Non-transition metal N-heterocyclic carbene complexes

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Since their isolation in 1991, N-heterocyclic carbenes (NHCs) have become ubiquitous in organometallic chemistry. In more recent years investigations into the coordination of NHCs to other elements have expanded, and there are examples of their coordination to elements across the whole periodic table. This report gives an overview of NHC complexes of non-transition metal elements, ranging from the s-block elements, through the p-block and on to the lanthanides.

1. Introduction

Due to their steric and electronic properties N-heterocyclic carbenes (NHCs) are a rapidly expanding area of research, particularly in transition metal chemistry. Besides their role as excellent ligands in metal-based catalytic reactions, organocatalytic carbene catalysis has emerged as an exceptionally fruitful research area in synthetic organic chemistry, and this area has recently been reviewed. Coordination of NHC ligands is not only limited to transition metals; there is an expanding range of examples in which NHCs have been used in combination with groups 1, 2, 13, 14, 15, 16, 17 and also the lanthanides. NHCs are Lewis base 2-electron donors and don’t necessarily require backbonding in their complexes, making them suitable for coordinating to a range of different centres. This report describes many of the interesting NHC complexes formed with elements of the s-block and p-block and also the lanthanide ions, most of which have emerged during the past decade, particularly over the past few years. The carbene interactions range from being covalent to more ionic in nature, and can be evaluated by comparison of bond lengths and angles in the solid state, and in solution by chemical shift changes in the NMR spectra. This report focuses on singlet 5-membered NHCs, and the diagrams of the complexes are represented in the same way as the paper they correspond to.

2. s-Block-carbenes

In 1998, Siebert and co-workers reported a 3-borane-1,4,5-trimethylimidazol-2-ylidene (1) which was formed through deprotonation of 3-borane-1,4,5-trimethylimidazole using n-butyl lithium. The $^{13}$C NMR spectrum shows a shift in the C2 carbon from 213.7 ppm in the non-coordinating carbene to 191.3 ppm, which is consistent with the carbene interacting with a lithium metal centre. The authors described this as a Li(thp)\(^{+}\)\(1^{-}\) (thp = tetrahydro-pyran) salt, and the solid state structure reveals dimeric units of two carbene centres which are connected by two lithium ions (Fig. 1). The N1C2N3 angle of 104.0(2)\(^{\circ}\) is enlarged by approximately 2.5\(^{\circ}\) when compared to the non-coordinating carbene, which can be explained by the interaction of the

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carbene centres with the lithium ions. For each of the lithium cations a short (Li1C2' 2.169(5) Å) and a longer (Li1C2 2.339(5) Å) contact with the carbene C2 atoms are observed. The coordination around the lithium cation is completed by the thp molecule and a weak interaction with the anionic BH3 group. This was the first reported example in which an NHC interacts with a group 1 metal.

The first example of lithium-NHC complexes, in which the lithium is coordinated only to carbon centres, was reported by Arduengo and co-workers. Stable NHCs were reacted with lithium 1,2,4-tris(trimethylsilyl) cyclopentadienide to give 2 (Fig. 2). A single crystal X-ray structure reveals a complex in which the lithium centre is coordinated in a η⁵-fashion to the cyclopentadienyl ring, with a single σ-interaction between the lithium and carbene centre. The lithium centre lies 2.155(4) Å from the carbene centre hence has a closer contact than in the previous example, possibly as a result of the carbene interacting with only one lithium centre.

Polydentate ligands that combine NHC ligands with an anionic functional group, to stabilise higher oxidation states and Lewis acidic metal centres, have become a popular area of research over the past few years. One of the common routes used to generate NHCs is deprotonation at the C2 position of the imidazolium precursor using a base, of which potassium t-butoxide is the most commonly reported. As more N1- and N3-functional groups are incorporated into NHC ligands to improve catalysis and increase diversity, more complexes in which the group 1 metal cation is incorporated have been reported. In fact, group 1 NHC salts are becoming competitors to silver(I) adducts as effective and less costly transmetallation reagents in systems where the non-coordinating NHC ligand is unavailable. One of the first groups to demonstrate this was Arnold and co-workers. An
alkylammonium imidazolium bromide was deprotonated in sequential steps using $n$-butyl lithium, to afford a lithium bromide adduct of an amine carbene (3) (Scheme 1). The solid state structure comprises a dimeric unit of two amine carbene groups which are connected by two lithium bromide bridging groups. The lithium-NHC distance of 2.197(4) Å is relatively long when compared to the previous structures, possibly as a result of the ligand being relatively bulky and too large for closer contact with the lithium ion. The ligand was successfully transferred on to lanthanide ions, an area which is discussed later in this review.

The first group 1 carbene complex with an N-bound anionic functional group was reported in 2004. An alkylamino carbene is readily deprotonated using $n$-butyl lithium to afford 4 (Fig. 3). The solid state structure comprises a discrete dimer via bridging amido groups. Although there is severe distortion of the lithium-NCN bond (147.9° compared to the closer to linear 161.8° in 3), the lithium-NHC bond distance of 2.124(4) Å is still short, suggesting that the interaction is predominantly ionic.

A few years later Arnold and co-workers also reported the synthesis of lithium complexes of the neutral and anionic salts of a tridentate amino bis-carbene ligand (Scheme 2). Treatment of the cationic amino bis-imidazolium salt with three equivalents of $n$-butyl lithium affords the lithium amino bis-carbene chloride complex (5). Deprotonation with four equivalents of $n$-butyl lithium affords the lithium amide salt (6). Although the complexes were not characterised in the solid state, characteristic shifts in the multinuclear NMR spectra and elemental analysis are consistent with the lithium complexes being formed. NMR spectra of 5 suggest formation of a cluster of lithium chloride ions with lithium-NHC bonds ($^{13}$C NMR: NCN 203.9 ppm) and NH-chloride bonding interactions. Following further deprotonation to form 6 the complex also retains lithium chloride and exhibits a similar C2 chemical shift ($^{13}$C NMR: NCN 203.4 ppm).
Arnold and co-workers also reported the deprotonation of alkoxy imidazolium iodides with $n$-butyl lithium to yield lithium alkoxide carbenes (Scheme 3). Single crystals of one of the complexes were grown from a diethyl ether solution, and revealed a dimer of LiL with lithium iodide incorporated to form a tetramer of lithium cations (7). The lithium-NHC bond distance of 2.131(6) Å is similar to that of the lithium amide carbene 4. Also as in 4 there is distortion of the lithium-NCN bond which has an angle of 152.3°. The C2 carbon resonates at 200 ppm in the $^{13}$C NMR spectrum which is a relatively high-frequency, possibly as a result of the incorporated lithium iodide. The lithium salts were able to act as ligand transfer reagents and react with copper (II) chloride or triflate to afford mono- or bis-substituted copper(II) alkoxy carbene complexes.

Similar alkoxide ligands enabled the first crystallographic characterisation of a potassium-NHC complex. Previous attempts to isolate potassium-NHC complexes had led to migration of the N-hydrocarbyl group to the C2-position to form cyclic imines. By using O-functionalised N-alkyl arms, thermally stable potassium salts of NHCs were isolated. Following reaction of an alcohol-functionalised imidazolium iodide with excess potassium hydride in THF, single crystal X-ray crystallography revealed a polymeric structure, based on a network of potassium-NHC tetramers with cube-shaped $K_4O_4$ cores (8) (Scheme 4). Each potassium centre is four-coordinate, with three O atoms and a carbene from the ligands. The average potassium-NHC bond-length is 3.045 Å which is, as expected,
longer than when interacting with the smaller lithium centre. The backbone C4 and C5 atoms also display close intermolecular contact with potassium centres, which is noteworthy due to the number of ‘abnormal’ carbenes arising due to a [1,4] H shift. It is unlikely, however, that an ‘abnormal’ carbene is generated in this case, as upon dissolution in NMR solvent the original ‘normal’ carbene is generated. The $^{13}$C NMR spectrum shows a high-frequency C2 chemical shift of 208.4 ppm.

When a bulky bis(adamantylethoxy) imidazolium salt was treated with potassium hydride the reaction did not afford the expected potassium-carbene. Instead, elimination of one alcohol arm produced a mono (adamantylethoxy) imidazole (9) (Scheme 5). Treatment of this with isopropyl iodide resulted in the alcohol imidazolium iodide salt, which undergoes deprotonation with lithium hexamethyldisilazide to afford the lithium alkoxy carbene (10) which was characterised by mass spectrometry and multinuclear NMR spectroscopy. The C2 carbon in 10 resonates at 186.3 ppm in the $^{13}$C NMR spectrum, which is a significantly lower frequency than the similar ligand in 7 which has lithium iodide incorporated into the structure.

Danopoulos and co-workers reported on the preparation of NHC ligands with pendant indenyl and fluorenyl groups. Deprotonation of the alkylindene or -fluorene imidazolium salts with one equivalent of potassium hexamethyldisilazide leads to NHCs functionalised with neutral indene or fluorene moieties (IndH-NHC and FlH-NHC). Further deprotonation with
a second equivalent of potassium hexamethyldisilazide affords anionic indenyl and fluorenyl NHC species [(Ind-NHC) –K⁺ and (Fl-NHC) –K⁺] (11) (Scheme 6). The ¹³C NMR spectra for (Ind-NHC) –K⁺ and (Fl-NHC) –K⁺ exhibit C2 resonances at 211.0 ppm and 206.0 ppm respectively, which is consistent with the previously described potassium-NHC complex 8. The structure of (Fl-NHC) –K⁺ (11) was determined by single crystal X-ray diffraction, and comprises polymeric zigzag chains with potassium atoms and bridging fluorenyl units. The potassium coordination sphere comprises two phenyl rings which sandwich the metal and a tethered NHC group, with a potassium-NHC bond distance of 2.896(5) Å.

![Scheme 6 Synthesis of 11.](image)

The first magnesium-NHC adducts were reported by Arduengo and co-workers in 1993.²⁰ Stable NHCs were reacted with diethyl magnesium to afford the corresponding magnesium-NHC complexes in good yields (Scheme 7). Relative to the non-coordinating carbenes the C2 carbons are shifted substantially upfield by 25–30 ppm in the ¹³C NMR spectra (R = adamantyl 180.1 ppm, R = mesityl 194.8 ppm). Single crystal X-ray structures revealed that the N-adamantyl-substituted carbene complex has a monomeric solid state structure, while the less bulky N-mesityl complex is dimeric in the solid state. The dimeric structure is formed through bridging of one ethyl unit from each magnesium centre, and is likely as a result of the mesityl units providing insufficient steric protection in the imidazole plane. The dimer comprises a magnesium-carbene bond distance of 2.279(3) Å.

![Scheme 7 Synthesis of magnesium-NHC complexes.](image)

In 1998, the same group reported the synthesis of magnesium metallocene NHC complexes, in addition to metallocene NHC complexes of other group 2 elements.²¹ The adducts show an interesting trend in the nature of the metal-carbene bonds which increase as metal radii increase. The trends are reflected in both the solid state structures (metal-carbene bond length increases) and the NMR spectra (downfield shift of C2) of the adducts (Table 1). In addition to mono-NHC complexes, the heavier alkaline earth elements (Sr and Ba) are capable of forming stable bis-NHC adducts.
In 2001, Schumann and co-workers reported a similar set of metallocene complexes with 1,3-di-iso-propyl-4,5-dimethylimidazoly-2-ylidene. X-ray crystallography and NMR studies confirmed a similar trend between metal-carbene bond strength and alkaline earth metal as that found by Arduengo and co-workers. Additionally they showed that as the steric bulk of the cyclopentadienyl ligand increases the metal-carbene bond distance is elongated.

The first group 2 amido NHC complex was reported in 2004. An amino carbene is readily deprotonated by half an equivalent of dimethylmagnesium to afford MgL2 (Scheme 8). Despite the diagonal relationship between Li+ and Mg2+ there is virtually no distortion about the M-NCN bond as seen in complex 4. The magnesium bis-(amido NHC) chelate has short magnesium-N bond lengths and average magnesium-NHC bond distances (2.263(2) Å and 2.2697(16) Å).

An anionic aryloxy-bound NHC ligand was reported by Zhang and co-workers (Scheme 9). Initially, attempts were made to isolate the sodium aryloxy NHC through deprotonation of the imidazolium-substituted phenol using sodium hexamethyldisilazide. A monoanionic carbene ligand is generated at −78 °C, though on warming to room temperature a 1,2-migration rearrangement results in an aryloxy substituted imidazole. The sodium salt was therefore generated in situ at −78 °C and transferred on to magnesium forming an [ML]2 dimer with bridging aryloxy groups (13).

<table>
<thead>
<tr>
<th>Metal-carbene bond length (Å)</th>
<th>13C NMR: C2 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg 2.194(2)</td>
<td>185.7</td>
</tr>
<tr>
<td>Ca 2.562(2)</td>
<td>196.2</td>
</tr>
<tr>
<td>Sr 2.861(5)</td>
<td>198.2</td>
</tr>
<tr>
<td>Ba 2.951(3)</td>
<td>203.5</td>
</tr>
<tr>
<td>Ligand</td>
<td>213.7</td>
</tr>
</tbody>
</table>

Scheme 8 Synthesis of 12.
magnesium centre is tetrahedral with two bridged oxygen atoms, an NHC carbon and a mesitylene carbon. The closest magnesium-carbon interaction of 2.224(4) Å is with that of the NHC.

Magnesium complexes of a tridentate monoanionic bis-carbene ligand have recently been reported (Scheme 10). Treatment of the cationic amino bis-imidazolium salt with methylmagnesium chloride leads to the formation of a magnesium chloride adduct (14), with a C2 chemical shift of 194.0 ppm in the $^{13}$C NMR spectrum. The remaining amino proton can be removed through heating the magnesium chloride adduct in THF to give $\text{Mg}_2(L)\text{Cl}_3$.
Deprotonation of 14 can also be achieved by reaction with lithium hexamethyldisilazide. Following deprotonation of the amino group the $^{13}$C NMR spectrum exhibits a resonance at 182.3 ppm for the C2 carbon, suggesting a stronger interaction of the carbene with the magnesium centre.

A number of heavier amido group 2-NHC complexes have been reported in which the NHC ligand does not possess an anionic tether. These are prepared by addition of the group 2-amide to the corresponding imidazolium salt, or addition of the stable NHC to a solvent-free group 2-amide. Solid state studies are consistent with the formation of monomeric three-coordinate group 2 species in which the NHC binds through donation of the lone pair to the electrophilic metal centre. Multinuclear NMR studies suggest that this coordination is retained in solution, though the labile NHC ligand is readily displaced upon reaction with protic substrates or other Lewis bases. The metal-carbene bond lengths and C2 chemical shifts in the $^{13}$C NMR spectra are similar both in values and trends to those reported in the previous group 2 metal-carbene complexes (Table 2).

<table>
<thead>
<tr>
<th>Metal-carbene bond length (Å)</th>
<th>$^{13}$C NMR: C2 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca 2.6285(16)</td>
<td>194.1</td>
</tr>
<tr>
<td>Sr  2.731(3)</td>
<td>199.0</td>
</tr>
<tr>
<td>Ba  2.915(4)</td>
<td>Not observed</td>
</tr>
</tbody>
</table>

NHCs have been shown to form stable complexes with many of the s-block metals in both groups 1 and 2. Complexes both with and devoid of an anionic tether have been reported and demonstrate that a tether does not necessarily bring the carbene into closer proximity with the metal centre. Other factors such as steric bulk and other substituents should be considered. In general, moving from group 1 to group 2 decreases the metal-carbene bond distance as the Lewis acidity of the metal centre increases. Moving down the groups increases the metal-carbene bond distance as the metal radius increases.

3. **p-Block-carbenes**

In 2002, Jones and co-workers reported bidentate NHC complexes of group 13 trihydrides and trihalides. It was found that the M(H)$_3$ fragments form mono-NHC four-coordinate complexes, with the ligand bridging two metal centres, whereas with InBr$_3$ and TICl$_3$ the bis-NHC ligand coordinates in a chelating fashion (Scheme 11). This suggests that the halides are stronger Lewis acids than the hydrides, and highlights the ability of the larger metals.
to achieve higher coordination numbers. Solid state structures of alu-
minium-mono-NHC, indium-mono-NHC and indium-bis-NHC exhibit
metal-carbene bond distances of 2.067(2) Å, 2.3069(16) Å and 2.233(6) Å
respectively.

The same group also reported on the reaction of GaI and InCl with
mono-NHCs. A product was isolated using GaI only when it was reacted
with a bulky NHC, and resulted in an anionic complex and imidazolium
cation, with the imidazolium proton likely being abstracted from the solvent
(16) (Fig. 4). The gallium-NHC bond length of 2.070(7) Å is very similar to
the GaH₃(NHC) discussed previously. Reaction of a less sterically hindered
NHC with InCl affords the unusual oxo-bridged dimer 17, likely as a result
of adventitious oxygen in the reaction mixture, as a product could not be
isolated when the reaction was done under strict anaerobic conditions. The
average indium-NHC bond length of 2.234 Å is similar to the InBr₃(NHC)₂
discussed previously, and shorter than the InH₃(NHC).

In 2004 an indium-NHC complex was reported which was prepared from
an air stable imidazolium salt precursor. Reaction of one equivalent of
imidazolium salt with InMe₃ affords (NHC)InMe₂Cl 18 (Scheme 12). The
indium-NHC bond distance of 2.267(2)Å is shorter than that of
InH₃(NHC), though longer than the bis-NHC InBr₃(NHC)₂. Mono-triflate
(19) and bis-triflate (20) complexes can also be prepared by treatment of 18
with trimethyl silyl triflate and treatment of 19 with triflic acid respectively.
The indium-NHC bond distance of 2.264(2) Å in 19 barely changes from the trichloride adduct 18, though the indium-NHC bond distance of 2.183(2) Å in 20 is the shortest of the three complexes, reflecting the dicationic nature of the metal centre.

The first example of a thallium-NHC complex was reported by Meyer and co-workers in 2003. A tris-NHC ligand, of which there were previously no metal complexes reported, was reacted with Tl(OTf) in THF at −35 °C, resulting in a thallium-tris-NHC complex (21) (Scheme 13). The highly temperature sensitive complex was characterised by single crystal X-ray diffraction which confirmed the tridentate conformation. The three carbene ligands are not symmetrically bound to the thallium as they exhibit slightly different thallium-NHC bond distances, with an average bond length of 2.952 Å.

The $^{13}$C NMR spectra of the group 13-NHC adducts exhibit C2 resonances that are upfield from the uncoordinated carbene and downfield from
that of the imidazolium salt. This, and the relatively long M-NHC bond lengths, suggest that the electronic structures are intermediate between those of the stable free NHC and the imidazolium ion.

The first group 14 adduct of an NHC was reported by Arduengo and co-workers in 1993.\textsuperscript{30} Germanium diiodide was reacted with a stable carbene to afford the germanium-NHC adduct 22 (Fig. 5). The C2 carbon is shifted upfield in the \textsuperscript{13}C NMR spectrum by 60.88 ppm relative to the uncoordinated carbene, from 219.69 ppm to 158.81 ppm. The most interesting feature of this compound is that the geometry around the germanium centre is pyramidal, with a germanium-NHC bond distance of 2.102(12) Å. This is quite different to the geometry of a germaethene where the germanium and carbon atoms exhibit trigonal planar coordination and a shorter germanium-carbon bond length of 1.803 Å.\textsuperscript{31} The length and orientation of the germanium-NHC bond in 22 and the NMR spectroscopy data indicate a highly polarised structure rather than a double bond.

A similar pyramidal structure was reported two years later when a stable carbene was reacted with bis(2,4,6-triisopropylphenyl)stannylene (Scheme 14).\textsuperscript{32} The C2 carbon of the complex 23 is shifted upfield in the \textsuperscript{13}C NMR spectrum compared to the uncoordinated carbene, though only by 28 ppm which is significantly less than in the germanium adduct 22. The solid state structure has a tin-NHC bond length of 2.379(5) Å.

In the same year Kuhn and co-workers reported a series of silicon- and tin-NHC complexes (Scheme 15).\textsuperscript{33} The pentacordinated silicon and tin structures 24 and 28 were determined by single crystal X-ray crystallography, and possess metal-NHC bond lengths of 1.911(7) Å and 2.179(3) Å respectively. The monomeric stannylene complex 29 was also

\textbf{Fig. 5}  Diagram of 22 as observed in the solid state.

\textbf{Scheme 14}  Synthesis of 23.
characterised by single crystal X-ray crystallography and has a tin-NHC bond distance of 2.290(5) Å. As in previous cases the geometry around the metal centre is pyramidal.

The single crystal X-ray structure of the silylene-NHC adduct 30 also comprises a pyramidal geometry around the silicon, with a long silicon-NHC bond of 2.162(5) Å (Fig. 6).34 The NMR spectral data indicate significant C\(^+\)–Si\(^-\) bond polarity and DFT calculations are also consistent with this. The single crystal X-ray structure of 31 is also consistent with a zwitterionic species made up from a partially cationic carbene and a partially anionic stannylene.35 Compound 32 was the first example of an NHC-stabilised transient diorganogermylene and exhibits the expected pyramidal geometry around the germanium centre.36 The germanium-NHC bond distance is 2.078(3) Å.

The same group also described the synthesis and structural characterisation of a number of NHC-stabilised germanium(II) compounds derived from the dichloro derivative 33 via substitution chemistry (Fig. 7).37 They demonstrated that the length of the germanium-NHC bond is significantly
influenced by the π-donating ability of the substituents on germanium. For example, when one of the chloride substituents in 33 is replaced by triflate the germanium-NHC bond is reduced in length from 2.106(3) Å to 2.068(2) Å. The observations are consistent with the germanium having a δ+ charge due to the electron-withdrawing triflate group.

In 2006, Jones and co-workers reported the reaction of anionic gallium(I)-NHC analogues with the heavier group 14 (E) alkene analogues (Scheme 16). The complexes formed exhibit long gallium-E bonds with that of E = Sn being 2.7186(6) Å in the mono-NHC and an average of 2.6485 Å in the dianionic bis-NHC. The nature of the gallium-E bond was probed by DFT calculations and was shown to be closely related to the neutral NHC adducts of group 14 dialkyls. Various other group 14-NHC analogues have also been reported and the area has recently been reviewed.

The first group 15 adduct of an NHC was reported by Arduengo and co-workers in 1997. A stable carbene was reacted with pentaphenylicaclopentaphosphine to form the carbene-phosphonidene 34 (Scheme 17). The C2 chemical shift in the 13C NMR spectrum appears at 169 ppm, 44.7 ppm upfield from the uncoordinated carbene, and the single crystal X-ray structure shows a phosphorus-NHC bond length of 1.794(3) Å. This is relatively long for typical phosphaalkenes indicating that the bond is highly polarised, which is also indicated in the NMR data.

Fig. 7 Diagram of 33.

Scheme 16 Group 14 adducts of gallium(I) NHC analogues.
Similar phosphorus- and arsenic-NHC adducts have also been reported by Arduengo and co-workers with varying N-substituents (Me, Mes), C3 and C4 substituents (H, Me) and group 15 substituents (Ph, CF3, C6F5). The high field 31P NMR chemical shift, the upfield shift of the C2 carbon in the 13C NMR spectra and the long phosphorus- or arsenic-NHC bond length are consistent with all the adducts being highly polarised.42,44

The same group reported the first carbene complex of a phosphorus(V) centre.45 A stable carbene was reacted with phenyltetrafluorophosphorane affording 35 (Scheme 18). The 13C NMR signal for the C2 carbon appears at 164.7 ppm, 55 ppm upfield from the uncoordinated carbene. The single crystal X-ray structure comprises an octahedral geometry around the phosphorus, with a phosphorus-NHC bond length of 1.91(4) Å. The longer phosphorus-NHC bond length and larger upfield shift of the C2 resonance compared to compound 34 is consistent with 35 being even more polarised.

Kuhn and co-workers reported the reaction of a stable carbene with POCl3 to yield the [(NHC)POCl2][Cl] salt which, following partial hydrolysis, affords 36 (Scheme 19).46 The solid state single crystal X-ray structure comprises a phosphorus-NHC bond length of 1.843(2) Å, which is consistent with the P–C bond being polarised.
Clyburne and co-workers investigated the reaction of a stable carbene with diazokane to afford azines.\textsuperscript{47} Reaction with diazafluorene affords \textit{37}, and reaction with diphenyl diazamethane affords \textit{38} (Fig. 8). Both the C-N bond lengths in both compounds (1.325(3) Å and 1.304(3) Å in \textit{37} and 1.312(3) Å and 1.294(3) Å in \textit{38}) are longer than typical C-N double bonds (ca. 1.29 Å), with the asymmetry suggesting that the compounds are polarised. The longer C-N bond length in both compounds is between the nitrogen and the NHC fragment, and compound \textit{37} appears to be the most ionic of the two, likely as a result of increased delocalisation.

![Fig. 8](https://example.com/fig8.png)  
\textbf{Fig. 8} NHC-stabilised azines.

In 2005, Bielawski and co-workers reported the reaction of a stable carbene with an aryl azide to give the triazine \textit{39} (Scheme 20).\textsuperscript{48} Both the E- and the Z- isomers were identified in the solid state and were found to have nitrogen-NHC bond lengths of 1.339(3) Å and 1.330(3) Å respectively, hence is even more polarised than compound \textit{37}.

![Scheme 20](https://example.com/scheme20.png)  
\textbf{Scheme 20} Synthesis of \textit{39}.

While many stable carbenes tend to be unreactive towards oxygen in the absence of a catalyst, Denk and co-workers found that a stable carbene could be oxidised to the urea \textit{40} in the presence of a catalyst or by reaction with NO (Scheme 21).\textsuperscript{49} The solid state structure exhibits an oxygen-NHC bond length of 1.237(3) Å, and the C2 carbon resonates at 152.7 ppm in the $^{13}$C NMR spectrum, 60.2 ppm upfield from the uncoordinated carbene. The bond length is elongated compared to a typical C=O double bond.

![Scheme 21](https://example.com/scheme21.png)  
\textbf{Scheme 21} Synthesis of \textit{40}.
(ca. 1.20 Å) and the large shift of the C2 carbon in the $^{13}$C NMR spectrum is consistent with a polarised compound.

Reaction of a stable carbene with SCl$_2$ results in the hypervalent sulfur compound 41 (Scheme 22).$^{50}$ The sulfur-NHC bond length of 1.732(3) Å is significantly longer than that of a typical C=S double bond (ca. 1.60 Å) indicating a highly polarised compound.

![Scheme 22](image)

Scheme 22  Synthesis of 41.

Bildstein and co-workers prepared an N-iminoisopropyl NHC ligand that forms adducts with sulfur and selenium through reaction of them in their elemental form (42) (Fig. 9).$^{49}$ The solid state structures exhibit a sulfur-NHC bond length of 1.681(2) Å, and a selenium-NHC bond length of 1.840(2) Å. The C2 resonance in the $^{13}$C NMR spectrum where E=S is 161.0 ppm, an upfield shift of 55.3 ppm compared to the uncoordinated carbene, and the C2 carbon when E=Se resonates at 153.8 ppm, an upfield shift of 62.5 ppm. This indicates that on going down Group 16 the E–NHC bond becomes more polarised. The sulfur-NHC bond does not appear to be as polarised as in the hypervalent sulfur compound 41, in which the sulfur atom also possesses electron withdrawing groups. The selenium-NHC bond in 43 also appears to be highly polarised, with a bond length of 1.884(9) Å.$^{51}$ This is significantly longer than a typical Se=C double bond (Se=C=Se = 1.698 Å)$^{52}$ and nearer to that of an Se–C single bond (ca. 1.94 Å).

![Fig. 9](image)

Fig. 9  Sulfur- and selenium-NHC adducts.

The tellerium-NHC adduct 44 was isolated and described as having a mesomeric structure (Fig. 10).$^{53}$ This is confirmed by the dramatic upfield shifts in the $^{13}$C NMR spectrum and also the $^{125}$Te NMR spectrum. The solid state structure exhibits a long tellerium-NHC bond length of 2.087(4) Å.

One of the first Group 17-NHC adducts was isolated by Arduengo and co-workers in 1991.$^{54}$ A stable carbene and iodopentafluorobenzene exist in

*Organomet. Chem.*, 2010, **36**, 1–28 | 17
equilibrium with the adduct in solution as evidenced by averaged NMR chemical shifts in the presence of excess of either reagent (Scheme 23). After several hours in solution at room temperature it appears that the I–C bond is cleaved resulting in pentafluorobenzene and the iodo-imidazolium ion. Compound 45 was isolated and characterised by single crystal X-ray diffraction and comprises an iodine-NHC bond distance of 2.754(3) Å and iodine-C(phenyl) bond distance of 2.159(3) Å.

From the above reaction it can be considered that the lone pair of an NHC interacts with the $\sigma^*$-orbital of a halogen to generate a reverse ylide (Scheme 24). The resulting product is ionic, similar to hydroimidazolium salts. Crystalline adducts of NHCs with iodine, bromine and chlorine have all been reported.

Reaction of a stable carbene with iodine results in compound 46, which can be considered an isolated transition state which models the nucleophilic attack of the carbene on the iodine molecule (Scheme 25). The iodine-iodine bond is significantly lengthened and the carbon iodine bond distance of 2.104(3) Å is slightly elongated when compared to that of iodoarenes. The authors report that protic solvents promote ionic dissociation to the 2-iodoimidazolium ion which is isoelectronic with the tellerium adduct 44.

A stable carbene reacts with 2-iodo-1,3-dimesityl imidazolium salt to form the bis(NHC) iodine complex 47 (Scheme 26). The central C-I-C unit
is almost linear with a small difference between the two iodine-NHC bond distances (2.286 Å and 2.363 Å). In solution the iodine anion does not appear to compete with the carbene for complexation to the 2-iodoimidazolium salt. This structure is in contrast to the previous compound 46 in which the iodine does not appear to exchange between cations.

Reaction of a stable carbene with sulfuric chloride results in abstraction of the chloride cation to give the adduct 48 (Scheme 27).\(^{57}\) The C2 carbon resonates at 133.05 ppm in the \(^{13}\)C NMR spectrum and the solid state structure exhibits a chlorine-NHC bond distance of 1.696(9) Å. The fluorine-NHC analogue was prepared by Kuhn and co-workers by reaction of the stable carbene with SO\(_2\)F\(_2\).\(^{50}\) The solid state structure exhibits a fluorine-NHC bond distance of 1.291(14) Å.

Reports from Kuhn and co-workers identified the reaction of stable carbenes with 1,2-dichloroethane to yield 2-chloro-1,3-disubstituted imidazolium chloride salts.\(^{58}\) The versatility of these salts has been demonstrated by Ishikawa and co-workers.\(^{59}\) Due to its strong electrophilicity, 2-chloro-1,3-dimethylimidazolium chloride can be used in chlorination, oxidation, reduction and rearrangement reactions, in addition to being used as a dehydrating agent.

Jones and co-workers investigated reactions of the stable carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene with a series of halide sources
Compounds display a chlorine-NHC bond length of 1.677(5) Å which is comparable to that of 48. The C2 carbon resonates at 135.7 ppm in the 13C NMR spectrum. Reaction with 1,2-dibromoethane yields the bromo-analogue (50) of the product reported by Kuhn and co-workers through reaction with 1,2-dichloroethane. Following the reaction by NMR spectroscopy using 1 molar equivalents of 1,2-dibromoethane reveals that the 2-hydroimidazolium salt (51) is also formed in the reaction. Reaction with dibromine yields compound 50 only. The bromine-NHC bond distance is 1.861(4) Å and the C2 carbon resonates at 126.4 ppm in the 13C NMR spectrum.

Kuhn and co-workers reported on the syntheses and structures of some 2-bromo-1,3-diisopropyl-4,5-dimethylimidazolium derivatives. The stable carbene reacts with bromine to give the bromine adduct (52) (Fig. 11). The bromine-NHC bond length of 1.881(5) Å is as expected for imidazolium ions. By use of excess tetrabromomethane instead of bromine the CBr4 adduct 53 was isolated, and the bromotellurate salt 54 is obtained by reaction with TeBr4. Incorporation of the tetrabromomethane molecule into the unit cell does not significantly influence the structure of the Br–Br–NHC unit, though coordination of the bromide ion at TeBr4 lowers the nucleophilic character of the anion and the closest Br–Br bond length increases significantly.

(Scheme 28)\(^{60}\) Compound 49 displays a chlorine-NHC bond length of 1.677(5) Å which is comparable to that of 48. The C2 carbon resonates at 135.7 ppm in the 13C NMR spectrum. Reaction with 1,2-dibromoethane yields the bromo-analogue (50) of the product reported by Kuhn and co-workers through reaction with 1,2-dichloroethane. Following the reaction by NMR spectroscopy using 1 molar equivalents of 1,2-dibromoethane reveals that the 2-hydroimidazolium salt (51) is also formed in the reaction. Reaction with dibromine yields compound 50 only. The bromine-NHC bond distance is 1.861(4) Å and the C2 carbon resonates at 126.4 ppm in the 13C NMR spectrum.

Kuhn and co-workers reported on the syntheses and structures of some 2-bromo-1,3-diisopropyl-4,5-dimethylimidazolium derivatives.\(^{61}\) The stable carbene reacts with bromine to give the bromine adduct (52) (Fig. 11). The bromine-NHC bond length of 1.881(5) Å is as expected for imidazolium ions. By use of excess tetrabromomethane instead of bromine the CBr4 adduct 53 was isolated, and the bromotellurate salt 54 is obtained by reaction with TeBr4. Incorporation of the tetrabromomethane molecule into the unit cell does not significantly influence the structure of the Br–Br–NHC unit, though coordination of the bromide ion at TeBr4 lowers the nucleophilic character of the anion and the closest Br–Br bond length increases significantly.
In general, on moving down the groups of the p-block, the M-NHC bond length increases as the M centre becomes softer. On moving across the rows the M-NHC bond length decreases and the bonding becomes more ionic, with the bonding of X–NHC (X = halogen) being as expected for imidazolium ions. Other factors that influence the bonding are the sterics and electronics of substituents both on the NHC fragment and the M centre.

4. f-Element-carbenes

The first lanthanide-NHC complexes were isolated by Arduengo and co-workers in 1994. A stable carbene displaces THF in bis(pentamethylcyclopentadieny1)-samarium-THF to form the samarium(II)-NHC complex 55 (Scheme 29). The addition of a second equivalent of NHC resulted in the isolation of the bis(NHC) adduct 56. Compound 56 was characterised in the solid state by single crystal X-ray diffraction and exhibits samarium–NHC bond distances of 2.837(7) Å and 2.845(7) Å, which are longer than the M–C bond in σ-bonded alkyl lanthanide complexes.

Addition of the same NHC to Eu(thd)₃ (thd = tetramethylheptanedioate) affords the europium(III) adduct Eu(thd)₃(NHC). The europium-NHC bond distance of 2.663(4) Å is shorter than that of the samarium(II) complex and is consistent with the higher oxidation state of the lanthanide centre. The yttrium(III) analogue was also prepared and characterised by NMR spectroscopy. The C2 carbon resonates at 199 ppm in the ¹³C NMR spectrum, with a ¹³Y₂ coupling constant of 33 Hz. This indicates that the NHC remains bound to the metal centre in solution and does not dissociate on the NMR timescale.

The synthesis of Y[N(SiHMe₂)₂]₃(NHC)₃ (NHC = 1,3-dimethylimidazolin-2-ylidene, x = 1, 2) was achieved by displacement of THF ligands in Y[N(SiHMe₂)₂]₃(THF)₂ by the stable carbene. The structural data reveal...

Organomet. Chem., 2010, 36, 1–28 | 21
that the carbene ligands affect the coordination mode of the bis(di-methylsilylamide) ligands by forcing them to form β-H-yttrium agostic interactions. Organometallic uranyl complexes of monodentate NHC adducts have also been reported (Fig. 12).^64–66

NHCs are Lewis base 2-electron donors, but have no necessary requirements for back-bonding, making them perfectly suited for the f-elements. NHCs are relatively soft ligands, thus a tethered anionic moiety represents a viable method for covalent attachment to the hard electropositive metal centre. The anionic component forms a strong covalent interaction with the metal centre and brings the NHC into close proximity. As previously discussed, NHC ligands with an OH or NH tether may be deprotonated to form s-block alkoxide or amido salts, in which the NHC group in the chelate binds to the metal centre. These adducts can be used as transmetallation agents for early metal and f-element complexes. Treatment of a potassium alkoxide with UI$_3$(THF)$_4$ in THF affords tetravalent uranum(IV) complexes $57$ or $58$, with the outcome being dependent upon stoichiometry (Scheme 30).^67 Variable temperature NMR studies on $57$ display a fluxional process in solution which is assumed to be the exchange of free for uranium-coordinated NHC. The same potassium alkoxide adduct reacts with uranyl dichloride [UO$_2$Cl$_2$(THF)$_2$]$_2$ to afford [UO$_2$(L)$_2$],^68 and the lithium amide adduct affords the analogous [UO$_2$(L)$_2$].^12

The imidazolium protons and the alcohol and amino protons are sufficiently acidic that monoprotonated proligands can be used in transamination reactions to afford f-element functionalised-NHC adducts.
Transamination of the lithium bromide NHC amine 3 (Scheme 1) with \( \text{Sm}[\text{N(SiMe}_3\text{)}_2]_3 \) proceeds cleanly to afford the dark yellow air-sensitive \( \text{Sm(L)[N(SiMe}_3\text{)}_2]_2 \) \( (59) \) (Scheme 31).\textsuperscript{11} The lithium bromide adduct gives better product yields than the free base, and no lithium or bromide ions remain in the coordination sphere of the lanthanide metal. The samarium–NHC bond length of 2.588(2) Å is shorter than those of the monodentate lanthanide-NHC adducts. The yttrium(III),\textsuperscript{11} europium(III)\textsuperscript{68} and neodymium(III)\textsuperscript{69} analogues have also been isolated. The yttrium-NHC bond distance of 2.501(5) Å is even shorter, reflecting the smaller size and increased Lewis acidity of the yttrium(III) centre, and the adduct exhibits a large \( ^1J_{\text{YC}} \) coupling constant of 54.7 Hz in solution. The larger neodymium (III) centre renders complex \( 62 \) significantly more air-sensitive than the others. The free base could not be used to prepare NHC adducts of the larger cerium(III) metal, hence the cerium(III) analogue of \( 59 \) could only be prepared \textit{via} the lithium bromide adduct.\textsuperscript{70} Ligand exchange between the product and lithium bromide resulted in the bridged complex \{\text{Ce(L)[N(SiMe}_3\text{)}_2(\mu-\text{Br})]_2\}. Presumably this is due to the lower Lewis acidity of cerium(III) enabling lithium to compete for the amide ligand.

\[
\begin{align*}
\text{LiYb(N}^\text{Pr}_2\text{)}_4 & + \text{Ln}[\text{N(SiMe}_3\text{)}_2]_3 \xrightarrow{\text{PhMe, Reflux}} \text{Ln}[\text{N(SiMe}_3\text{)}_2]
\end{align*}
\]

\( \text{Ln = Sm (59), Y (60), Eu (61), Nd (62)} \)

\textbf{Scheme 31} Synthesis of lanthanide amide-NHC complexes.

The transamination of the anionic amido ytterbium complex \( \text{LiYb(N}^\text{Pr}_2\text{)}_4 \) with aryloxo-functionalised NHC imidazolium salt precursors affords bis-aryloxo-NHC monoamido ytterbium(III) complexes (Scheme 32).\textsuperscript{71} The complexes are isostructural with one another in the solid state and exhibit average ytterbium–NHC bond distances of 2.487 Å (R = Me) and 2.535 Å (R = \text{\textsuperscript{1}Pr}). These are comparable to the monodentate lanthanide(III)-NHC bond lengths where the ligand possesses and amido tether, though a direct comparison with like-for-like metal centre is not possible. The longer ytterbium-NHC bond length where R = \text{\textsuperscript{1}Pr} is likely as a result of the increased bulk of the ligand.

\[
\begin{align*}
\text{t-Bu} & \text{OH} \xrightarrow{\text{LiYb(N}^\text{Pr}_2\text{)}_4, \text{THF}} \text{t-Bu} \\
\text{t-Bu} & \text{N}^\text{Pr}_2 \text{N} \end{align*}
\]

\( \text{R = \text{\textsuperscript{1}Pr, Me}} \)

\textbf{Scheme 32} Synthesis of bis-aryloxo-NHC monoamido ytterbium complexes.
Treatment of the yttrium(III) adduct 60 with potassium naphthalenide in dme-diethyl ether mixture results in deprotonation of the C4 carbon and migration to afford the ‘abnormal’ carbene complex 63 (Fig. 13). The C2 binding carbon migrates from the yttrium(III) centre to the incorporated potassium(I) cation. The C4 carbanion forms a short bond with the yttrium(III) centre in the solid state (2.447(2) Å) and exhibits a large $^{1}J_{YC}$ coupling constant of 62 Hz in solution. Complex 63 may be quenched with a variety of electrophiles. For example, reaction with Me3SiCl silylates the NHC backbone to afford 64.

Transamination between the lithium salt of the tridentate amino bis-carbene (6) and Y[N(SiMe3)2]3 affords an yttrium bis-NHC complex Y(L)[N(SiMe3)2]Cl. The $^{13}$C NMR spectrum exhibits a C2 resonance at 194.3 ppm with a $^{1}J_{YC}$ coupling constant of 48.0 Hz, which is slightly lower than that of the mono-NHC yttrium complex bearing two amido groups. The yttrium-NHC bond length of 2.574(3) Å is also slightly longer than in the mono-NHC complex.

Lanthanide complexes of NHC ligands bearing indenyl groups have also been reported. Transamination of the imidazolium-bromide salt in Scheme 6 with Y(CH2SiMe3)3(THF)2 affords the bromide bridged complex {Y(L)(CH2SiMe3)(μ-Br)}2. Reaction with anionic LiLn(CH2SiMe3)4(THF)4 (Ln = Y, Lu, Sc), however, yields the monomeric halide-free Y(L)(CH2SiMe3)2. This product can also be achieved by deprotonation of the imidazolium salt using lithium hexamethyldisilazide to give the stable carbene, followed by reaction with Ln(CH2SiMe3)3(THF)2. In all the complexes the monoanionic Ind-NHC ligand bonds to the metal centre in an η⁵-fashion through the 5-membered ring of the indenyl unit, and the strong electron-donating carbene coordinates to the metal centre preventing THF coordination. The yttrium-NHC bond distance of 2.501(3) Å in Y(L)(CH2SiMe3)2 is the same as that of the amide tethered ligand in 60.

Shen and co-workers reported a method for preparing lanthanide-NHC halides through protonolysis. Reaction of the imidazolium bromide salt with anionic LiLn(NiPr)4 affords salicylaldiminato-functionalized NHC-lanthanide bromides (Scheme 33). The complexes were all characterised by single crystal X-ray diffraction and exhibit capped octahedral geometries. The NHC–Ln–NHC bond angles decrease Nd > Sm > Er > which is consistent with decreasing ionic radii, and the Ln-NHC bond lengths also
decrease $2.717(3) \text{Å} \ (\text{Nd})$, $2.685(6) \text{Å} \ (\text{Sm})$, $2.568(7) \text{Å} \ (\text{Er})$ with decreasing ionic radii.

Cui and co-workers have reported the first xylene-bridged bis-NHC-ligated CCC-pincer lanthanide metal dibromides.\textsuperscript{76} They were prepared by reaction of the imidazolium salts with $\text{LnCl}_3$ in the presence of $n$-butyl lithium (Scheme 34). Single crystal X-ray diffraction analysis revealed that the overall molecular structure of these complexes is an isostructural monomer of a THF solvate. The monoanionic xylene-bridged bis-NHCs bond to the central metal as a tridentate CCC-pincer moiety in a $\kappa_C:\kappa_C:\kappa_C'$ mode which, in combination with the two trans-located bromo units, generates a twisted tetragonal bipyramidal geometry. The average lanthanide-NHC bond lengths of $2.585(7) \text{Å} \ (\text{Sm})$, $2.484(7) \text{Å} \ (\text{Lu})$ and $2.309(8) \text{Å} \ (\text{Sc})$ are on the short side when compared to other lanthanide-NHC bonds.

The metal-carbene bond in lanthanide-NHC complexes is clearly weaker and more reactive than in late metal systems. The use of bidentate and tridentate ligands bearing anionic tethers can be effective in stabilising lanthanide-NHC complexes, generating systems with shorter metal-carbene bonds. The area is still relatively underdeveloped, though the lanthanide-NHC complexes are already displaying a range of chemistry in homogeneous catalysis and small molecule activation, some of which is unseen in late transition metal-NHC chemistry.

**Conclusion**

The coordination chemistry of NHCs with non-transition metal centres has expanded rapidly in recent years. It is clear that NHCs are able to form a range of interactions, ranging from being covalent to more ionic in nature. Their interaction with elements across the whole periodic table has improved our understanding of these highly tuneable and versatile ligands.
References

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