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Stable abnormal N-heterocyclic carbenes and their applications

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Although N-heterocyclic carbenes (NHCs) have been known as ligands for organometallic complexes since the 1960s, these carbenes did not attract considerable attention until Arduengo *et al.* reported the isolation of a metal-free imidazol-2-ylidene in 1991. In 2001 Crabtree *et al.* reported a few complexes featuring an NHC isomer, namely an imidazol-5-ylidene, also termed abnormal NHC (aNHCs). In 2009, it was shown that providing to protect the C-2 position of an imidazolium salt, the deprotonation occurred at the C-5 position, affording imidazol-5-ylidenes that could be isolated. Over the last ten years, stable aNHCs have been used for designing a range of catalysts employing Pd(II), Cu(I), Ni(II), Fe(0), Zn(II), Ag(I), and Au(I/III) metal based precursors. These catalysts were utilized for different organic transformations such as the Suzuki–Miyaura cross-coupling reaction, C–H bond activation, dehydrogenative coupling, Huisgen 1,3-dipolar cycloaddition (click reaction), hydroheteroarylation, hydrosilylation reaction and migratory insertion of carbenes. Main-group metal complexes were also synthesized, including K(I), Al(III), Zn(II), Sn(II), Ge(II), and Si(II/IV). Among them, K(I), Al(III), and Zn(II) complexes were used for the polymerization of caprolactone and *rac*-lactide at room temperature. In addition, based on the superior nucleophilicity of aNHCs, relative to that of their nNHCs isomers, they were used for small molecules activation, such as carbon dioxide (CO_2), nitrous oxide (N_2O), tetrahydrofuran (THF), tetrahydrothiophene and 9-borabicyclo[3.3.1]nonane (9BBN). aNHCs have also been shown to be efficient metal-free catalysts for ring opening polymerization of different cyclic esters at room temperature; they are among the most active metal-free catalysts for ε-caprolactone polymerization. Recently, aNHCs successfully accomplished the metal-free catalytic formylation of amides using CO_2 and the catalytic reduction of carbon dioxide, including atmospheric CO_2, into methanol, under ambient conditions. Although other transition metal complexes featuring aNHCs as ligand have been prepared and used in catalysis, this review article summarize the results obtained with the isolated aNHCs.

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Introduction

The importance of N-heterocyclic carbenes (NHCs) as ligands for organometallic complexes became first apparent, in the 1960s and early 1970s, from independent works by Öfele,[1] Wanzlick,[2] and Lappert.[3] Despite considerable progress accomplished by these groups, the topic did not attract widespread consideration until Arduengo *et al.* reported the isolation of the first metal-free N-heterocyclic carbene **1**[4,5] (Fig. 1). This finding, which followed the discovery of the first stable carbene, namely a (phosphino)-(silyl)carbene **2**,[6,7] marked a turning point in carbene chemistry. The ongoing popularity of this research area is primarily due to the development of extremely active organocatalysts[8] and transition metal catalysts based on carbenes.[9] This is clearly demonstrated by the second-generation Grubbs' olefin metathesis catalyst, in which the phosphine ligand of the first generation has been replaced by an NHC.[10]

Arduengo-type NHCs coordinate to a metal center *via* the C2 carbon, and we will refer these carbenes hence forth to as normal N-heterocyclic carbenes (nNHCs).[11,12] However, later it was realized that the C4/5-centers of the imidazolium ring are also susceptible to metallation *via* C–H activation. Indeed, in 2001, Crabtree and co-workers first reported the cationic iridium complex **3**, starting from a 2-pyridylmethylimidazolium (Fig. 1).[13] This type of binding *via* the C5-positions of NHCs is referred to as abnormal binding mode of NHCs and these compounds are named abnormal NHCs (aNHCs), and sometimes mesoionic carbenes (MICs) or non classical carbenes.[14] The location of the carbene center at C5 makes aNHCs less thermodynamically stable and stronger donor than nNHCs. Energy decomposition analyses have shown that the energy-gap between the parent nNHC and aNHC is about 19 kcal mol^{-1}.[15,16] In 2004, Yates[17,18] calculated the acid dissociation constant of imidazolium cations, and found that the aqueous pK_a value of the C2-bound hydrogen was 24.9 whereas for the C5 it was 33.0, which indicates a higher barrier for the metallation of the latter. Several experimental methods have been used to evaluate the electronic nature of the C5-carbene and they consistently indicated that aNHCs are more electron-donating than their nNHC analogues.[19–22]

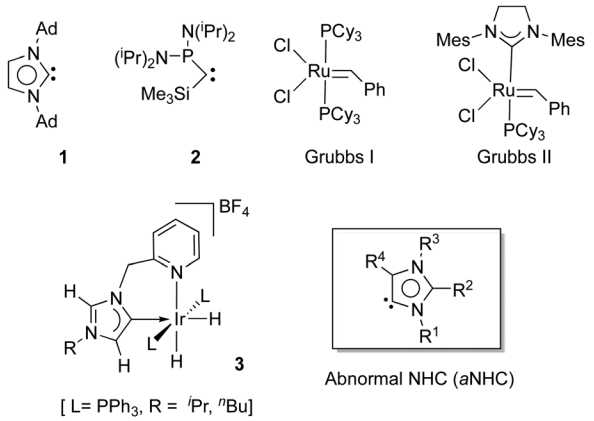
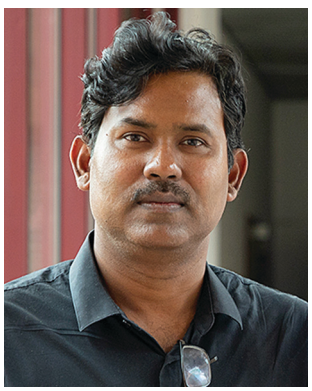


Fig. 1 The first stable NHC **1** and the first isolated carbene **2**; the first and second generation Grubbs' catalysts; the first C5 bound imidazolylidene metal complexes **3**; the abnormal NHCs, which are the topic of this review.



Swadhin K. Mandal

Swadhin K. Mandal obtained his doctoral degree in 2002 from Indian Institute of Science, Bangalore. He has been a post-doctoral fellow at the University of California, Riverside and at the University of Göttingen as an Alexander von Humboldt fellow. He is currently a professor at the Department of Chemical Sciences, IISER Kolkata. He has received SERB Distinguished Investigator Award-2018 and CRSI Bronze Medal-2019. He was awarded with the prestigious Shanti Swarup Bhatnagar Prize in Chemical Sciences for 2018 by Govt. of India.

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Michèle Soleilhavoup received her PhD in 1993 from the University of Toulouse under the supervision of Guy Bertrand. After two years at BASF AG at Ludwigshafen, she became Chargèe de Recherche CNRS at University Paris VI. From 2000 to 2001, she worked in the Laboratoire de Chimie de Coordination in Toulouse, before joining the UCR/CNRS Laboratory and in 2012 the UCSD/CNRS Joint Research Laboratory at the University of California, San Diego.

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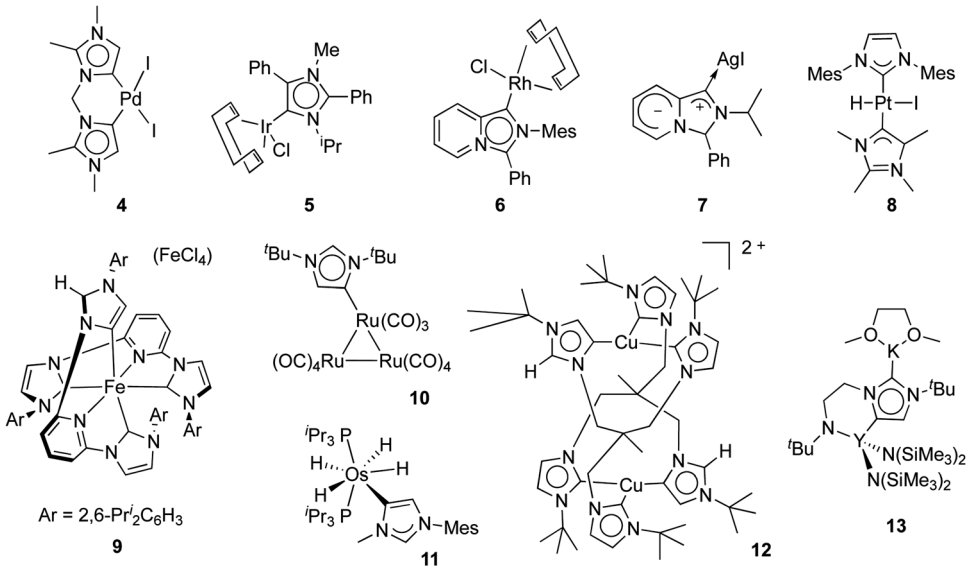
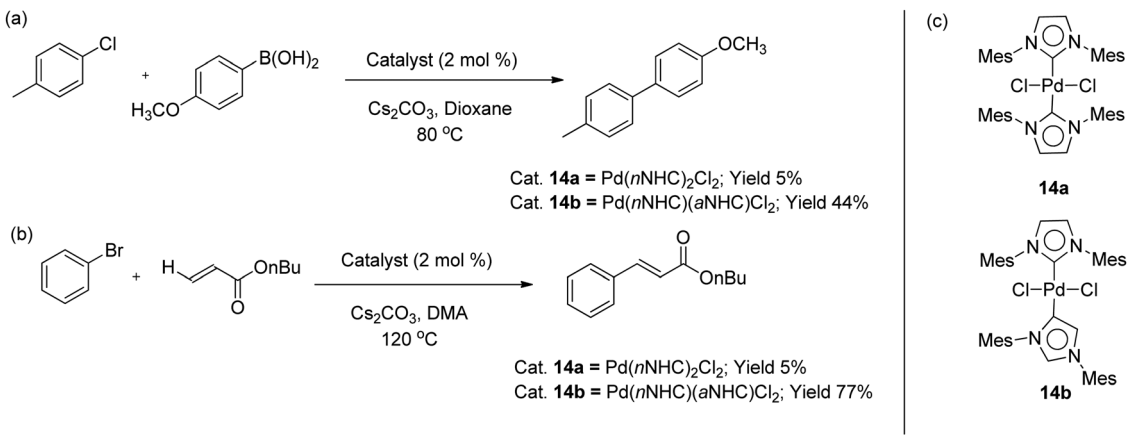


Fig. 2 Metal complexes *via* C5 metallation without isolating the corresponding free aNHC.

The more electron-donating nature of aNHCs, compared to nNHCs, was considered to be a desirable property for designing better catalysts, and prompted the development of aNHC-organometallic chemistry. For example, Albrecht and co-workers performed the reaction of C2-protected imidazolium salt with $Pd(OAc)_2$ and obtained the C5-bound dicarbene palladium diiodide **4** (Fig. 2).[23] Similarly, Crabtree *et al.* prepared the iridium complex **5**,[22] and Lassaletta synthesized the rhodium(I) (**6**) and silver(I) (**7**) complexes.[24] Cavell and co-workers[25] observed the formation of aNHC based Pt complex **8** by mixing [Pt(norbornene)$_3$], IMes (1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene) and the C2 blocked NHC in a molar ratio of 1 : 1 : 1.8. Other aNHC complexes were obtained serendipitously during attempts to make nNHC complexes, as illustrated by complexes **9**,[26] **10**,[27] **11**,[28] **12**[29] and **13**.[30]

Already in 2004, Lebel and co-workers[31] reported convincing catalytic experiments showing the superiority of the aNHCs palladium complex **14b** over the analogous nNHC complex **14a** in the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions as shown in Scheme 1. Similarly, a Rh–(aNHC)$_2$ complex effectively catalyzes the transfer hydrogenation of ketones using iPrOH as hydrogen source[32] whereas the analogous nNHC complex Rh-(nNHC)$_2$ is not efficient under identical conditions.

As mentioned at the beginning of this introduction, the first stable metal-free nNHC was isolated by Arduengo in 1991,[4] but it was only in 2009 that the first metal-free aNHC was isolated.[33] At that time, Albrecht wrote "*normal carbenes rapidly became a key tool for organometallic chemistry and organic synthesis once they were available as stable free ligands some 20 years ago. Given the unique impact of abnormal carbenes on the reactivity of transition metals, the accessibility of free abnormal carbenes may become another cornerstone in this field, and it will be exciting to witness developments in these directions.*"[34] This review article describes these developments.



Scheme 1 (a) Suzuki–Miyaura reactions using nNHC complex **14a** and aNHC complex **14b**; (b) Mizoroki–Heck reactions using complexes **14a** and **14b**; (c) NHC palladium complexes **14a** and **14b**.

Isolation of the first abnormal NHC

Bertrand and co-workers designed the imidazolium salt **15** as a precursor for the stable abnormal N-heterocyclic carbene (aNHC) **16** (Scheme 2).[33] Because the C5-bound proton of imidazolium salts is much less acidic than the C2-bound proton,[17,18] the C2 position was protected by a phenyl group.

When **15** ($HCl{\cdot}Cl^-$) was treated with two equivalents of a lithium base, *n*-butyllithium (*n*BuLi) or lithium diisopropylamide (LDA), aNHC-lithium adduct **18** was isolated (Scheme 2). However, when the deprotonation of imidazolium salt **15** ($HCl{\cdot}Cl^-/HBr{\cdot}Br^-$) was performed with two equivalents of potassium bis(trimethylsilyl)amide (KHMDS) in tetrahydrofuran, a clean reaction occurred and the metal-free aNHC **16** was isolated, and fully characterized including by a single crystal X-ray diffraction study (Scheme 2b). In the solid state, **16** features a planar 5-membered ring confirming the delocalization of the π system. Although aNHC **16** is highly air sensitive, and quantitatively rearranges into **17** upon heating in benzene at 50 °C for 48 hours, it is stable at room temperature under inert atmosphere for a few days both in the solid state and in solution. Calculations predict aNHC **16** to be 14.1 kcal mol^{-1} less stable than its isomeric nNHC (phenyl group bonded to C5 instead of C2). The HOMO of **16** (−4.403 eV) is a σ-type lone-pair at C5 and the HOMO−1 (−4.879 eV) is a C5–C4 π-bonding orbital (Fig. 3). These molecular orbitals are higher in energy than those of the isomeric nNHC (−5.000 and −5.279 eV, respectively), which confirms that aNHCs are more basic than the corresponding nNHCs.

In a subsequent paper,[35] it was shown that electron-withdrawing groups at C-4 stabilize aNHCs, whereas electron-donating substituents destabilize them to the extent that the free carbenes cannot be isolated. Interestingly, according to the Tolman Electronic Parameters, aNHCs are stronger electron-donors than NHCs, even when there is an electron-withdrawing substituent at C4. Note, that the substituent at C-2 only slightly affects the electronic properties aNHCs.

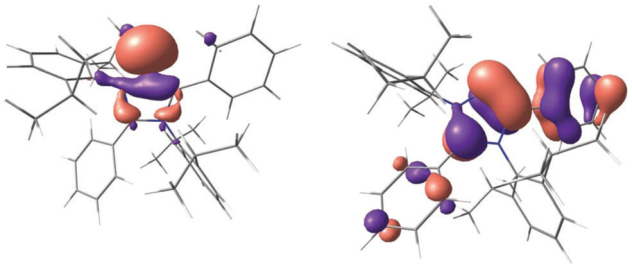
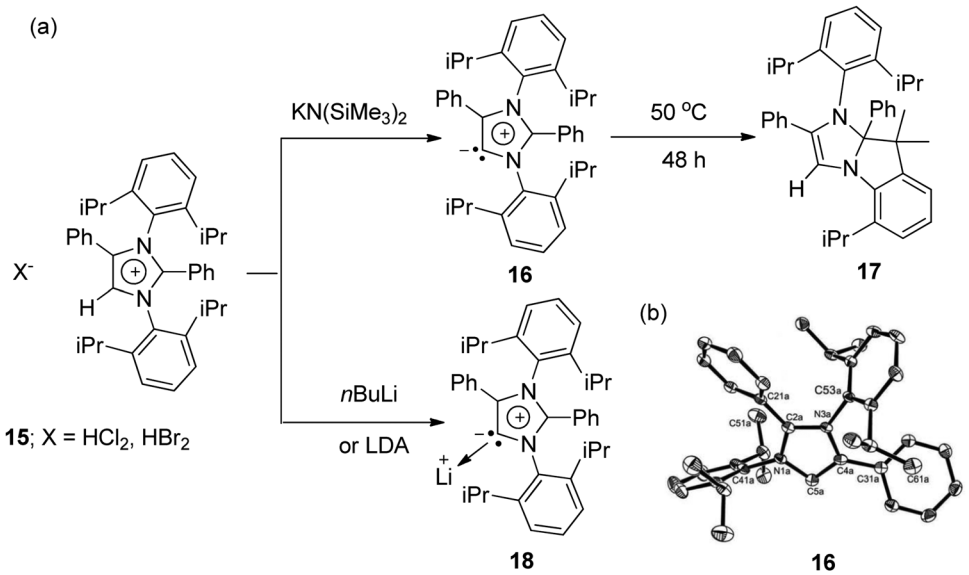


Fig. 3 MO pictures of two highest-lying occupied orbitals HOMO (left) and HOMO−1 (right) of **16**.

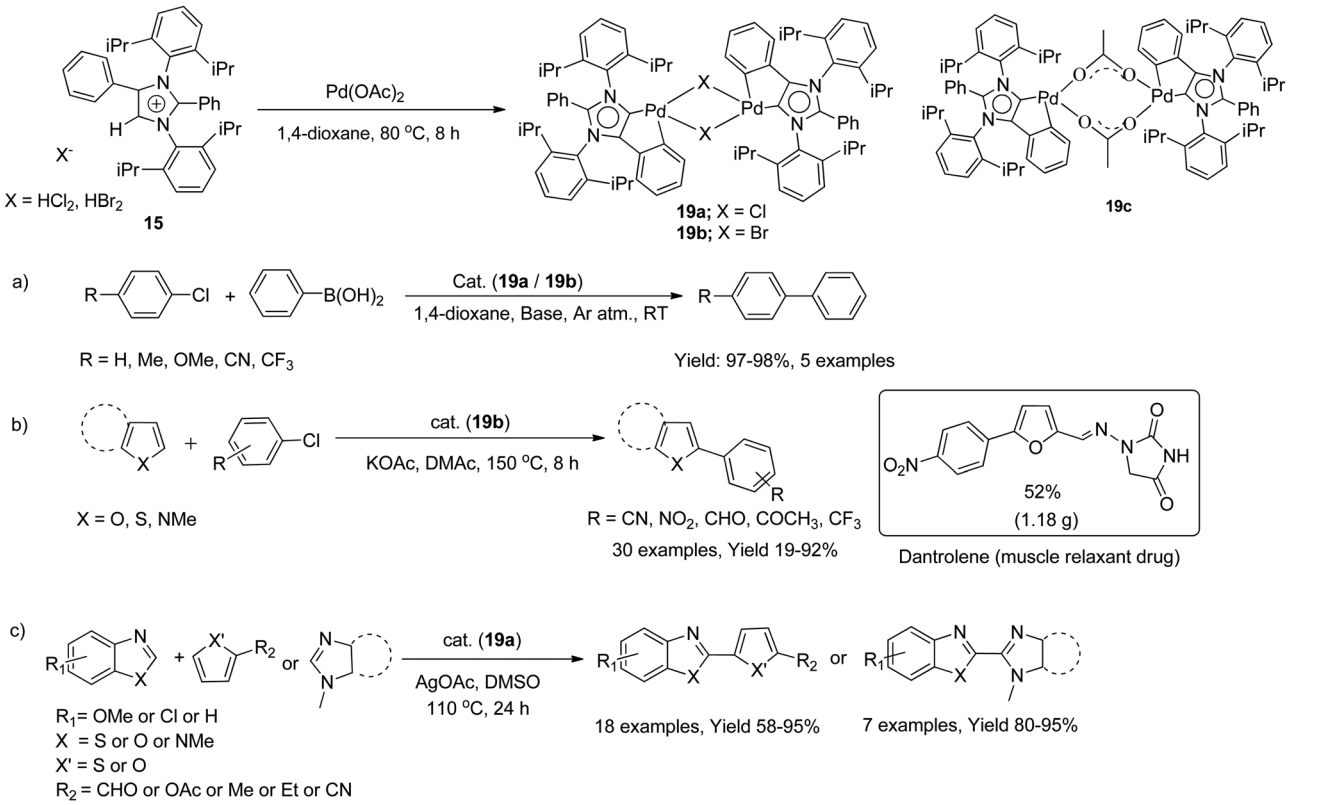
Transition metal complexes from isolated aNHCs for catalytic coupling reactions

It is a challenging task to utilize an inert aryl chloride partner in Suzuki–Miyaura coupling.[36,37] In this context, Mandal and co-workers have reported that halo-bridged C–H activated palladium dimer **19**[38] are active catalysts for the Suzuki–Miyaura cross-coupling of a number of aryl chlorides affording the biaryls in nearly quantitative yields at room temperature with low catalyst loading (up to 0.005 mol%; Scheme 3a). Importantly, complex **19a** remained active for 10 successive catalytic runs without any loss of activity, confirming the robustness of the Pd–aNHC bond.

The palladium bromide analogue **19b** was also used as a catalyst for the direct C–H arylation of heteroarenes (1-methylpyrrole, 1-methylindole, furan, thiophene, furfural and *N*-benzyl-1,2,3-triazole) using activated aryl chloride substrates (Scheme 3b).[39]



Scheme 2 (a) Isolation of the first aNHC; (b) molecular view of free aNHC **16** in the solid state.



Scheme 3 (a) Suzuki–Miyaura cross-coupling reaction of aryl chlorides at room temperature; (b) direct arylation of heteroarenes with aryl chlorides and synthesis of muscle relaxant drug dantrolene in gram scale; (c) catalytic cross dehydrogenative heterocoupling of heteroarenes.

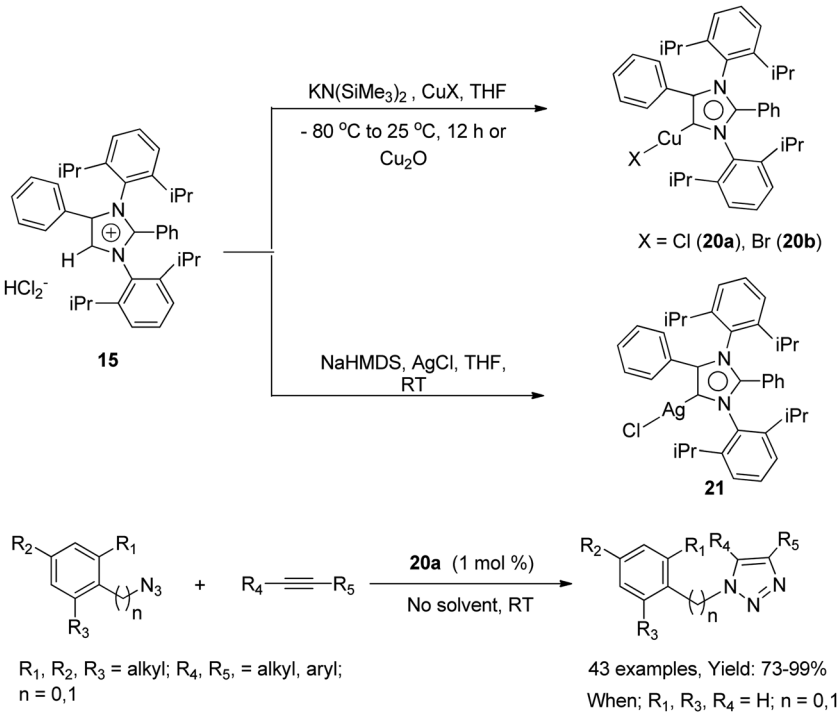
This protocol allowed for the development of a one-pot synthesis of the muscle relaxant drug dantrolene[40] in gram scale. More recently, complex **19a** was reported to be an active catalyst for the dehydrogenative cross-coupling using a variety of heteroarenes (Scheme 3c) such as benzothiazole, benzoxazole, 2-formyl thiophene, furfural and *N*-methyl benzimidazole.[41] The active catalyst for dehydrogenative cross-coupling was isolated by performing stoichiometric reaction between complex **19a** and silver acetate and it was characterized as an acetate bridged dimer (**19c**) as revealed by a single crystal X-ray study.

The same aNHC was used as ligand for less expensive transition metals such as Cu(I) and Ni(II). The aNHC–Cu(I) complexes **20a** and **20b**, prepared by *in situ* deprotonation of **15** in the presence of CuX,[42] efficiently catalyzed Huisgen 1,3-dipolar cycloaddition reactions of azides with alkynes (''click'' reaction)[43] to give 1,4-substituted 1,2,3-triazoles in excellent yields at room temperature within short reaction times under solvent-free conditions (Scheme 4). The reaction went smoothly even for sterically hindered azides and alkynes, including internal alkynes, which usually requires higher temperatures.[44] The longevity of catalyst **20a** was demonstrated up to 10 successive catalytic cycles. Interestingly, Cazin *et al.* generalized the use of Cu_2O for the preparation of same copper(I) chloride complex **20a**,[45] and they reported that this complex is significantly more efficient than its nNHC analogue. Recently Aldeco-Pérez, Cuevas-Yañez and co-workers demonstrated that aNHC–Ag complex **21** also catalyzes [3+2] cycloadditions of a variety of azides with alkynes without any copper additives.[46]

To utilize the acidic C–H proton of triazole, Mandal and co-workers extended the use of Cu(I) complex **20b** for one-pot consecutive catalysis. This study integrates organometallic catalysis and organocatalysis whereby the product of the first catalytic cycle acts as the catalyst component for the next catalytic cycle (Scheme 5).[47] The abnormal N-heterocyclic carbene copper based organometallic catalyst **20b** promotes the click reaction giving a triazole, which after activation through an alkylation step acts as an efficient organocatalyst for different organic transformation *e.g.* aza-Michael addition or multi component reactions (MCR) in a consecutive fashion in the same reaction pot (Scheme 5).

As a part of their ongoing interest in developing catalysts based on the isolated aNHC ligand **16**, Mandal and co-workers established that $Ni(COD)_2$/aNHC combination can perform hydroheteroarylation of vinyl arenes with benzoxazole to furnish selectively 1,1-diarylalkanes (Scheme 6a).[48] Transition metal catalyzed hydroheteroarylation of olefins through C–H bond activation offers a highly atom-economical system for the preparation of 1,1- or 1,2-diarylalkanes[49,50] which are part of a variety of pharmaceuticals and biologically active molecules.[51]

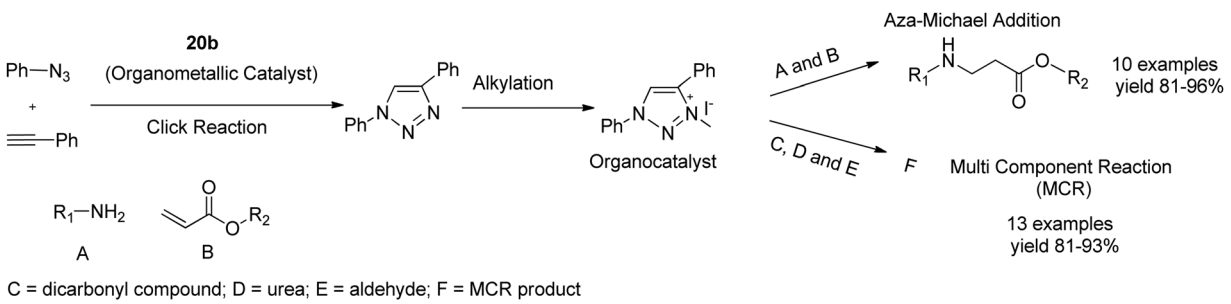
In order to characterize the catalytically active Ni(0) complex and gain insight into the catalytic cycle, several stoichiometric reactions were performed between $Ni(COD)_2$ and aNHC **16**.



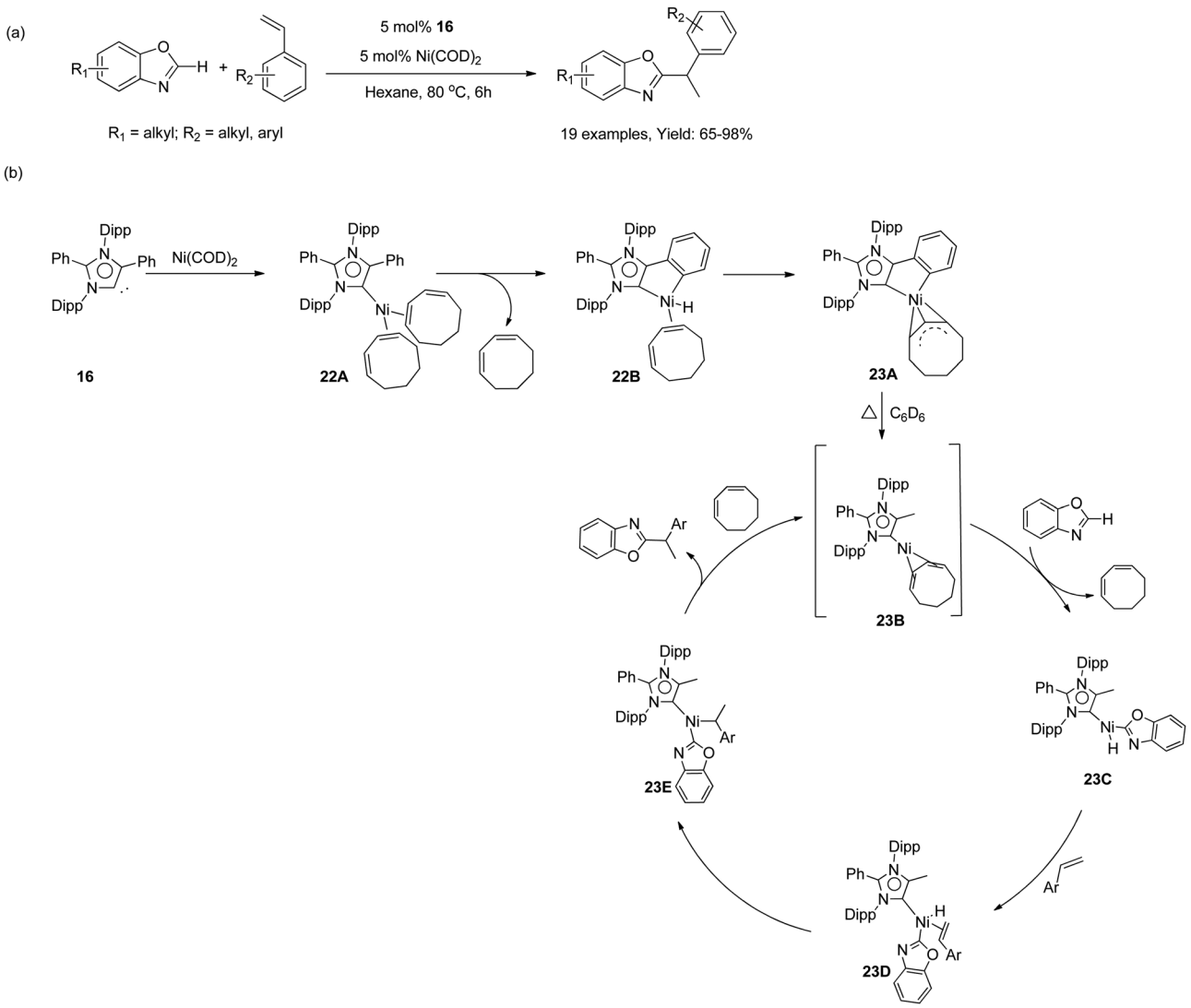
Scheme 4 Synthesis of aNHC–Cu and –Ag complexes; Huisgen 1,3-dipolar cycloaddition (click reaction) with complex **20** under solvent-free conditions at room temperature.

Surprisingly, formation of an aryl C–H activated nickel(II) cyclooctenyl complex **23A** was observed instead of the anticipated aNHC–Ni(0) complex (Scheme 6b). The metal center is in a distorted square planar environment where nickel(II) binds to a carbene carbon, a C–H activated *ortho* aryl carbon, and a cyclooctenyl ligand in an η^3 fashion. The reaction affording the nickel(II) cyclooctenyl complex **23A** was explained by the isomerization of 1,5-COD to 1,3-COD followed by loss of a 1,3-COD ligand. Subsequent orthometallation of one of the adjacent aryl groups would lead to the formation of a Ni–H species; lastly nickel hydride migration to the 1,3-COD ligand leads to the η^3-allyl mode of binding to Ni(II). This reaction pathway is in agreement with a previous report by Caddick, Cloke *et al.*,[52] and with an upfield ^{1}H signal at δ −11.33 ppm which supports the involvement of the Ni–H complex **23C**. Based on the above experimental remarks and earlier literature reports,[53] a mechanistic pathway for the hydroheteroarylation reaction was proposed (Scheme 6b). Further, **23A** was utilized for the catalytic C(sp^2)–H borylation of a range of arenes at 80 °C.[54]

Bertrand and co-workers prepared (aNHC)AuCl complex **24** (Scheme 7a) in 79% isolated yield by simply reacting **16** with chloro(dimethylsulfide)gold(I) in THF.[33] Recently, Toste and co-workers stabilized Au(+III) oxidation state with the same aNHC backbone (**25** and **26**) (Scheme 7). These complexes can participate in rapid migratory insertion of carbenes derived from silyl- or carbonyl-stabilized diazoalkanes into Au–C bonds at temperatures ≥ −40 °C (Scheme 7b).[55] This is the first example of migratory insertion of carbenes derived from diazoalkanes into an Au–C bond (Scheme 7b). This study paves the way for homogeneous gold-catalyzed processes integrating carbene migratory insertion steps.



Scheme 5 Integration of organometallic catalysis with organocatalysis where the product of the first organometallic catalytic step acts as organocatalyst for the next catalytic cycle.

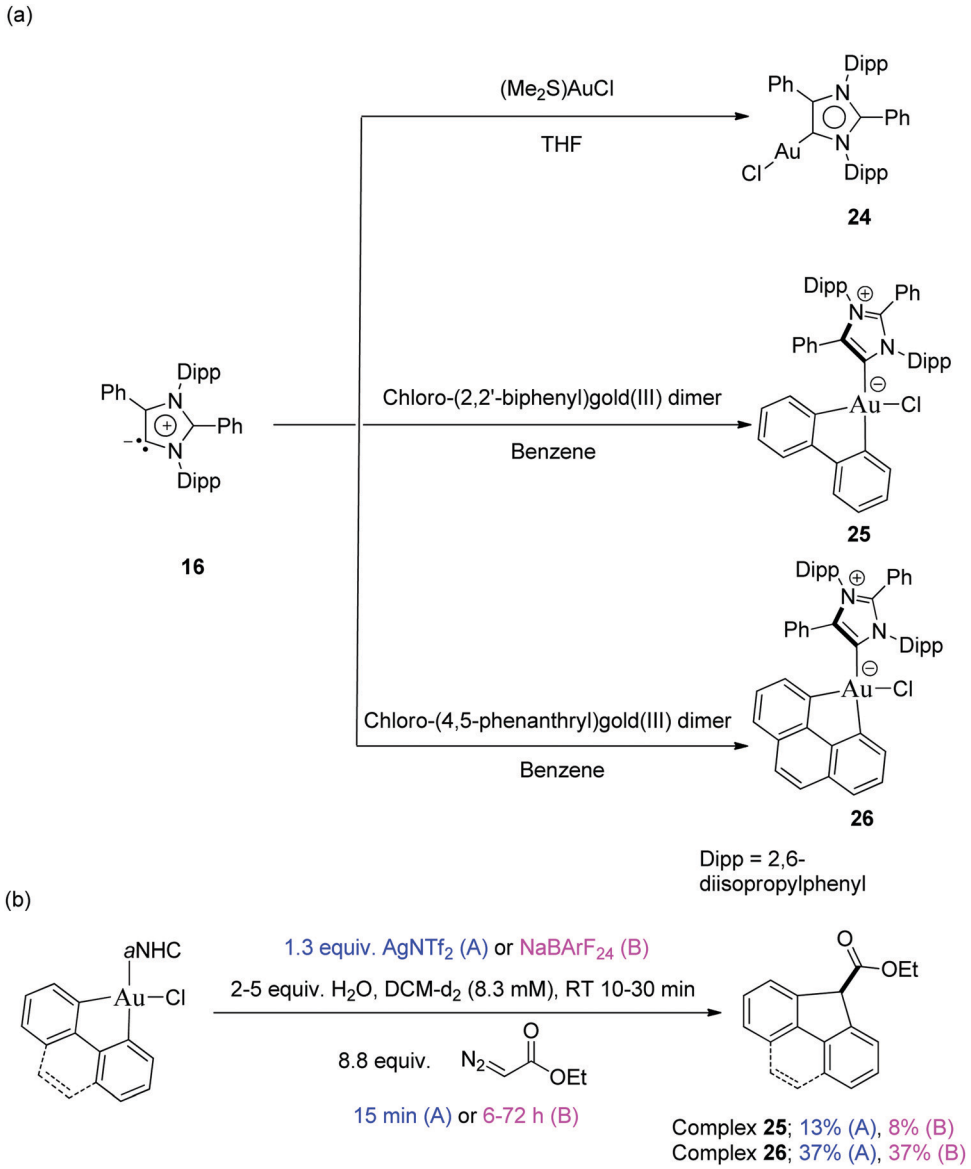


Scheme 6 (a) Hydroheteroarylation of vinylarenes with benzoxazole using $Ni(COD)_2$/aNHC combination; (b) plausible mechanistic cycle.

Transition metal complexes from isolated aNHCs for catalytic hydrosilylation reactions

Hydrosilylation, the addition of a Si–H bond across a multiple bond[56] has been described as the "most important application of platinum in homogeneous catalysis."[57] In recent years, there have been ongoing efforts to replace Pt metal. In this context, Mandal and co-workers used Cu(I), Ni(II) and Fe(0) complexes bearing the aNHC **16** for the chemoselective hydrosilylation of ketones, aldimines and nitro groups, respectively. The reduction of carbonyl moiety to alcohol *via* hydride transfer is a universal method for the production of fine chemicals leading to molecules with hydroxy functionalities.[58] Mandal and co-workers found the copper(I) complex **20a** (Scheme 8a) to be a versatile, selective, and highly efficient catalyst for the reduction of carbonyl functionality *via* hydrosilylation in presence of $PhSiH_3$ or polymethylhydrosiloxane (PMHS); **20a** acts under low catalyst loading (0.25 mol%) at ambient temperature (Scheme 8a).[59] Note also that nickel complex **27** is an effective catalyst for the hydrosilylation of nitroarenes into amines with good chemoselectivity (Scheme 8b).[60]

The use of Fe based catalysts for various reactions, including the hydrosilylation, has gained attention in recent years.[61,62] Mandal and co-workers prepared the abnormal NHC based iron(0) complex **28**[63] by treatment of free aNHC **16** with commercially available diiron nonacarbonyl $[Fe_2(CO)_9]$ in a 2 : 1 ratio at room temperature (Scheme 9a). Complex **28** selectively hydrosilylates a variety of aldimines and ketimines to amines under low catalyst loading at room temperature with high turnover numbers (up to 17 000). The reduction is applicable to a wide range of imine substrates with excellent functional group tolerance and chemoselectivity (Schemes 9b and c). Additionally, **28** was active for the hydrosilylation of sugar moieties containing highly functionalized imines, which provides a simple access to their *N*-alkylated derivatives (Scheme 9d; 5 examples, yield 82–86%). A combined theoretical and experimental study reveals that the imine



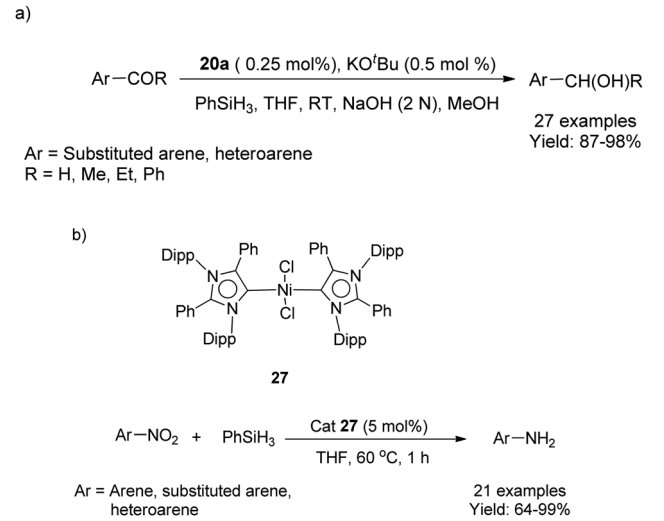
Scheme 7 (a) Synthesis of Au(I) and Au(III) metal complexes from aNHC **16**; (b) migratory insertion of carbenes into Au(III)–C bonds.

hydrosilylation reaction occurs *via* the iron hydride complex **30** (Fe–H, δ = −9.22 ppm, ^{29}Si, δ = −6.1 ppm)[64] followed by the hydride migration to the inserted imines (Scheme 9e). The crucial role of the Fe-hydride species **30** in the catalytic cycle was demonstrated by its stoichiometric reaction with *N*-(4-methoxybenzylidene)-4-methylaniline in DMSO-d_6 at slightly elevated temperature; the hydride signal disappeared completely and ^{1}H NMR signals corresponding to **32** (benzylic proton at δ = 4.13 ppm) were observed.

Main group based organometallic catalysts from isolated aNHCs

Main group elements are far more ubiquitous than transition metals, not only on Earth but also in the entire universe. As a consequence, catalysis by main group compounds is currently gaining overwhelming interest.[65,66] Here we summarize recent efforts to develop main group complexes using isolated abnormal NHCs, and their applications towards catalysis.

Ghadwal, Roesky, Dittrich and co-workers compared the reactivity of aNHC *vs.* nNHC towards $HSiCl_3$ and H_2SiCl_2.[67] A dismutation of $HSiCl_3$ occurred in the presence of aNHC resulting in the five coordinated aNHC·$SiCl_2H_2$ adduct **34** (Scheme 10a) with concomitant elimination of $SiCl_4$. In contrast, an nNHC reacts with $HSiCl_3$ to produce dichlorosilylene **37** with reductive elimination of HCl (Scheme 10b). Similarly, a five coordinated **34** (Scheme 10a) and a six coordinated silicon adduct **38** (Scheme 10b) were obtained by the reaction of aNHC and nNHC with H_2SiCl_2, respectively. In a subsequent study, the same authors established that an aNHC easily substitutes an nNHC from an NHC·$SiCl_2$ adduct to afford compound **39** (Scheme 10c).[68] This result again confirms the stronger nucleophilic nature of aNHCs compared normal NHCs. Furthermore, dichlorogermylene



Scheme 8 (a) Catalytic hydrosilylation of functionalized aldehydes/ketones with aNHC–Cu **20a**. (b) Hydrosilylation of nitroarenes to anilines with aNHC–Ni **27**.

aNHC·$GeCl_2$ (**40**) and aNHC·$SnCl_2$ (**41**) were synthesized by treatment of Cl_2Ge.dioxane and $SnCl_2$, respectively, with aNHC in a 1 : 1 molar ratio (Scheme 10e). The molecular structure of **40** discloses a distorted trigonal pyramidal geometry.[69] The aNHC adducts have shorter M–C(carbene) bond lengths {(1.908(2) Å (**34**) and 2.071(2) Å (**40**))} in comparison with that of the nNHC analogue **37** and the reported nNHC·$GeCl_2$ {2.112(2) Å}.[69]

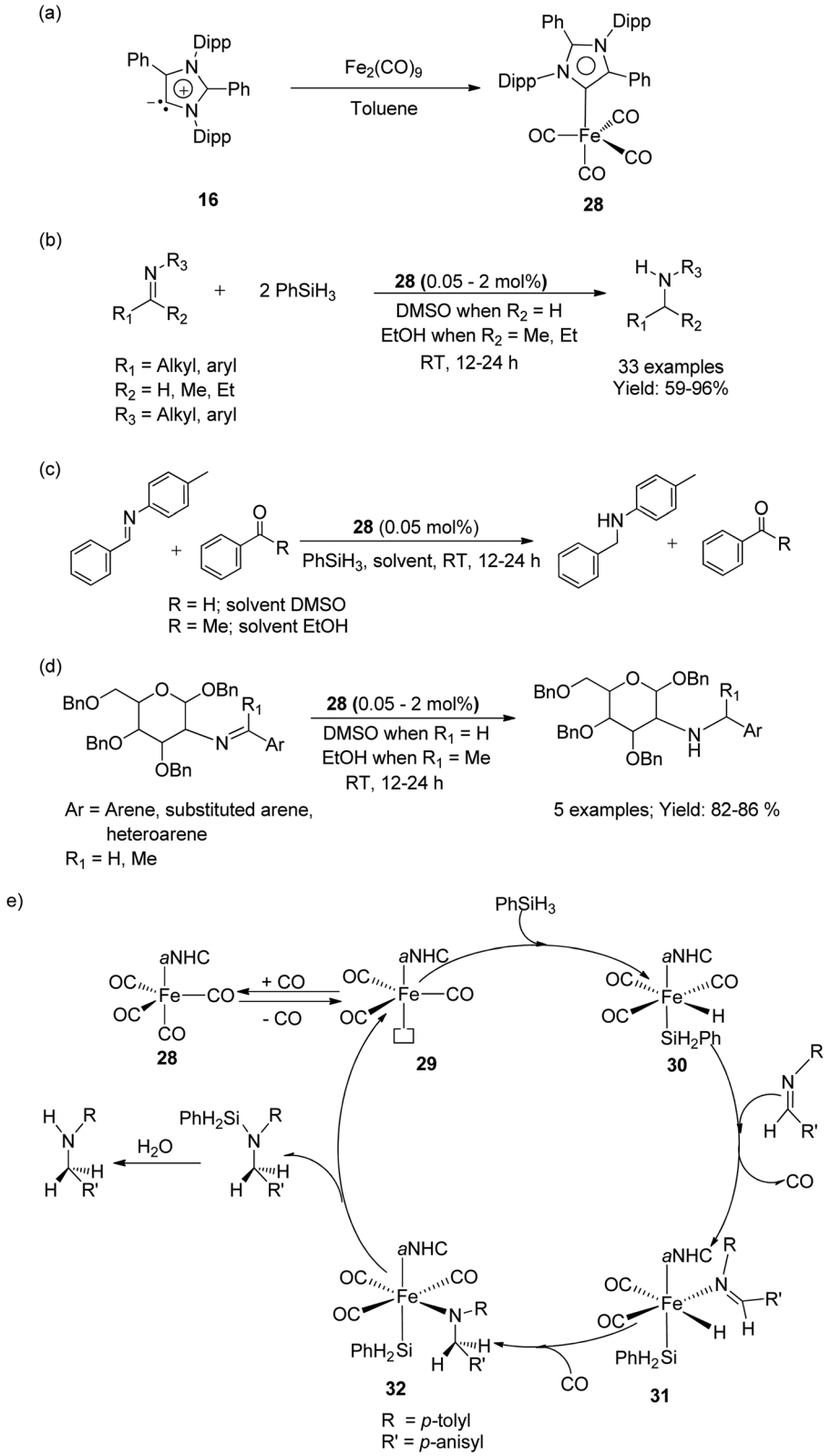
Catalytic applications of aNHC main group complexes remain largely unexplored. Mandal and co-workers introduced the aNHC organozinc (**43**) and aNHC organoaluminum (**44**) adducts (Scheme 11a) as catalysts for the ring opening polymerization of cyclic esters.[70] It may be noted that there has been enormous interest in developing main group element based catalytic systems for the production of biodegradable and biocompatible polycaprolactides (PCL), polylactides (PLA), and polyvalerolactones (PVL).[71–74] The aNHC adducts, **43** and **44** were synthesized from $ZnEt_2$ and $AlMe_3$ (Scheme 11a).[70] Formation of complex **43** was rationalized by considering that **42** reacts with $HN(SiMe_3)_2$ during crystallization, with elimination of ethane (Scheme 11a).[70] These adducts (**43** and **44**) were found to be quite efficient catalysts for the polymerization of *rac*-lactide (*rac*-LA) (Scheme 12a). Both complexes (**43** and **44**) were active towards other cyclic esters such as ε-caprolactone (ε-CL) and δ-valerolactone (δ-VL). In addition, aNHC zinc adduct **43** was even used as a catalyst for the synthesis of tri-block copolymers (Scheme 12b).

Mandal and co-workers also synthesized aNHC **16** s-block metal adducts for ring opening polymerization. The potassium complex **45** was prepared by treatment of the free aNHC with potassium bis(trimethylsilyl)amide at room temperature (Scheme 11c).[75] The X-ray crystal structure of **45** showed a dimeric structure in which $N(SiMe_3)_2$ bridges two potassium ions (Scheme 11d). The average $K–C_{aNHC}$ bond length in **45** appeared to be quite elongated (2.973 Å), even though it is slightly shorter than that observed by Hill in the case of $[(nNHC)KN(SiMe_3)_2]_2$ complex (3.0291(17) Å); this is in agreement with the aNHC's superior σ-donation capability.[76] The ^{13}C NMR spectrum of **45** reveals a resonance at δ = 197.2 ppm, assignable to the C-5 carbon bound to the potassium center, which is only slightly shifted upfield from the corresponding chemical shift of free aNHC (δ = 201.9 ppm).[33] Such a negligible ^{13}C NMR chemical shift is attributable to the weak interaction between K(I) and the carbene carbon and it is also comparable with earlier reported potassium complexes.[77] This weak interaction was exploited to develop highly efficient ring-opening polymerization catalysts for ε-caprolactone and *rac*-lactide. Compound **45** induces the polymerization of *rac*-LA in toluene at room temperature with 96% conversion within 2.5 h (Scheme 12c).

Metal-free catalysis with aNHCs

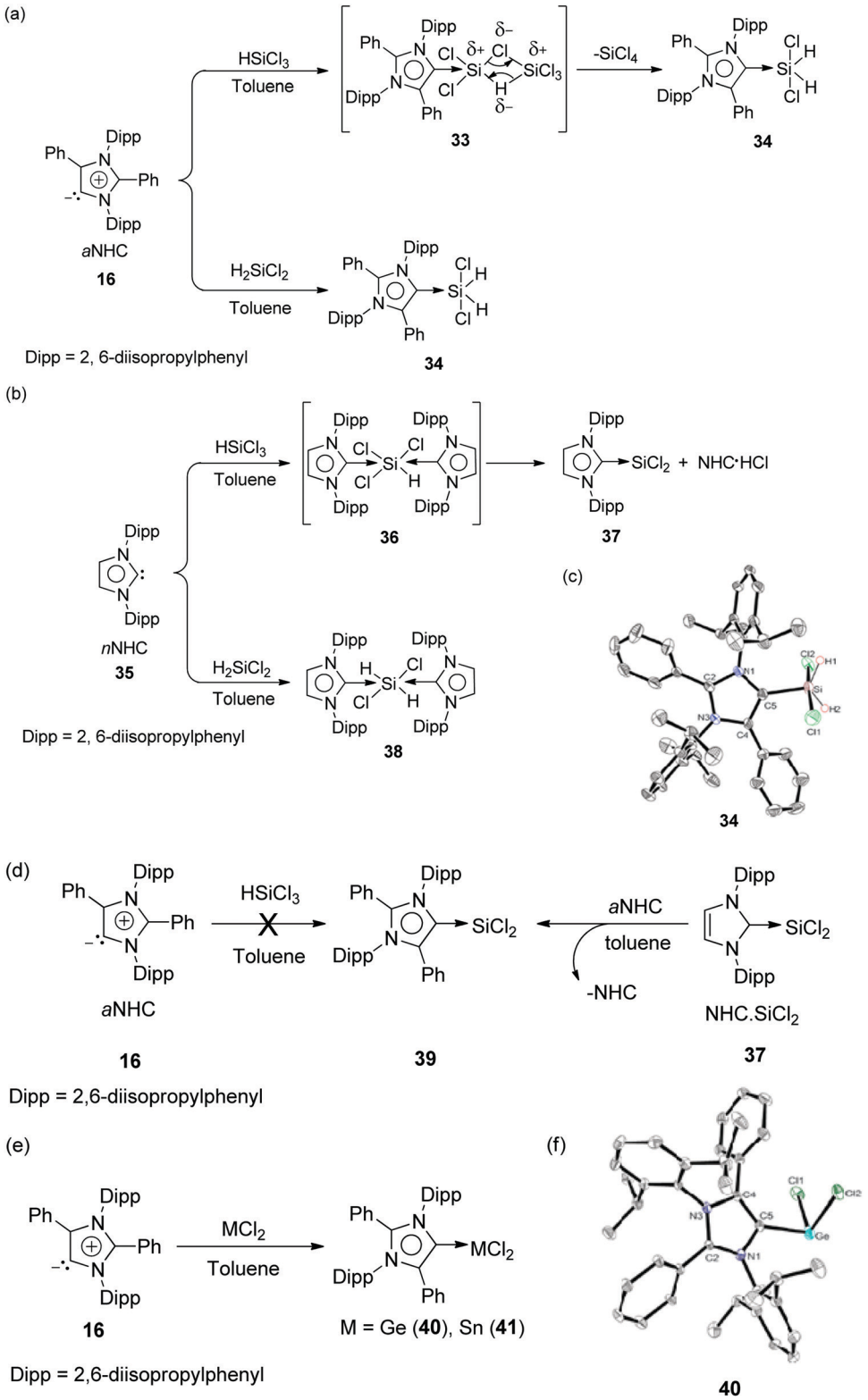
Organocatalyzed reactions represent an attractive alternative to metal-catalyzed processes notably because of their lower cost and benign environmental impact in comparison to organometallic catalysis. In this context, N-heterocyclic carbenes (NHCs) have been studied for their ability to promote primarily the benzoin condensaion. Lately, dramatic progress in understanding their intrinsic properties and in their synthesis have made them available to organic chemists. This has resulted in a tremendous increase of their scope and in a true explosion of the number of papers reporting NHC-catalyzed reactions. Here, we highlight the ever-increasing number of reactions that can be promoted by N-heterocyclic carbenes. Organocatalyzed reactions represent an attractive alternative to metal-catalyzed processes notably because of their lower cost and benign environmental impact in comparison to organometallic catalysis. In this context, N-heterocyclic carbenes (NHCs) have been studied for their ability to promote primarily the benzoin condensation. Lately, dramatic progress in understanding their intrinsic properties and in their synthesis have made them available to organic chemists. This has resulted in a tremendous increase of their scope and in a true explosion of the number of papers reporting NHC-catalyzed reactions. Here, we highlight the ever-increasing number of reactions that can be promoted by N-heterocyclic carbenes. Metal-free catalytic reactions are attractive substitutes to metal-catalyzed processes because of their lower cost and lower environmental impact. N-Heterocyclic carbenes (NHCs) have been used as organocatalysts due to their ability to act as strong Lewis bases.[78] As mentioned in the previous section, theoretical calculations demonstrated that aNHCs are more basic than their nNHC isomers.[79] Mandal and co-workers tested the efficacy of the aNHC **16** in combination with $B(C_6F_5)_3$ (Frustrated Lewis Pairs) towards small molecule activation such as tetrahydofuran (THF), tetrahydrothiophene as well as nitrous oxide (N_2O)[80] (Scheme 13a). Interestingly, aNHC forms a stable Lewis acid-base adduct [aNHC·$B(C_6F_5)_3$] **49** and [aNHC·9BBN][81] **50** with $B(C_6F_5)_3$ and 9BBN, respectively, (Scheme 14).

The superior Lewis basicity of free aNHC **16** was exploited in 2011 for metal-free ring opening polymerization.[82] The aNHC **16** can act as an excellent catalyst at 25 °C for polymerization of three different monomers, *rac*-lactide (*rac*-LA), ε-caprolactone



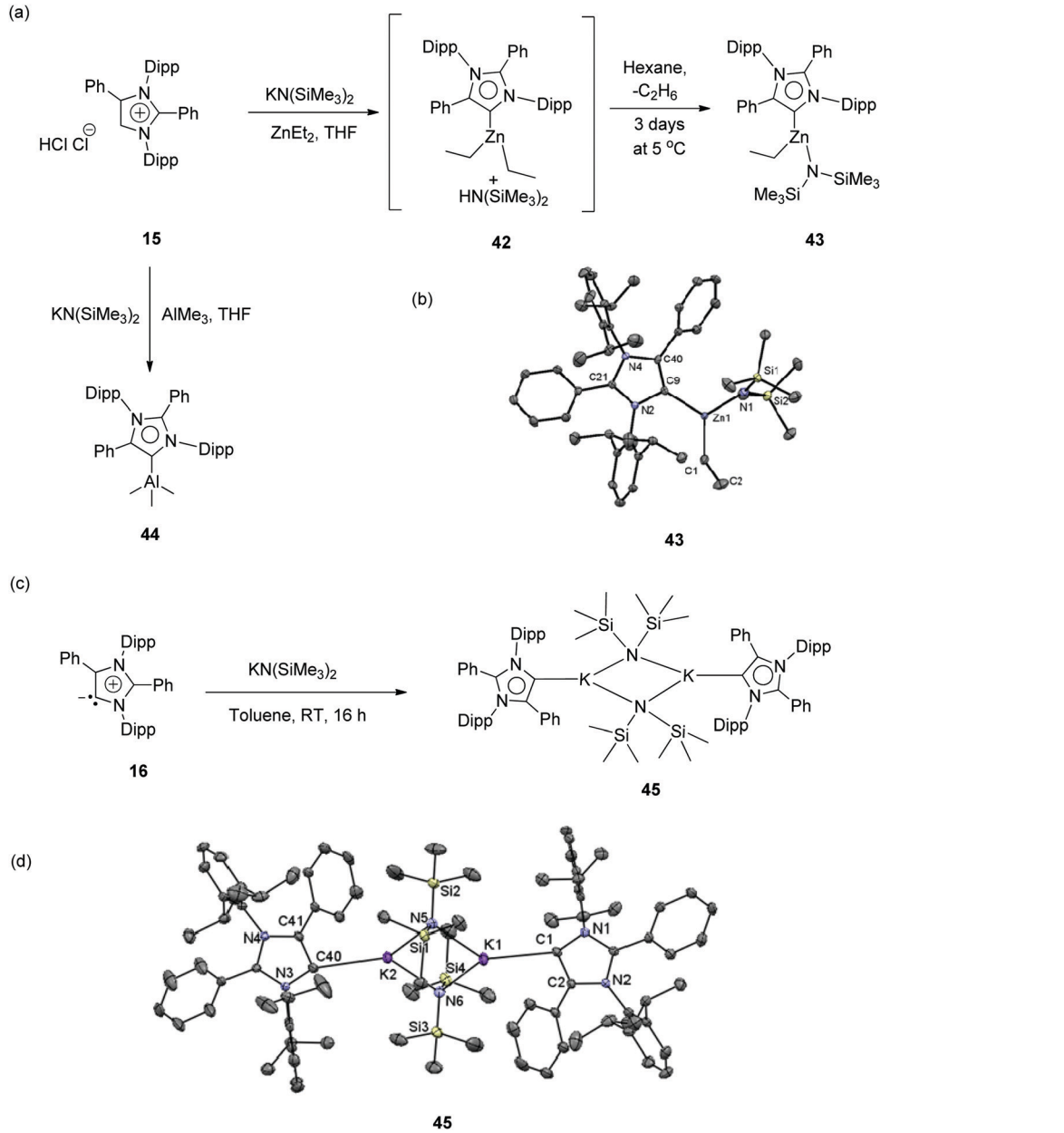
Scheme 9 (a) Synthesis of Fe(0) complex **28** using aNHC **16**; (b) hydrosilylation of various aldimines/ketimines; (c) chemoselective hydrosilylation; (d) hydrosilylation of imines bearing sugar derivatives; (e) plausible catalytic cycle for the hydrosilylation of imines by complex **28**.

(ε-CL) and δ-valerolactone (δ-VL) in the presence of benzyl alcohol (BnOH) as an initiator (Scheme 15). Note an earlier report by Hedrick and co-workers on the use of an nNHC for such ROP at room temperature.[83]



Scheme 10 (a) Reaction of aNHC with $HSiCl_3$, H_2SiCl_2; (b) reaction of nNHC with $HSiCl_3$ and H_2SiCl_2; (c) molecular view of **34** in the solid state; (d) replacement of nNHC with aNHC; (e) reaction of aNHC with $GeCl_2$ and $SnCl_2$; (f) molecular view of **40**.

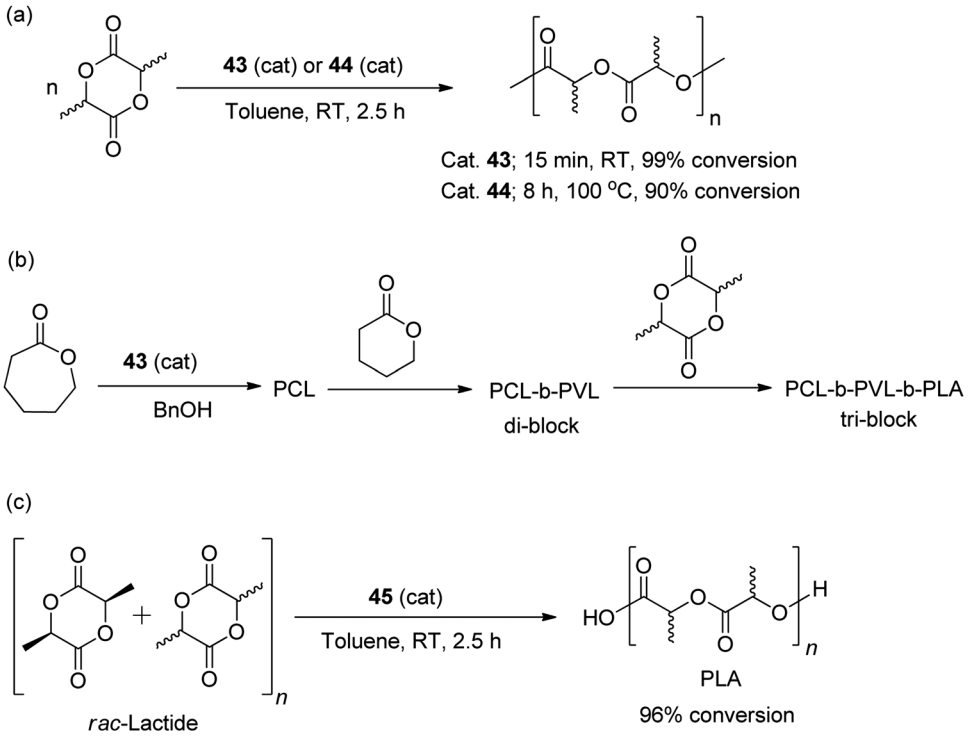
To have insights into the mechanism, several stoichiometric reactions and preliminary DFT calculations were carried out. In the reaction of **16** with a stoichiometric amount of benzyl alcohol, a new highly deshielded ^{1}H signal at δ = 11.5 ppm was observed. The significant shift of free –OH proton ($\Delta\delta$ = 10.3 ppm) in the presence of **16** indicates the creation of a hydrogen bonded



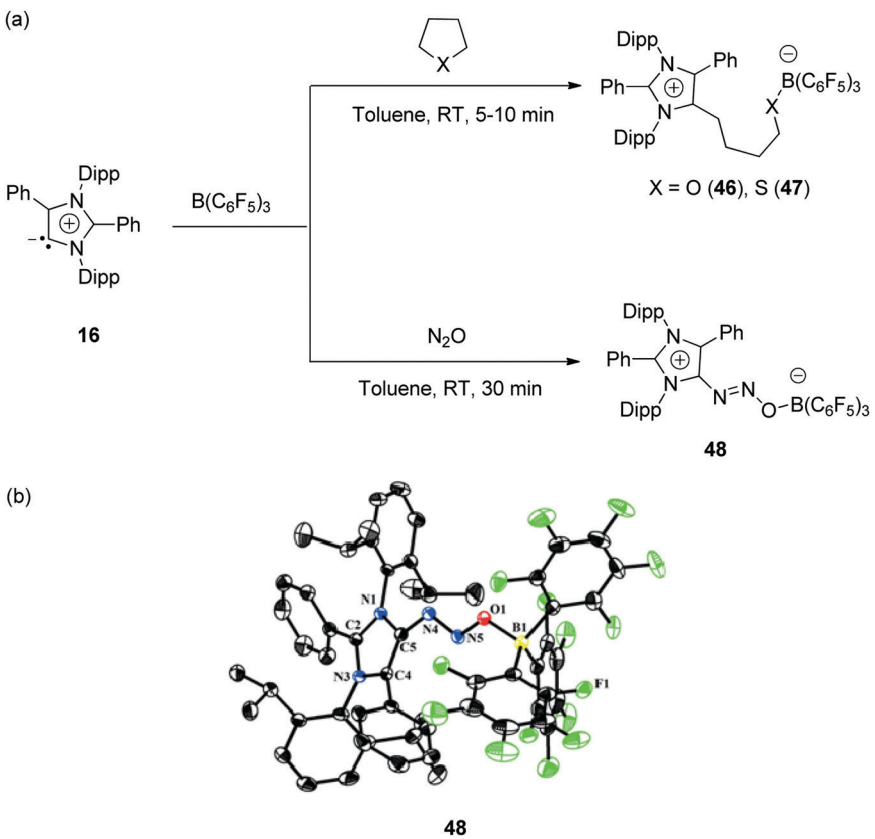
Scheme 11 (a) Synthesis of organozinc (**43**) and organoaluminum (**44**) aNHC complexes; (b) molecular view of **43** in the solid state; (c) synthesis of aNHC based potassium complex; (d) molecular view of **45** in the solid state.

adduct **16a** (Scheme 15b), which was supported by ^{1}H–^{13}C HSQC 2D NMR spectroscopy. The DFT study was carried out on both aNHC **16** and its normal N-heterocyclic carbene analogue. Remarkably, when the HOMO of hydrogen bonded aNHC···BnOH adduct (**16a**) is compared to that of the nNHC···BnOH, a number of important differences appear. The HOMO of the nNHC adduct is lower in energy (−5.151 eV) than the HOMO of the aNHC adduct (−4.947 eV) (Fig. 4). In addition, the NPA (Natural Population Analysis) charge on the carbene carbon of the adduct is significantly less (−0.117 e in aNHC···BnOH, **16a**) compared to that in nNHC···BnOH, (0.108*e*) at the BP86/TZVP//BP86/SVP level of theory.[84] Taking all these data into account, the better nucleophilic character of the carbene carbon in (aNHC···BnOH) explains that aNHCs are more efficient than their nNHC analogues in ring opening polymerization. Motivated by the above observation, the aNHC was further utilized towards the activation of CO_2. Mandal and co-workers established that aNHC reacts with $B(C_6F_5)_3$ in presence of CO_2 to form $[aNHC{\cdot}CO_2{\cdot}B(C_6F_5)_3]$, **51** in 86% yield at room temperature in a very short period of time (Scheme 16a);[88] however, compound **51** could not be reduced further.

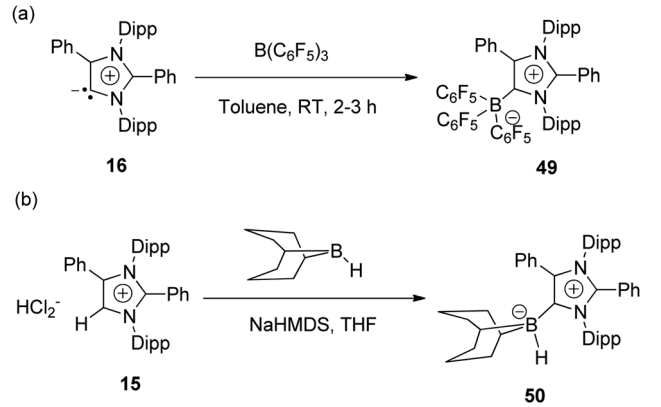
There are two possibilities for the effective utilization of CO_2; (i) its reduction into methane, methanol, formic acid, formaldehyde *etc.*; (ii) its functionalization into urea, polycarbonates, cyclic carbonates *etc.* Combining reduction and functionalization of CO_2, one may consider reductive functionalization



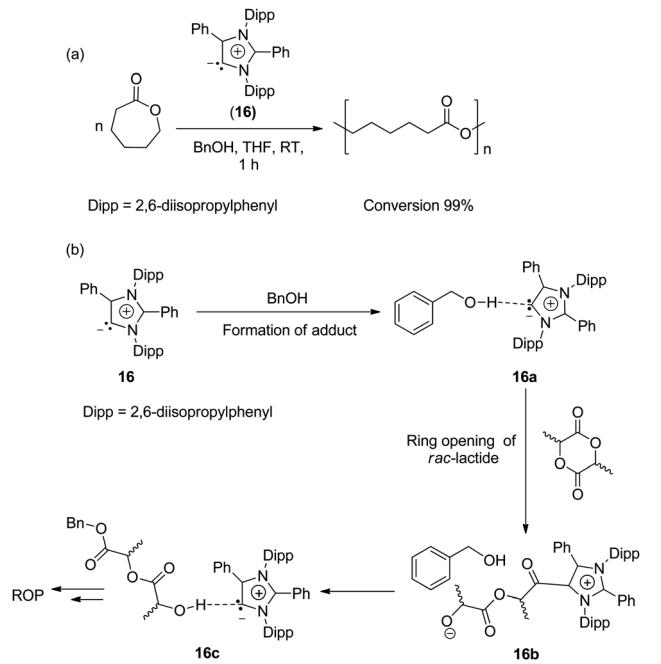
Scheme 12 (a) Ring opening polymerization of *rac*-lactide with **43** and **44**; (b) synthesis of tri-block copolymer **43**; (c) ring opening polymerization of *rac*-LA at room temperature with **45**.



Scheme 13 (a) Activation of small molecules using the first isolated aNHC **16**; (b) molecular view (50% thermal ellipsoids are shown) of **48** in the solid state.



Scheme 14 (a) Lewis acid–base adduct [aNHC·B(C_6F_5)$_3$] **49** with isolated aNHC **16**; (b) Lewis acid–base adduct [aNHC·9BBN] **50** with aNHC salt **15**.



Scheme 15 (a) Polymerization of ε-caprolactone using an aNHC as a catalyst; (b) plausible mechanism for polymerization of cyclic ester with **16**.

which has been well documented as "diagonal transformation" by Cantat *et al.*[85] The reductive functionalization of CO_2 leads to versatile chemicals and energy-storage materials, such as formamides, aminals, and methylamines *etc.*[86,87] Mandal and co-workers reported the first catalytic formylation of amides with CO_2 under ambient and metal-free-conditions (Scheme 17a) expanding the horizon of the "diagonal transformation".[88] A variety of electron-rich and electron-poor amides including heterocycles were tested. The reaction gave rise to the formylated product in good to very good isolated yield.

Several stoichiometric reactions were carried out in order to support the mechanism depicted in Scheme 17b. In the first step, the aNHC **16** captures CO_2 to form the aNHC-carboxylate adduct **52** (Scheme 16b), as previously reported.[33] In the next step, the carboxyl moiety of **52** attacks the Lewis acidic silane

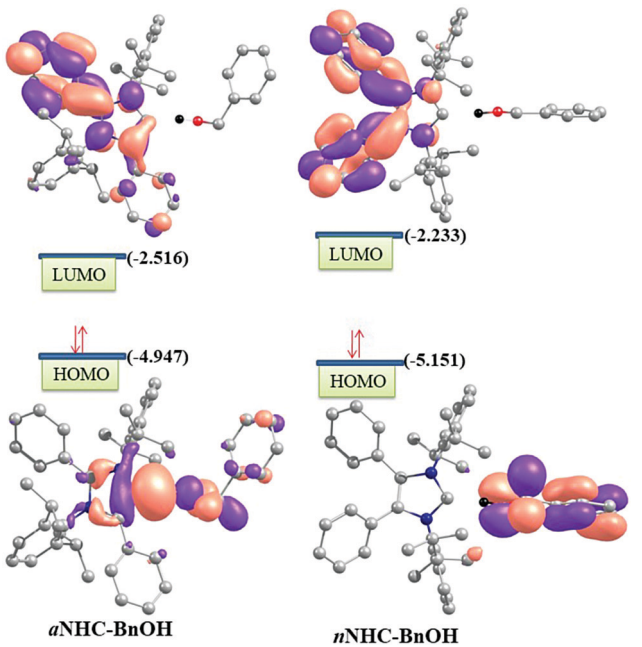
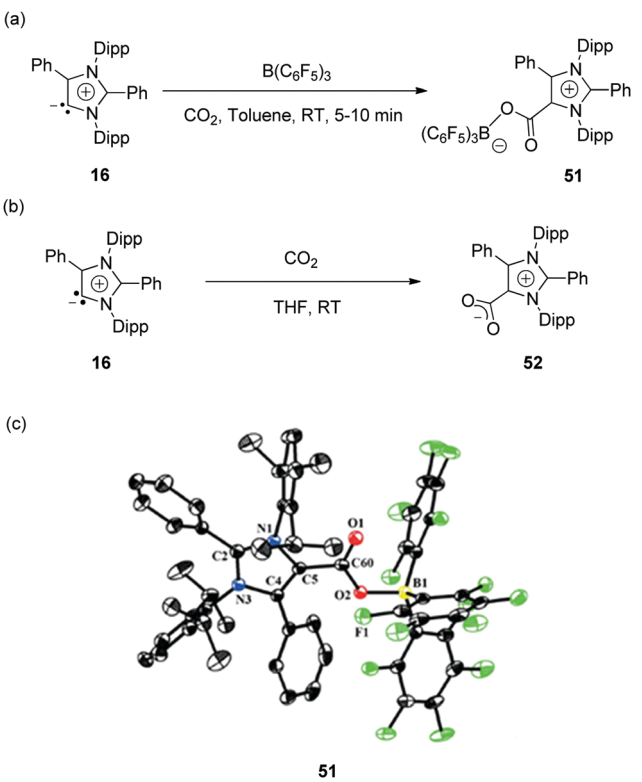
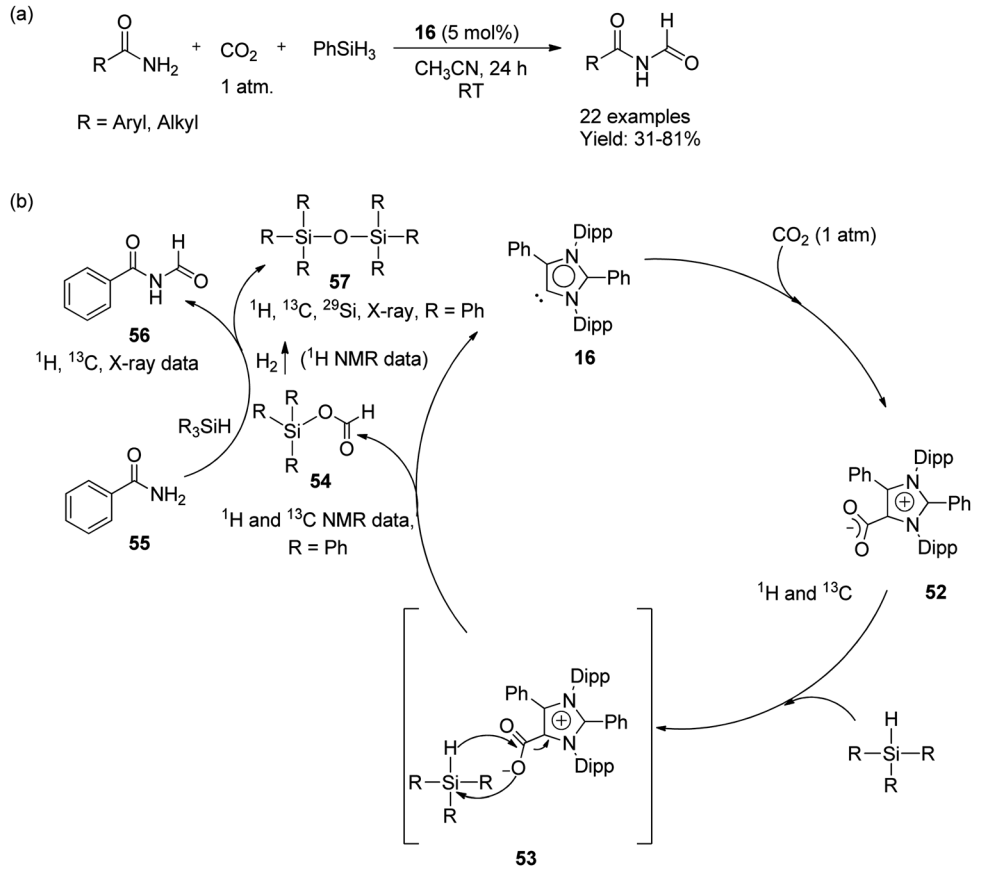


Fig. 4 (a) Frontier KS-molecular orbitals for (aNHC···BnOH) adduct **16a**; (b) Frontier KS-molecular orbitals for (nNHC···BnOH) adduct. The orbital energies are in eVs.

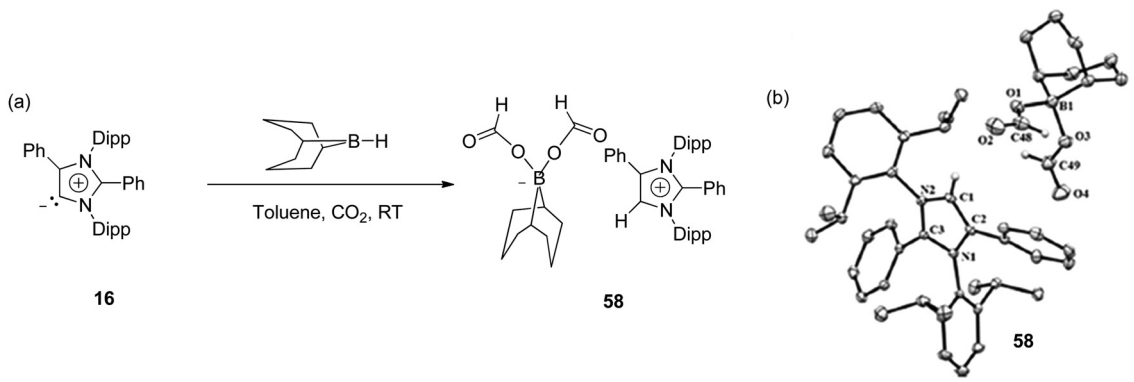


Scheme 16 (a) Activation of carbon dioxide by aNHCB(C_6F_5)$_3$ adduct; (b) activation of carbon dioxide without aNHCB(C_6F_5)$_3$ adduct; (c) molecular view (50% thermal ellipsoids are shown) of **51** in the solid state.

and facilitates the hydride transfer to form formoxysilanes **54**. Simultaneously, the amide **55** undergoes activation with another



Scheme 17 (a) Metal-free formylation of amides with CO_2 under ambient conditions in presence of aNHC **16**. (b) Plausible catalytic cycle.

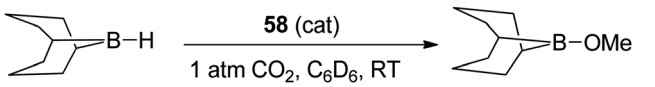


Scheme 18 (a) Isolation of the borondiformate compound **58** as a reaction intermediate; (b) perspective ORTEP view of the borondiformate compound **58**. Hydrogen atoms (except CH-imidazolium and two formate H) have been omitted for the sake of clarity.

molecule of silane in the presence of **16**, which triggers a formyl transfer, affording product **56** with the elimination of $Ph_3SiOSiPh_3$ **57**.

The catalytic reduction of CO_2 into CH_3OH is an important chemical transformation because it can potentially address global warming and provide an alternative source of renewable energy since methanol is considered one of the most promising synthetic fuels.[89–91] Mandal and co-workers used **16** and its CO_2 adduct **52** as efficient metal-free catalysts for the reduction of carbon dioxide to methanol under ambient conditions (CO_2: 1 atm; room temperature) with the help of a range of borane hydrides {HBR_2 = HBcat (catecholborane), HBpin (pinacolborane), 9-BBN (9-borabicyclo[3.3.1]nonane), $BH_3{\cdot}SMe_2$ and $BH_3{\cdot}THF$}.[92] To gain information on the catalytic cycle, several stoichiometric reactions were carried out. A catalytically active compound, [aNHC-H·9BBN$(OCOH)_2$] **58** (Scheme 18) was isolated. The latter exhibited a TON of 6000 for the catalytic reduction of CO_2 to methoxyborane, which is among the highest TON values

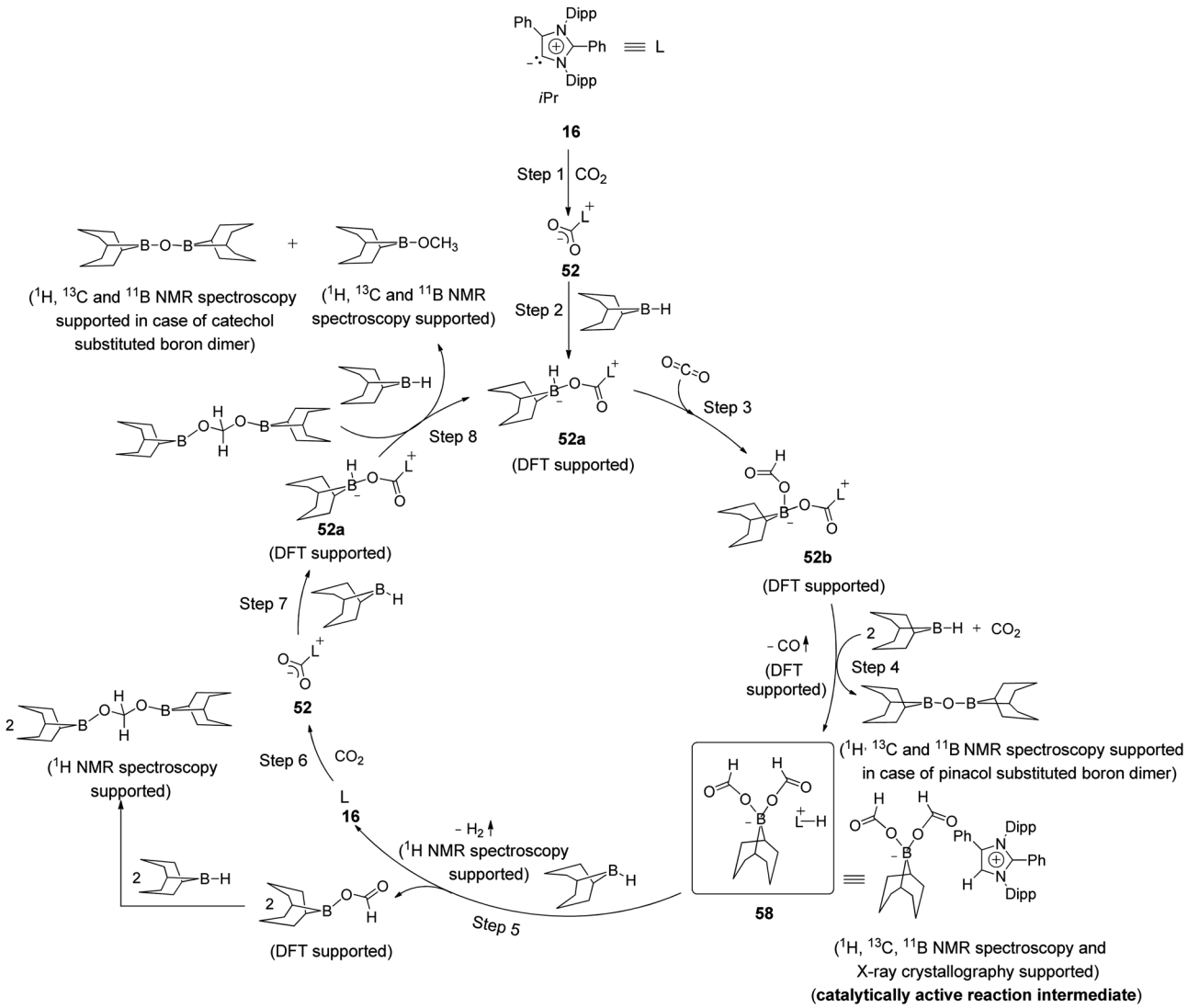
Table 1 Catalytic reduction of CO_2 with hydroborane (9BBN) using **58** as a catalyst under different catalyst loading[a]



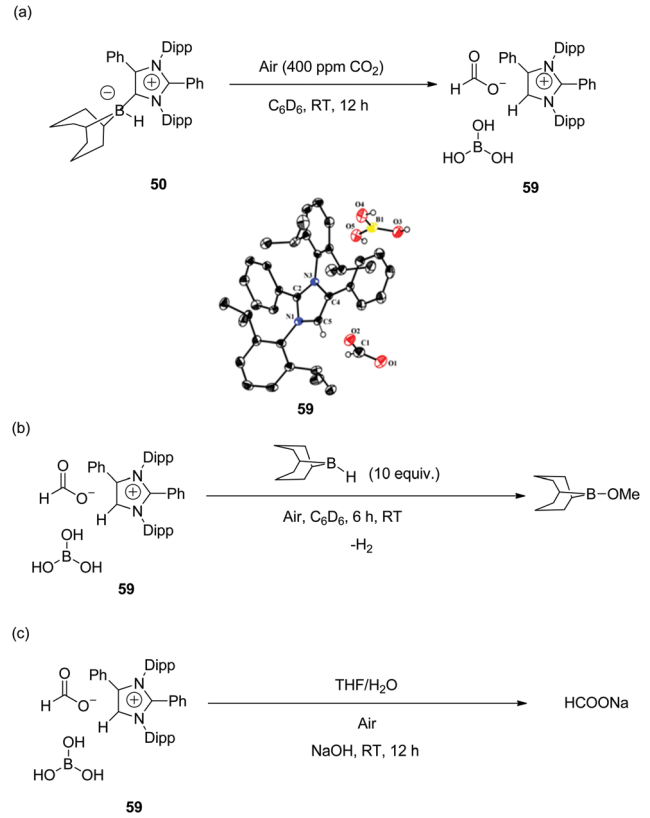
Entry	Catalyst **58** (mol %)	Time (h)	TON[b]
1	0.10	6	380
2	0.01	8	3500
3	0.005	12	6000

[a] Reactions were performed in a 25 mL J. Young Schlenk tube: catalyst **58**, 9-BBN and hexamethylbenzene in 2 mL of C_6D_6 under 1 atm. pressure of CO_2 at RT. [b] Based on the integration of the signal for the methoxy group of CH_3OBR_2, as determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard.

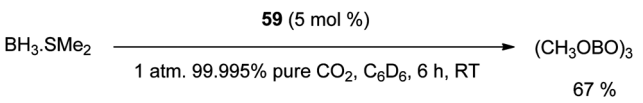
reported under homogeneous and ambient conditions (Table 1). Tandem experimental and computational experiments (Scheme 19) showed that **16** first reacts with CO_2 to give aNHC–CO_2 adduct **52**, which then undergoes a nucleophilic addition to 9-BBN affording **52a**. Subsequent insertion reaction of CO_2 into the B–H bond of **52a** results in a four coordinate compound **52b**, which reacts with 9-BBN to generate the borondiformate salt **58**. Then, another molecule of 9-BBN reacts with **58** to regenerate **16** with the formation of boronformate, which is reduced by 9-BBN to its acetal form $H_2C(OBBN)_2$ and ultimately to methoxyborane, which upon hydrolysis produced methanol. The CO_2 gas used in this study was 99.995% pure. However it is an open challenge to capture carbon dioxide from a low-concentrated source such as air and to reduce it into an alternative fuel under ambient conditions.[93–100] Mandal and co-workers recently reported the metal-free capture of CO_2 from air and its reduction to methoxyborane and sodium formate at room temperature.[101] When a C_6D_6 solution of aNHC–9BBN adduct **50** was left open to ambient air overnight **59** was formed and isolated (Scheme 20a). The single-crystal X-ray study of **59** confirmed that a CO_2 molecule from air was fixed as a formate anion. Treatment of



Scheme 19 Proposed mechanism for the reduction of CO_2 with 9-BBN catalyzed by aNHC **16**.



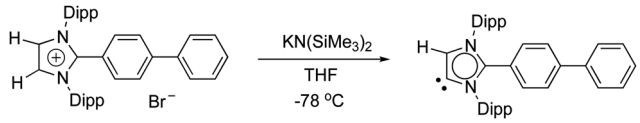
Scheme 20 (a) Capture of carbon dioxide from air with compound **50** and ORTEP view of **59**; (b) reduction of carbon dioxide into methoxyborane in air; (c) reduction of carbon dioxide into sodium formate in air.



Scheme 21 Metal-free catalytic reduction of carbon dioxide into trimethoxyboroxine under ambient conditions.

59 with 10 equivalents of 9-BBN in presence of air quantitatively afforded CH_3OBBN within 6 h (Scheme 20b). Moreover, treatment of **59** with sodium hydroxide at room temperature resulted in the formation of sodium formate (Scheme 20c).

Additionally compound **59** can act as an efficient catalyst for the conversion of CO_2 into trimethoxyboroxine[102] under ambient conditions in presence of a less expensive borane, $BH_3{\cdot}SMe_2$ (Scheme 21).



Scheme 23 Synthesis of stable C-4 protonated aNHC.

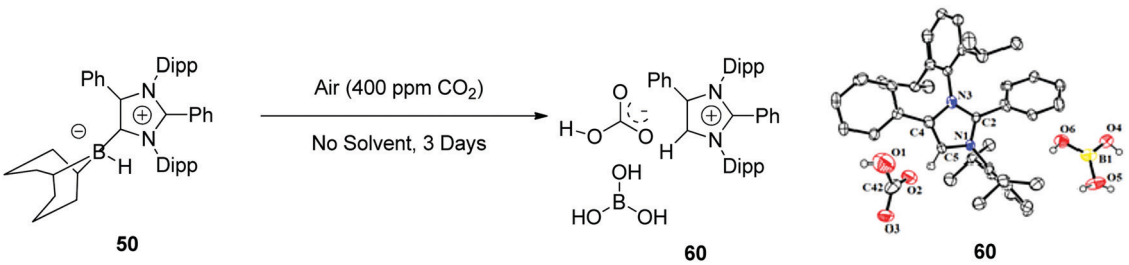
Interestingly, when compound **50**, as a fine powder, was exposed to air for 3 days, the formation of **60** featuring the bicarbonate anion was observed (Scheme 22).[103–105]

Conclusions and perspectives

Although calculations predict aNHCs are less thermodynamically stable than their nNHC isomers by some 10–20 kcal mol^{-1}, they can be isolated. The HOMO is a σ-type lone-pair at C-5 and the HOMO−1 is a C5–C4 π-bonding orbital, both of these MOs are higher in energy than those of nNHCs. Consequently, aNHCs are more basic than the corresponding nNHCs, a statement confirmed by all experimental and computational studies. The substituent at the C-4 of the isolated aNHC **16** is a non-bulky benzene ring, suggesting that a variety of substitution patterns should be tolerated without precluding isolation of the corresponding aNHC. Indeed, a very recent paper by Ghadwal reports the isolation of a C-4 protonated aNHC (Scheme 23).[106] Interestingly, the substituent at C-4 is in conjugation with the carbene center, which opens the possibility of substantially modulating the electronic character of the ring system.

Some aNHC transition metal complexes can be prepared from the imidazolium salts, but this is not the case for aNHC main group adducts, which have already found many applications as exemplified by the aNHC–9BBN adduct which is active for hydrogenation reactions. Obviously, for organocatalysis, stable aNHCs are a must. In this area, the first results are very encouraging as shown by the formylation of amides using CO_2, the reduction of carbon dioxide into methanol in the presence of pure carbon dioxide gas as well as from ultra low concentrated CO_2 sources such as air.

In their excellent review, Glorius *et al.*[9h] wrote "From these beginnings as academic curiosities, N-heterocyclic carbenes today rank among the most powerful tools in organic chemistry, with numerous applications in commercially important processes." Considering that bottle-able NHCs have been discovered almost two decades before aNHCs, we believe that the future of the latter is very exciting.



Scheme 22 Capture of carbon dioxide from air by compound **50**.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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