ni complexes have been rarely used because of their high toxicity and, in some cases, their instability. Instead, the synthesis and analysis of easier-to-handle *cis*-[IrCl(CO)₂(NHC)] and *cis*-[RhCl(CO)₂(NHC)] complexes is preferred. Reference studies by Crabtree and co-workers[33] and by Nolan and co-workers[25k] have made it possible to correlate the values obtained from the iridium complexes to the nickel-based TEP values [Eq. (1)].[34]

Ir to Ni : $\text{TEP } [\text{cm}^{-1}] = 0.8475\tilde{\nu}_{CO}^{\text{av/Ir}} [\text{cm}^{-1}] + 336.2 [\text{cm}^{-1}]$ (1)

Along the same lines, Wolf and Plenio nicely correlated the averaged carbonyl frequencies of several dicarbonylchlororidium and dicarbonylchlororhodium carbene complexes.[35,36] By slightly expanding Plenio's dataset using additional $\tilde{\nu}_{CO}^{\text{av}}$ values reported in the literature (Table 3; the formulas for compounds **7** and **8** are in Figure 4), one arrives at the modified linear regression equations [Eq. (2) and Eq. (3)] with a very good regression coefficient $R^2 = 0.98$. Figure 5 shows the graphical presentation of the data set used for this extended correlation. Naturally, this data also allows a correlation between the data of Rh and Ni complexes [Eq. (4)].[37] The Equations (1)–(4) allow the calculation of so far unknown $\tilde{\nu}_{CO}$ values for Ir, Rh, or Ni complexes and, thus, the direct comparison of these systems with each other (e.g., entries with footnote [e] in Table 4). However, it is important to note that data can only be properly compared, if the IR measurements were carried out in the same manner; for example, the same solvent (most often in CH₂Cl₂) is used. Otherwise the $\tilde{\nu}_{CO}$ values can vary significantly and a direct comparison is not advisable.[38]

Rh to Ir : $\tilde{\nu}_{CO}^{\text{av/Ir}} [\text{cm}^{-1}] = 0.9441\tilde{\nu}_{CO}^{\text{av/Rh}} [\text{cm}^{-1}] + 98.9 [\text{cm}^{-1}]$ (2)

Ir to Rh : $\tilde{\nu}_{CO}^{\text{av/Rh}} [\text{cm}^{-1}] = 1.0356\tilde{\nu}_{CO}^{\text{av/Ir}} [\text{cm}^{-1}] - 56.9 [\text{cm}^{-1}]$ (3)
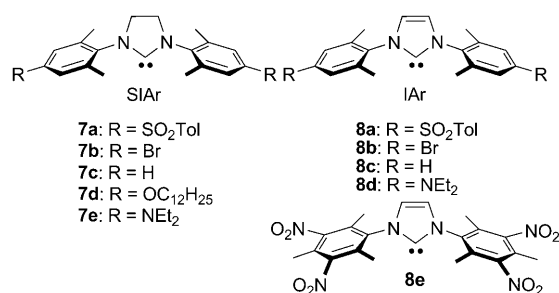
Rh to Ni : $\text{TEP } [\text{cm}^{-1}] = 0.8001\tilde{\nu}_{CO}^{\text{av/Rh}} [\text{cm}^{-1}] + 420.0 [\text{cm}^{-1}]$ (4)

Table 3: $\tilde{v}_{CO}^{av}$ Values for [IrCl(CO)$_2$(NHC)] and [RhCl(CO)$_2$(NHC)] complexes measured in CH$_2$Cl$_2$.

Entry	Ligand	$\tilde{v}_{CO}^{av/Rh}$	$\tilde{v}_{CO}^{av/Ir}$	TEP[a]	Entry	Ligand	$\tilde{v}_{CO}^{av/Rh}$	$\tilde{v}_{CO}^{av/Ir}$	TEP[a]
1	**29**[b]	2045.7	2032.5	2058.7	10	IMes	2038.5	2023.1	2050.8
2	**7a**[g]	2046.0	2030.5	2057.0	11	**7d**[g]	2037.5	2022.0	2049.8
3	**33a**[c]	2046.0	2030.0	2056.6	12	**32b**[c]	2035.0	2022.0	2049.8
4	**7b**[g]	2043.5	2027.5	2054.5	13	**8d**[g]	2035.5	2021.0	2049.0
5	**8b**[g]	2042.0	2025.5	2052.8	14	**26**[d]	2035.5	2020.5	2048.6
6	**7c**[g]	2040.5	2025.0	2052.4	15	IpTol	2035.5	2019.5	2047.7
7	SIMes	2040.5	2024.6	2052.0	16	**37**[e]	2032.0	2017.5	2046.0
8	**8c**[g]	2040.5	2024.0	2051.5	17	**24**[d]	2030.5	2015.5	2044.3
9	IiPr	2037.5	2024.0	2051.5	18	**9**[f]	2016.0	2002.0	2032.9

[a] Values calculated by linear regression using the Equation (1).[25k] [b] See Figure 11. [c] See Scheme 3. [d] See Figure 10. [e] See Figure 14. [f] See Figure 6. [g] See Figure 4.

7a: R = SO$_2$Tol
7b: R = Br
7c: R = H
7d: R = OC$_{12}$H$_{25}$
7e: R = NEt$_2$

8a: R = SO$_2$Tol
8b: R = Br
8c: R = H
8d: R = NEt$_2$

Figure 4. Plenio's series of NHC ligands with tuned electronic properties.[35, 37]
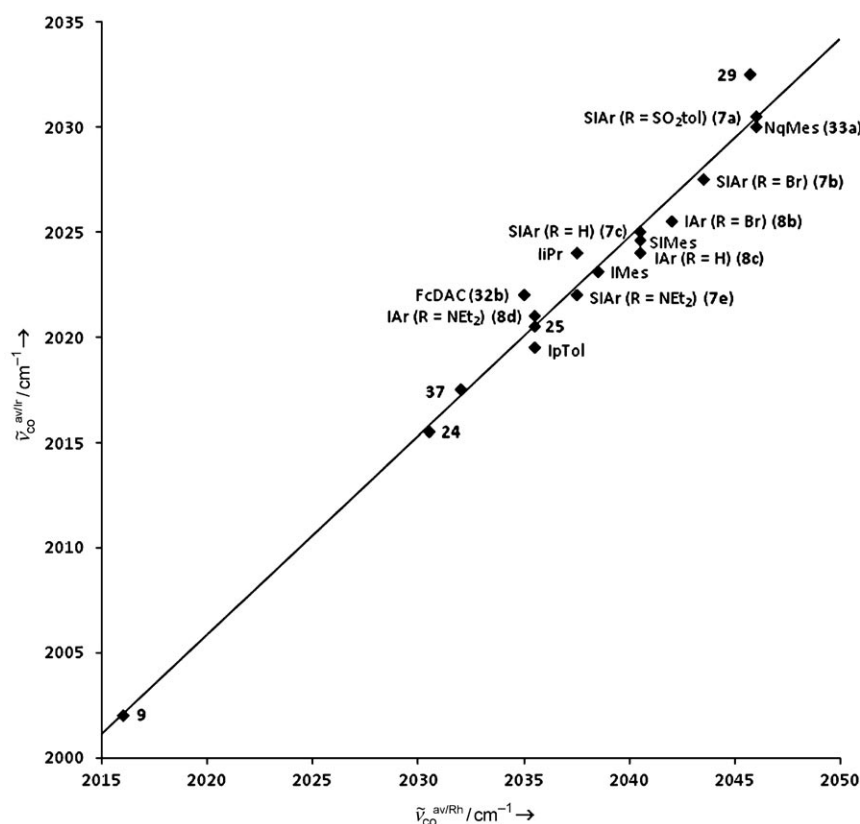
Figure 5. Correlation of the $\tilde{v}_{CO}^{av}$ values of [IrCl(CO)$_2$(NHC)] and [RhCl(CO)$_2$(NHC)] complexes, resulting in Equation (2).

Alternatively, the $\tilde{v}_{CO}$ values can also be obtained with high fidelity by quantum chemical calculations, as was shown in numerous excellent publications very recently.[39] These calculations are time efficient and, intriguingly, NHC ligands can be investigated regardless of their synthetic availability. Consequently, these calculations hold great promise as a predictive tool for deciding which ligand might provide the desired electronic properties for a given application.

The TEP values obtained clearly show the electron richness of the NHC ligands (Table 4; the formulas for compounds **9—11** are in Figure 6), most of them being significantly more electron rich than phosphine ligands. Remarkably, the commonly employed NHC ligands like IMes or IPr vary only slightly in their electronic properties. A reason for this might be that—unlike for other ligands—the substituents are not directly linked to the donor atom, but only attached to the periphery of the ligand system. However, the breadth of the electronic variation of NHCs has been expanded dramatically in recent years and three interesting developments should be highlighted:

a) Development of families of NHC ligands having slight variations in the electronic properties
b) Variation of the electronic properties by appropriate choice in the heterocycle
c) Switchable NHCs

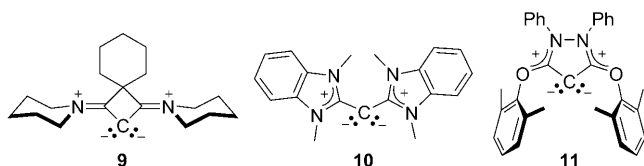### 3.1. Development of Families of NHC Ligands having Slight Variations in Their Electronic Properties

In a systematic study, Plenio and co-workers[29c] prepared a series of *N,N'*-diaryl-substituted NHCs that only differ in the *para* substituents (**7**; Figure 7). This substitution allowed the variation of the electronic properties over a wide range, with the sulfone-substituted ligand **7a** being electronically comparable to PCy$_3$ and the NEt$_2$-substituted **7e** being comparable to IAd (Table 4, entries 11 and 33; Δ(TEP) = 7.2 cm^{-1}). A comparable shift was obtained by Bertrand and co-workers[41] for the variation of the boron substituents on boron-containing cyclic six-membered NHCs (**12**, Figure 7; Table 4, entries 28, 42, and 49; Δ(TEP) = 7.4 cm^{-1}). Intriguingly, Fürstner et al.[38] altered the electronic properties of pyridine-derived imidazolylidenes (**13**) by an elegant through-space interaction (Figure 7). Organ et al.[42] (**14a–c**), Glorius et al.[43] (**15a–d**), Bielawski et al.[44] (**16a–c**), and Herrmann et al.[45] (**17a–c**) modified the electronics by

Table 4: Comparison of $\tilde{v}_{CO}^{av/Ir}$ and calculation of TEP values for several NHCs.

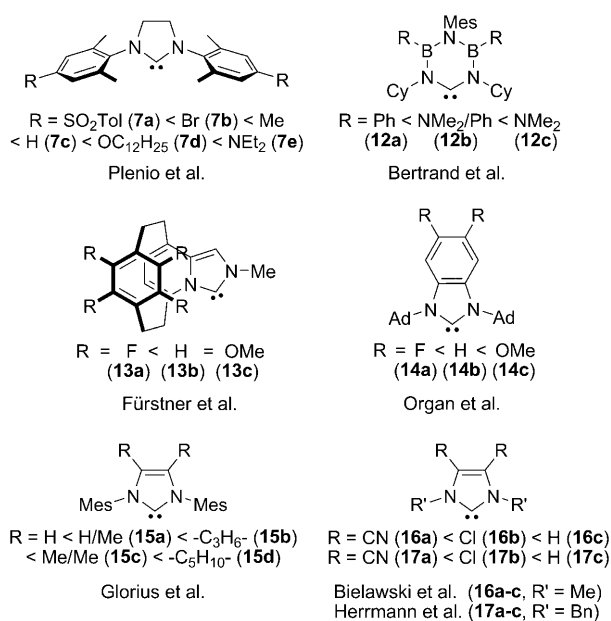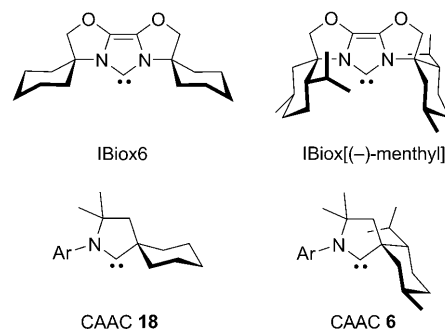| Entry	Ligand	$\tilde{v}_{CO}^{av/Ir}$	TEP[a]	Entry	Ligand	$\tilde{v}_{CO}^{av/Ir}$	TEP[a]
1	PPh₃	–	2068.9[b]	28	**12a**[k]	2023.2[e]	2050.8
2	**21**[f]	–	2065.3[c]	29	IMes	2023.1	2050.7[b]
3	**20**[f]	–	2061.5[c]	30	ICy	2023.0	2049.6[b]
4	**31a**[g]	2035.0	2060.9	31	ItBu	2022.3	2050.1
5	**32a**[g]	2035.0	2060.9	32	**32b**[g]	2022.0	2049.8
6	**8e**[m]	2034.5[d]	2060.4	33	**7e**[m]	2022.0	2049.8
7	**19**[f]	–	2060.0[c]	34	IAd	2021.6	2049.5
8	**34a**[g]	2032.7	2058.9	35	**8d**[m]	2021.0	2049.0
9	**29**[h]	2032.5	2058.7	36	**26**[i]	2020.5	2048.6
10	TPT	2030.8	2057.3	37	CAAC **18**[i]	2020.4[e]	2048.5
11	**7a**[m]	2030.5	2057.0	38	**22**[i]	–	2048.3[c]
12	**33a**[g]	2030.0	2056.6	39	**31b**[g]	2020.0	2048.2
13	PCy₃	2029.5	2056.2[b]	40	IpTol	2019.5	2047.7
14	**8a**[m]	2029.5	2056.2	41	**15d**[k]	2019.1	2047.4
15	IPrCl	2028.3	2055.2	42	**12b**[k]	2018.6[e]	2046.9
16	**7b**[m]	2027.5	2054.5	43	**23**[i]	2018.1[e]	2046.6
17	SIDM	2026.0	2053.2	44	**33b**[g]	2017.5	2046.0
18	IDM	2025.0	2052.4	45	**37**[l]	2017.5	2046.0
19	**7c**[m]	2025.0	2052.4	46	**27**[i]	2017.2[e]	2045.8
20	SIPr	2024.9	2052.3[b]	47	**34b**[g]	2016.2	2044.9
21	SIMes	2024.6	2051.5[b]	48	**24**[i]	2015.5	2044.3
22	**7d**[m]	2024.6[e]	2052.0	49	**12c**[k]	2014.4[e]	2043.4
23	**25**[i]	2024.1[e]	2051.6	50	CAAC **6**	2013.0	2042.2
24	**8b**[m]	2024.0	2051.5	51	**10**[n]	2004.8[e]	2035.2
25	IiPr	2024.0	2051.5	52	**28**[i]	2003.0	2033.7
26	IPr	2023.9	2051.5[b]	53	**9**[n]	2002.0	2032.9
27	IBiox6	2023.5	2051.1	54	**11**[n]	2000.6[e]	2031.7

[a] Values calculated by linear regression using the Equation (1).[25k] [b] Determined experimentally.[30,53] [c] Quantum chemically calculated.[39a] [d] Value calculated by the correlation of experimentally determined E_0 and $\tilde{v}_{CO}$ [(NHC)Ir(CO)₂Cl] values.[35,37] [e] Values calculated by linear regression taking the experimentally determined $\tilde{v}_{CO}^{av}$ of the [RhCl(CO)₂L] complex and using Equation (2). [f] See Figure 9. [g] See Scheme 3. [h] See Figure 11. [i] See Figure 10. [j] See Figure 8. [k] See Figure 7. [l] See Figure 14. [m] See Figure 4. [n] See Figure 6.

Figure 6. Some bent allenes and carbodicarbenes.[40]

Figure 7. Series of NHCs with tunable electronic properties.

Figure 8. Closely related cyclohexyl- and menthyl-substituted IBiox and CAAC ligands; Ar = 2,6-diisopropylphenyl.

electron richness (**18** compared to **6**: Δ(TEP) = -6.3 cm^{-1}; Table 4, entries 37 and 49).

3.2. Variation of the Electronic Properties by Appropriate Choice in the Heterocycle

The nature of the NHC heterocycle, particularly the position and choice of the heteroatoms, has a major influence on the electronic properties of the NHC. Thus, oxazolylidene **19**, thiazolylidene **20**, and triazolylidene **21** are among the least electron-rich NHCs (Figure 9). Even though the TEP

Figure 9. Quantum chemically calculated TEP values of less electron-rich NHCs.[39e]

substituting the NHC backbone (Figure 7). However, in the case of **14** (long distance) and **15** (alkyl substituents) only a rather small variation was observed, whereas the ligand families **16** and **17** showed a much larger variation.
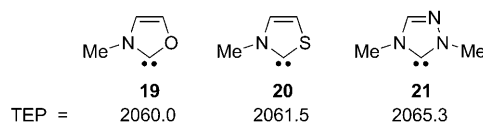
Remarkable also are the IBiox[13k,46] and CAAC[24] families of ligands, the prominent members of which are shown in Figure 8. Whereas the cyclohexyl-substituted ligands IBiox6 and CAAC **18** are conformationally flexible and exhibit flexible steric bulk,[46b,c] IBiox[(−)-menthyl][46e] and CAAC 6[24a,b] bear additional *i*Pr and Me substituents and are rather rigid. Not only does this lead to an enormously increased steric demand, but also to a remarkably increased
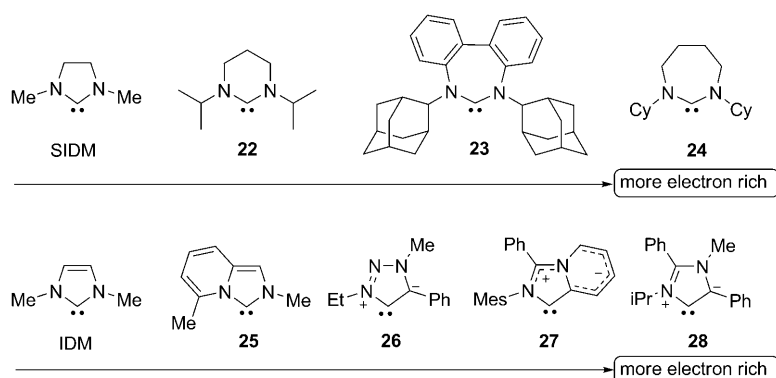
Figure 10. Comparison of five-, six- and seven-membered NHCs (top) and of normal and abnormal NHCs (bottom).

values for these systems have not yet been determined experimentally, quantum chemical calculations provided reliable data (Table 4, entries 7, 3, and 2, respectively).[39e]

In addition, increasing the ring size to six-[39e] and seven-membered carbenes[47] results in an increased electron richness (Table 4, entries 38, 43, and 48; the formulas for **22** and **23** are shown in Figure 10). In addition, abnormal pyridyl-annulated carbene **27** (Table 4, entry 45) reported by Lassaletta and co-workers, is remarkably more electron donating as a ligand (Δ(TEP) = −5.8 cm^{-1}) than the corresponding "normal" NHC imidazol[1,5-a]pyridine-3-ylidene (**25**) (Table 4, entry 23).[48] Moreover, among abnormal NHCs, the abnormal 1,2,3-triazolylidene carbene **26** (Table 4, entry 36) synthesized by Albrecht and co-workers[49] is less electron rich than **27**, whereas **28**, developed by Crabtree and co-workers, is significantly more electron rich (Figure 10).[50]

Interesting is the comparison of the structurally closely related six-membered NHCs **29** and **30** (Figure 11): whereas neutral NHC **29** is one of the least electron-donating NHCs reported to date (Table 4, entry 9), anionic NHC **30** is a much more electron-rich NHC.[51,52]
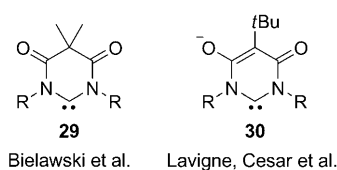

Figure 11. R = 2,4,6-trimethylphenyl.

3.3. Switchable NHCs

Recently developed NHC ligands that allow the reversible and controlled switching of their electronic properties have been reported. Bielawski and co-workers[53] have changed the electronic properties of NHCs **31**–**33** by the electrochemical oxidation/reduction of NHC–carbonyl complexes (Table 4, entries 4, 39; 5, 32; 12, 44; Scheme 3). The difference in the TEP values between the two electronic states of these systems is in a range of 10.6–12.7 cm^{-1} (for comparison: the Δ(TEP) between PPh$_3$ and PCy$_3$ is also 12.7 cm^{-1}).

Incorporation of a carbonyl group into the imidazolylidene backbone generates another rather electron-poor NHC ligand (**34a**, Scheme 3, Table 4, entry 8). Formation of the enolate by deprotonation results in the very electron-rich system **34b** (Table 4, entry 46). Protonation returns the electron-poor [Ir(CO)$_2$Cl(**34a**)] starting system. This demonstrated for the first time the switching ability of the electron-donor properties by a simple and reversible deprotonation/protonation strategy.[54]

Figure 12 demonstrates the differences in the electronic states of the respective switchable NHCs, and summarizes the electron richness of selected NHC ligands (see also Table 4).
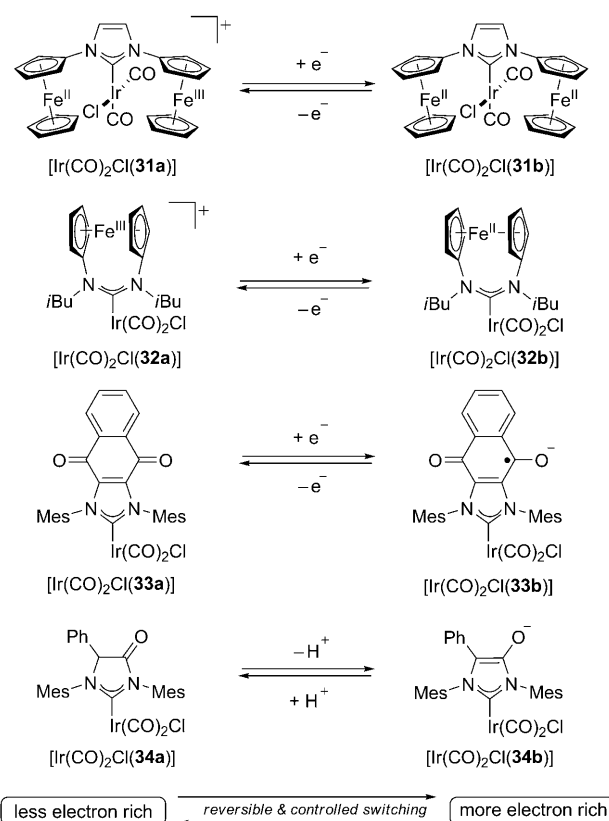
Scheme 3. Electronically switchable NHC ligands.

4. Steric Demand of NHCs and Metal–NHC Bond Lengths

It is a challenge to describe the shape and steric demand of a NHC-ligand in a general way since they strongly depend upon the N substituents. In addition NHCs possess an anisotropic structure and there is a massive variation in steric interactions upon rotation around the metal–NHC bond.

The 'buried volume' method, currently being developed and refined by Nolan, Cavallo, and co-workers, elegantly quantifies the steric demand of various NHCs using a single
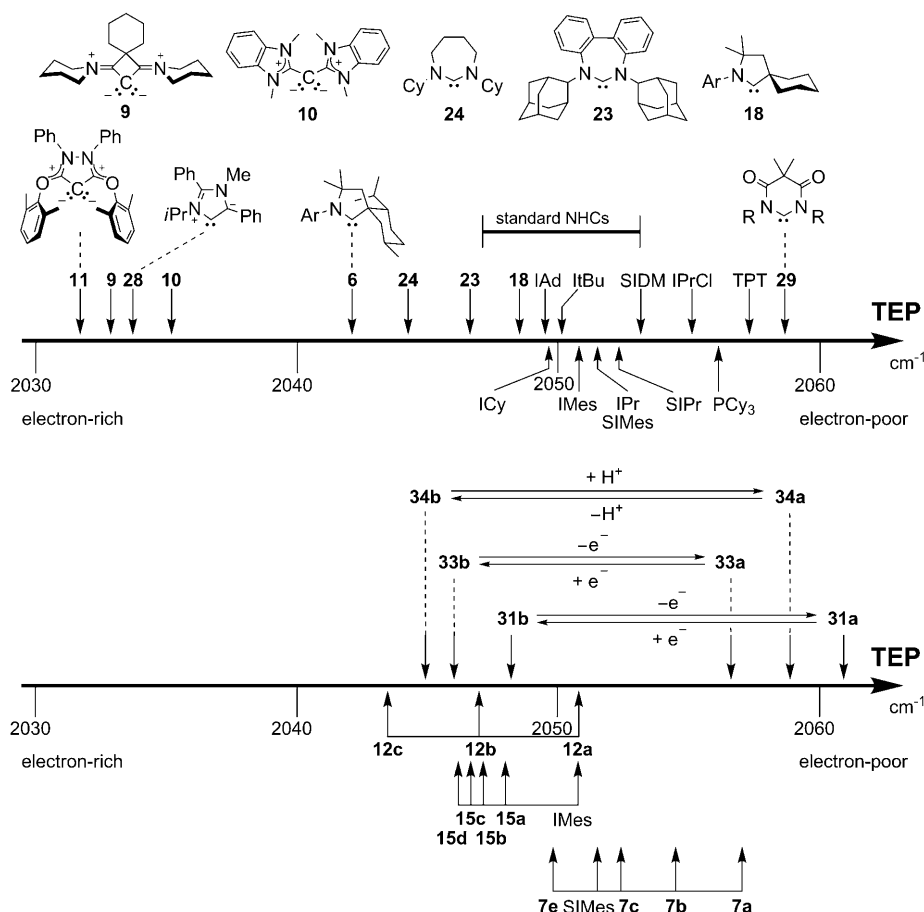
Figure 12. An overview: Tolman's electronic parameter for selected NHC ligands.

parameter only.[26a,56] The buried volume %V_{bur} represents the part of a sphere around the metal (with a certain radius r) that is buried by the atoms of the ligand under investigation. The more sterically demanding (within the coordination sphere of the metal)[56d] a ligand, the larger the %V_{bur} value (Figure 13).

As an attractive feature, the buried volume method is not limited to a certain class of ligands and, thus, can be used for the comparison of all kinds of ligands, such as mono- or bidentate ligands, NHCs, phosphines, or cyclopentadienyl-based ligands. Naturally, it is important that the same set of parameters is used to determine the %V_{bur} of a ligand class otherwise it is not possible to compare the results. A radius of 3.5 Å for the sphere and a distance of 2.0 Å (Table 5) between
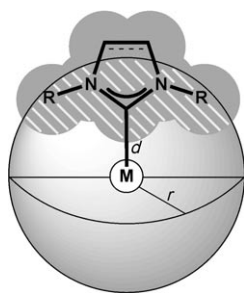

Figure 13. Graphical illustration of the buried volume (%V_{bur}) concept.

the metal and coordinating carbene atom seems to be a good choice to describe the steric demand.

Furthermore, it is important to note that the structure of the NHC can be derived from crystallographic or quantum chemically calculated data. In addition, different objects (the free NHC, the azolium salt, or any metal complex derived thereof) can be the basis for analysis. These different data sources often lead to different results and great care has to be taken in comparing %V_{bur} values.

In an excellent and exhaustive study, Clavier and Nolan examined the buried volume of many NHCs that formed complexes with coinage metals.[58] These complexes are ideally suited as their linear geometry leads to the minimization of the steric influence of additional spectator ligands on the metal center. In the case of phosphines, gold(I) chloride proved to be advantageous as several crystal structures are available and the gold(I) complexes do not tend to form dimeric or tetrameric structures as do copper(I) and silver(I) complexes. Numerous complexes and X-ray structures of [(NHC)AuCl], [(NHC)AgCl], and [(NHC)CuCl] can be found and there is a good match between the buried volume calculated from these different metal-containing complexes (Table 6). In addition, Clavier and Nolan showed that there is no big influence of the counterion upon the buried volume of the phosphine–gold complexes, and that the same is true for the analogous NHC

Table 5: Metal–NHC bond distances [Å] derived from X-ray crystal structures of different NHC transition-metal complexes.

Entry	Metal-NHC	Complex	Lit.	Entry	Metal-NHC	Complex	Lit.
1	1.983	[(ItBu)AuCl]	[57a]	16	1.997, 1.990	[(IMes)$_2$Pd]	[25p]
2	1.999	[(IMes)AuCl]	[25i]	17	1.957	[(ItBu)Ni(CO)$_2$]	[55]
3	1.983	[(SIMes)AuCl]	[25i]	18	1.971	[(IMes)Ni(CO)$_3$]	[55]
4	1.942	[(IPr)AuCl]	[25i]	19	1.960	[(SIMes)Ni(CO)$_3$]	[55]
5	1.979	[(SIPr)AuCl]	[25i]	20	1.979	[(IPr)Ni(CO)$_3$]	[55]
6	2.016	[(ItBu)AuBr$_3$]	[25h]	21	1.962	[(SIPr)Ni(CO)$_3$]	[55]
7	2.010	[(IMes)AuBr$_3$]	[25h]	22	2.114	[(ItBu)Ir(CO)$_2$Cl]	[25k]
8	2.052	[(SIMes)AuBr$_3$]	[25h]	23	2.108	[(IMes)Ir(CO)$_2$Cl]	[25k]
9	2.048	[(IPr)AuBr$_3$]	[25h]	24	2.121	[(SIMes)Ir(CO)$_2$Cl]	[25k]
10	2.042	[(SIPr)AuBr$_3$]	[25h]	25	2.079	[(IPr)Ir(CO)$_2$Cl]	[25k]
11	2.062	[(ItBu)Pd(allyl)Cl]	[25n]	26	2.071	[(SIPr)Ir(CO)$_2$Cl]	[25k]
12	2.032	[(IMes)Pd(allyl)Cl]	[25n]	27	2.105	[Cp*Ru(IMes)Cl]	[57b]
13	2.028	[(SIMes)Pd(allyl)Cl]	[25n]	28	2.083	[Cp*Ru(SIMes)Cl]	[26]
14	2.043	[(IPr)Pd(allyl)Cl]	[25n]	29	2.086	[Cp*Ru(IPr)Cl]	[57c]
15	2.040	[(SIPr)Pd(allyl)Cl]	[25n]	30	2.087	[Cp*Ru(SIPr)Cl]	[26]

Table 6: Comparison of %V_{bur} values in [(NHC)CuCl], [(NHC)AgCl], and [(NHC)AuCl] complexes of important NHCs.[a]

Entry	NHC	%V_{bur} (Cu)	%V_{bur} (Ag)	%V_{bur} (Au)
1	ICy[b]	28.8[59a]	27.7[25m]	27.4[5]
2	IMes	36.3[59b][c]	36.1[59c]	36.5[25i]
3	SIMes	36.9[59a]	36.1[25m]	36.9[25i]
4	IPr	47.6[59d]	46.5[59e]	44.5[59f]
5	SIPr	46.4[59g]	44.5[59e]	47.0[25i]
6	IBiox[(−)-menthyl]	50.4	49.4[46e,b]	47.7

[a] NHC structures extracted from crystal structures ($r = 3.5$ Å, $d = 2.0$ Å, Bondi radii scaled by 1.17). [b] ICy = dicyclohexylimidazolin-2-ylidene. [c] Bromide as the anion.

complexes.[58] Therefore, it is legitimate to compare the %V_{bur} for several coinage-metal complexes exhibiting a linear geometry.

As anticipated, the smallest NHCs are those with methyl groups on N. Naturally, the buried volume of the NHCs increases with increasing steric demand of the N substituents. The buried volume for some of the most commonly used NHCs ranges from 36.5% to 47.0% (Table 6, entries 2–5) when considering their AuCl complexes (or from 33.5% to 38.0% for the [IrCl(CO)$_2$] complexes). These %V_{bur} values clearly show the extraordinarily high steric demand of NHCs and the strong deviations obtained for different data sets.

As indicated above, switching from the linear [(NHC)AuCl] to the square-planar [(NHC)IrCl(CO)$_2$] complexes results in a decrease of buried volume of (S)IMes and (S)IPr (Figure 14). Obviously, the final ranking of the steric hindrance of different kinds of NHCs is variable and dependent upon the nature of the metal complexes. For highly coordinated complexes the buried volume decreases in the following order: ItBu/IAd > SIPr/IPr > SIMes/IMes > ICy > IDM. For two-coordinated metal complexes, however, the increase of the %V_{bur} value for IPr and SIPr is very pronounced, thus changing the order of buried volume: SIPr/IPr > ItBu/IAd > SIMes/IMes > ICy > IDM. This change is caused by distinctly different conformations adopted by the NHC ligands in the different complexes. Arguably, these differences in %V_{bur} point to a weakness of the buried volume concept, that is, the calculated steric demand represents only a snap-shot, and the level of flexibility/rigidity of different parts of the NHC is not taken into account.[13k] Gratifyingly, a very recent paper
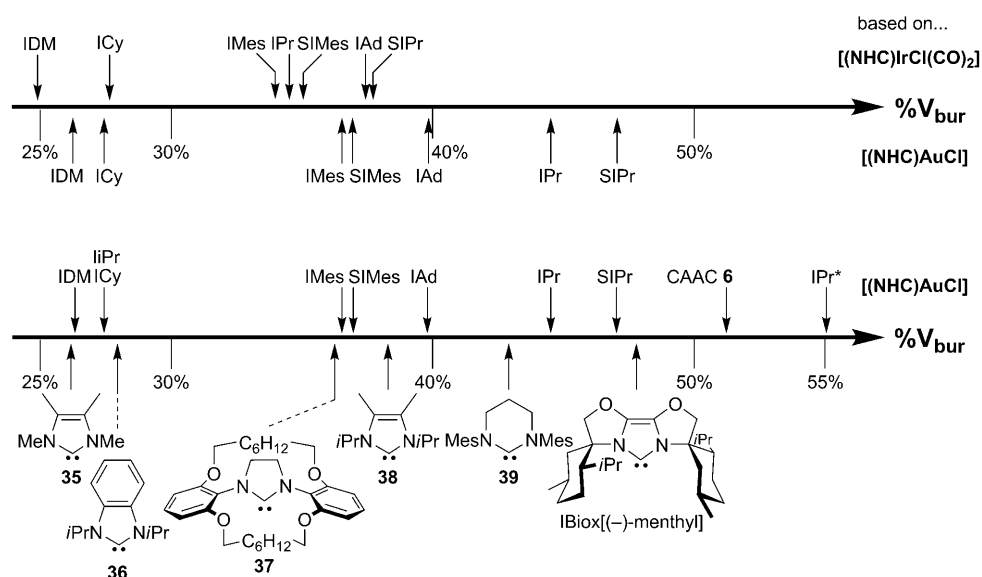
Figure 14. Upper scale: comparison of %V_{bur} values of seven prominent NHCs determined starting from two different metal complexes; bottom scale: [Au(NHC)Cl] complex derived %V_{bur} values for some representative NHCs.

by Cavallo and co-workers takes into account the impact of the flexibility of NHC ligands and, arguably, represents the starting point for a dynamic model that more precisely describes the actual metal environment during catalysis.[60]

The effect of backbone (un)saturation or annulation upon the steric demand is quite small (Table 7, entries 3 and 5, 7

Table 7: Calculation of the buried volume of different NHC-metal complexes.

Entry	NHC	%V_{bur} [(NHC)AuCl][a]	%V_{bur} [(NHC)IrCl(CO)$_2$][a]	%V_{bur} [(NHC)IrCl(CO)$_2$][b]
1	**35**	26.1[25i]	–	–
2	IDM	26.3[64a]	–	24.9
3	IiPr	27.4[64b]	–	–
4	ICy	27.4[25i]	27.6[25k]	–
5	**36**	27.9[64c]	–	–
6	**37**	36.2[63][c]	–	–
7	IMes	36.5[25i]	33.8[25k]	31.6
8	SIMes	36.9[25i]	35.0[25k]	32.7
9	**15d**	–	35.2[43]	33.4[65]
10	**38**	38.4[25i]	–	–
11	**39**	42.9[64d,c]	–	–
12	IPr	44.5[59f]	34.5[25k]	33.6
13	ItBu	–	37.6[25k]	35.5
14	SIPr	47.0[25i]	37.7[25k]	35.7
15	IAd	39.8[25i]	37.4[25k]	36.1
16	IBiox[(−)-menthyl]	47.7	–	–
17	CAAC **6**	51.2[64e]	–	–
18	IPr*	55.1[62b]	–	–

[a] NHC structures extracted from X-ray crystal structure ($r = 3.5$ Å, $d = 2.0$ Å, Bondi radii scaled by 1.17). [b] NHC structures extracted from DFT-optimized structure of [(NHC)IrCl(CO)$_2$] complexes ($r = 3.5$ Å, $d = 2.1$ Å).[56a] [c] Silver chloride complex was used.

and 8; Figure 14), but variation of the substituents on the 4- and 5-positions allows the fine tuning of the steric properties (Table 7, entries 7 and 9). In some selected cases, backbone substitution can exhibit a rather strong effect upon the buried volume (Table 7, entries 3 and 10). Increasing the NHC ring size from five- to six-membered cycles (and even seven- and eight-membered cycles)[61] also has a substantial effect upon the steric demand (Table 7, entries 8 and 11). Finally, the chiral CAAC **6**[24a,b] and IBiox[(−)-menthyl],[46d] as well as the achiral IPr*[62] (1,3-bis[2,6-bis(diphenylmethyl)-4-methylphenyl]imidazol-2-ylidene, Figure 1) are among the most sterically demanding monodentate carbene ligands.

5. Bond Dissociation Energy

The common assumption that NHC ligands bind more strongly to late transition metals than to phosphines can be proven by the bond dissociation energy (BDE) of the metal–ligand bond. For example in Ru^{II} and Ni^0 complexes, NHCs possess a higher BDE than phosphines do (Table 8). There are recent reports concerning existence of σ/π donation and π backdonation in some metal–NHC bonds.[66] The relative strength of the metal–NHC bond can also be dependent on

Table 8: BDE values (in kcal mol^{-1}) for CO and L (= NHC or phosphine) determined by calorimetric studies and calculations.

Entry	Ligand	BDE of CO in [Ni(CO)$_3$L]	BDE of L in [Ni(CO)$_2$L]	BDE of L in [Cp*RuCl(L)]
1	IMes	28.3	46.5	15.6
2	ICy	27.0	46.3	21.2
3	SIMes	26.8	47.2	16.8
4	IPr	26.7	45.4	11.1
5	SIPr	25.6	46.1	12.1
6	ItBu	13.3	44.3	–
7	IAd	7.6	46.5	6.8
8	PPh$_3$	30.4	30.0	-
9	PtBu$_3$	27.4	34.3	–
10	PCy$_3$	–	–	10.5

the steric properties of the NHC ligands, such as in the crowded [Cp*RuCl(NHC)] and [(NHC)Ni(CO)$_3$] complexes.[26,55,57a] The steric demand of some NHCs can induce the dissociation of other ligands. Consequently, the BDE of the third CO ligand in [Ni(CO)$_3$(NHC)] complexes (NHC = IAd and ItBu) is quite small, resulting in the facile formation of the corresponding dicarbonyl complex. Additionally, in some cases the dissociation/substitution and reductive elimination of NHC ligands was observed.[67]

6. Conclusion

NHCs have had a spectacular development from being a curiosity to serving as the workhorses of organometallic chemistry and catalysis. Understanding and tuning their distinct properties has been and will be key to the success for improving catalytic activity and other applications. The investigation of the electronics of NHCs, especially using the TEP method, is now firmly established. Moreover, whereas the electronic variation of the first reported NHCs was very limited, more and more NHCs with greatly varied electronic properties have been developed. In addition, series of structurally similar but electronically different NHCs, and the evolution of (reversibly) switchable NHCs have significantly expanded the chemists' toolbox.[53,54]

The determination of the steric demand of NHCs is significantly more challenging than the measurement of the electronic properties. In this regard, the buried volume concept represents a major breakthrough, although an additional improvement is required since the flexibility of the ligands is not taken into account.[60] In addition, it is unclear, if the buried volume is also relevant to describe the steric properties of NHC organocatalysts. Additional research along these lines seems rewarding. Furthermore, the design of distinct NHC architectures such as NHCs having exceptional buried volumes of and above 50%,[24a,46e,61,62] or ones exhibiting restricted flexibility[68] will enable new catalytic applications.

These and other exciting developments in the area of NHCs will eventually allow the synthesis of sophisticated, tailor-made catalysts. Since Arduengo's first isolation of an NHC in 1991, NHCs will soon leave their teenage phase; the best is yet to come!

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