From the reactivity of *N*-heterocyclic carbenes to new chemistry in ionic liquids

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N-Heterocyclic carbenes have numerous applications in synthetic chemistry. We detail the reactivity and chemistry of these molecules including investigations into their reactions with small reagents, their use for the preparation of polarised azines and their potential application as **NLO** materials. The chemistry of imidazolium salts, which are related to **NHC**s by the addition of a proton, is also discussed. New chemistry for ionic liquids is also revealed.

Introduction

For the past two decades, synthetic inorganic chemistry has focused on the preparation of highly reactive molecules with unusual bonding modes. Through the use of bulky ligands[2,3] and the concept of electronic stabilisation,[1] numerous examples of unusual bonding modes and low coordinate compounds have been prepared. These materials are of interest not only due to their potential synthetic versatility for applications in materials chemistry and catalysis,[4] but also as models for reaction intermediates.[5]

Three ligand designs stand out as reliable substituents in preparing unusual bonding modes. The first ligand design, based upon the diazabutadiene dianion (**1**) (Chart 1), has been used to prepare numerous examples of low coordinate molecules including phosphorus-,[6,7] arsenic-[7] and gallium-containing[8] ions, germylenes,[9] silylenes[10] and carbenes.[11] Perhaps the most important of these molecules are the *N*-heterocyclic carbenes (**NHC**s), particularly 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**2**) (Chart 1) that has been extensively used in transition metal chemistry to stabilise low oxidation state metal complexes.[12]

The second ligand design is the *m*-terphenyl ligand (**3**) (Chart 1). These ligands are known for their bowl-shaped pocket formed by the out-of-plane twisting of two aryl substituents *meta* to one another on a central phenyl ring. With these steric constraints, the ligands can reliably enforce low coordination numbers and unusual geometries at the atoms placed within the pocket. These ligands have been used to showcase a variety of highly unusual bonding modes for both main group and transition metals.[2,3,13] Our group has employed these ligands to produce compounds ranging from single molecules[14] to 2-D clay-like materials[15] and self assembled monolayers.[16]

The fourth reliable ligand design is the β-diketiminato ligand **4**, *aka* **NacNac**.[17] Perhaps most relevant to this review is the

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Diane A. Dickie was born in Truro, Nova Scotia in 1979 and earned her BSc (Honours) in Chemistry at Mount Allison University in Sackville, New Brunswick under the supervision of Dr Stephen Westcott in May 2001. She began her PhD studies with Dr J. A. C. Clyburne at Simon Fraser University in September 2001. She was the recipient of a Natural Sciences and Engineering Research Council of Canada post-graduate scholarship (NSERC PGS-B) from May 2003–April 2005. Her research is focused on the synthesis of organometallic complexes of substituted m-terphenyl ligands. She intends to pursue postdoctoral research in low-valent main group chemistry after completing her PhD in early 2006.

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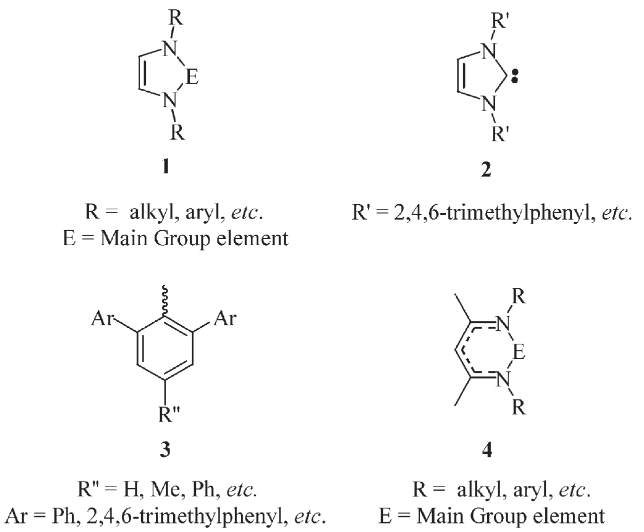


Chart 1 The diazabutadiene ligand (**1**), *N*-heterocyclic carbene (**NHC**) (**2**), *m*-terphenyl ligand (**3**), and **NacNac** ligand **4**.

fact that this tuneable monoanionic ligand has been used to prepare group 13 carbene analogues.[18] Although not a major feature of this article, we note that many of the studies we have performed are relevant to main group complexes of the **NacNac** ligand *vis a vis* carbene chemistry.

The chemistry of **NHC**s and *m*-terphenyl ligands are closely related. As illustrated in Fig. 1, these two ligand designs have an *isosteric* relationship. It is from this point that we began our two-pronged studies into the use of these ligands: in the first case, we used **NHC**s and related molecules to understand the chemistry of low coordinate carbon with a variety of reagents, and in the second case we used the reliability of steric enforcement of unusual coordination numbers and geometries to prepare novel or unusual metal-containing materials.[14–16] This review will focus on our work on **NHC**s and related molecules. Our studies into derivatives of *m*-terphenyl ligands will appear in a later review.

Carbenes and their reactivity with small reagents

Carbenes are neutral molecules with a dicoordinate carbon atom having two non-bonding electrons.[12,19] **NHC**s have attracted interest due to their numerous applications in synthetic chemistry.[19,20] **NHC**s have revolutionised aspects of catalysis,[21,22] have also been used in transition metal chemistry to stabilise low[23] and more recently, high[24,25] oxidation state transition metal complexes. For these reasons, understanding the chemistry of **NHC**s with small organic reagents is of great importance.

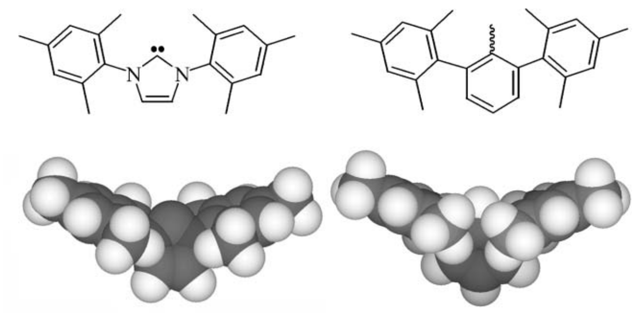
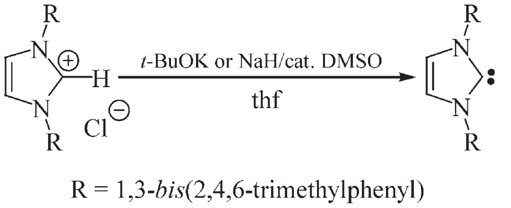


Fig. 1 Space-filling model of **NHC** (**2**) (left) and 1,3-bis(2,4,6-trimethylphenyl)benzene (right).

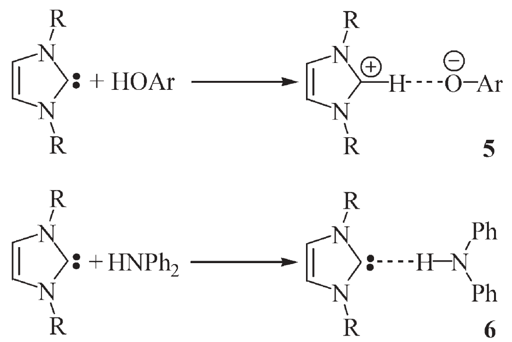


Scheme 1 Synthesis of **NHC** (**2**) by deprotonation of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride.

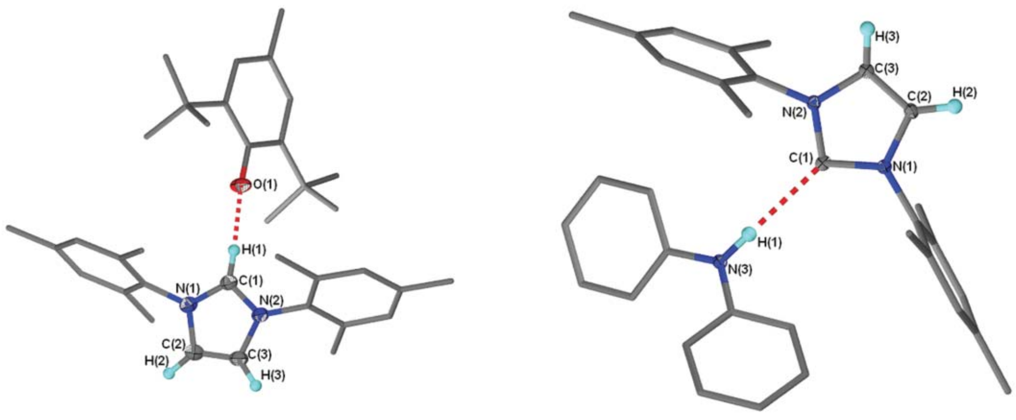
The most commonly used method to prepare **NHC**s is the deprotonation of imidazolium ions (Scheme 1).[26,27] **NHC**s are among the most basic neutral compounds known, with pK_a values ranging from 22 to 24 in DMSO.[28,29] Because of the high basicity of **NHC**s, we began the examination of their reactions with a variety of protic reagents. This work was done in collaboration with Professor Matthew Davidson, at the University of Bath.

Previously, the Davidson group had performed some elegant studies on the protonation of phosphoranes, which have comparable basicity, and they identified numerous examples of unusual hydrogen bonds.[30] As expected, **NHC**s behave as strong bases towards weak acids such as phenols (Scheme 2).[31] The **NHC** (**2**) will deprotonate a phenol to produce a [cation···anion] pair that exhibits one of the shortest [C–H···O] hydrogen bonds (1.759(4) Å, H···O length) yet reported (Fig. 2).[31,32] The shortness of this bond can be rationalised using the concept of charge assistance.[33] Another unprecedented bonding motif for C/H/N was identified by the reaction with the weak acid, diphenylamine (Scheme 2), where the carbeneic carbon acted as the acceptor to the N–H hydrogen producing a [C···H–N] hydrogen bond (Fig. 2).[31]

Since treatment of a carbene with a proton (H^+) produces a carbocation, in principle addition of a hydrogen atom ($H^•$) should produce a tricoordinate radical related to the methyl radical. At the time of our studies, the dearth of reports on the



Scheme 2 Interaction of Brønsted acids with an **NHC** (**2**).



5

6

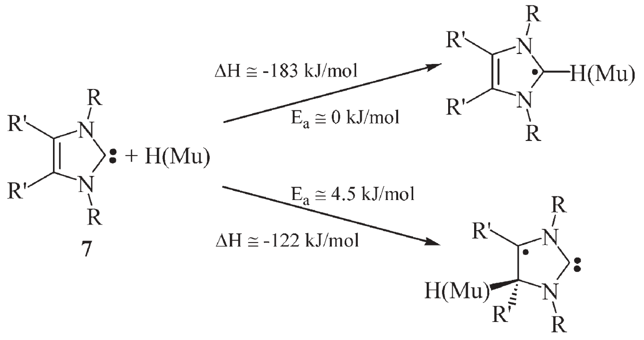
Fig. 2 Solid state structures of **5** and **6**. (Reproduced with permission from reference 32. Copyright 2002 Taylor and Francis.)

reactivity of stable carbenes or the group 14 analogues with any free radical species was surprising.[34] For **NHC**s it was not previously known how the hydrogen atom would react, especially given theoretical evidence for electron delocalisation around the **NHC** central ring.[35–37] Scheme 3 shows the possible addition sites for a hydrogen atom on an **NHC**. We were able to study these addition reactions computationally and found that the addition of a hydrogen atom was both thermodynamically and kinetically favoured at the carbeneic site.

We then extended the computational studies to the reaction of a hydrogen atom with a model (**8**) of a β-diketiminatoaluminium(I) complex, which is a group 13 carbene analogue.[38] As shown in Scheme 4, the reaction of hydrogen at the four most likely addition sites on **8** occurs exothermically.[39] The addition of the hydrogen atom to the Al centre was the most exothermic (-202 kJ mol^{-1}), which is similar to the result of the addition of H to the carbeneic carbon in **7** (-183 kJ mol^{-1}). This provides an illustration of the parallel reactivity of group 13 carbene analogues and an **NHC**. The single electron reduction of **8** was also investigated and it was determined that unpaired spin density of both **[8-H1]** and the reduction product of **8** is located entirely on the β-diketiminato ligand. These results clearly showed that the β-diketiminato ligand is redox active, and the redox behaviour is observed structurally through the elongation of the C=N bond.[39]

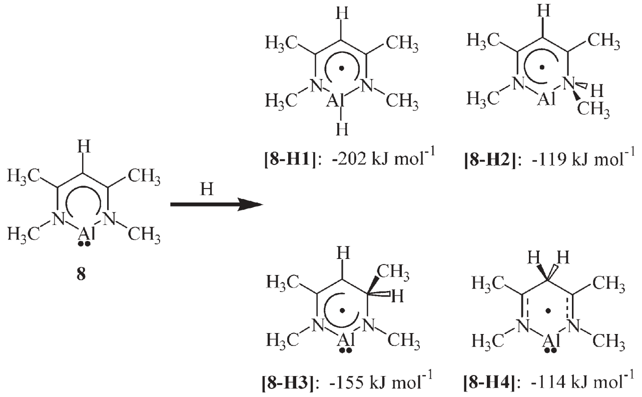
Perhaps the most exciting aspect of the hydrogen atom study was that we were able to confirm experimentally the computational results through SFU's access to Canada's meson facility, TRIUMF. Here, in collaboration with Professor Paul W. Percival, his former graduate student Dr Iain D. McKenzie (University of Stuttgart) and Dr Jean-Claude Brodovitch, we had access to muonium,[40] which is considered a light isotope of hydrogen. Muon spin rotation and muon level crossing spectroscopy were used to determine the muonium, ^{13}C, and ^{15}N hyperfine coupling constants (hfcs) for the radical produced by muonium addition to **NHC**s (Fig. 3).[41] Agreement was observed between the experimental and calculated hfcs, confirming that muonium, and hence hydrogen, adds exclusively to the carbeneic site. An optimised structure (UB3LYP/6-311G** calculations) of the radical detected is shown in Fig. 4.

In order to perform the muonium study, we had to prepare a ^{13}C labelled carbene,[42] and such labelled carbenes have proved invaluable in a variety of instances. The synthesis of ^{13}C labelled **NHC**s, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene



R = isopropyl R' = methyl

Scheme 3 Possible reactions of **NHC**s with the hydrogen atom and its "isotope" muonium, Mu.



Scheme 4 Possible sites of hydrogen atom addition to **8** and calculated heats of reaction (UB3LYP/6-31G^{++}(d,p)). (Reproduced with permission from reference 39. Copyright 2005 Royal Society of Chemistry.)

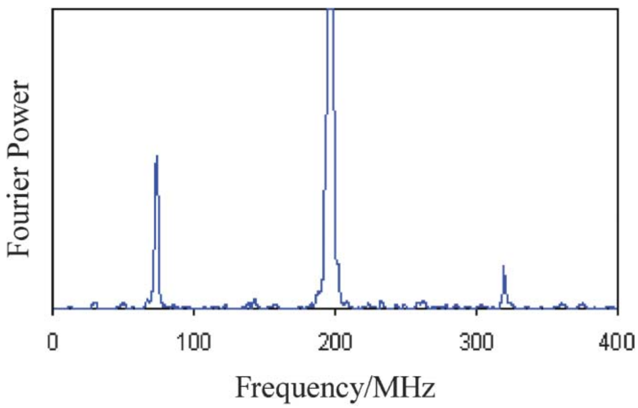


Fig. 3 Transverse field μSR spectrum at 14.4 kG of **7-μ** in thf at 298 K. The pair of peaks at *ca*. 73 MHz and 320 MHz are due to a muoniated radical. (Reproduced with permission from reference 41. Copyright 2003 American Chemical Society.)

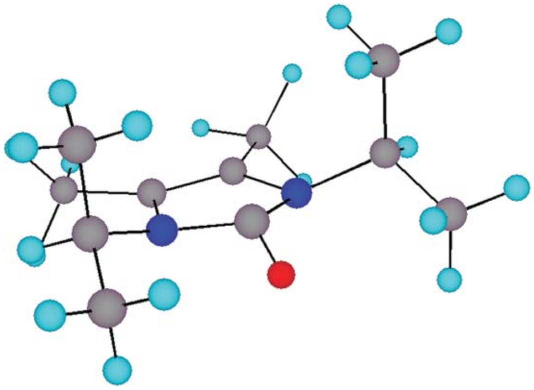
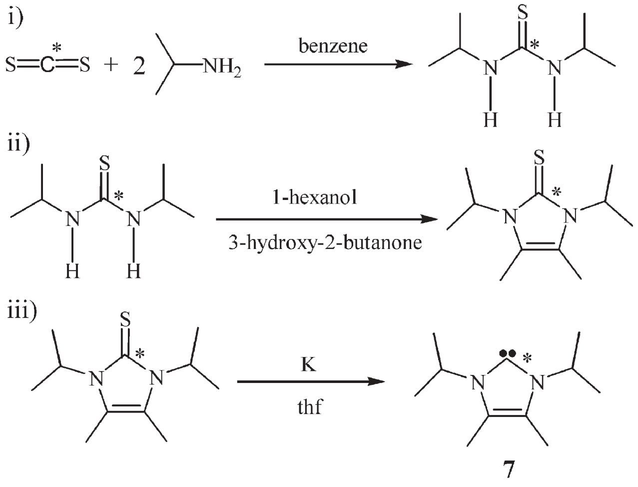


Fig. 4 Optimised structure of **7-μ** showing the non-planar radical centre at C2. (grey = C; royal blue = N; light blue = H) (Reproduced with permission from reference 41. Copyright 2003 American Chemical Society.)

(**2**) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**7**), for muon addition and muon-level-crossing spectroscopy,[41] as well as for the characterisation of a carbene–silver complex (see below) by solution and solid state ^{109}Ag and ^{13}C CP/MAS NMR spectroscopy,[43] has been one of the major advances in our laboratory. **NHC** (**7**) was synthesised as shown in Scheme 5.[44] Two equivalents of isopropyl amine were reacted with ^{13}C labelled carbon disulfide in benzene and the isolated product was then heated to reflux for 12 hours with one equivalent of 3-hydroxy-2-butanone in 1-hexanol to give a thione. Reduction of the thione with an excess of potassium metal (2.5 equivalents)[45] gave labelled carbene **7** in 80% yield.

Recently, we reported the synthesis, structure and a CP/MAS study of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene silver(I) chloride complex (**9**). This complex was prepared by reacting 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride with Ag_2O, and the X-ray crystal structure shows a monomer with C_2 symmetry and a head-to-tail alignment (Fig. 5).[43]



Scheme 5 Synthesis of ^{13}C labelled **7**.

Solution and solid-state multinuclear NMR studies were carried out on the ^{13}C-enriched analogue. This allowed the observation of both ^{13}C and ^{109}Ag nuclei in the NMR spectra. Two doublets were observed at 185 ppm in the ^{13}C solution NMR spectrum, consistent with splitting by two spin ½ nuclei, ^{109}Ag and ^{107}Ag. A broadened doublet centred at 184 ppm was observed in the ^{13}C solid state NMR spectrum. The solid state ^{109}Ag resonances on the other hand were found at 532 ppm (Fig. 6), with the solution ^{109}Ag resonance at 597 ppm.[43] Orientations of the chemical shift tensors were also assigned for this molecule, providing much data for the understanding of this system.

Silver(I) carbene complexes are of interest because they are easy to make and can be used as an air and moisture stable carbene transfer agent without requiring the extreme anaerobic conditions necessary for the synthesis of free **NHC**s. Monomeric silver(I) carbene complexes are rare because silver(I) carbene complexes usually oligomerise *via* silver–silver interactions, bridging halides or even Ag–(μ_2-C$_{carbene}$)–Ag interactions.[46]

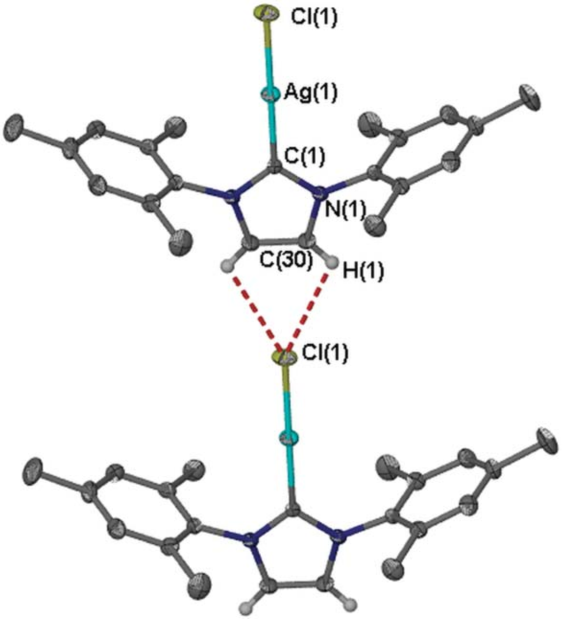


Fig. 5 Solid state structure of **9**. (Reproduced with permission from reference 43. Copyright 2003 American Chemical Society.)

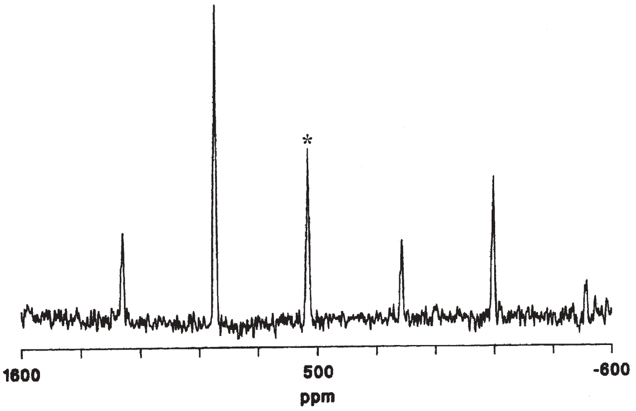
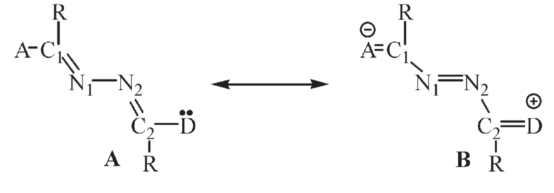


Fig. 6 Solid state ^{109}Ag NMR spectrum of **9**. The isotropic chemical shift (*) is at 532 ppm. (Reproduced with permission from reference 43. Copyright 2003 American Chemical Society.)

As part of our continued studies of carbene chemistry, we produced azines ($R_2C{=}N{-}N{=}CR_2$) through the treatment of **NHC**s with diazoalkanes. Because of their unusual reactivity and spectral properties,[47] azines have been explored as potential nonlinear optical (**NLO**) materials,[48] and have been used as ligands in organometallic compounds.[49] Although these compounds are analogous to 1,3-butadiene, prior to our studies with strong push–pull systems there was little evidence for delocalisation within the azine backbone (Scheme 6).[50] It has been noted that there is a high degree of polarisation in the double bonds between the carbeneic carbon and main group elements,[51] which we hoped to exploit by making azines derived from **NHC**s. Azines **10–15** were prepared by the addition of a diazoalkane to an **NHC** and are shown in Chart 2.

The preferred resonance structure (**A**/**B** Scheme 6) can be inferred by a measure of the N_1–N_2 and C_1–N_1/C_2–N_2 bond lengths. It was found that in **10** the N_1–N_2 bond lengths were shorter and the C_1–N_1/C_2–N_2 bond lengths were longer when compared to the non-**NHC** containing azines, **17–19**. This suggests an increased contribution of resonance form **B** in **10** compared to the other compounds. In fact, the N–N bonds in the **NHC** containing azines **10–15** are the shortest and the C–N bonds the longest reported for all structurally characterised azines.[47] These compounds (**10–15**) were calculated to have dipole moments ranging from 4.9 D for **8** to 6.9 D for **12**.[47] The azine–carbene link in **10–15** is not planar but instead has a twist of 11–32° between the N–N bond and the **NHC** central ring. The "twist" in **10–15** is significantly less than that found in other azines. This suggests a continuum of conjugated orbitals in the azine linkage, and suggests that polarisation of the azine unit has been achieved in these complexes. These materials (**10–15**) were found to exhibit **NLO** behaviour in both a theoretical study and by surface second harmonic generation (**SHG**) experiments on submonolayer films.[47]



Scheme 6 Resonance structures of an azine. (Reproduced with permission from reference 47. Copyright 2004 Royal Society of Chemistry.)

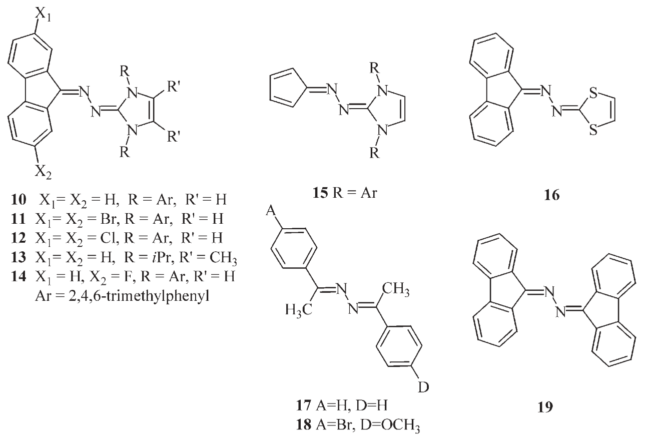


Chart 2 Azine bound **NHC**s. (Reproduced with permission from reference 47. Copyright 2004 Royal Society of Chemistry)

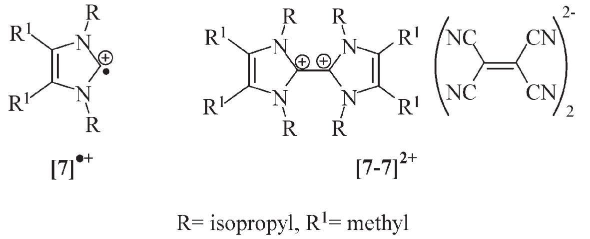


Chart 3 Reaction of an **NHC** with **TCNE**.

To further our study on the reactivity of carbenes with small reagents we decided to examine their electrochemistry. We noted that whereas one-electron reductions of **NHC**s had been reported,[52] simple one-electron oxidation reactions had not. Since **NHC**s are good carbon based electron donors, we decided to observe their reaction with a good carbon based electron acceptor, namely tetracyanoethylene (**TCNE**).[53]

Treatment of **NHC**s with **TCNE** resulted in the formation of an insoluble red precipitate that was not suitable for analysis by X-ray crystallography; however using spectroscopic techniques we were able to assign the structure[53] to the previously reported dication, $[\mathbf{7}\text{–}\mathbf{7}]^{2+}$ shown in Chart 3.[54] We rationalise the formation of this material by invoking the possible transient radical cation $[\mathbf{7}]^{\bullet+}$ as an intermediate.[55] Although we were unable to spectroscopically confirm the presence of this radical cation intermediate, its structure was examined using computational approaches. The results of this study are presented in Table 1.

The most notable feature of the putative radical cation is the high spin density located on the carbeneic carbon. The shape of the singularly occupied molecular orbital (SOMO) suggests the potential for dimerisation through carbeneic carbon–carbeneic carbon bond formation (Fig. 7).[53] Attempts to date to experimentally confirm the presence of this radical intermediate have not been successful. We note a recent review suggesting alternative reaction mechanisms for carbene dimerisation.[56]

Table 1 Selected calculated bond lengths and angles for **7**, $[7]^{\cdot+}$, and $[7\text{–}7]^{2+}$. (Reproduced with permission from reference 53. Copyright 2004 Royal Society of Chemistry). Numbering is shown in Fig. 7

Parameter	**7**	$[7]^{\cdot+}$	$[7\text{–}7]^{2+}$ (calc.)	$[7\text{–}7]^{2+}$ (exp.)[54]
C_2–N_2	1.379	1.337	1.370	1.351(3)
N_2–C_3	1.416	1.423	1.395	1.370(3)
C_3–C_4	1.371	1.381	1.390	1.363(4)
C_2–C_2	—	—	1.462	1.463(3)
N_1–C_2–N_2	102.3	111.6	107.7	108.4(2)
C_2–N_3–C_3	112.9	107.2	109.0	108.6(2)
N_2–C_3–C_4	105.9	106.9	107.1	107.4(2)
N_1–C_2–C_2–N_2	—	—	90.04	88.1

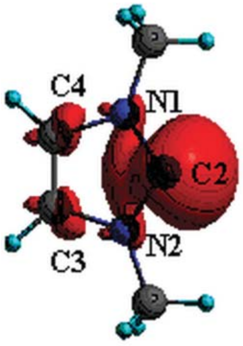


Fig. 7 Total electron spin density of $[7]^{\cdot+}$. (Reproduced with permission from reference 53. Copyright 2004 Royal Society of Chemistry.)

Chemistry of imidazolium ions and their relevance to ionic liquids

During our studies of **NHC**s with small reagents, we realised that similar studies on imidazolium ions would be informative and have direct relevance to the chemistry observed in ionic liquids. Ionic liquids have come to the forefront as an important component of "Green" chemistry. They appear ready to replace classical volatile organic compounds (**VOC**s) in many industrial applications.[57] This shift from problematic organic solvents could have significant environmental impacts. Moreover, it is the author's opinion (JACC) that most of the exciting chemistry/applications for ionic liquids will not come from their use as a replacement solvent but from their use in chemistry and technology unique to ionic liquids (such as separation techniques and materials chemistry).

The most extensively studied class of ionic liquids is based upon the imidazolium ion. The relationship between an imidazolium ion and a carbene is the removal of a proton and although several authors had suggested a clear link for the fast chemical conversion of an imidazolium ion to an **NHC** through a redox process, this was not supported by product analysis. This was surprising to us, since this reaction represents a simple electrolysis of the imidazolium ion, a process similar to the electrolysis reaction of water. Indeed, the imidazolium ion is the conjugate acid of the carbene as water is the conjugate acid of hydroxide ion.[58]

The cyclic voltammogram (CV) of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **2** is shown in Fig. 8. It shows an irreversible reduction of the imidazolium ion and the presence of a significant peak on the return scan that corresponds to a single electron event, implying that the species initially produced in the reaction is the radical shown in Scheme 7.

This radical (**[2-H]$^{\cdot}$**) was not detected spectroscopically; however, as described above, we were able to fully characterise its muoniated analogue at the TRIUMF facility.[41] The peak at −0.19 V lies at the potential measured for the oxidation of **NHC**s, suggesting that **NHC**s are produced *via* electrolysis of imidazolium ions. The electrochemical reduction of the imidazolium ion was experimentally confirmed through a large-scale reduction of the imidazolium ion with metallic potassium (Scheme 8).[59] Potassium reduction was also performed on 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride giving the corresponding 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene in high yield. This chemical reduction produces carbenes in high yields and is perhaps the most

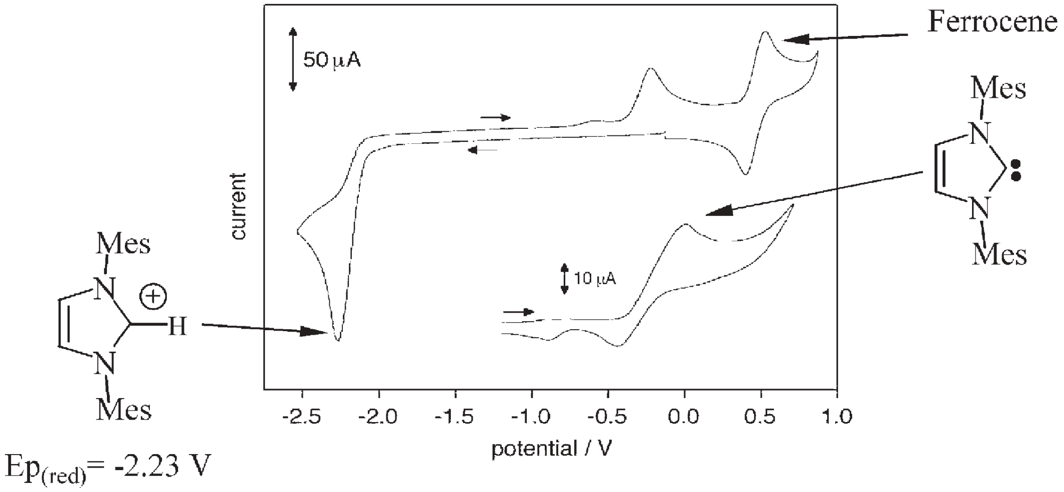
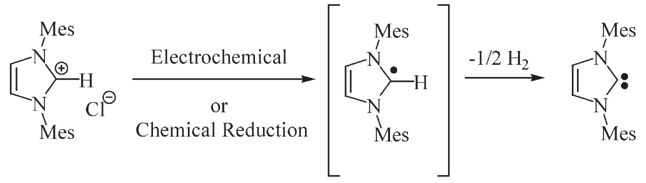
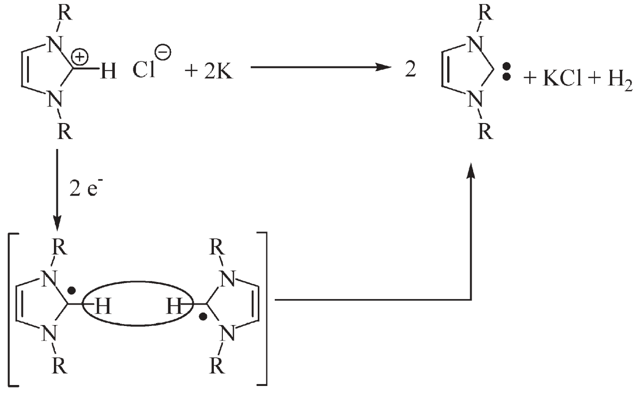


Fig. 8 Cyclic voltammogram of a DMF solution (2×10^{-3} M) of **[2-H][Cl]** containing tetrabutylammonium hexafluorophosphate (0.1 M) at 300 mV s^{-1} in the presence of ferrocene (1.5 mM). The inset shows the cyclic voltammogram of a THF solution of carbene **2** (4.2×10^{-2} M) at 300 mV s^{-1} containing 0.1 M tetrabutylammonium hexafluorophosphate.[53] (Reproduced with permission from reference 59. Copyright 2004 Royal Society of Chemistry.)



[2-H][Cl] **[2-H]$^\bullet$** **2**

Scheme 7 Reduction of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride **[2-H][Cl]** produces **NHC 2**. (Reproduced with permission from reference 59. Copyright 2004 Royal Society of Chemistry.)



Scheme 8 Proposed mechanism for the reduction of **[2-H][Cl]** with metallic potassium.

straightforward and reliable procedure for the preparation of **NHC**s.

A surface mediated mechanism cannot be ruled out for this reaction. We note that subsequent studies on metal nanoparticles in imidazolium ionic liquids suggest the involvement of carbenes in ionic liquids formed through a redox activity that broadly parallels the results observed here.[60]

We also examined the reaction of hydride sources with imidazolium ions. For example, it is shown in Scheme 9 that imidazolium ion reacts with sodium borohydride to produce a borane complex, **[2-BH$_3$]**.[61] Lithium aluminium hydride reacts analogously to produce the alane complex **[2-AlH$_3$]**.[62] We propose that there is a transitory "dihydrogen bond"[63] formed between the two ions which evolves H_2, giving **[2-BH$_3$]**. Remember that H_2 has the strongest homonuclear single bond strength.[64] Although the structure of **[2-BH$_3$]** was not interesting in itself, its *supramolecular* structure revealed unusual dihydrogen bonding that, in part, resulted in a high melting point (Fig. 9). Subsequent work by the Ito group showed a similar reaction between imidazolium ions and the super hydride $LiHBEt_3$.[65]

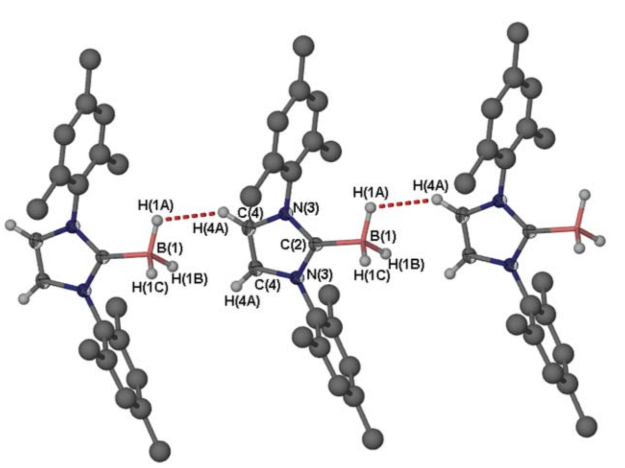
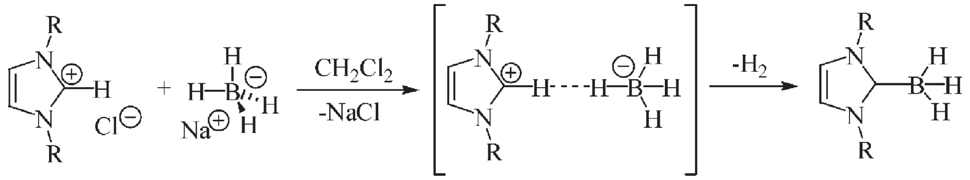


Fig. 9 Structure of **[2-BH$_3$]**. Hydrogen atoms on the aryl substituents have been removed for clarity.

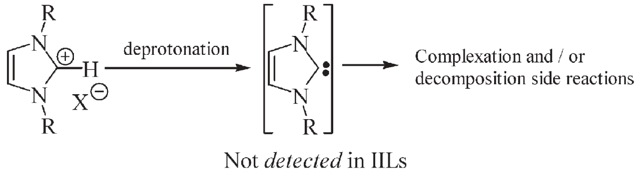
The chemistry that we identified above is relevant to the chemistry of the most common imidazolium-based ionic liquids (**IIL**s). Although ideally the imidazolium ion should be inert as a solvent, it can react under basic conditions to produce a carbene (Scheme 10). While this may be detrimental or beneficial, depending on the reaction,[66,67] it became clear to us that the prevention of such side reactions would be a worthwhile endeavour.

Previous experience in phosphorus chemistry gained by Dr Clyburne while pursuing a PhD under the supervision of Dr Neil Burford (Dalhousie University), suggested that side reactions could be prevented or minimised by using related phosphonium-based ionic liquids (**PIL**s) (Chart 4). Preliminary and as yet unpublished results indicate that the reduction of phosphonium ions [$P(C_6H_{13})_3(C_{14}H_{29})$][Cl], $Ep_{red} = -2.93$ V) is much harder than the reduction of imidazolium ions (**[2-H][Cl]**, $Ep_{red} = -2.23$ V).[68] Furthermore, we have recently shown that strong bases such as **NHC**s and Grignard reagents are compatible with **PIL**s.[69] This discovery should have a significant impact on future developments in the chemistry of ionic liquids[70] since we know that other green solvents, such as **IIL**s, carbon dioxide, water, and alcohols, are incompatible with strong bases.[71] Carbenes are highly basic and we were surprised that deprotonation of the **PIL**s to give the phosphorane (Chart 5) does not occur. The inertness of **PIL**s towards reaction with bases appears to be couched in kinetic arguments (Fig. 10). Because the imidazolium rings in **IIL**s are rigid, steric protection of the carbeneic site is minimal but due to the flexible alkyl chains of **PIL**s there is considerable steric congestion around the reactive C–H site therefore access is limited.



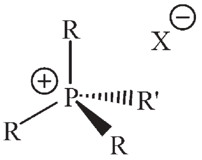
R = 2,4,6-trimethylphenyl **[2-H][BH$_4$]** **[2-BH$_3$]**

Scheme 9 Synthesis of **[2-BH$_3$]**.



R = alkyl or aryl
X = Cl, Br, $AlCl_4$, BF_4, etc.

Scheme 10 Deprotonation of an imidazolium ion in an **IIL**.



X = Cl, Br, $C_{10}H_{19}COO$, $[(CF_3)SO_2]N$
R = C_6H_{13}, R' = $C_{14}H_{29}$

Chart 4 Structure of **PIL**s with a partial list of commercially available anions.

As described above, we have shown that imidazolium ions could be easily converted to nucleophilic carbenes by their treatment with metallic potassium.[59] We also found that **PIL**s do not react with reducing agents such as potassium since potassium can be used to dry the **PIL**s. Thus, treatment of a suspension of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride in **PIL** with potassium results in the formation of **NHC 2** (Scheme 11). If stored under an inert atmosphere, this highly viscous, light brown carbene–**PIL** solution is stable in excess of months. Formation of **2** is unambiguously assigned by the observation of the carbon signal for the carbeneic carbon at 216 ppm in the ^{13}C NMR spectrum.

Conclusion and outlook

In this review we have examined the reaction of **NHC**s with small reagents including protons, the hydrogen atom, and an electron. The use of **NHC**s for the preparation of polarised azines was investigated and their potential application as **NLO** materials was explored. The preparation of ^{13}C labelled **NHC**s was described as well as the isolation of a carbene transfer agent. The chemistry of imidazolium salts, which are related to the **NHC** by an addition of a proton, was also investigated. The conversion of an imidazolium salt to an **NHC** through a redox process was investigated along with their reaction with a hydride source. This conversion was shown to also occur in traditional organic solutions and in **PIL**s. Strong bases, such as **NHC**s were found to be compatible with **PIL**s. These studies have allowed us to explore the fundamentals of carbene chemistry. Further studies of the reactions of **NHC**s with small molecules are continuing, as is the investigation of strong bases and hydride sources in **PIL**s.

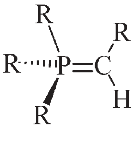


Chart 5 A phosphorane, the anticipated product resulting from deprotonation of a **PIL**.

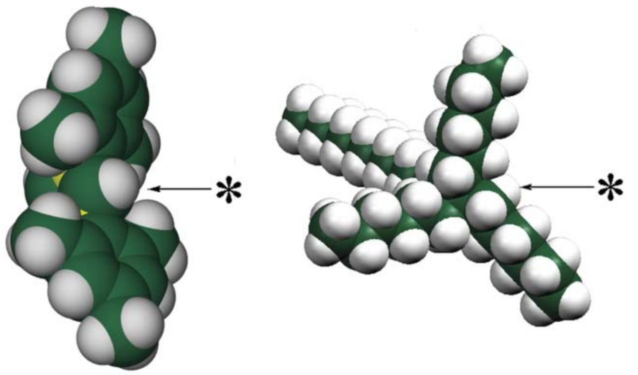
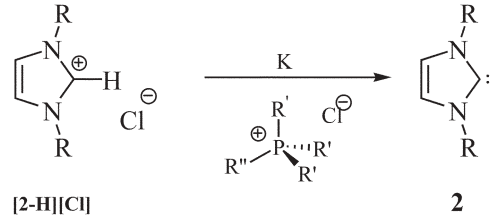


Fig. 10 Space filling diagram of 1,3-bis(2,4,6-trimethylphenyl)imidazolium ion (left) and tetradecyl(trihexyl)phosphonium ion (right). Highlighted (*) are the reactive C–H fragments in the different molecules.



R = 2,4,6-trimethylphenyl R' = C_6H_{13} R'' = $C_{14}H_{29}$

Scheme 11 Reduction of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride in **PIL**s.

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