1
N-Heterocyclic Carbenes

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1.1
Introduction

Over the past few decades, stable carbenes have received a great deal of attention from a number of researchers [1]. In the singlet carbene compounds, a carbon center bears a lone pair of electrons in an sp^2 hybridized orbital while a p orbital remains vacant (Figure 1.1a). Triplet carbenes are also known, where each of the two electrons occupy a degenerate p orbital (Figure 1.1b).

   N-Heterocyclic carbenes (NHCs) are a specific form of this class of compound, where the carbene is located on an *N*-heterocyclic scaffold. While these species were initially not widely applied in chemistry, they have now been employed in a broad range of fields, including organocatalysis [2] and organometallic chemistry [3]. Hundreds of different NHCs are known in the literature, and much has been learned about their properties and reactivity. Various experimental and theoretical techniques have been applied toward this aim, including density functional theory (DFT) studies, which have allowed an insight into the bonding and orbital arrangements in NHCs. This chapter details the discovery and isolation of stable NHCs, the characterization of the electronic nature of this species, the factors that render them stable, and the nature of their bonding to metal centers. In addition, some of the ways in which the electronic and steric properties of these species can be explored and quantified will be discussed.

1.2
Structure and Properties of NHCs

Prior to the isolation of stable NHCs, some information was known about the properties of these species. As early as the 1960s, researchers such as Wanzlick were active in probing the reactivity of NHCs generated *in situ* from, for example, the thermolysis of the corresponding dimers [4]. In this way, the nucleophilic reactivity of these species with a number of reagents was characterized
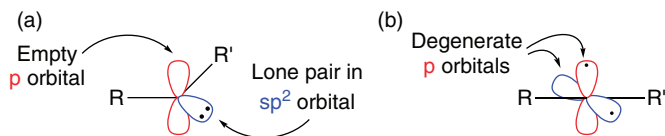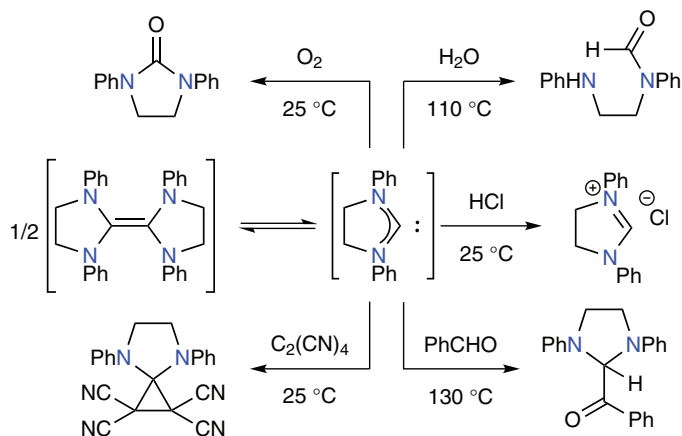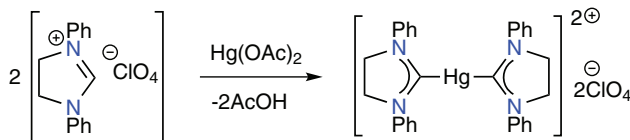
Figure 1.1 (a) Singlet carbenes; (b) triplet carbenes.

(Scheme 1.1). In addition, reaction with HCl yielded the corresponding imidazo-lium chloride salts. Metal–carbene complexes were also prepared by Wanzlick and Schönherr, without isolation of the free carbene itself (Scheme 1.2) [5].


Scheme 1.1 Early studies of the reactivity of N-heterocyclic carbenes. [4].

Scheme 1.2 Synthesis of an NHC-mercury complex [5].

The isolation of stable NHCs was a key event in the chemistry of this valuable class of compound, as this allowed the preparation of material for detailed characterization. In addition, many modern syntheses of NHC–metal complexes rely on the use of isolated NHCs. In 1991, when Arduengo *et al.* exposed imidazolium chloride **1** to NaH and catalytic DMSO in THF, stable carbene **2** was isolated (Scheme 1.3) [6]. This species, also known as IAd, could be characterized by various methods, including X-ray crystallography and NMR spectroscopy.

Initially, it was unclear whether steric or electronic effects were the source of the stability of **2**. A subsequent publication from Arduengo *et al.* reported a further four stable carbenes **3–6** (**3** is typically referred to as ITME, and **4** as IMes) with various *N*-substituents, which were prepared in the same manner as **2**
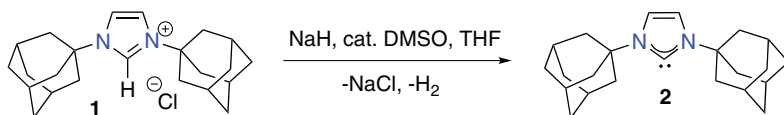
Scheme 1.3 Synthesis of IAd [6].

4 R = Me, R' = Me
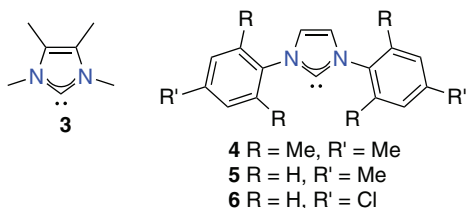**5** R = H, R' = Me
6 R = H, R' = Cl

Figure 1.2 Stable NHCs isolated by Arduengo *et al.* [7].

(Figure 1.2) [7]. Notably, these were far less sterically hindered, suggesting that the origin of their stability was electronic, rather than steric, or was a combination of these factors.

The aromatic nature of the imidazolium ring was thought to be critical to the stability of NHCs. However, in 1995, NHC **7** (SIMes) bearing a saturated backbone and bulky mesityl *N*-substituents was obtained by deprotonation of the corresponding imidazolium chloride **8**, and was characterized by Arduengo *et al.* (Scheme 1.4) [8].
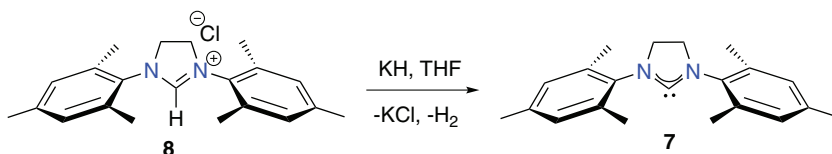
Scheme 1.4 Synthesis of SIMes [8].

With a robust route to synthesize and isolate free carbenes in hand, several researchers applied a number of tools to investigate their properties and reactivity. A thorough understanding of these properties is essential to understand how these species can be applied in chemistry, and to inform the rational design of new NHCs. X-ray photoelectron spectroscopy (XPS) and DFT studies of a model carbene **9** (I^{t}Bu) confirmed the presence of a lone pair of electrons in the plane of the imidazolylidene ring, and an empty p orbital on the same carbon center [9]. However, there was initially some debate as to whether the carbene was best considered as a carbene or as an ylide (Figure 1.3); that is, whether a resonance contribution from the lone pair centered on nitrogen was a part of the bonding arrangement in NHCs. Understanding this aspect of the structure of NHCs was important in order to understand both how the structure of the
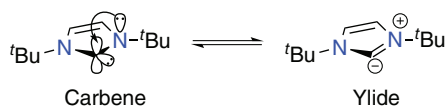
Figure 1.3 Carbenic and ylidic resonance forms of *N*-heterocyclic carbenes (**9** (I^{t}Bu) is pictured).

NHC might affect reactivity, as well as allowing for the tuning of reactivity *via* structural modifications.

Initial studies by Dixon and Arduengo suggested that the ylidic form was not a major contributor to the structure of imidazolium-based NHCs [10]. Subsequent electron distribution mapping of a model carbene, **3**-d_{12} (ITME-d_{12}) using X-ray and neutron radiation also suggested very little contribution from the ylidic form; these methods relied on mapping the electron distribution 0.7 Å above the plane of the NHC, which the authors proposed should indicate whether p_π–p_π delocalization occurred. The lengthened C−N bonds in imidazolylidenes compared to the corresponding imidazolium salts were proposed to be further evidence of negligible interaction of the nitrogen lone pairs with the empty p orbital at the carbene. Visualization of the electron density using this method showed π electron density between C4 and C5 corresponding to the double bond, and the *p* electrons of the nitrogen; no evidence for an ylidic form was found. In addition, the ^{13}C shielding tensor σ_{11} was revealed to be negative, suggesting that the carbenic resonance form was dominant [11]. However, later work by Boehme and Frenking suggested that the method of electron density mapping that was employed was not appropriate, as it suggested negligible π-delocalization in pyridine and pyrrole, which are known to be aromatic [12]. *In silico* calculations by these authors, particularly those involving natural bond order (NBO) calculations, strongly suggested that p_π–p_π delocalization was significant in both imidazol-2-ylidenes and imidazolidin-2-ylidenes, but more pronounced in the former.

A detailed study, published at the same time by Heinemann *et al.*, explored this p_π–p_π delocalization in NHCs, and aimed to understand whether imidazol-2-ylidenes were aromatic species [13]. Three key characteristics of NHCs were explored: thermodynamic stability, geometric structure, and the charge distribution. Isodesmic calculations on acyclic carbenes and aminocarbenes showed that even when conjugation was not possible, the carbene was stabilized by adjacent amino groups due to their σ electron-withdrawing properties. Conjugation further increased stabilization; imidazolidin-2-ylidenes were more stable again, while imidazol-2-ylidenes were most stable (Figure 1.4). Similarly, structural data were consistent with π-delocalization. Calculated magnetic susceptibility anisotropies (Δχ) were suggestive of cyclic π-delocalization, but to a lesser extent than in benzene. All of these results strongly suggest the involvement of p_π–p_π delocalization from the nitrogen lone pair into the empty orbital at the carbene, and that imidazol-2-ylidenes show some aromatic character. In a later study by Bielawski and coworkers, it was shown that the electronic properties of acyclic
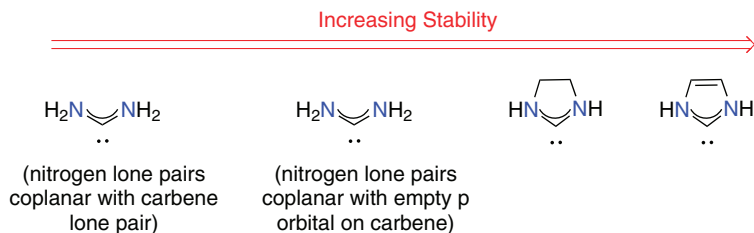
Increasing Stability

(nitrogen lone pairs coplanar with carbene lone pair)

(nitrogen lone pairs coplanar with empty p orbital on carbene)

Figure 1.4 Stability of some carbenes, as determined by isodesmic calculations for the reaction of each carbene with methane to generate NHC·H_2 and dihydrocarbene [13].
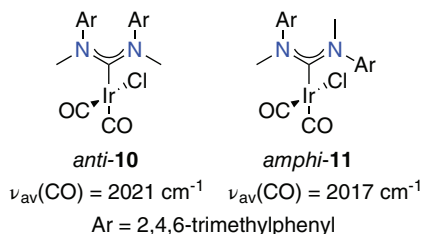

anti-**10**

amphi-**11**

$\nu_{av}(CO) = 2021$ cm^{-1} $\nu_{av}(CO) = 2017$ cm^{-1}

Ar = 2,4,6-trimethylphenyl

Figure 1.5 [IrCl(CO)$_2$(L)] complexes in which the differing degrees of p$_\pi$–p$_\pi$ conjugation affects the electronic properties of the metal center [14].

diaminocarbenes (as probed using the infrared spectra of [IrCl(CO)$_2$(L)] complexes **10** and **11**, shown later) were dependent on the ligand conformation, due to differing degrees of p_π–p_π delocalization (Figure 1.5) [14].

Clearly, this delocalization is a key component of the bonding in NHCs, and for this reason NHCs are typically drawn with the inclusion of a curve between the nitrogen atoms in order to emphasize this aspect of their electronic structure.

1.3
Abnormal Carbenes

While the majority of reports of imidazolylidenes bound to metal centers involve coordination *via* the C2 position (i.e., imidazol-2-ylidenes), there has been recent and growing interest in so-called abnormal carbenes, often referred to as aNHCs, where binding occurs *via* the C4 or C5 position (Figure 1.6) [15]. Often the substitution pattern is chosen to block the C2 position. The resulting imidazolylidenes are stabilized by only one nitrogen moiety, as the π-donating and σ-accepting properties of the second nitrogen atom are greatly reduced. Such species provide great scope for achieving different properties from so-called normal carbenes.

These species tend to show quite different electronic properties to their normally bound congeners. They are considerably more electron-donating due to
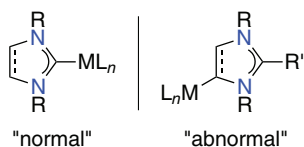
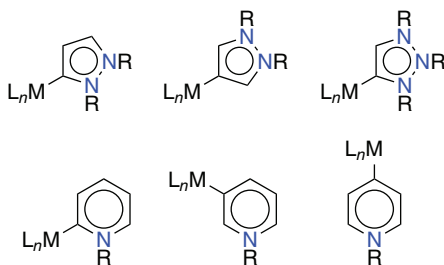**Figure 1.6** Normally versus abnormally bound imidazolylidenes.

Figure 1.7 NHC species with reduced heteroatom stabilization [15].

the reduced σ-withdrawal from the carbene center, as evidenced by calculated Tolman electronic parameter (TEP) [16] values (shown later) for a range of these species [17]. In addition, they have been shown to be more π-accepting (due to reduced p_π–p_π delocalization), as determined by analysis of the ^{31}P chemical shifts of the corresponding phosphinidene adducts [18]. The different properties of these ligands will naturally confer different properties and reactivity to the metal centers to which they are coordinated.

Other species with reduced heteroatom stabilization are also known; these include isomers of imidazolylidenes (e.g., 1,2-imidazol-3-ylidenes, 1,2-imidazol-4-ylidenes), 1,2,3-triazoly-4-lidenes, and pyrimidazolylidenes (Figure 1.7) [15].

1.4
Why Are NHCs Stable?

Prior to the isolation of NHCs, various studies were carried out on species generated *in situ* [4]. However, once Arduengo succeeded in isolating a series of stable species, attention naturally turned to identifying *why* some species were stable and isolable, while others were not.

Heinemann and Thiel [19] and Carter and Goddard [20] both applied theoretical methods to investigate the singlet–triplet gap in prototypical carbene compounds, showing that this factor was key in the stability of NHCs. Triplet carbenes are known to be much less stable than singlet species [21]. Some of the factors affecting the singlet–triplet gap have been established for some time, such as the influence of the geometry of the carbene and the presence of
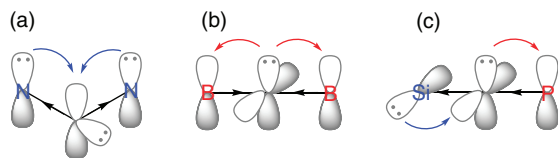
Figure 1.8 Bonding arrangements in some stable carbene systems [1].

neighboring π systems [22]. Importantly, the two otherwise degenerate empty p_x and p_y orbitals on the carbene must be rendered different in energy (e.g., by bending the carbene in one plane), and the energy gap between the singlet and triplet forms must be as large as possible.

Bertrand and coworkers have discussed, with the use of illustrative examples, the various means by which carbenes can be stabilized [1]; the three examples employed are reproduced here (Figure 1.8). In Figure 1.8a, which is a typical arrangement in NHCs, electron density from the lone pair of an adjacent hetero-atom is donated into the empty p orbital, while the inductive σ-electron-withdrawing nature of the heteroatom reduces the electron density at the carbene center. In Figure 1.8b, the (linear) carbene is stabilized by donation of electron density from the carbene into adjacent π-accepting heteroatoms (such as boron), which are σ-donating. In Figure 1.8c, the combination of π-donating/σ-withdrawing and π-withdrawing/σ-donating heteroatoms acts to stabilize the linear carbene.

Boehme and Frenking probed the stability difference between saturated and unsaturated carbene species, considering various factors such as the optimized geometries (MP2/6-31G(d)), energies of hydrogenation and NBO analysis of imidazol-2-ylidene and imidazolidin-2-ylidene [12]. The enthalpy of hydrogenation of imidazol-2-ylidene was lower than that of imidazolidin-2-ylidene (about -20 and -40 kcal mol^{-1}, respectively), in agreement with the higher thermodynamic stability of the former. NBO analysis showed that, despite the longer C2—N bonds in the former, the p_π(C2) occupancy was higher, suggesting a greater contribution from the nitrogen lone pair. The contribution of σ donation to the electronics of C2 was shown to be similar in both systems, suggesting that the difference in stability must result from greater π donation from the nitrogen atoms in unsaturated analogs.

Cavallo and coworkers have shown that the stability of a singlet carbene (with respect to dimerization) can be ascertained *via* calculation of two key properties of a carbene [23]. The steric bulk is quantified using percent of buried volume, %V_{bur} (shown later) [24], while the electronic nature is quantified using the singlet–triplet energy gap (E_{S-T}). It was shown that a linear correlation ($R^2 = 0.93$ or 0.88, for gas-phase or THF data, respectively) exists between the energy of dimerization (E_{dim}) and a linear combination of %V_{bur} and E_{S-T} (Equation 1.1). Importantly, the value of E_{dim} can be used to predict the behavior of a carbene. For carbenes where E_{dim} was predicted to be ≤ -20 kcal mol^{-1}, the NHC was found (experimentally) to be stable as a dimer. In cases where $E_{dim} \geq 0$ kcal mol^{-1},

the NHC was found to be stable as a monomer. For intermediate cases, the NHC exists as a mixture of the free carbene and dimer at equilibrium.

$$E_{dim} = A \cdot \% V_{bur} + B \cdot E_{S-T} + C \tag{1.1}$$

1.5
Bonding of NHCs to Metal Centers

One of the major applications of NHCs is as ligands for transition and main group metal centers. Therefore, understanding the way in which NHCs bond to and influence the properties of metal(loid) centers is of great importance. In this section, the nature of bonds to NHCs will be discussed, highlighting how this important characteristic has been probed experimentally and theoretically. Section 1.6 deals with the characterization of NHCs, and includes a discussion of the various metrics that can be used to *quantitatively* describe the way in which different NHCs can affect the properties of species to which they are bound.

N-Heterocyclic carbenes and phosphine ligands can bind metal centers in a somewhat similar fashion: *via* dative coordination using a lone pair of electrons. Therefore, phosphines are often considered to be the closest neighbors to NHCs in terms of organometallic chemistry. However, the properties of these two classes of compounds can be quite different, and can yield, for example, catalysts with quite different reactivity. The use of NHCs in olefin metathesis [25] and in palladium catalysis [26], for example, has allowed the preparation of highly active and stable species that are now at the forefront of their fields. Various studies have been conducted to explore the nature of bonding between NHCs and metal centers. Díez-González and Nolan reviewed some aspects of NHC coordination to metal centers in 2007 [27].

One of the key issues was the degree of σ and π bonding between the NHC and the metal center. Initially, NHCs were thought to be purely σ donors, but later studies revealed contributions from π-bonding also. Structural data for NHC–Cu complexes suggested C—Cu bond lengths that were shorter than those that would be expected for purely σ bonds [28]. Later studies by Hu *et al.* revealed the structure of molecular orbitals in a number of NHC–Ag complexes [29]. Initially, significant π interactions were observed between the p_π orbitals of the carbene (i.e., perpendicular to the plane of the imidazolylidene ring) and the metal d_{xz} and d_{yz} orbitals [29a], suggesting that π-backbonding comprised a significant part of the NHC–Ag bond. This contribution was later quantified at 15–30% of the total orbital interaction energy, while Frenking and coworkers calculated a value of about 20% [30], underlining its importance in NHC–metal bonding [29b].

Hu *et al.* also used structural data for [Z(IMes)$_2$] (Z = Ni^0, Ag^I, I$^+$) compounds (**12–14**) to illustrate the importance of π backbonding (Figure 1.9) [29b]. In the nickel example, the metal is relatively electron rich (d^{10}), and so can donate electron density from the *d* orbitals into the C—N π^* orbital of the NHC,
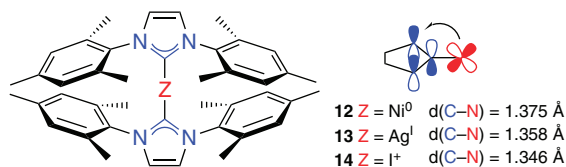
Figure 1.9 Probing the effect of π-backbonding in bis(NHC) compounds [29b].

lengthening the C−N bond. In the silver example, the metal center is less electron rich (and is cationic), so it is less able to participate in $d \rightarrow \pi^*$ backbonding, and the C−N bond is less elongated as a result. Iodine does not have filled d orbitals at all, and so the C−N bond in the NHC is shorter still, being unaffected by $d \rightarrow \pi^*$ backbonding.

Scott *et al.* have explored the bonding in some bis(NHC) iridium and rhodium complexes in which the NHCs are present in a *trans* arrangement [31]. The metal–carbene bonding in complex $[IrCl(\kappa^2\text{-}I^tBu)_2]$ **15** was found to involve π donation from the NHC to the metal (Figure 1.10). The bond lengths from the iridium center to the carbenes differed by about 0.2 Å, both by X-ray crystallographic analysis and by density functional theory studies. In addition, NBO analyses showed that the bonds had quite different orders (0.62 and 0.51). These different bond lengths were rationalized by visualizing the molecular orbitals of the complex; the shorter bond involves partial $\pi \rightarrow d$ donation from the highest occupied molecular orbital (HOMO) of the NHC (a π orbital) to the empty d orbitals of the electron-deficient metal center.

A later study by Jacobsen and coworkers systematically evaluated the various contributions of π donation and π backbonding in a variety of metal complexes of imidazol-2-ylidene (Figure 1.11) [32].

The systems studied covered a wide range of metals, d-configurations, geometries, and oxidation states. The authors studied the enthalpies of the metal–NHC bonds by assessing the energies of the complexes versus systems in which the NHCs were separated from the metal; however, the new fragments were not allowed to rearrange and so the bond enthalpy in each case was termed BE_{snap}, that is, only the energy required to "snap" the bond. Applying an energy decomposition analysis to the results allowed the separation of σ and π bonding, and the separation of the latter into π donation and π backbonding. Orbital interactions were found to dominate, with stronger bonds found in cationic species and
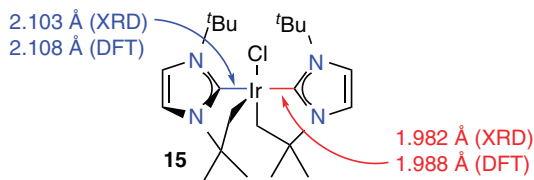

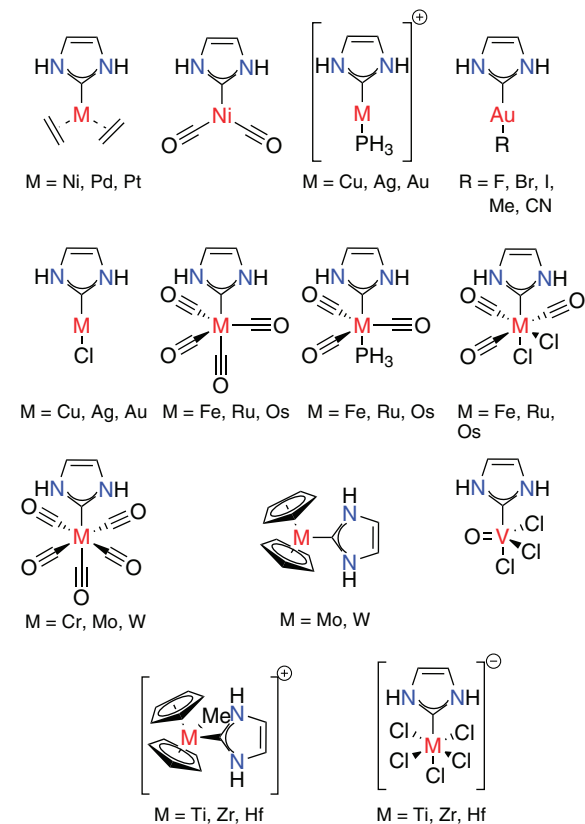**Figure 1.10** Ir−C bond lengths in $[IrCl(I^tBu)_2]$ [31].

Figure 1.11 Model complexes studied by Jacobsen and coworkers to evaluate the contributions of π-donation and π-backbonding to metal–carbene bonds [32].

those with high d-electron counts. Furthermore, bond energies were found to change when ligands with different π-donor or π-acceptor properties were used, strongly suggesting that π bonding to the metal is a significant factor in the NHC–metal bond. In a further step, π donation and π backbonding were separated in two subsequent calculations by removing the empty metal d orbitals and then the empty NHC π orbitals, respectively. The authors therefore concluded that three types of bonding were significant: σ bonding from the lone pair into the d_{z^2} orbital, π donation, and π backbonding between the π system localized on the NHC and the d_{xz} (or d_{yz} orbitals) (Figure 1.12). This is quite a complex bonding arrangement, and means that the M–NHC interaction is dependent not only on the structure and properties of the NHC, but also on the electronic arrangement at the metal center. Surprisingly, even metal centers that are formally d^0 exhibited considerable π backbonding, with this contribution increasing with d electron count.

Three key systems have been studied experimentally to investigate the contribution of π bonding to metal–NHC bonding. Fantasia *et al*. prepared a series of
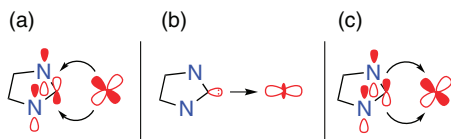
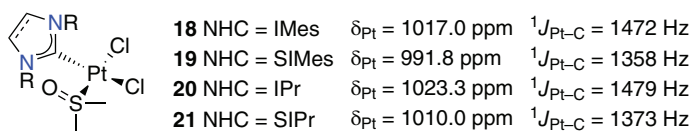**Figure 1.12** Contributions to the metal–carbene bond: (a) π-backbonding, (b) σ-donation, and (c) π-donation.

18	NHC = IMes	δ_{Pt} = 1017.0 ppm	$^1J_{Pt–C}$ = 1472 Hz
19	NHC = SIMes	δ_{Pt} = 991.8 ppm	$^1J_{Pt–C}$ = 1358 Hz
20	NHC = IPr	δ_{Pt} = 1023.3 ppm	$^1J_{Pt–C}$ = 1479 Hz
21	NHC = SIPr	δ_{Pt} = 1010.0 ppm	$^1J_{Pt–C}$ = 1373 Hz

Figure 1.13 Characterization of *cis*-[PtCl$_2$(DMSO)(NHC)] complexes [33].

cis-[PtCl$_2$(DMSO)(NHC)] complexes **18–21** (Figure 1.13), in which the NHC was the only potential π-accepting ligand [33]. Analysis of the ^{195}Pt NMR chemical shifts and the ^{195}Pt − ^{13}C ^1J coupling constants reveal information about the influence of the carbene ligand on the properties of the metal center. Larger coupling constants are indicative of more electron density in the σ bond between carbene and metal; therefore, the larger constants observed for complexes bearing unsaturated NHCs suggested that these bind the platinum center with more σ character than their saturated congeners. However, the ^{195}Pt chemical shifts revealed that Pt centers coordinated to saturated NHCs were more electron rich (lower δ_{Pt}). This was rationalized using computational studies, which supported the experimental evidence that saturated NHCs are both better σ donors and π acceptors, and form stronger bonds to the Pt center.

Bielawski and coworkers utilized [RhCl(COD)(NHC)] and [RhCl(CO)$_2$(NHC)] complexes to investigate π backbonding by spectroscopic means (Figure 1.14). Of particular interest were NHCs **22** and **23**, which contain spectroscopic probes (carbonyl and nitrile, respectively) for IR analysis. The frequency of signals corresponding to these probes can be altered by changing the degree of π
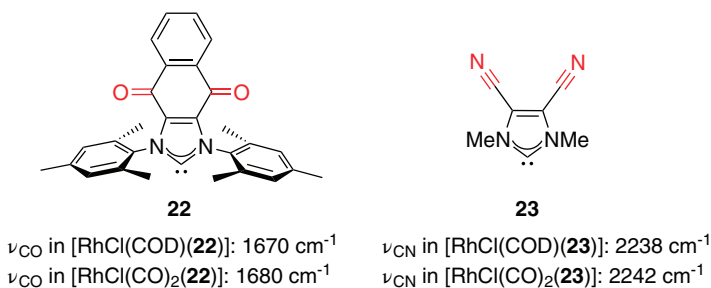

22

ν_{CO} in [RhCl(COD)(**22**)]: 1670 cm^{-1}
ν_{CO} in [RhCl(CO)$_2$(**22**)]: 1680 cm^{-1}

23

ν_{CN} in [RhCl(COD)(**23**)]: 2238 cm^{-1}
ν_{CN} in [RhCl(CO)$_2$(**23**)]: 2242 cm^{-1}

Figure 1.14 Spectroscopic investigation of π-backbonding in [RhCl(COD)(NHC)] and [RhCl(CO)$_2$(NHC)] complexes.

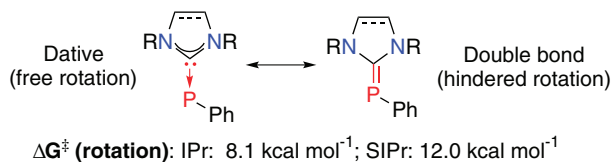ΔG‡ **(rotation)**: IPr: 8.1 kcal mol^{-1}; SIPr: 12.0 kcal mol^{-1}

Figure 1.15 NHC-phosphinidene adducts, and rotational barriers at room temperature for two examples.

backbonding from the metal center. The corresponding [RhCl(COD)(NHC)] complexes were exposed to CO to produce [RhCl(CO)$_2$(NHC)] complexes, in which the COD ligand was replaced with two CO ligands, which are better π acceptors. An increase in the stretching frequency of the probes was found to occur, indicative of strengthening of the bonds from the weaker π backbonding from the Rh center in the dicarbonyl species.

Most recently, phosphinidene adducts have been used to probe the nature of π bonding to NHCs [18]. The bonding in these adducts can be considered to be somewhere between dative coordination to the phosphorus atom, and double bond character between the carbene and the phosphorus (Figure 1.15). Adducts bearing the IPr and SIPr NHCs were studied; the former showed free rotation around the C−P bond (equivalent *iso*-propyl moieties) at room temperature, while the latter did not. Variable temperature NMR studies allowed the barrier to rotation in each species to be quantified, revealing a greater degree of double-bond character between phosphorus and the saturated NHC. This was put forward as further evidence of the contribution of π bonding in bonds to NHCs. Furthermore, the ^{31}P chemical shift was shown to vary considerably (about −60 to 130 ppm), depending on the ability of the NHC under examination to undergo d → π backbonding.

While the various contributions from σ and π bonding are a function of the electronic configuration of the metal center, they also depend on the structure of the NHC ligands. Bertrand and coworkers reported an NHC ligand **24** where one of the nitrogen atoms was confined in an orientation where π-delocalization into the empty p orbital was restricted (Figure 1.16) [34]; therefore, the carbene is stabilized by the σ-inductive withdrawing effects of two nitrogen atoms, but only accepts π electron density from one. The new ligand was as nucleophilic and σ-donating as analogs such as **25**, but was found to have a smaller singlet–triplet energy gap and was more π-accepting, as a result of the interaction with only one nitrogen lone pair.
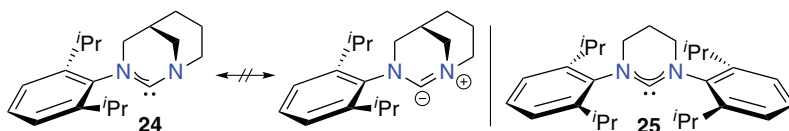

Figure 1.16 Tuning the properties of NHC ligands through structural confinement of the nitrogen substituents.

1.6
Quantifying the Properties of NHCs

With such a vast range of NHCs known from the literature and a wider still range accessible using established organic chemistry methodologies [35], it becomes important to be able to compare this catalog of ligands quantitatively. To achieve this aim, a number of metrics have been employed. A fuller discussion of the latest models that can be used to describe NHCs can be found in a subsequent chapter, but a brief discussion is presented here, divided into steric impact and electronic properties. Given the similarity of NHCs to phosphanes, in that both are neutral two-electron σ-donor ligands, some of these metrics bear relation to those employed in the chemistry of phosphanes. Other metrics are newer, and take advantage of recent increases in the capabilities of analytical equipment and molecular modeling software. However, the inherent simplicity of quoting a single number for steric impact and a single number for electronic properties render $\%V_{bur}$ and TEP [16] the current metrics of choice for describing NHC ligands.

1.6.1
Steric Impact

For phosphanes, the Tolman cone angle, defined as a cone extending from a metal center (2.28 Å from the phosphorus of the phosphine ligand) that encompasses the substituents, provides the most common measure of steric impact [16]. However, NHCs are typically a very different shape from phosphanes. Initially, a metric based on the "wedge" shape of NHCs was proposed, using two parameters to describe the size of an NHC [36]. However, this was quickly superseded by the concept of percent of buried volume ($\%V_{bur}$) [24], which is defined as the proportion of a sphere, centered on the metal, which is occupied by the ligand (Figure 1.17). This scale can be used to describe NHCs and phosphanes, and in theory any other ligands also. Cavallo and coworkers have
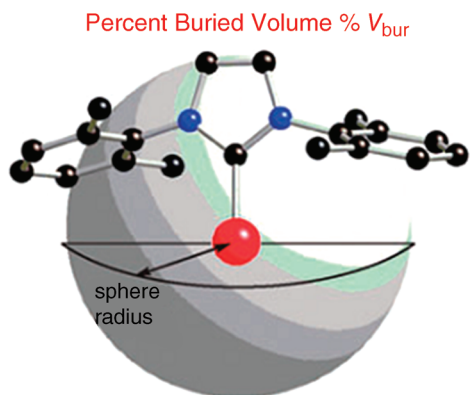

Percent Buried Volume $\% V_{bur}$

sphere radius

Figure 1.17 Percent of buried volume for characterizing the steric properties of NHC ligands [24].
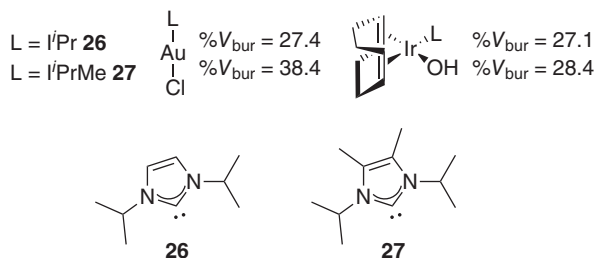
Figure 1.18 Comparison of %V_{bur} using different metal complexes.

developed a simple Web-based software that allows %V_{bur} to be calculated quickly from crystallographic data [37].

The percent of buried volume is heavily dependent on both the nature of the ligand under investigation and on the geometry of the complex to which it is coordinated. It is therefore very difficult to compare values of %V_{bur} obtained using different families of complexes. For example, NHCs **26** (I^{i}Pr) and **27** (I^{i}Pr^{Me}) differ only in the methylation of the imidazolylidene backbone. When the linear two-coordinate [AuCl(NHC)] complexes are considered, there is a significant difference in %V_{bur} (23.5% versus 33.9%; where the M–NHC distance is 2.28 Å) (Figure 1.18) [24]. However, in square planar [Ir(COD)(NHC)(OH)] complexes, the difference is far less stark (27.1 and 28.4%), but still sufficient to change the way in which the ligand and metal interact [38]; I^{i}Pr^{Me} was found to add only once to [IrCl(COD)]$_2$ to form [IrCl(COD)(I^{i}PrMe)], while I^{i}Pr added twice, yielding [Ir(COD)(I^{i}Pr)$_2$][Cl]. For this reason, the steric properties of new NHCs are typically evaluated on at least two systems, and often three; for example, linear two-coordinate [AuCl(NHC)], square planar [IrCl(CO)$_2$(NHC)], and tetrahedral [Ni(CO)$_3$(NHC)], where the IR spectrum of the latter complex is also used to determine the TEP.

However, %V_{bur} does have some limitations as a metric. Values are typically calculated from X-ray diffraction data or DFT-derived structures, which represent the solid state and gas phase, respectively. It can therefore be difficult to infer the structure in the solution phase; the vast majority of the most commonly used computational solvation models do not take into account specific solvation effects, and instead apply an electric field to simulate the effect of solvent. In addition, %V_{bur} is a static measure, and only takes into account the steric impact of the specific conformation examined. In solution, many ligands will adopt a number of conformations. Although it is possible to conduct very elegant and detailed studies assessing the dynamic behavior of ligands in specific environments [39], these studies are time-consuming and computationally expensive.

1.6.2
Electronic Properties

The TEP is the typical method used to investigate the electronic properties of phosphanes [16], and has been extended to describe NHCs [40].
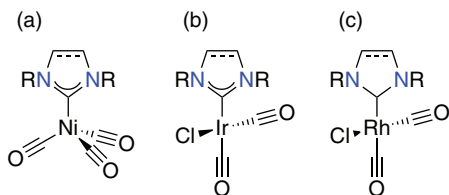
Figure 1.19 Systems commonly used to determine TEP for NHCs: (a) [Ni(CO)$_3$(NHC)], (b) [IrCl(CO)$_2$(NHC)], and (c) [RhCl(CO)$_2$(NHC)].

This parameter is determined by the preparation and analysis of the corresponding [Ni(CO)$_3$(NHC)] complex. Electron-rich ligands will increase the π donor ability of the metal center, leading to donation into the π^*_{CO} antibonding orbital. As a result, the C−O bond distance lengthens and the stretching frequency ν_{CO}, observable by IR at ~2000–2100 cm^{-1}, will decrease. The frequency of the A$_1$ vibration of [Ni(CO)$_3$(NHC)] complexes can therefore be used as a quantitative measure of their electron-donating abilities. However, synthesis of the necessary complexes requires the reaction of the free carbene with volatile, pyrophoric, and highly toxic [Ni(CO)$_4$] (Figure 1.19a).

Alternative systems have been utilized by researchers. A linear correlation between the A$_1$ frequency in the IR spectra of [Ni(CO)$_3$(NHC)] complexes and the average ν_{CO} in the IR spectra of the corresponding [IrCl(CO)$_2$(NHC)] complexes (Figure 1.19b) has been shown (Equation 1.2) [41]:

$$TEP = 0.847 \cdot \nu_{CO}(\text{av., Ir}) + 336 \text{ cm}^{-1}. \tag{1.2}$$

The latter complexes can be prepared in a straightforward manner from the corresponding [IrCl(COD)(NHC)] complexes; these can, in turn, be prepared from various synthetic routes, including the reaction of free carbenes or [AgCl(NHC)] complexes with [IrCl(COD)]$_2$, or the reaction of [Ir(OR)(COD)]$_2$ (R = Me, Et, ^{t}Bu) with the NHC salt.

Later, it was shown that the use of [RhCl(CO)$_2$(NHC)] complexes (Figure 1.19c) was also a practical alternative for the determination of TEP, with a good linear correlation between the iridium- and rhodium-derived data sets (Equation 1.3) [42].

$$\nu_{CO}(\text{av., Ir}) = 0.8695 \cdot \nu_{CO}(\text{av., Rh}) + 250.7 \text{ cm}^{-1}. \tag{1.3}$$

The commercially available complex [Rh(CO)$_2$Cl]$_2$ can be used to prepare [RhCl(CO)$_2$(NHC)] compounds in one synthetic step, or carbonylation of [RhCl(COD)(NHC)] can also be employed as a synthetic route, analogous to the method in which the iridium species are prepared.

The use of TEP is also not without some drawbacks. The weakening of the CO bond *via* back-donation into the π^*_{CO} antibonding orbital is dependent on the ability of the metal center to undergo $d \rightarrow \pi^*_{CO}$ backbonding; while this is typically correlated to the electron density of the metal center, it also depends somewhat on the π-acceptor nature of the NHC ligand. Nolan, Jacobsen, and Cavallo

28
TEP = 2069.0 cm^{-1} (Ir)

29
TEP = 2057.3 cm^{-1} (Ir)

30
TEP = 2055.0 cm^{-1} (Ir)

31
TEP = 2051.5 cm^{-1} (Ni)

32
TEP = 2050.7 cm^{-1} (Ni)

33
TEP = 2049.1 cm^{-1} (Ir)

34
TEP = 2046.7 cm^{-1} (Ir)

35
TEP = 2046.1 cm^{-1} (Ir)

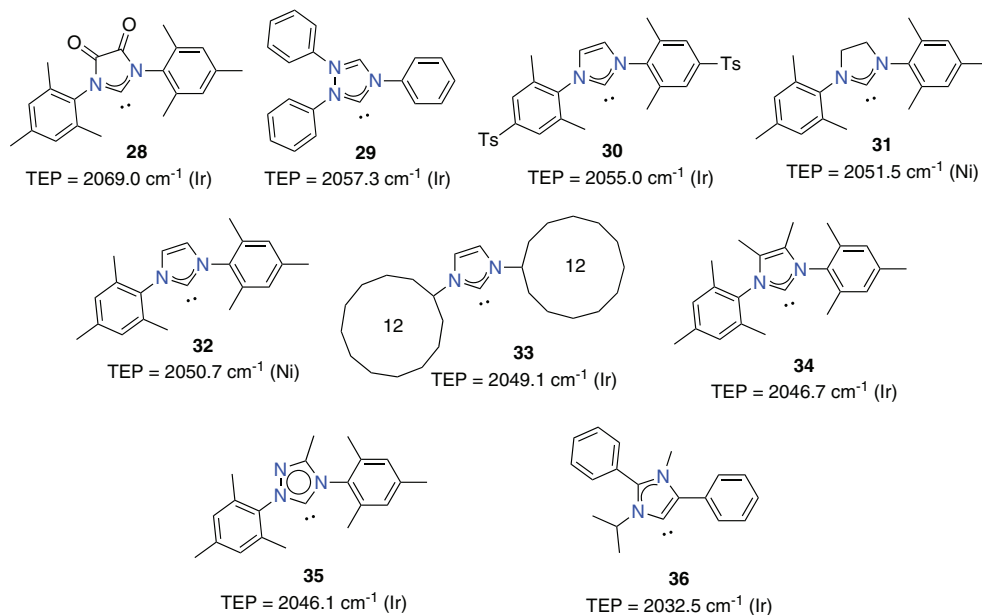**36**
TEP = 2032.5 cm^{-1} (Ir)

Figure 1.20 Examples of NHCs that have been characterized by TEP measurements [40,41b,43].

later used a series of platinum complexes to show that saturated NHCs are more electron donating *but* are better π acceptors.

A vast number of NHCs have been characterized using the three systems in Figure 1.19. A sample of some of these data can be found in Figure 1.20 (for carbenes **28**–**36**); a more detailed collection of TEP values can be found in the literature [44].

1.7
N-Heterocyclic Carbenes in the Context of Other Stable Carbenes

Due to the efforts of a number of researchers, a wide range of stable carbenes have been isolated and characterized. NHCs form only one subset of this class of compounds, and therefore it is interesting to consider their properties in the context of the wider range of stable carbene compounds at the fundamental level and by understanding how their electronic and steric properties compare. A full discussion of this topic is beyond the scope of this chapter, so a limited overview is provided here.

In an early study, Arduengo *et al*. conducted XPS and DFT studies on a model carbene, and on the analogous silylene and germylene [45]. While such studies showed a localized lone pair in the plane of the imidazolylidene ring, with an empty *p* orbital perpendicular to this, the electronic structures of the silylene and germylene analogs were quite different. The HOMOs in these compounds
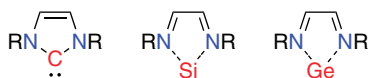
Figure 1.21 Proposed bonding models in *N*-heterocyclic carbenes, silylenes, and germylenes [45].
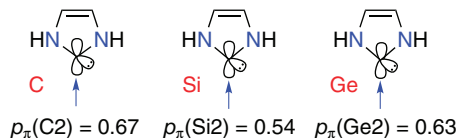

$p_\pi(C2) = 0.67$ $p_\pi(Si2) = 0.54$ $p_\pi(Ge2) = 0.63$

Figure 1.22 Calculated p_π occupancy of the carbene center in model carbene, silylene, and germylene compounds [13].

were shown to be derived from π orbitals instead. These were more localized on the Ge center than in the Si center, in their respective compounds. In some respects, the Si and Ge analogs were proposed to be similar to chelated diimine compounds, rather than carbenes (Figure 1.21). However, work by Boehme and Frenking emphasized that the influence of π-donation to the carbene/silylene/germylene center was still a considerable factor [12].

Later studies by Heinemann *et al.* suggested that p_π–p_π delocalization is still a key aspect of the bonding in *N*-heterocyclic silylenes and germylenes, albeit with lower p_π occupancy at the carbene center (Figure 1.22) [13]. The heats of hydrogenation of the silylene and germylene compounds were also found to be less exothermic than those of the corresponding carbene, due to their weaker bonds to hydrogen.

Other carbon-centered ligands, flanked by heteroatoms other than nitrogen, are known. Kassaee *et al.* studied a range of compounds (aminocarbenes, imidazol-2-ylidenes and imidazolidin-2-ylidenes) stabilized by one heteroatom (Figure 1.23). Characteristics such as the singlet–triplet energy gap (E_{S-T}), nucleophilicity, electrophilicity, and proton affinity were assessed. Acyclic compounds with no heteroatom stabilization often preferred the triplet state, while for cyclic species the singlet state was more stable (E_{S-T} of −4.2–5.7 kcal mol^{-1}). Amino groups, which are σ-accepting but π-donating, stabilized carbenes (E_{S-T} of 27.8–51.8 kcal mol^{-1}), while silyl groups (σ-donating; π-accepting) destabilized them (E_{S-T} of −7.0 to −15.9 kcal mol^{-1}), and phosphane (σ-donating; π-donating) was only moderately stabilized (E_{S-T} of 8.6–12.2 kcal mol^{-1}). The latter effect was ascribed to the difficulty of achieving planarity at phosphorus. Oxygen (weaker π donor, strong σ donor) and sulfur heteroatoms lead to some stabilization of the
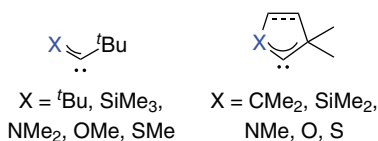

X = ^{t}Bu, SiMe$_3$,   X = CMe$_2$, SiMe$_2$,
NMe$_2$, OMe, SMe   NMe, O, S

Figure 1.23 Compounds studied computationally by Kassaee *et al.* [46].

singlet state ($E_{S-T} = 29.0–37.3$ and $18.7–29.9$ kcal mol^{-1}, respectively). In each case, the cyclic species were more stable, due to the restricted geometry at the carbene center. While NHCs are typically the most stable species, there is clearly great potential for other species as ligands. In addition, a number of oxazol-2-ylidene and thiazol-2-ylidene ligands are known in the literature, providing other means by which the reactivity of NHCs can be tuned.

Bertrand and coworkers have reviewed the topic of stable carbenes based on scaffolds other than diaminocarbenes [47]. Diphosphinocarbenes, aminophosphinocarbenes, cyclic (alkyl)amino carbenes, cyclic (amino)ylidic carbenes, cyclopropenylidenes, cyclic bent allenes, carbodiphosphoranes, and vinylidenephosphoranes have all been reported (examples **37**–**44**, respectively, in Figure 1.24a). Use of the [RhCl(CO)$_2$(L)] system for measuring TEPs allows the electron-donating ability of these systems to be ranked and compared to those of NHCs and abnormally bound NHCs (Figure 1.24b).
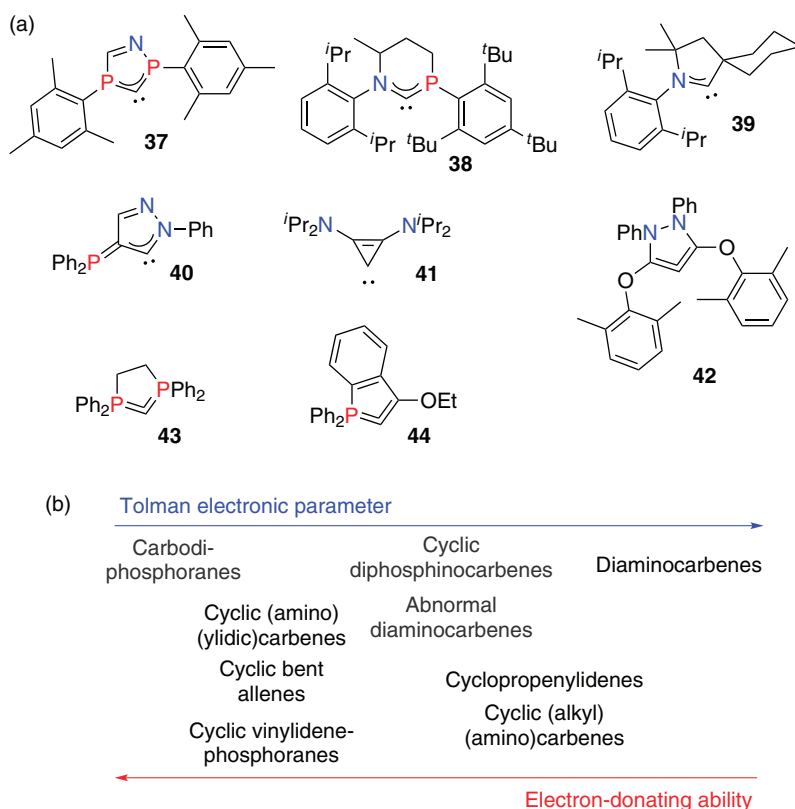

Figure 1.24 (a) Nondiaminocarbene species employed as ligands; (b) electron-donating ability of NHCs and relatives thereof.

1.8
Synthesis of NHCs

The synthesis of NHCs can generally be approached *via* two main routes, which require the preparation of different precursor compounds. Examples are presented here of how some common motifs can be approached. A full discussion of every synthetic route is beyond the scope of this chapter, but some representative examples are presented here. Interested readers are referred to a recent review of the topic [35]. A step-by-step guide to the synthesis of some common NHCs (IPr and IMes) has been published [48].

The first route is *via* the deprotonation of the corresponding salt using a strong base, typically NaH or KH in the presence of a catalytic quantity of KO^{t}Bu (Scheme 1.5) [48]. Imidazolium chloride salts are typically poorly soluble in organic media, so often the corresponding tetrafluoroborate, hexafluorophosphate, or tosylate salt is employed instead. The reaction is typically conducted in THF; filtration of the reaction mixture through celite followed by removal of the solvent *in vacuo* and/or crystallization yields the free carbene. This method is suitable for multigram preparations of free carbene, but requires the use of an inert atmosphere glovebox to manipulate the carbene thus formed. The precursor salts are typically prepared using one of two routes: disconnection at the backbone is preferred for unsaturated *N*-alkyl imidazolium salts, while disconnection at the C2–N1 and C2–N3 bonds is preferred for most other species. Species bearing saturated backbones can be obtained by reduction of the diimine before cyclization. Both methods of preparing the imidazolium salts are typically practical and high yielding on a large scale, and are routinely employed in our research laboratories on scales of up to about 1 kg. Free carbene liberation is routinely performed on scales of up to about 50 g, as larger-scale work is limited by the size of the requisite glassware and by the need to work in a glovebox. Free carbenes generated using this method can also be generated *in situ* in Schlenk glassware, either in the presence of a metal precursor or with the subsequent addition thereof. However, this approach requires the use of a strong base each time, and additional experimental time for the deprotonation reaction. Where a glovebox is available, the use of isolated pure free carbenes is more convenient.
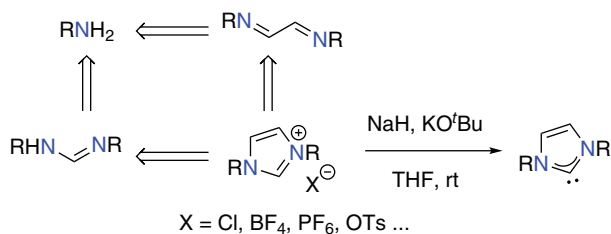
Scheme 1.5 General approach to free carbenes derived from imidazolium salts.
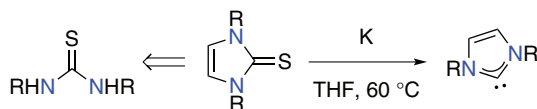
Scheme 1.6 Synthesis of NHCs *via* thione species.

The reduction of thiones can also be used to generate free carbenes (Scheme 1.6) [49]. A solution of thione is heated in the presence of potassium, and then the resulting solution can be filtered and worked up to yield carbene. While this route is typically very clean, it does require the use of elemental potassium, which can be hazardous. The thione compounds can be prepared from the corresponding thioureas, for which a variety of synthetic routes are known. Again, the scale of this synthetic route is limited by the need to work in the glovebox.

Both of these routes rely on very stable precursors that can typically be stored under ambient conditions for considerable periods of time. In contrast, the free carbenes generated from these methods are highly unstable to oxygen and moisture, but can be stored for extended periods (months) in the solid state in a freezer under an argon atmosphere.

Synthetic routes to NHCs are very flexible, and a vast number of structures are possible. NHCs based on imidazole and imidazolidine cores are the most common, although 1,2,3- and 1,2,4-triazole and oxazole, thiazole, and benzimidazole cores have also been used (among others). Several researchers, most notably Cavell and coworkers, have also explored the chemistry of so-called "ring-expanded" NHCs, where a six-, seven-, or eight-membered ring forms the core of the NHC [50]. By suitable modification of the synthetic route, it is possible to introduce a variety of substituents on the backbone of the core, or at the *N*-substituents. This enormous flexibility has contributed to the rapid growth of this area of chemistry.

1.9
Salts and Adducts of NHCs

A key drawback of the use of free NHCs as synthetic tools in organometallic chemistry is the inherent air and moisture sensitivity of these species. Synthetic routes that are used to prepare free carbenes are therefore limited in scale, requiring equipment that can be introduced to the glovebox and manipulated therein. To overcome this obstacle, a number of stable NHC precursors have been employed as NHC equivalents in organometallic synthesis.

Early in the study of NHCs, Wanzlick and Schikora showed that thermolysis of a chloroform adduct of an NHC liberated the free carbene *in situ*, although in these instances the free carbene was not isolated (Scheme 1.7) [51]. Adducts of NHCs with chloroform and alcohols can be stable to ambient conditions, while others are less stable and can decompose.
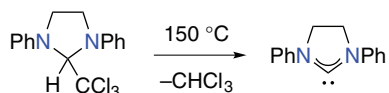
Scheme 1.7 Generation of a free carbene from thermolysis of the corresponding adduct.

Such adducts can be prepared by various routes. Arduengo *et al.* have explored the insertion of free carbenes into a number of C−H bonds, characterizing this aspect of carbene reactivity [52]. For applications in organometallic chemistry, especially where larger-scale syntheses are desired, more convenient methods exist that avoid the need to generate the free carbene (Scheme 1.8). These routes include reaction of the imidazolium salt with an alkoxide base (such as sodium methoxide or potassium *tert*-butoxide) to form the corresponding alcohol adduct (Scheme 1.8a) [53] and deprotonation in chloroform solution to form the chloroform adduct (Scheme 1.8b) [53]. Alternatively, condensation of an intermediate diimine with the corresponding aldehyde can yield the adduct directly, without the need to first prepare the imidazolium salt (Scheme 1.8c) [54]; adducts of NHCs with various aryl groups have been prepared in the latter manner [54], as well as chloroform adducts [51].

Thermolysis of these adducts, usually in refluxing solvent, yields the corresponding free carbene *in situ*. Typically, this is carried out in the presence of a metal precursor, and under rigorously inert conditions. In this way the handling of solid free carbene is avoided.

Carboxylate adducts of NHCs have been prepared and used in organometallic synthesis [55], as well as in organocatalysis [56]. These are typically prepared from exposure of the corresponding free carbene species to carbon dioxide, upon which they conveniently precipitate from THF solution (Scheme 1.9). While their preparation requires the use of sensitive free carbene species, the final products are air and moisture stable and can be worked up and isolated
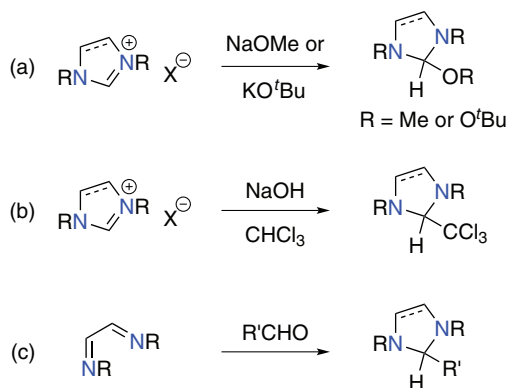
Scheme 1.8 Synthesis of NHC adducts [51,53,54].
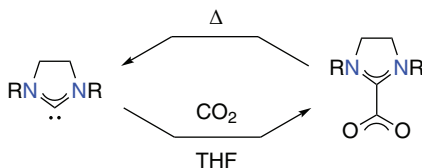
Scheme 1.9 Carboxylates as masked NHCs [55].

using reagent-grade solvents under ambient conditions. The free carbene is liberated by heating.

While chloride, tetrafluoroborate, hexafluorophosphate, and tosylate salts are typically used when the free carbene is prepared via deprotonation, it has been shown that hydrogen carbonate salts can liberate free carbenes upon thermolysis, without the need to use a base [56b].

These methodologies do present some drawbacks, as thermolysis is typically necessary to liberate the free carbene. If the free carbene is particularly unstable and subsequent reaction with the metal precursor is slow, or if a thermally sensitive organometallic complex is to be formed, decomposition may compromise the yield of the reaction.

1.10
Summary

In summary, this chapter presents an overview of *N*-heterocyclic carbenes as chemical species. The electronic characteristics of these ligands were discussed, detailing how p_π–p_π delocalization and σ electron withdrawal stabilizes the carbene center. The bonding to metal centers was also discussed, whereby the potential for σ donation, π donation, and π backbonding was highlighted. A brief introduction to how these species can be classified was presented, although the latest developments on this topic are detailed in a subsequent chapter. In addition, an overview is presented of how these compounds, and stable adducts thereof, can be prepared in the laboratory. This chapter has hopefully provided the reader with a foundation from which the myriad applications of NHCs can be appraised and understood, en route to stimulating or developing the use of NHCs in the reader's chemical research.

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