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N-Heterocyclic Carbene Mediated Activation of Tetravalent Silicon Compounds: A Critical Evaluation

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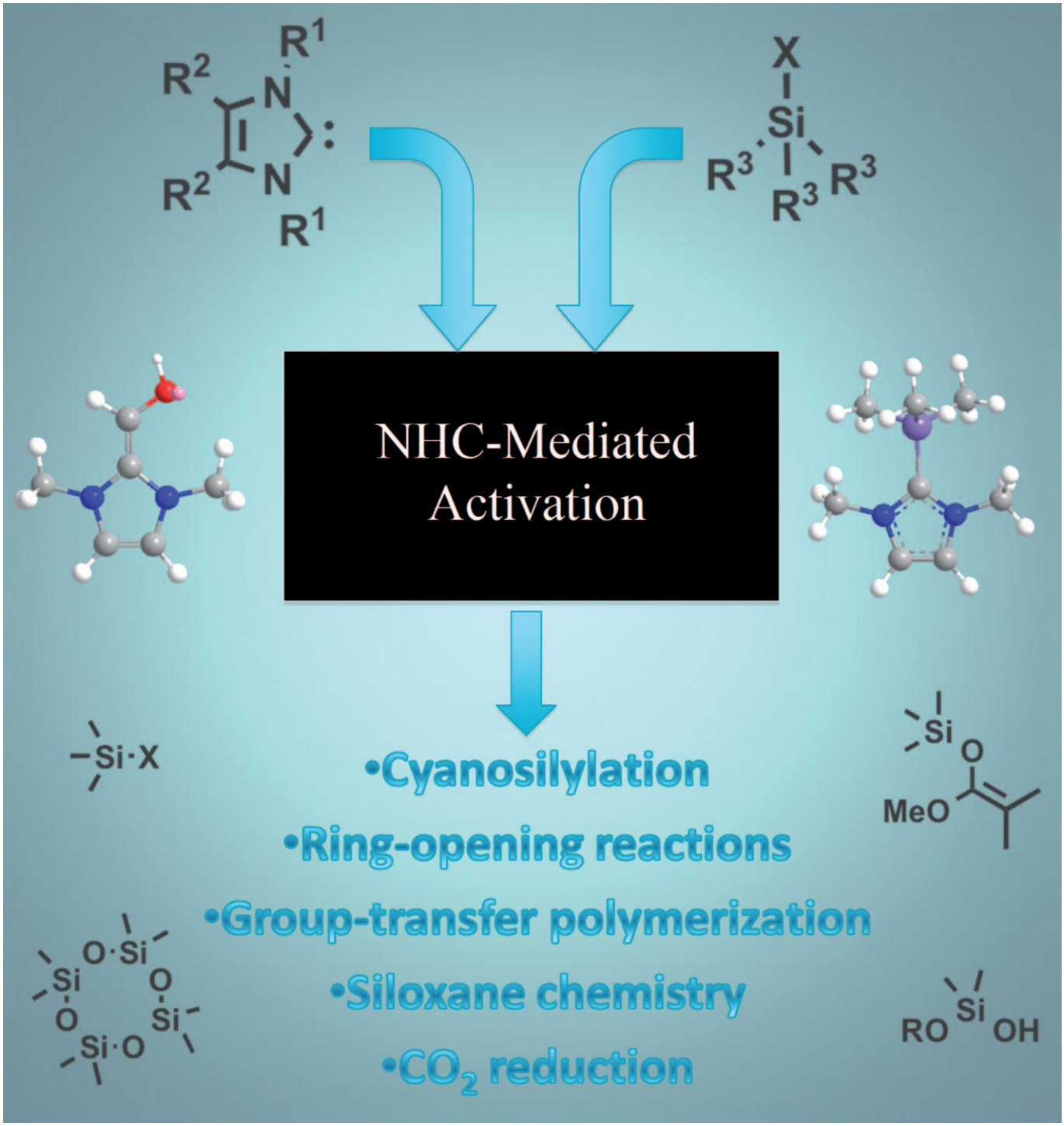


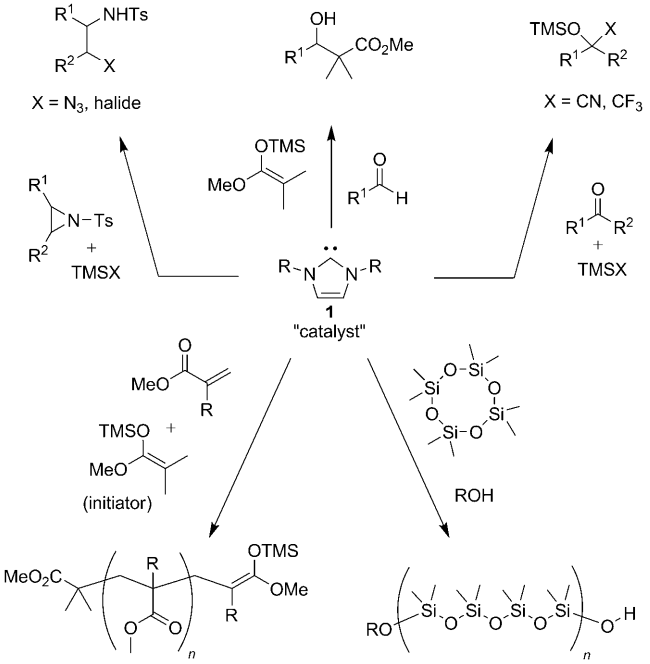
Abstract: An overview of the recent bibliography concerning the N-heterocyclic carbene (NHC)-mediated activation of tetravalent silicon compounds is presented. Diverse reactions are discussed, such as the NHC-mediated addition of silyl pronucleophiles to a variety of electrophiles, NHC-promoted organic and inorganic polymerisation and the reduction of CO_2 by hydrosilanes as facilitated by NHCs. The review concludes with a discussion of the current knowledge regarding the role of Lewis acid–base NHC–Si interactions in the mechanistic course of these reactions.

Keywords: carbenes · Lewis bases · organocatalysis · polymers · silanes

Introduction

The utility of N-heterocyclic carbenes (NHCs) in synthesis is expanding dramatically. From catalytic procedures in small-molecule synthesis to polymer preparation, the usefulness of these stable, neutral, electron-pair donors is becoming increasingly apparent.[1] One area that has provided particularly dramatic examples is the field of main-group chemistry, in which stoichiometric NHC σ donors stabilise low-valent *p*-block elements.[2] Arguably the most impressive example in this regard is the isolation of a stable silicon(0) species that contains an Si=Si double bond stabilised by an NHC.[3] This minireview, however, is concerned with an alternative interaction of NHCs and silicon: the NHC-mediated activation of tetravalent silicon reagents.

NHCs have been reported as catalysts or initiators of a wide variety of organic transformations that involve silicon compounds, including the cyanosilylation of aldehydes, ketones and imines,[4] the trifluoromethylsilylation of aldehydes and ketones,[5] Mukaiyama aldol reactions[6] and aziridine addition reactions[7] (Scheme 1). They have also been proposed to facilitate σ-bond metathesis between silanes and copper alkoxides,[8] promote the group-transfer polymerisation of acrylate monomers in the present of silyl ketene acetal initiators,[9] facilitate ring-opening polymerisation of cyclic siloxanes,[10] catalyse the dehydration of disilanol oligomers[11] and facilitate the reduction of CO_2 by hydrosilanes.[12] This minireview will summarise the developments in this area, highlighting the mechanistic scenarios proposed and ending with a detailed discussion of the current knowledge regarding the role of Lewis acid–base NHC–Si interactions in the mechanistic course of these reactions.



Scheme 1. Reactions in which NHCs mediate the reaction. **1a**: R = 2,4,6-trimethylphenyl; **1b**: R = *t*Bu; **1c**: R = cyclohexyl; **1d**: R = adamantyl; **1e**: R = Me.

NHC-Mediated Reactions of Silyl Pronucleophiles

Cyanohydrins, formed by formal addition of hydrogen cyanide across a C=O double bond, represent highly valuable synthetic intermediates in light of their ready elaboration into other building blocks, such as α-hydroxy carbonyl species. A large body of work concerns the development of cyanohydrin syntheses, which due to safety considerations often utilise trimethylsilyl cyanide (TMSCN) as the pronucleophile of choice to give silyl cyanohydrin products. A plethora of reagents have been shown to facilitate the transfer of a cyano group from TMSCN to carbonyl compounds,[13] although reports regarding the use of NHCs are of particular relevance to this account.

Kondo, Aoyama and co-workers were the first to report that IMes, mesitylene-substituted carbene **1a** (R = 2,4,6-trimethylphenyl) formed in situ from the corresponding imidazolium salt and potassium *tert*-butoxide, facilitated the cyanosilylation of aldehydes.[4a] This was followed in quick succession by several other related reports on the NHC-mediated cyanosilylation of aldehydes, ketones and imines (Scheme 2).[4] In their original report, Kondo, Aoyama and

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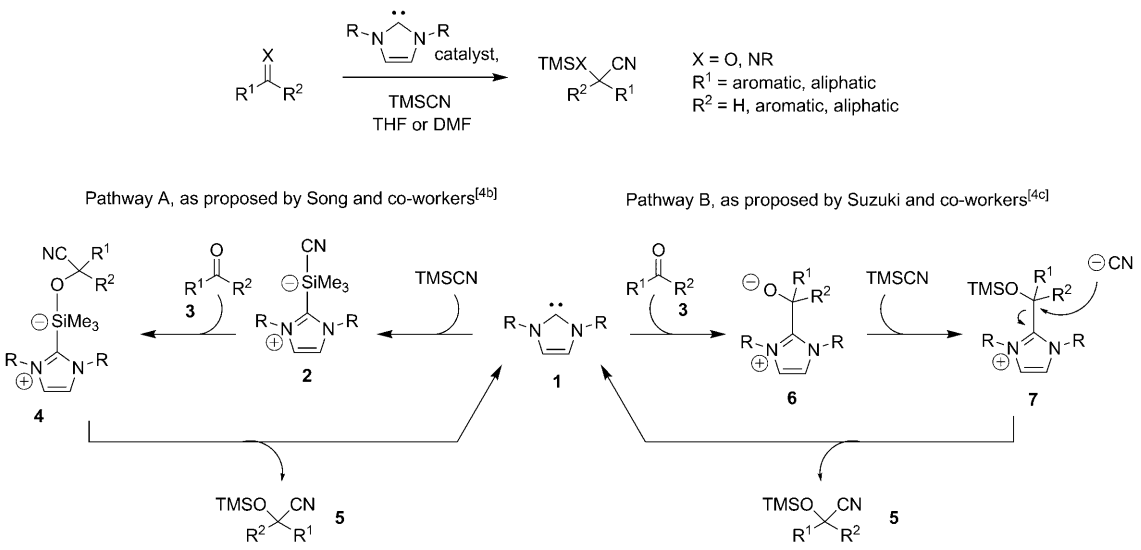


Scheme 2. NHC-mediated cyanosilylation.

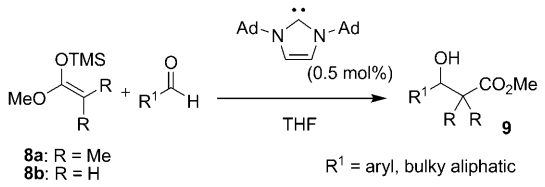
co-workers demonstrated that both enolisable and aromatic aldehydes were suitable substrates in the presence of **1a** (10 mol%) in THF, and the products were isolated in high yield (83–98%).[4a] This report was shortly followed by the studies of Song and co-workers, who used pre-isolated carbene reagents rather than ones generated in situ.[4b] Impressively, by switching to I*t*Bu (**1b**, R = *t*Bu) as the catalyst, they demonstrated that as little as 0.1 mol% catalyst loading was sufficient to facilitate the reaction, although they generally used 0.5 mol% to increase the reaction rate. Once again, they demonstrated that enolisable and aromatic aldehydes were suitable substrates in THF and gave the products in high yields. They also reported that enolisable and non-enolisable ketones could be cyanosilylated under the reaction conditions, although a solvent switch to DMF was required. Subsequent studies by Suzuki, Sato and co-workers demonstrated that other NHCs (including ones derived from imidazolium, benzimidazolium, imidazolinium, thiazolium and triazolium salts) were competent in mediating the reaction, although these appear to be less active than **1b**.[4c] Using **1a** as a catalyst, Kondo, Aoyama and co-workers also recognised that enolisable and non-enolisable ketones could be cyanosilylated if DMF was used as a solvent,[4e] albeit by using a higher catalyst loading (5 mol%) than the studies of Song and co-workers. They also reported that N-tosyl ketimines were suitable substrates, isolating the products in good yield. By switching to ICy (**1c**, R = cyclohexyl), Maruoka and co-workers demonstrated that DMF was no longer required for ketone substrates and reported that enolisable and non-enolisable ketones and ketimines with a variety of nitrogen substituents (Ts, Bn) could be cyanosilylated by using 1 mol% of the catalyst in THF.[4d] Because highly enantioselective cyanosilylations have been reported for certain chiral Lewis bases,[12] it should be possible to use chiral NHCs to mediate stereocontrol in these reactions. Currently, however, there is only a single attempt to effect asymmetric catalysis in this regard, in which the product was isolated in a low *ee* of 22%.[4c]

Throughout these studies, two mechanistic scenarios have been envisaged for catalysis (Scheme 2). Pathway A, proposed by Song and co-workers,[4b] hypothesises an interaction of the NHC with TMSCN to form a hypercoordinate intermediate **2**. This activating interaction, in keeping with other Lewis base catalysts,[13] was proposed to facilitate transfer of the cyano group to the electrophile to give adduct **4**, which could release product **5** and regenerate the free carbene. Pathway B, on the other hand,[4c] suggests that the carbene interacts first with the carbonyl species to give zwitterionic intermediate **6**. This intermediate is then silylated by TMSCN (to generate **7**), followed by displacement of the carbene adduct by the cyanide anion. Note that to date none of the cyanosilylation studies involving NHCs have provided any experimental proof of these mechanistic proposals.[4]

Matthew Fuchter completed his PhD research under the supervision of Professor A. G. M. Barrett, FRS, FMedSci at Imperial College London. He undertook postdoctoral appointments at Imperial College London and at CSIRO, Australia, where he worked with Professor A. B Holmes, FRS. He was subsequently appointed as an RCUK Academic Fellow at The School of Pharmacy, London, before moving to his current position of Lecturer in Synthetic and Medicinal Chemistry at Imperial College London. His research involves the development of innovative methods in organic synthesis and medicinal chemistry, including the use and applications of N-heterocyclic carbenes.

NHCs have also been reported as mediators of the trifluoromethylsilylation of aldehydes and ketones,[5] in close analogy to cyanosilylation above. Song and co-workers reported that 0.5 mol% of IAd (**1d**, R = adamantyl) was sufficient to mediate the trifluorosilylation of a variety of enolisable and non-enolisable aldehydes by using $TMSCF_3$. DMF was required for practical reaction rates and the products were generally isolated in moderate to good yield (54–90%). Ketones were generally unreactive under the developed reaction conditions, although a single example was presented in which a higher catalyst loading could drive the reaction of an aromatic ketone with an electron-withdrawing group forward.

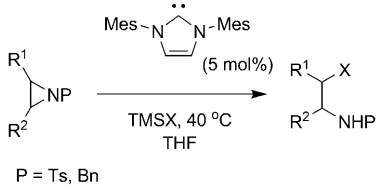
The Mukaiyama aldol reaction is a mainstay of synthetic organic chemistry and has been under intensive investigation for more than 30 years. Both Lewis acid and Lewis base catalysts are effective in mediating the reaction, and in the context of this review Song and co-workers have reported an NHC-mediated Mukaiyama aldol reaction (Scheme 3).[6]



Scheme 3. NHC-mediated Mukaiyama aldol reaction.

Low loadings of **1d** gave products **9** in moderate to good yield for silyl ketene acetal **8a** (60–91%). A variety of aromatic substrates were tolerated, as were bulky aliphatic aldehydes. Attempts to effect the Mukaiyama aldol reaction of acetophenone were unsuccessful, however. For silyl enol ether **8b**, further optimisation was required, such as lowering the temperature to 0°C to suppress byproduct formation. Electron-deficient aromatic aldehydes were found to be suitable substrates, but electron-rich aromatics or aliphatic systems only gave a low yield of the products.

Aziridines are highly versatile building blocks that can be ring-opened under a variety of conditions to give many nitrogen-containing scaffolds. In line with the previously demonstrated Lewis base catalysed ring-opening of aziridines with silyl pronucleophiles, Wu and co-workers reported the ability of NHCs to mediate aziridine addition reactions (Scheme 4).[7] They found that 5 mol% of **1a** could mediate

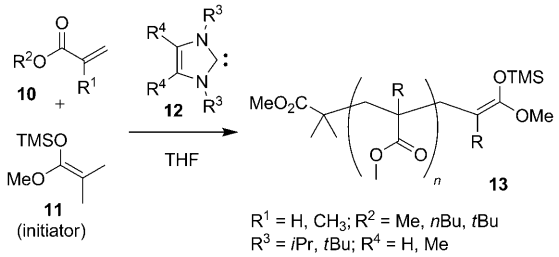


Scheme 4. NHC-mediated aziridine ring-opening reaction.

the addition of $TMSN_3$ and TMSX (X = Cl, I) to aziridines in good yield (89–99%). N-Tosyl and N-benzyl groups were tolerated and aziridines derived from cyclohexene and cyclopentene were suitable substrates, along with simple aliphatic systems.

Polymerisation Chemistry

Recently, independent reports from Taton, Gnanou and co-workers[9a,c] and Hedrick, Waymouth and co-workers[9b] have detailed the use of NHCs as activators of silylketene acetals, which initiate the polymerisation of a variety of (meth)-acrylic monomers **10**. (Scheme 5) This type of polymeri-



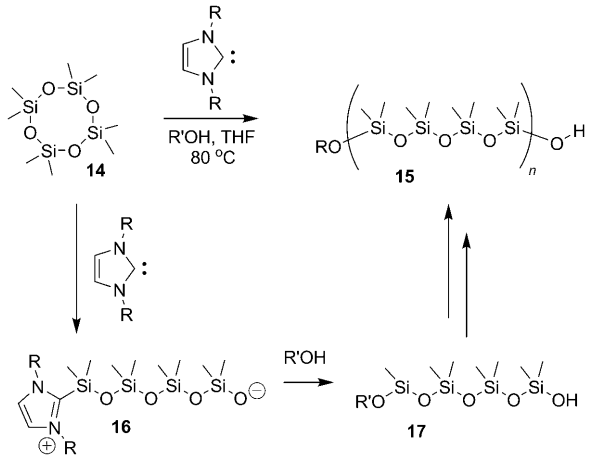
Scheme 5. NHC-mediated GTP reaction.

sation, termed group-transfer polymerisation (GTP), was developed in the 1980s, and activation of the silylketene acetal initiators has been previously demonstrated with either nucleophilic or Lewis acidic catalysts.[9] Several NHCs **12** were shown to be effective catalysts that mediate the GTP of methyl methacrylate (MMA), *tert*-butyl acrylate (TBA) and *n*-butyl acrylate in the presence of silyl ketene acetal initiator **11** (Scheme 5).[9] In general, high levels of conversion were achieved for all the monomers, with polydispersities of around 1.2. Importantly, evidence was provided for living chain ends and, therefore, the conditions developed were suitable for block co-polymer formation.

The mechanism of nucleophilic GTP has been under considerable debate, largely concerning the identity of the propagating species: either pentacoordinated silicon intermediates or anionic enolates. Reactions proceeding via pentacoordinated silicon intermediates are termed "associative" and those via anionic enolates are "dissociative". Müller produced a comprehensive literature based on kinetic modelling to account for the mechanism of GTP induced by different catalysts.[14] Extrapolating these mechanistic studies to the use of NHC activators, there is a conflict in the studies by Taton, Gnanou and co-workers[9c] and Hedrick, Waymouth and co-workers.[9b] Whereas Taton and Gnanou favour an associative mechanism for GTP polymerisation activated by NHCs (such as **12a**, $R^3 = i$Pr, $R^4 = H$; **12b**, $R^3 = t$Bu, $R^4 = H$), Hedrick and Waymouth favour a dissociative mechanism, albeit for a slightly different NHC activator (**12c**, $R^3 = i$Pr, $R^4 = Me$). Both groups provide kinetic reasoning for their preference by comparing the rate of GTP to

the concentration of initiator as outlined by Muller.[14] However, Taton, Gnanou and co-workers also provide additional evidence for their hypothesis, including ^{13}C and ^{29}Si NMR spectroscopy. No change was observed in the ^{13}C NMR spectra, and the ^{29}Si signal for the $SiMe_3$ group was only shifted downfield by 2 ppm from $\delta = 17$ ppm upon addition of NHC **12a** to the silylketene acetal **11**.[9c] Clearly, this is evidence against the formation of either a stable pentacoordinated intermediate (the chemical shift of which should be expected much further upfield[9c]), or the subsequent ionisation of such a species. The authors suggest that the lack of shift is indicative of the weak interaction between the NHC and the silicon acceptor.

The reported use of NHCs in polymer chemistry is not restricted to the preparation of organic polymers. Baceiredo and co-workers have reported the use of NHCs in the polymerisation of cyclic siloxanes (Scheme 6).[10] Exposure of

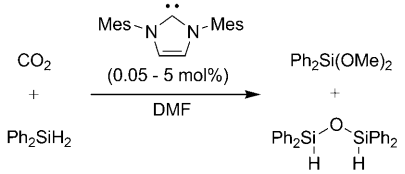


Scheme 6. NHC-mediated polymerisation of cyclic siloxane D_4 (**14**).

cyclic siloxane D_4 (**14**) to substoichiometric quantities of NHC **1b** or **1c** and an alcohol initiator produced poly(dimethylsiloxane) polymers (PDMS). The polymerisations proceeded with approximately 85% conversion, and more efficient molecular weight control was obtained by using primary alcohols (MeOH and BnOH). The authors propose a mechanism initiated by nucleophilic attack of NHCs **1b** or **1c** on **14** to give zwitterionic compound **16**, followed by NHC displacement by the alcohol to give silanol **17**, which can further condense to form the polymer (Scheme 6). The evidence presented for this consists of the inability of **1a** to catalyse the reaction, which was attributed to increased bulk, and the dependence of the rate of polymerisation on the concentration of the NHC (increased rate with increased concentration of NHC). It seems unlikely, however, that the NHC would nucleophilically ring-open **14** via the intermediacy of a pentacoordinated silicon in light of the predicted NHC–Si interaction energy of 3–5 kcal mol^{-1} for unhindered NHC **1d** (R = Me) and silicone oligomer (MeO-$[SiR_2O]_3$Me).[15]

CO_2 Reduction

Zhang, Ying and co-workers reported the organocatalytic reduction of CO_2 by hydrosilanes mediated by NHCs (Scheme 7).[12] Either imidazolium carboxylates or in situ



Scheme 7. NHC-mediated CO_2 reduction.

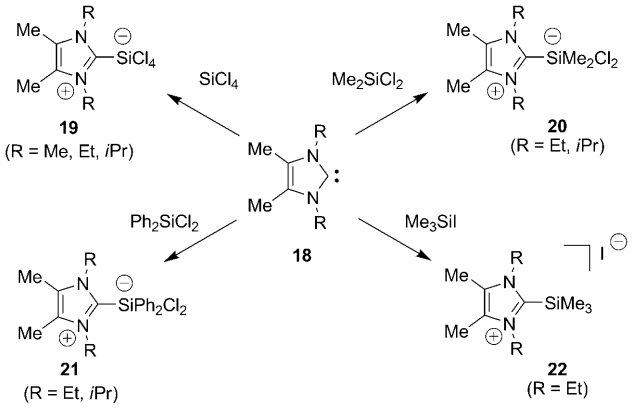
generated **1a** (via deprotonation of the imidazolium salt) were suitable catalysts and gave full conversion to the reduction products in 6–72 h, depending on the catalyst loading. Exposure of the reduction products to two equivalents of NaOH/H_2O gave methanol in over 90% yield. The turnover number (TON) and turnover frequency (TOF) for the NHC catalyst in this reaction reached 1840 and 25.5 h^{-1}, respectively. The mechanism for this reaction is unknown, but a hypothesis was put forward based on intermediates evidenced by GCMS and NMR spectroscopy.[41]

Mechanistic Understanding

Many of the studies highlighted above invoke a Lewis acid–base NHC–Si interaction as the catalytically relevant species. To consider this possibility, let us first examine the Lewis acid–base interactions of silanes. Lewis base interactions of NHCs with tetravalent silicon compounds can be classified as n–σ* interactions according to the system devised by Jensen.[16,17] Within this classification, n represents the non-bonding electron pairs of the Lewis base donor (the NHC), and σ* represents the anti-bonding orbitals of the acceptor (SiR_4) with σ character. The ability of the silicon atom to attain a hypercoordinate state, seemingly disobeying the octet rule, results from the ability of its 3p orbitals to engage in electron-rich three-centre-four-electron bonding (although this was previously assigned to the participation of d orbitals).[17,18] Binding of the Lewis base to the acceptor and formation of a hypercoordinate state results in redistribution of electron density throughout the adduct. Although this may formally render the silicon negatively charged in the case of adducts involving tetravalent silicon compounds, in fact the electron density is localised on the peripheral atoms with the silicon atom increasing in positive character.[17,19] Denmark has used this phenomenon to great effect in his Lewis base-catalysed, Lewis acid-mediated reactions.[17]

Many of the studies highlighted above cite a publication by Kuhn and co-workers as evidence of an NHC–Si interaction.[20] In 1995, this group prepared a number of stable

NHC–Si complexes starting from relatively Lewis acidic halosilane precursors (Scheme 8). NHCs with a variety of substituents were shown to readily form adducts with $SiCl_4$ and



Scheme 8. NHC–Si complexes reported by Kuhn and co-workers.[20]

the hypercoordinate complex of ethyl-appended NHC (**19**, R = Et) was unambiguously characterised by X-ray crystallographic analysis. Bond lengths within this crystal structure are indicative of the electronic redistribution alluded to above and, as expected of the polarised electron-rich three-centre-four-electron bond,[17] the electronegative chlorine atoms are located in the apical positions. Perhaps of more relevance to this discussion is the formation of formally cationic silicon adduct **22**, derived from coordination of the NHC to trimethylsilyl iodide. In a general sense, the n–σ* interaction exists as a continuum between a hypercoordinate state and an ionised one. Simple analogies can be drawn between this and the formation of a covalent bond, such as the S_N2 displacement. Whether a hypercoordinate (such as **19**–**21**) or an ionised (such as **22**) intermediate is isolated is dependent on a number of factors, including the Lewis basicity of the donor, the Lewis acidity of the acceptor, steric effects and the leaving group ability of the peripheral atoms. In the case of adduct **22**, the leaving group ability of the iodide coupled with the likely steric congestion of any hypercoordinate intermediate is likely to result in the formation of the ionised compound.

Although this nice example from the Kuhn laboratory clearly demonstrates the ability of certain NHCs to form stable adducts with relatively Lewis acidic halosilanes, it is far from assured that catalytically relevant NHC–Si interactions exist in other examples. In the absence of a unified scale of Lewis basicity,[17] the ability of NHCs to function as Lewis bases can be qualitatively divided into the strength of their donating ability to a given acceptor and the steric effects arising from such an interaction (ignoring solvent effects and chemical reactions following adduct formation for the time being). In terms of the strength of donating ability, imidazolium-derived NHCs (which are the focus of the chemistry discussed here) have a pK_a of approximately 24 (in DMSO),[21] which indicates that they are strong Brønsted bases. Although the usefulness of this scale in regards to Lewis basicity is debatable because it is clearly referenced against a proton rather than a Lewis acid, strongly solvent dependent and doesn't always provide a meaningful comparison,[22] it still provides a useful measure of the global basicity of imidazolium-derived NHCs.[17] This value is relatively independent of the R substituent and so many of the NHCs discussed herein can be considered to be strong bases. The Lewis acidity of the acceptor is another key metric to determine the strength of a Lewis acid–base interaction. In terms of tetravalent silicon compounds, their Lewis acidity is dependent on the electronegativity and polarisability of the ligands surrounding the silicon centre. Although halosilanes are relatively Lewis acidic, substitution of the halide ligand by alkyl or alkoxy groups leads to a significant loss in Lewis acidity.[23] This leads to uncertainty in comparing the adducts of NHCs with halosilanes to the proposed adducts with reagents such as TMSCN (see Scheme 2). Clearly the Lewis acidity of the silicon reagent must be taken into account when proposing such Lewis acid–base interactions. Hard–soft acid–base principles will also likely play a role in the formation of such Lewis pairs, but whether matched or mismatched Lewis pairs are more useful will depend on the catalytic processes in question.[24]

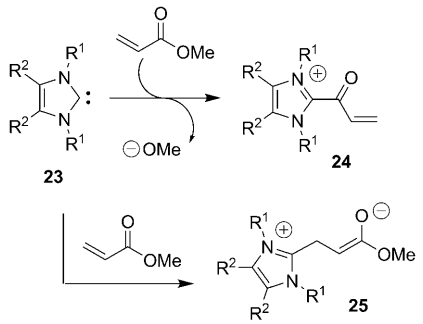
In light of the broadly similar basicity of the imidazolium-derived NHCs, perhaps the most important issue when considering the possibility of NHC–Si adducts is the steric consequences of complex formation. Although the steric bulk around the silicon reagent must be taken into account when predicting favourable complexation, if we assume that we are looking for Lewis pairs formed from a given silicon compound (e.g., TMSCN) and a collection of Lewis bases, then the bulk of the NHC is the limiting factor to consider. It is perhaps illuminating that in the examples from Kuhn and co-workers, only the relatively unhindered ethyl-appended NHC **18** (R = Et) was suitable to form stable adducts with TMSI.[20] Nolan, Cavallo and co-workers have proposed a model to measure ligand steric bulk, termed "percentage buried volume" ($\%V_{bur}$).[25] This is defined as the percent of the total volume of a sphere occupied by a ligand, and offers a useful metric in comparing the bulkiness of NHCs. Using examples published in Nolan's recent review,[26] ethyl-appended NHC **18** can be approximated to have a $\%V_{bur}$ of around 28[27] for an NHC–element bond length of 2.00 Å (the crystallographic NHC–Si bond length in **19** is 1.91 Å[20]). This is a broadly similar value to that of PMe_3.[26] Taking the cyanosilylation reactions as an example, however, many of the reports typically favour the use of bulkier NHCs, such as **1a** or **1d**,[4] which have calculated $\%V_{bur}$ values of 36.5, and 39.8, respectively, for a NHC–E length of 2.00 Å, and are considerably more bulky than their ethyl-appended counterpart **18**.[26] This significant rise in steric bulk (which incidentally seems to lead to better reaction efficiency) brings uncertainties in regards to their ability to form NHC–Si interactions. Indeed, the steric bulk of NHCs has been used as a means to prepare "frustrated" Lewis pairs with (significantly Lewis acidic) boron acceptors.[28] Frustrat-

ed Lewis pairs can be described as a combination of Lewis acids and bases in which adduct formation is prevented by steric encumbrance, so clearly the bulk around the NHC donor can have dramatic effects on its ability to form Lewis acid–base interactions.

Taking these facts into account and using cyanosilylation as an example, there are uncertainties in the current mechanistic proposals (see Scheme 2). In light of the precedence for the interaction of NHCs with carbonyl species (predominantly aldehydes) to form adducts such as **6**,[1f] it would seem that pathway B is plausible. However, following the formation of intermediate **7**, alternative mechanistic pathways may emerge because displacement of the carbene adduct by the cyanide anion seems unlikely on purely steric grounds. Instead it seems possible that the released cyanide anion could instead go on to catalyse the cyanosilylation reaction without further intermediacy of the NHC. Indeed, almost 40 years ago Evans and co-workers reported catalysis of the cyanosilylation reaction by addition of 1 mol% of a soluble cyanide anion source.[29] If this hypothesis were valid, it would mean the cyanosilylation reaction is merely initiated and not catalysed by NHCs (Scheme 2). Indeed, in related studies by Scheidt and co-workers, two mechanisms were considered for the addition of silyloxyallenes to aldehydes.[30] One mechanism in which an NHC catalyses the process through formation of a Lewis acid–base adduct with the silyl moiety was dismissed in favour of a pathway initiated by the NHC via an adduct with the aldehyde. X-ray crystallographic evidence was provided for the intermediacy of the aldehyde adduct, which crystallised from a mixture containing the NHC, benzaldehyde and chlorodimethylphenylsilane.

Indeed, it is possible that cyanosilylation may in fact only be initiated by NHCs in many of the reported cases, and furthermore may not involve an NHC–Si interaction of any kind. Other plausible mechanisms could be developed based on the Brønsted basicity of NHCs[21] deprotonating ketone substrates, followed by silylation of the resulting enolate[31] to generate a free cyanide anion that once again, could catalyse the reaction (Scheme 2). Further uncertainties arise for the other cases in which the hypothesised NHC intermediates are generated in situ from alkoxide bases and imidazolium salts. Metallic alkoxides are non-innocent Lewis bases that have also been demonstrated as efficient catalysts of cyanosilylation.[13] Furthermore, in several examples the use of the highly Lewis basic solvent DMF is required, another previously demonstrated catalyst for cyanosilylation.[32]

Similar uncertainties arise for the other examples cited in this minireview. In GTP polymerisation (Scheme 5), for example, other mechanisms for initiation of the polymerisation could be considered. One option may be the intermediacy of acyl azolium species (such as **24**, Scheme 9). These are proposed to be the intermediates in a number of organocatalytic processes involving NHCs,[1f] including transesterification.[33,34] Within the context of these polymerisation studies, it may be possible for the carbene to react with the acrylate monomer to give acyl azolium compounds, releasing one



Scheme 9. NHC-mediated formation of azolium intermediates.

equivalent of methoxide anion in the process. This methoxide anion is likely to have a non-innocent effect on the polymerisation reaction. Indeed, it has been previously demonstrated that lithium methoxide is a capable initiator of a Michael reaction between silyl enolates and α,β-unsaturated compounds.[35] It has also been previously demonstrated that oxyanions are capable activators of GTP.[36] Note that highly basic oxyanions limit the living nature of the polymerisation (something that perhaps goes against the studies of Taton and Gnanou[9c]), but this effect can, in part, be countered by low concentrations,[36] such as would be present from slow acyl azolium formation. It is perhaps illuminating to note that Hedrick and Waymouth reported the ability of **12c** to initiate the polymerisation of *tert*-butyl acrylate in the absence of silyl ketene acetal, albeit with low conversion.[9b] This could plausibly occur via formation of acyl azolium species **24** and methoxide anion-initiated polymerisation. Another option could be Michael addition of the NHC to the α,β-unsaturated system (to give **25**), which would offer another means of initiation in the absence of an NHC–Si interaction.[37] Such NHC addition reactions have been previously reported in other organocatalytic pathways[38] and may be relevant here.

Furthermore, in the polymerisation of cyclic siloxanes (Scheme 6), rather than nucleophilic attack of the NHC on **14**, polymerisation may instead proceed by NHC activation of the alcohol towards nucleophilic ring-opening of **14** by hydrogen bonding. Hydrogen-bonded NHC–alcohol complexes have precedence,[39] and obviously the degree of proton transfer in these complexes is sensitive to steric interactions, alcohol acidity, NHC basicity and solvent effects. Indeed, ring-opening polymerisation of cyclic carbosiloxanes mediated by NHCs has been hypothesised to proceed via hydrogen-bond activation of the alcohol initiator.[40] The inability of **1a** to catalyse the reaction as compared with **1b** or **1c** may be a result of sterics as the authors predict, although the $\%V_{bur}$ values of **1a** and **1b** are comparable.[26] Alternatively, the poor activity of **1a** may be due to differences in basicity compared with **1b** and **1c**.[39] It is also apparent that the subsequent polymerisation of silicone oligomer produced by ring opening of **14** could be catalysed by NHCs through hydrogen bonding to the corresponding silanol.[11]

Overall, the fact that many of the silicon reagents used are only weak Lewis acids and many of the NHCs used are significantly bulky suggests that NHC–Si interactions may not be the catalytically relevant species, especially when other energetically favourable interactions are in competition (such as formation of carbonyl adducts, see Scheme 2). Indeed, in one of the few computational analyses in the literature, Baceiredo and co-workers have predicted an NHC–Si interaction energy of only 3–5 kcal mol^{-1} for unhindered NHC **1e** and silicone oligomer ($MeO[SiR_2O]_3Me$).[15] It should be stated at this point that the ability of NHCs to catalyse processes involving silicon compounds need not involve the intermediacy of stable NHC–Si Lewis pairs. Indeed, to catalyse a given process the NHC simply has to lower the activation barrier of the reaction, which could plausibly proceed via an energetically favourable transition state involving an NHC–Si interaction.[41] However, in the absence of any suitable kinetic data, it is once again impossible to provide conclusive evidence for this eventuality.

Summary and Outlook

Novel and efficient synthetic procedures involving NHCs continue to expand. Indeed, this minireview has summarised developments in the NHC-mediated addition of silyl pronucleophiles to a variety of electrophiles, NHC-promoted organic and inorganic polymerisation chemistry and the reduction of CO_2 by hydrosilanes as facilitated by NHCs. It is likely that new methodologies that utilise these highly versatile molecules through the activation of silicon compounds will continue to be discovered. However, note that although many of these procedures hypothesise a NHC–Si interaction during the mechanistic course of the reaction, there is little experimental evidence for this. In light of the lack of clarity surrounding the mechanistic understanding of the synthetic studies detailed to date, it seems apparent that further theoretical, experimental and particularly kinetic studies on NHC–Si interactions in catalysis will further the understanding of these processes and, therefore, facilitate the development of new reaction methodologies based on such principles.

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[41] Note added in proof (August 26, 2010): Recent computational mechanistic studies on the NHC-mediated reduction of CO_2 by hydrosilanes has revealed that this reaction proceeds via an energetically favourable transition state involving an NHC–Si interaction, despite the fact that the NHC–Si complex is thermodynamically unstable (F. Huang, G. Lu, L. Zhao, H. Li, Z.-X. Wang, *J. Am. Chem. Soc*. **2010**, DOI: 10.1021/ja103531z). This study also reveals the exact reaction pathway traversed and that the stability of plausible NHC–Si intermediates are dependent on the exact NHC used in the study. Alternatively, for a further example of a computational study on stable NHC–Si interactions (principally halosilanes), the reader is referred to the study by Nyulászi and co-workers (O. Hollóczki, L. Nyulászi, *Organometallics* **2009**, *28*, 4159–4164), alongside the corresponding experimental studies reported by Roesky and co-workers (R. S. Ghadwal, S. S. Sen, H. W. Roesky, G. Tavcar, S. Merkel, D. Stalke, *Organometallics* **2009**, *28*, 6374–6377).

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