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David Specklin, Christophe Fliedel, Samuel Dagorne. Recent Representative Advances on the Synthesis and Reactivity of N -heterocyclic-carbene-supported Zinc Complexes. *Chemical Record*, 2021, 21 (5), pp.1130-1143. 10.1002/tcr.202100041 . hal-03204158

HAL Id: hal-03204158

<https://hal.science/hal-03204158>

Submitted on 21 Apr 2021

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Recent Representative Advances on the synthesis and reactivity of *N*-heterocyclic-carbene-supported Zinc Complexes

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Dedicated to Professor Pierre H. DIXNEUF for his outstanding contributions to organometallic chemistry and homogeneous catalysis.

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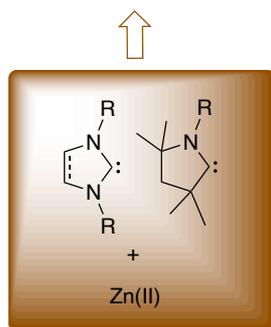
Abstract. The present account reviews the most recent noteworthy developments on the synthesis, structure and catalytic applications of Zn-NHC species, a class of complexes that have attracted attention over the past five to ten years due to their enhanced robustness and hydrolytic stability versus classical Zn organometallics. In particular, thanks to NHC stabilization, access to unprecedented Zn species were recently achieved, including two-coordinate Zn(II) organocations and thermally stable molecularly well-defined Zn hydride species, opening the way to effective Zn-mediated hydro-silylation/-boration catalysis of various unsaturated substrates under mild conditions. The potential of NHC-Zn species for the stabilization of unprecedented Zn species and use in various catalytic applications is only emerging and the vast array of readily available NHC structures should promote future developments of the field.

Keywords: Zinc, *N*-heterocyclic carbene, Lewis acids, catalysis

For Tables of Contents Only

Applications in catalysis

- Reduction of unsaturated substrates (including CO₂)
- Alkylation
- Cross-coupling catalysis



Novel classes of Zn(II) species

- Two-coordinate Zn(II) organocations
- Well-defined Zn(II) hydride species

Introduction

Over the past twenty years, *N*-heterocyclic carbenes (NHCs) have become an ubiquitous class of ligands for coordination to various transition/main group metal/heteroelement centers, which has led to numerous and diversified developments across chemical science, most notably in the areas of metal-mediated homogeneous catalysis, organometallic chemistry and related fundamental reactivity.^{1,2,3,4} The widespread use and success of NHC ligands take their source in the exceptional electronic properties (strong σ -donor) and steric tunability (primarily through the nature of the *N-R* group) of such entities, combined with well-established straightforward synthetic procedures to access NHCs.^{5,6,7,8} NHC coordination to various metal centers/heteroatoms (from carbo- to oxo-philic metals/heteroatoms) frequently provide unprecedented stabilization of the resulting organometallic fragments, which are features of interest for use in catalysis and the characterization of highly reactive organometallics.^{9,10,11,12,13,14,15} Additionally, recent and ongoing research efforts on the design/modifications of NHC heterocyclic backbone have already expanded the electronic/steric tunability (relative to those of classical Arduengo-type carbenes), and thus the potential scope of applications of these carbene ligands.^{8,16}

Zn-based species are notoriously known and have found widespread use as reagents for stoichiometric and catalytic chemical transformations, ranging from their use as Lewis acid catalysts to their frequent employment as alkylating agents for unsaturated substrates functionalization.¹⁷ Given that Zn is a cheap, environmentally benign and readily available metal source, Zn-based species, in particular well-defined Zn organometallics, have recently attracted increased attention for use in small molecules functionalization/activation.¹⁸ Since the first report on a NHC-stabilized Zn(II) species by Arduengo in 1993,¹⁹ NHC-Zn species, thanks to the remarkable kinetic stability of the Zn–Carbene bond, have played a major role in the

recent advancements of Zn organometallic chemistry, allowing access to unprecedented well-defined and highly reactive Zn entities.^{20,21} In addition to the structural interest of a number of NHC-Zn species recently reported, applications of NHC-Zn species in catalysis now spans from their use in alkyne dehydroboration/diboration, allylic alkylation, alkyne/alkene/ CO_2 hydrosilylation to polymerization catalysis of polar monomers. The present account highlights the most recent (5 to 10 years) noteworthy advances, including those from our lab, on the synthesis and reactivity studies of Zn complexes supported by NHCs.

Neutral NHC-Zn alkyl/aryl/halide complexes and related derivatives

ZnX_2 (X = Me, Et, halide) species are widespread reagents in organic chemistry as alkylating/reducing and Lewis acidic reagents/catalysts, but are typically highly moisture-sensitive. NHC adducts of the type $[(\text{NHC})\text{ZnX}_2]$ (X = Me, Et, halide) constitute easier-to-handle ZnX_2 sources and are thus of potential interest for various stoichiometric and catalytic organic reactions. Adducts of the type $[(\text{NHC})\text{ZnX}_2]$ are most frequently prepared by reaction of free NHC with ZnX_2 and afford monomeric ($[(\text{NHC})\text{ZnX}_2]$) or dimeric ($[(\text{NHC})\text{ZnX}_2]_2$) (**1-3**, Figure 1). Over the recent years, a number of monomeric NHC-bearing Zn di-alkyl/-aryl/-alkoxide derivatives were reported^{22,23,24,25} and were primarily used as polymerization catalysts (*vide infra*).^{21,22,26}

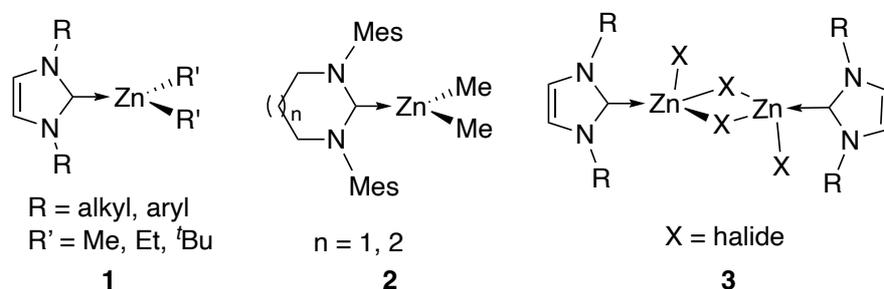
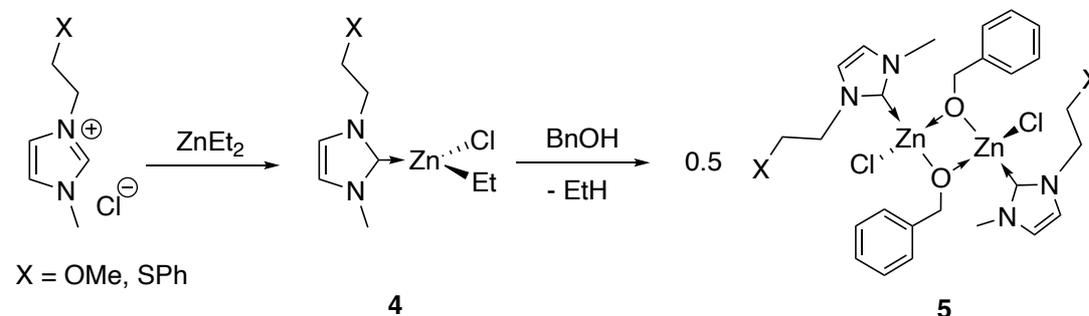


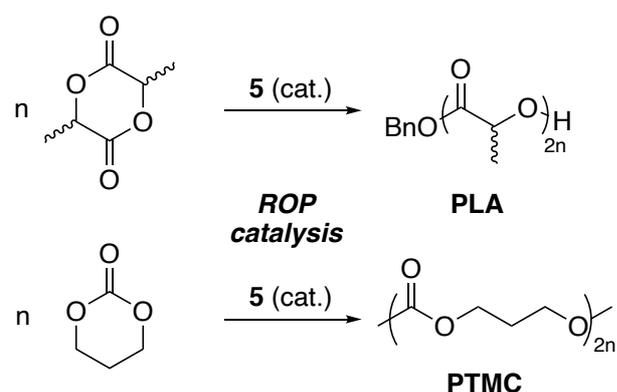
Figure 1. Monomeric $[(\text{NHC})\text{ZnX}_2]$ and dimeric $[(\text{NHC})\text{ZnX}_2]_2$ species

Mixed alkyl chloro derivatives (**4**, Scheme 1) are also accessible *via* a direct protonolysis reaction between ZnR_2 and the corresponding imidazolium chloride, and were readily converted dimeric NHC-Zn alkoxides **5**.^{27,28}



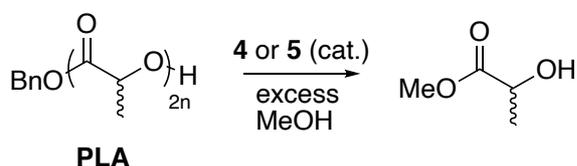
Scheme 1. Synthesis of NHC-Zn complexes **4** and **5**

Species of type **5** were shown to be highly effective ring-opening polymerization (ROP) catalysts of lactide (TOF up to 500 h^{-1} at room temperature), a bio-sourced monomer, for the production of well-defined PLA, a biodegradable polyester with numerous applications and of growing industrial importance (Scheme 2).²⁹ Likewise, trimethylenecarbonate (TMC), a cyclic carbonate available in a few synthetic steps from glycerol,³⁰ is also efficiently polymerized to yield narrow disperse polytrimethylenecarbonate (PTMC), a biodegradable material currently used on the biomedical area (Scheme 2).³¹ These ROPs proceed *via* initial monomer insertion/ring-opening into the Zn–OBn bond and subsequent chain growth, allowing access to chain-length-controlled poly-esters/-carbonates. All data suggest the non-involvement of the NHC moiety and thus with a stable Zn–NHC bond as the ROP proceeds.



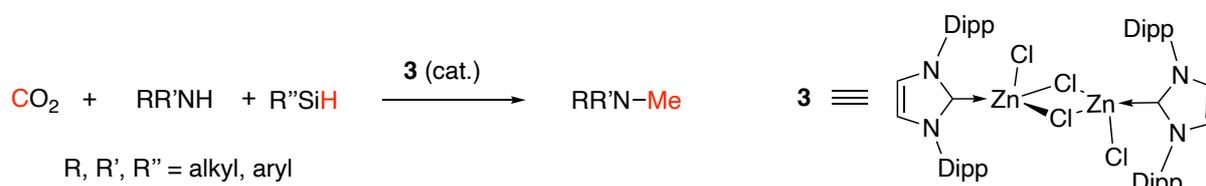
Scheme 2. ROP catalysis mediated by NHC-Zn benzyloxide species **5** for the production of biodegradable polyesters and polycarbonates.

Interestingly, NHC-Zn species **4** and **5** also catalyze the controlled degradation of PLA to methyl lactate at room temperature in the presence of a large excess of MeOH (100 equiv vs. **4** or **5**, Scheme 3). Remarkably, control experiments indicate the Zn-NHC bond essentially retains its integrity under such conditions, indicating the remarkable kinetic stability of the Zn-C_{carbene} bond towards methanolysis.²⁷



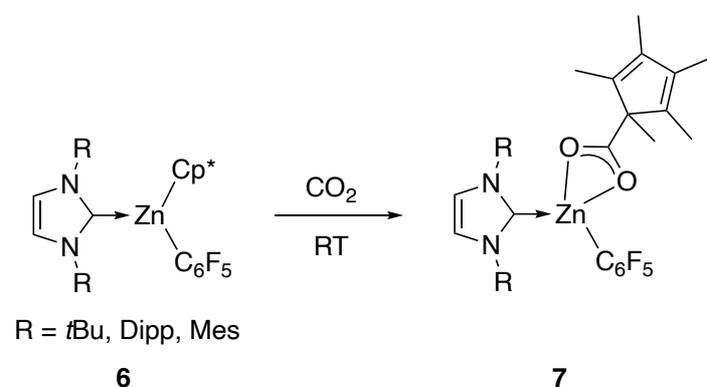
Scheme 3. Controlled degradation of PLA mediated by NHC-Zn species **4** and **5**

The robustness of [(NHC)ZnX₂] species was also exploited for stoichiometric and catalytic CO₂ functionalization/reduction. Thus, dimer [(IDipp)ZnCl₂]₂ was successfully used as catalyst for the efficient production of methylamines through methylation of secondary amines with CO₂ and hydrosilanes (Scheme 4).³² The catalytic formation of C-N bonds through the use of CO₂, a cheap and renewable C1 source, along with an inexpensive metal source such as Zinc is of interest. For instance, a *N*-methylaniline/PhSiH₃ mixture under CO₂ (1 bar) may be quantitatively converted to Me₂NPh (20 h, 100 °C). The role of the NHC-Zn moiety appears crucial for the catalysis to proceed efficiently since commercial ZnX₂ (X = Cl, Br) salts are much less effective catalysts. The reaction is proposed to occur *via* the formation of a formyl species, then hydrosilylated to the final product.



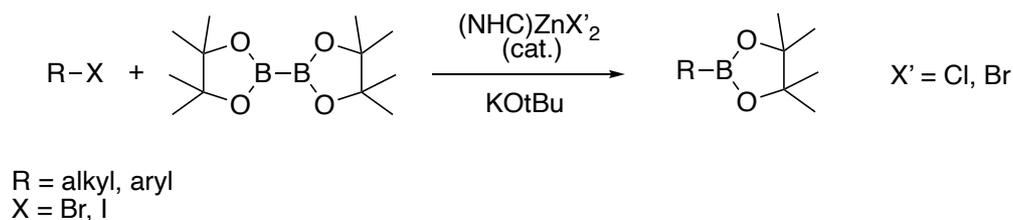
Scheme 4. Reductive methylation of secondary amines catalyzed by a NHC–ZnCl₂ species.

The reactivity of NHC-Zn adducts of the type [Cp*Zn(C₆F₅)(NHC)] (**6**, Scheme 5) with CO₂ was also studied.³³ Interestingly, the stoichiometric reaction of **6** with CO₂ exclusively proceeds through insertion into the C_{Cp*}–Zn bond to afford the corresponding mononuclear Zn carboxylate derivative **7** (Scheme 5), with thus the NHC–Zn moiety retaining its integrity. In the present system, NHC coordination is clearly beneficial since CO₂ insertion proceeds much faster and under milder conditions than that of “base-free” [Cp*Zn(C₆F₅)].



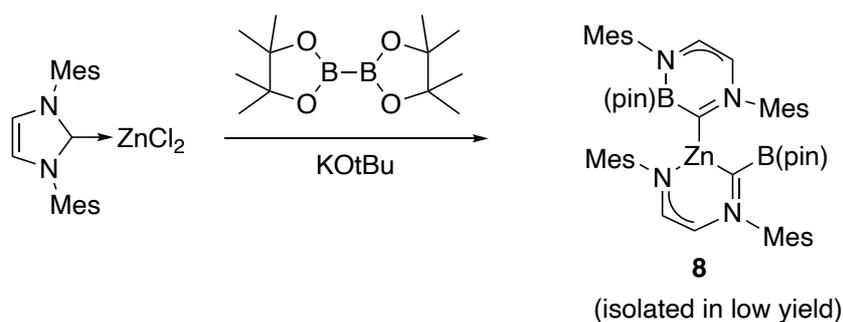
Scheme 5. CO₂ insertion reactivity of NHC-Zn adducts of the type [Cp*Zn(C₆F₅)(NHC)]

Several [(NHC)ZnX₂] (X = Cl, Br) adducts were recently shown to catalyze the cross-coupling of diboron reagent B₂(pinacolate)₂ with alkyl/aryl halides (Scheme 5).^{34,35} Such catalysis, which proceeds at room temperature, is most efficient with IMes as the NHC source. The mechanism of such Zn-catalyzed borylation of alkyl/aryl halides is likely to go through a radical process based on experimental data.



Scheme 5. Alkyl/aryl halides cross-coupling catalysis mediated by NHC-stabilized Zn(II) dihalides.

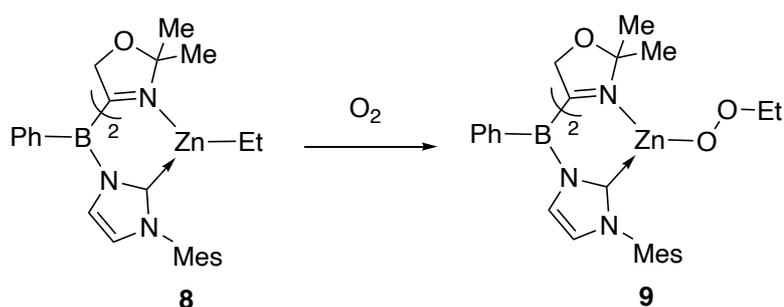
Control experiments on the reactivity of (NHC)ZnX₂ species with B₂(pinacolate)₂ in the presence of ^tBuOK evidenced the limited stability of the NHC-Zn moiety under such conditions. Thus, the stoichiometric reaction between [(IMes)ZnCl₂] with a 1/1 B₂(pinacolate)₂/^tBuOK mixture unexpectedly led to the isolation of the ring-expanded product **8** (Scheme 6), whose structure was confirmed through X-ray diffraction studies.³⁴ The formation of **8**, a compound that may be described as a di-carbenoid-type species, formally arises from Zn insertion into the C_{carbene}-N bond of a NHC while a B(pinacolate) group inserts in a similar manner in another NHC moiety.



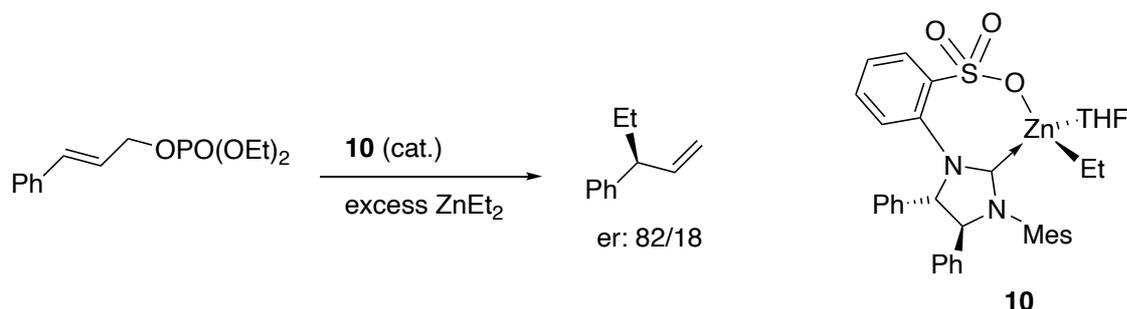
Scheme 6. Isolation of species **8** from the reaction of [(IMes)ZnCl₂] with a (pin)B-B(pin)/^tBuOK mixture

Chelating ligand platforms incorporating a NHC group were also investigated for coordination to Zn(II) and led to advances in fundamental reactivity and Zn-based catalysis. As noteworthy examples, the use of an anionic tridentate NHC-*bis*-oxazoline borate ligand for the stabilization of a rare example of well-defined Zn(II) peroxo derivative (**9**, Scheme 7), generated through an insertion reaction of O₂ with the corresponding Zn-Et precursor **8**.³⁶ Further, various (NHC)Zn supported by a chiral bidentate NHC-bearing ligand, such as **10** (Scheme 8), were demonstrated to be highly active catalysts for the enantioselective alkylation

of allylic substrates (using ZnEt_2 as an alkyl source) with an excellent regioselectivity ($> 98\%$) and a good enantioselectivity (enantiomeric ratio: 82/18; Scheme 8).³⁷ All experimental data are consistent with Zn(II) chelate **10** acting as a bifunctional catalyst: *i.e.* as a Lewis acid (with coordination of the allylic substrate to the Zn(II) center) and a Lewis base (with the coordination of the sulfonate function to ZnEt_2), such cooperation being crucial to the activity and selectivity of the catalytic process.



Scheme 7. O_2 insertion reactivity of NHC-Zn ethyl chelate **8** to afford (NHC)Zn peroxide **9**.

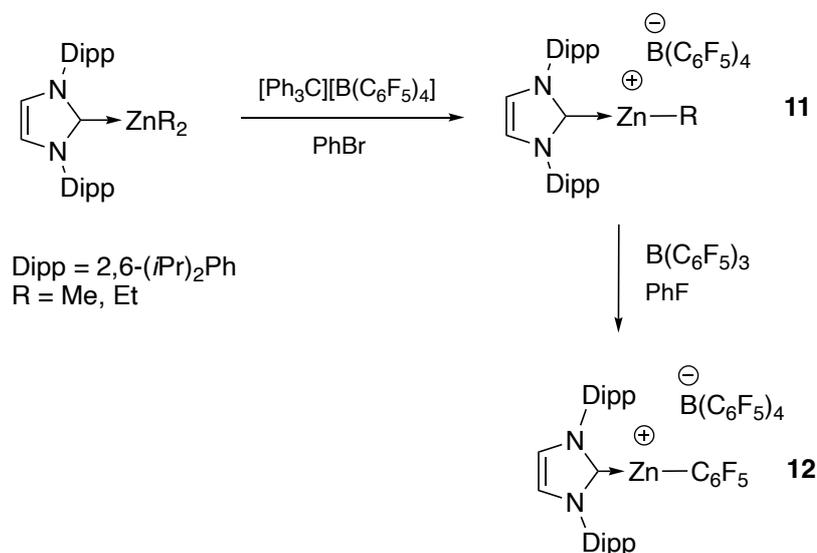


Scheme 8. Allylic alkylation catalyzed by chiral NHC-supported Zn(II) species **10**.

Low-coordinate NHC-stabilized Zn alkyl/aryl Cations

The exceptional σ -donating of NHCs recently allowed the isolation and structural characterization of the first two-coordinate Zn(II) organocations.³⁸ Thus, ionization of $[(\text{IDipp})\text{ZnR}_2]$ adducts ($\text{R} = \text{Me}, \text{Et}$) with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ led to the corresponding cations $[(\text{IDipp})\text{Zn-R}]^+$ (**11**, Scheme 9) as stable two-coordinate Zn(II) cations. Derivatization of the Zn-alkyl cations of type **11** with $\text{B}(\text{C}_6\text{F}_5)_3$ quantitatively yielded the more electrophilic $[(\text{IDipp})\text{Zn-C}_6\text{F}_5]^+$ cation **12** (Scheme 9), also a thermally stable Zn(II) cation. Lewis acidity

experimental estimation (using the Gutmann-Beckett method) of those cations agree with cation **12** being the most Lewis acidic of the series with a comparable Lewis acidity to landmark $\text{B}(\text{C}_6\text{F}_5)_3$. Yet, the DFT-estimated Fluoride Ion Affinity (FIA, calculated in the gas phase) of cation **12** suggests a stronger Lewis acidity than $\text{B}(\text{C}_6\text{F}_5)_3$. The molecular structures of cations **11** and **12**, depicted in Figure 2 in the case of **12**, display a nearly linear $\text{C}_{\text{carbene}}\text{-Zn-C}$ array (angles close to 180°). When crystallized from CH_2Cl_2 , the solid state data for salts [**11-12**][$\text{B}(\text{C}_6\text{F}_5)_4$] agree with discrete $[(\text{IDipp})\text{Zn-R}]^+$ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ions with no apparent cation/anion short contacts. Yet, in solution (CD_2Cl_2 , RT), ^1H and ^{19}F DOSY NMR data for $[(\text{IDipp})\text{Zn-Me}][\text{B}(\text{C}_6\text{F}_5)_4]$ are consistent with weakly interacting anions and cations, while data for $[(\text{IDipp})\text{Zn-C}_6\text{F}_5][\text{B}(\text{C}_6\text{F}_5)_4]$, which bears a more electrophilic but also slightly more sterically crowded Zn(II) center, agree with dissociated anions under the studied conditions.



Scheme 9. Synthesis of two-coordinate NHC-Zn cations **11** and **12**.

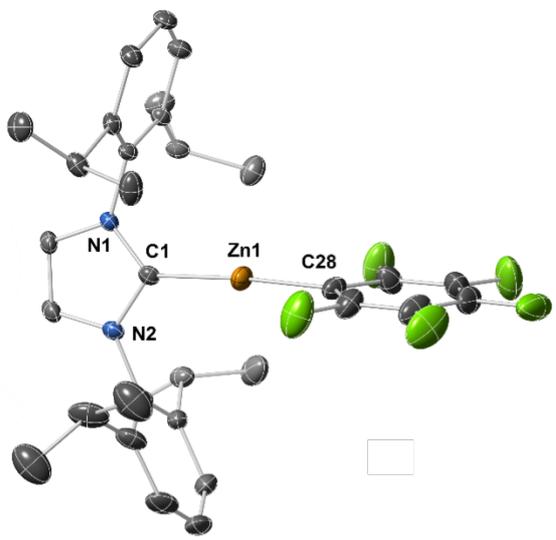
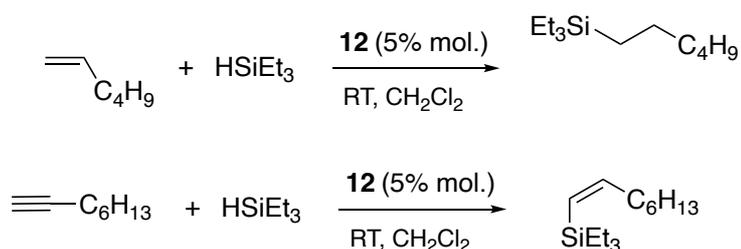


Figure 2. Molecular structure (ORTEP view) of cation **12**.

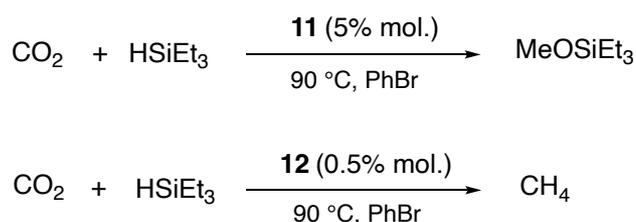
Thanks to its Lewis acidity, two-coordinate cation **12** is an effective catalyst for alkene and alkyne hydrosilylation. Cation **12** catalyzes 1-hexene hydrosilylation (with H–SiEt₃) at RT to selectively afford Et₃Si–C₆H₁₃ through an *anti*-addition of HSiEt₃ to the alkene moiety (Scheme 10). Likewise, it readily mediates 1-octyne hydrosilylation to selectively yield the corresponding *Z*-isomer vinylsilane product (Scheme 10). These hydrosilylations likely proceed through a Lewis-acid-type catalysis similar to those documented for strong group 13 element Lewis acids such as B(C₆F₅)₃.³⁹



Scheme 10. Alkene and alkyne hydrosilylation catalysis mediated by cation **12**.

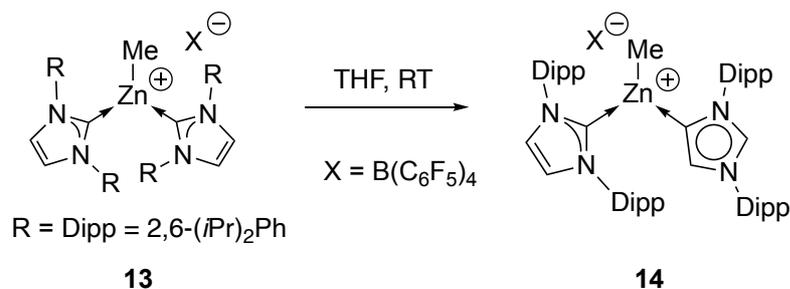
Interestingly, upon heating, cation **12** is also an efficient catalyst for CO₂ hydrosilylation to selectively afford methane along siloxane by-products (Scheme 11). At best, cation **12** (0.5 mol %) quantitatively converted a HSiEt₃/CO₂ mixture to methane within 23 h at 90 °C in PhBr,

reflecting the effectiveness and robustness of such NHC-stabilized Zn electrophiles. In the case of the less Lewis acidic Zn cations of type **11**, CO₂ hydrosilylation catalysis under identical reaction conditions led to the selective formation of the methanol-equivalent methoxy product MeO-SiEt₃. As a comparison, Et₂O-supported Zn-R⁺ cations of the type (Et₂O)₃Zn-R⁺ (R = Me, Et, C₆F₅) exhibit no alkene, alkyne and CO₂ hydrosilylation catalytic activity under similar reaction conditions.



Scheme 11. CO₂ hydrosilylation catalysis performed by NHC-Zn cations **11** and **12**.

Bis-NHC three-coordinate Zn(II) organocations such as **13** and **14** (Scheme 12) were also reported and illustrate the adaptability of NHC coordination to Zn(II) for improved stability and well-defined reactivity.⁴⁰ Thus, the initially prepared *tris*-organyl Zn(II) cation [(IDipp)₂Zn-Me]⁺ (**13**), a severely crowded species bearing two C2-bonded NHC ligands (Figure 3), readily isomerizes in the presence of a Lewis base such as THF to [(IDipp)(*a*IDipp)Zn-Me]⁺ (**14**, Scheme 12 and Figure 3), in which one of the NHC ligands is now C4/C5 bonded to the Zn(II) center. Steric relief for improved stability is clearly the driving force of the isomerization of **13** to **14**, as was further rationalized by DFT calculations.



Scheme 12. THF-catalyzed isomerization of *bis*-NHC Zn(II) cation **13** to **14**.

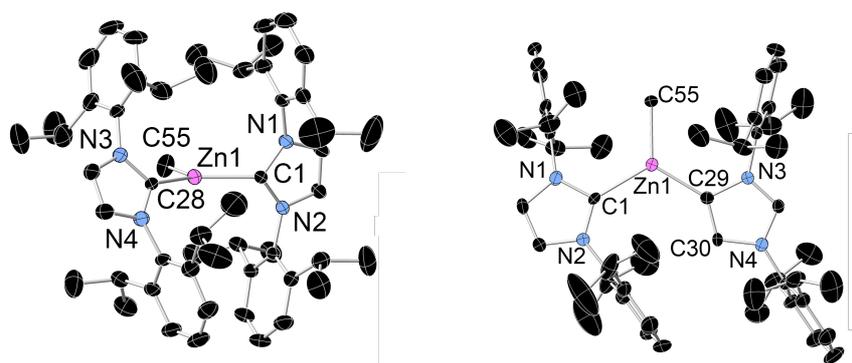
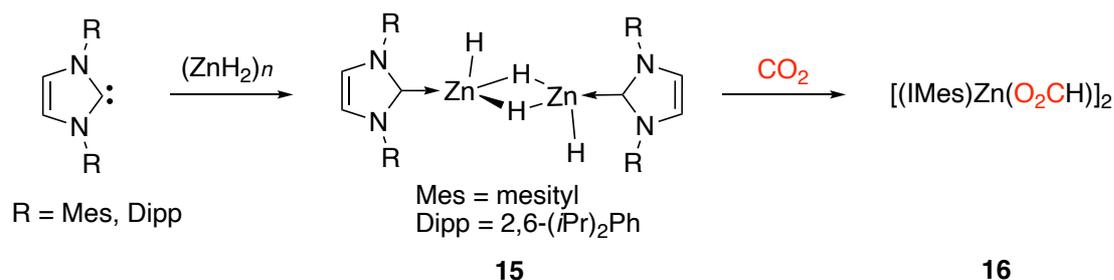


Figure 3. Molecular structures of *bis*-NHC Zn cationic isomers **13** (left) and **14** (right)

Unlike **13**, cation **14** cleanly reacts with CO₂ at RT through CO₂ insertion into the Zn–Me bond to produce [(IDipp)(*a*IDipp)Zn–OAc]⁺, the first instance of a well-characterized product from CO₂ insertion into a Zn–alkyl bond. Species **14** also mediates CO₂ hydrosilylation (using H-Si(OEt)₃ as a hydrosilane source) but, contrasting with the two-coordinate Zn(II) cations **11** and **12** (*vide supra*), the reduction catalysis stops at the first reduction formate product, *i.e.* HCO₂Si(OEt)₃, in line with a lower Lewis acidity for three-coordinate Zn species **14**.

NHC-supported Zn hydrides

Over the past few years, NHC coordination to Zn(II) has led to significant advances on the characterization and reactivity studies of molecularly well-defined Zn–H species, which are of interest as well-defined and soluble reduction agents.⁴¹ Thanks to NHC coordination, discrete molecular adducts of ZnH₂ were first reported as [NHC–ZnH₂]₂ dimeric adducts (**15**, Scheme 13 and Figure 4) by reaction of IDipp/IMes and ZnH₂.⁴²



Scheme 13. Synthesis of NHC-ZnH₂ adduct **15** and its insertion reactivity with CO₂.

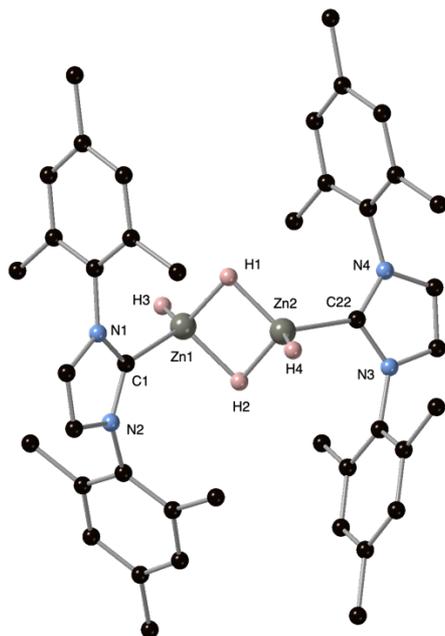
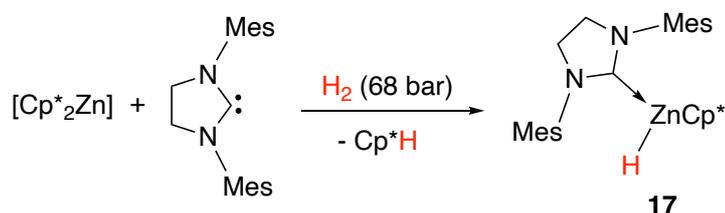


Figure 4. Molecular structure (ORTEP view) of [IMes-ZnH₂]₂ (**12**)

Species [IMes-ZnH₂]₂ readily reduces CO₂ under mild conditions through CO₂ insertion in the Zn-H bonds to quantitatively afford the formate insertion product [(IMes)Zn(O₂CH)]₂ (**16**, Scheme 13).^{42,43} Adduct **15** is also a highly effective catalyst for the catalytic dehydrogenative methanolysis of hydrosilanes to silylether products.

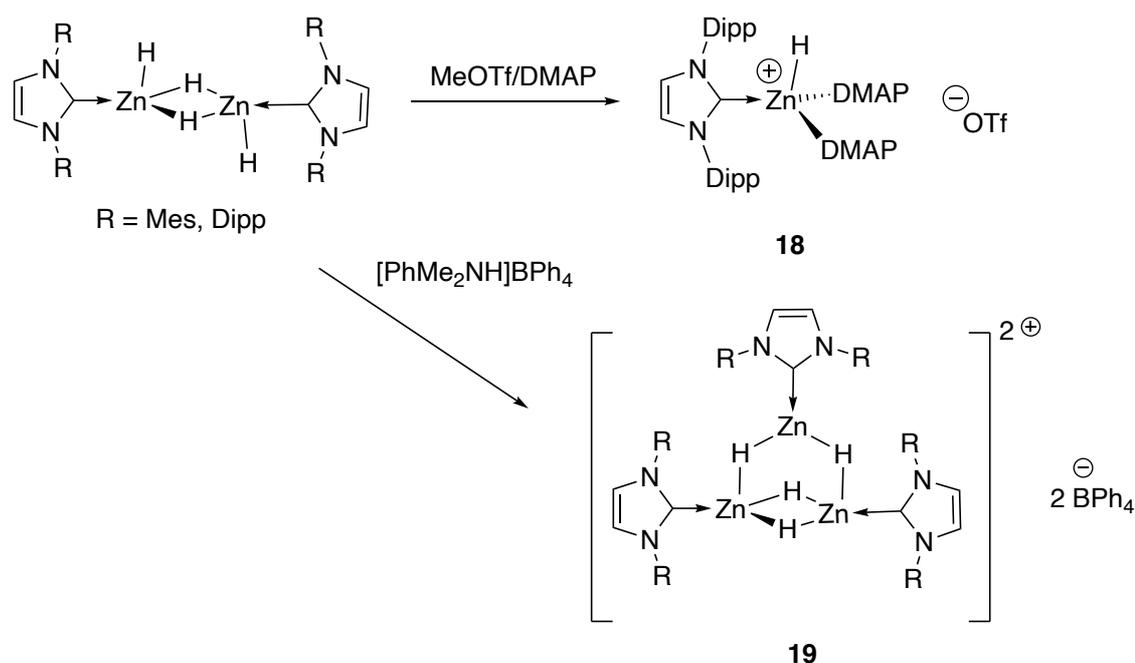
Monomeric (NHC)Zn-H species are also viable species as demonstrated by the preparation of complex **17** (Scheme 14) through hydrogenation of zincocene [Cp*₂Zn] (Cp* = pentamethylcyclopentadienyl) with H₂ (68 bar) in the presence of SIMes.⁴⁴ The Zn-H species

17 may be involved in Zn-catalyzed imine hydrogenation catalysis starting from a $[\text{Cp}^*_2\text{Zn}]/\text{NHC}$ mixture as pre-catalyst.⁴⁴



Scheme 14. Synthesis NHC-Zn hydride species **17** through hydrogenation of $[\text{Cp}^*_2\text{Zn}]$ in the presence of carbene SIMes.

The ability of NHCs to stabilize reactive Zn-based moieties was further evidenced by the recent synthesis and characterization of a monomeric NHC-supported Zn–H cation $[(\text{IDipp})\text{Zn}(\text{H})(\text{DMAP})_2]^+$ (**18**, DMAP = dimethylaminopyridine, Scheme 15 and Figure 5), the first instance of a molecularly well-defined Zn–H cation, *via* reaction of MeOTf with neutral precursor $[(\text{IDipp})\text{ZnH}_2]_2$ in the presence of DMAP.⁴⁵ Dimer $[(\text{IMes})\text{ZnH}_2]_2$ may also be ionized with $[\text{PhMe}_2\text{NH}][\text{BPh}_4]$ in the presence of THF to trinuclear Zn–H dication **19** (Scheme 15).⁴⁶



Scheme 15. Synthesis of NHC-supported Zn–H cations **18** and **19**.

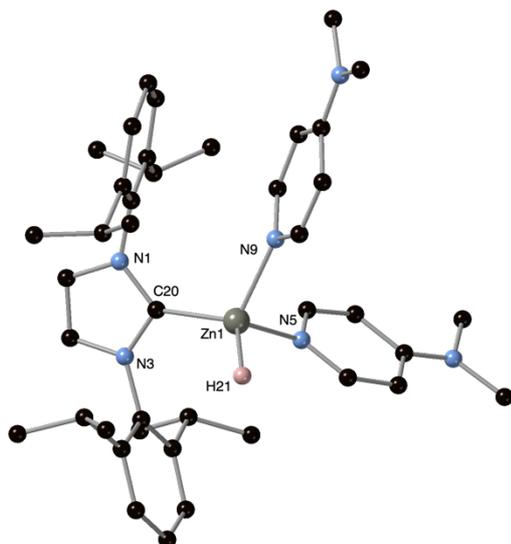
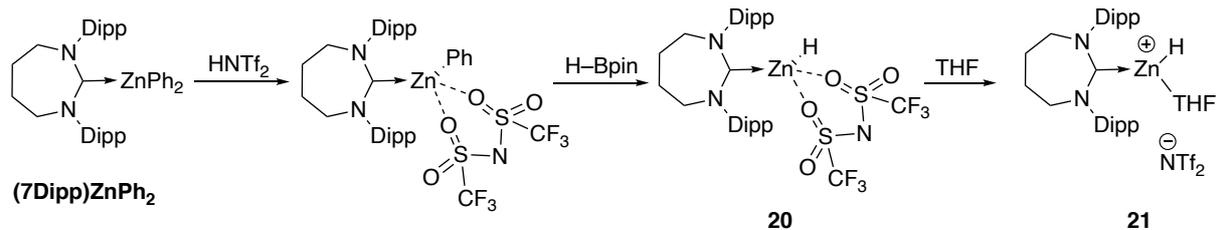


Figure 5. Molecular structure (ORTEP view) of cation [(IDipp)Zn(H)(DMAP)₂]⁺ (**18**).

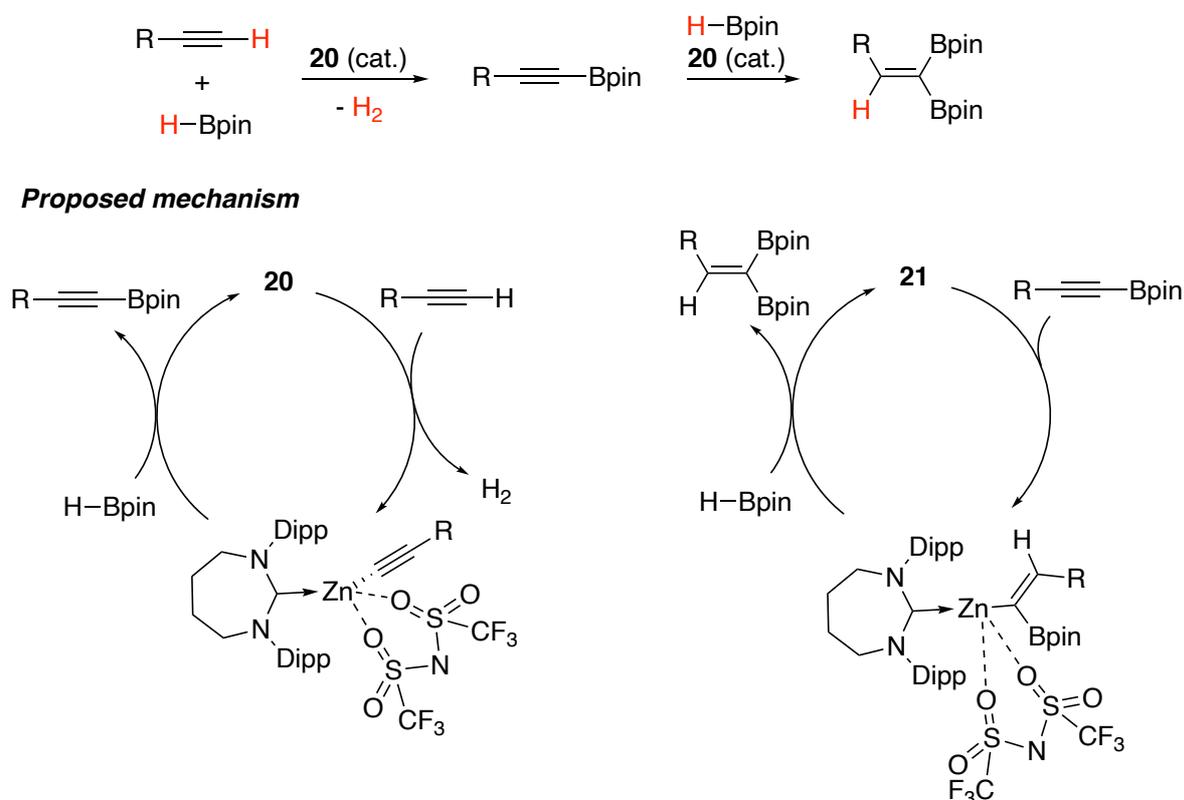
These electrophilic Zn–H cations may be used as catalysts for carbonyls and nitriles reduction under mild conditions, with insertion of the C=X (X = O, N) group into the Zn–H bond as the key reduction step. For instance, cation **19** (1 mol%) catalyzes CO₂ reduction (60 °C, 40 bar of CO₂) to form HCO₂Si(OEt)₃ as the major product (> 80%), while it mediates nitriles mono-hydrosilylation catalysis (to *N*-silylated imine products) at room temperature. Both cations **18** and **19** are highly efficient hydrosilylation catalysts of ketones (to the corresponding silyl ether products) at room temperature using down to 0.1 mol% of Zn catalyst and TOFs up to 475 h⁻¹.^{45,46}

The Zn–H ion pair [(7Dipp)Zn(H)][NTf₂] (**20**, 7Dipp = 1,3-bis(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-1H-1,3-diazepin-3-ium-2-ide; Scheme 16), in which the cationic Zn(II) center is supported by a more sterically protecting 7-membered ring NHC ligand (*vs.* classical 5-membered ring NHCs), was recently synthesized by a σ -bond Zn–C/H–B metathesis reaction, between [(7Dipp)Zn(Ph)][NTf₂] and pinacolborane (HBpin).^{47,48} Ion pair **20** readily dissociates in the presence of THF to afford a Zn–THF cationic adduct as a dissociated [NTf₂]⁻ salt (**21**, Scheme 16).



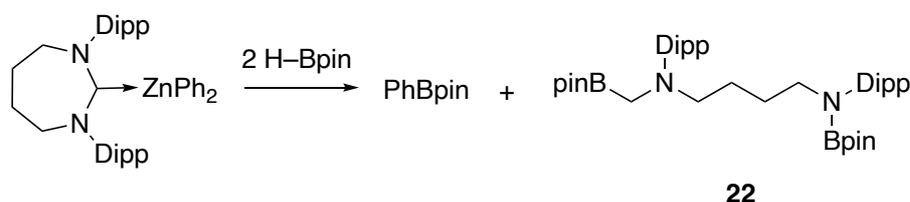
Scheme 16. Synthesis of the NHC-stabilized Zn–H compounds **20** and **21**.

Interestingly, compound **20** was successfully used in alkyne dehydroboration and alkynyl boronic esters hydroboration catalysis (Scheme 17). Thorough experimental and computational studies of these catalysis support the mechanistic proposal depicted in Scheme 17, in which σ -bond Zn–C/H–B metathesis and hydrozincation of the alkynyl dehydroboration product are two crucial reaction steps for these catalytic processes to occur.



Scheme 17. Sequential alkyne dehydroboration and hydroboration catalysis mediated by NHC-Zn species **20** and the associated mechanism.

It is important to note that the steric protection of Zn(II) provided by carbene 7Dipp provides an enhanced stability, which appears to be crucial for an effective catalysis under the reaction conditions. As a comparison, under identical reaction conditions, using IDipp instead of 7Dipp for coordination to Zn(II) only led to marginal catalytic activity due to decomposition of the Zn catalyst. The limited stability of the NHC–Zn moiety under hydroboration conditions was evidenced by the formation of the NHC-ring-opened product **22** (Scheme 18) from the reaction between [(7Dipp)ZnPh₂] with 2 equiv HB(pin).



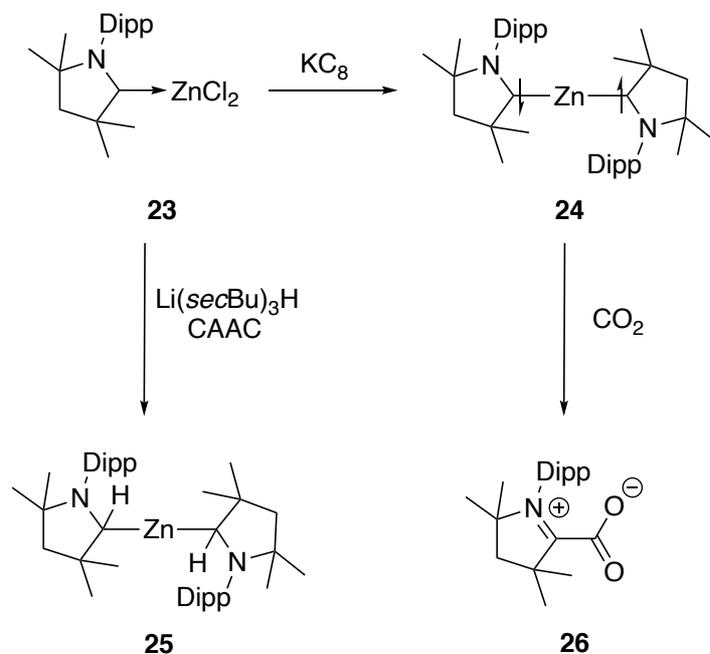
Scheme 18. Reaction of H–Bpin with adduct [(7Dipp)ZnPh₂]

CAAC-supported and diamido-carbene-supported Zn species

Cyclic Alkyl Amino Carbene (CAAC) ligands are NHCs displaying stronger σ -donating and π -accepting properties compared to classical Arduengo-type NHCs. As such, CAACs have drawn growing attention over the past few years due to their unique ability for the stabilization of various organometallic moieties, most notably low-valent metal centers, and the fact that CAAC metal/heteroelement species may display distinct reactivity relative to classical NHC-stabilized analogues.^{49,50}

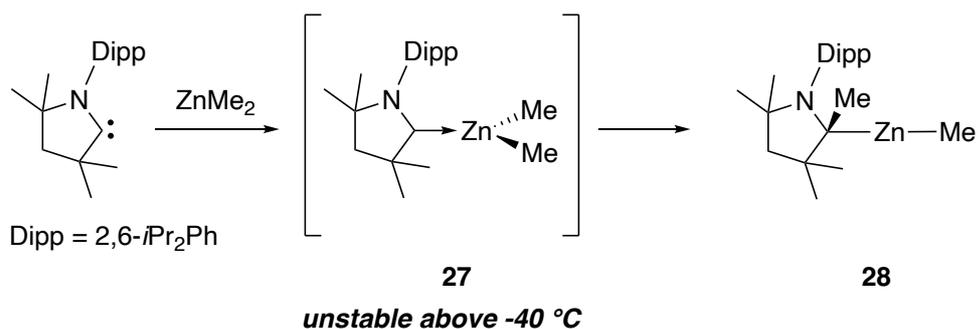
CAAC-supported Zn(II) species have been little explored to date but the couple of reports on the subject led to novel reactivity in organozinc chemistry. Thus, species (CAAC)ZnCl₂ (**23**, CAAC = 1-[2,6-bis(1-methylethyl)phenyl]-3,3,5,5-tetramethyl-2-pyrrolidinylidene, Scheme 19), a thermally stable adduct, may be reduced to afford an unprecedented singlet biradicaloid Zn(II) species, (CAAC)Zn (**24**, Scheme 19), in which each former carbene center now bears one electron.⁵¹ Reaction of adduct **23** with the hydride reagent

LiB(*sec*Bu)₃H yielded the (CAAC–H)₂Zn complex **25** (Scheme 19), in line with an electrophilic C_{CAAC} carbene center. The diradicaloid species **24** reacts rapidly with CO₂ at low temperature to afford zwitterion CAAC-CO₂ (**26**, Scheme 19), contrasting with the typical absence of reaction between neutral ZnR₂ species and CO₂ under such conditions.



Scheme 19. Studied reactivity of adduct [(CAAC)ZnCl₂] **23**.

The reactivity of CAAC carbene was also studied with simple ZnR₂ organometallics such as ZnMe₂ (Scheme 20).⁵² Unlike classical (NHC)ZnR₂ adducts (R = alkyl), which are thermally stable and robust entities,^{19,22,38} [(CAAC)ZnMe₂] adduct **27** is thermally unstable above -40 °C in solution and readily undergo carbene insertion into one of the Zn–Me bonds to produce **28** (Scheme 20, Figure 6). The instability of adduct **27** and its transformation to **28** reflect the more electrophilic character of the carbene center in CAAC *vs.* Arduengo-type NHCs.



Scheme 20. CAAC carbene insertion reactivity into a Zn–alkyl bond.

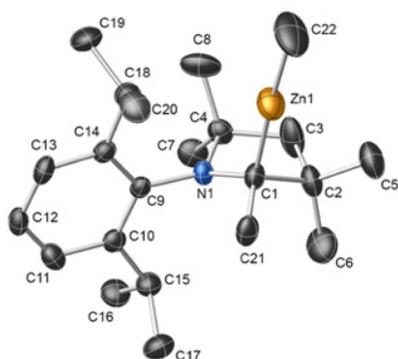
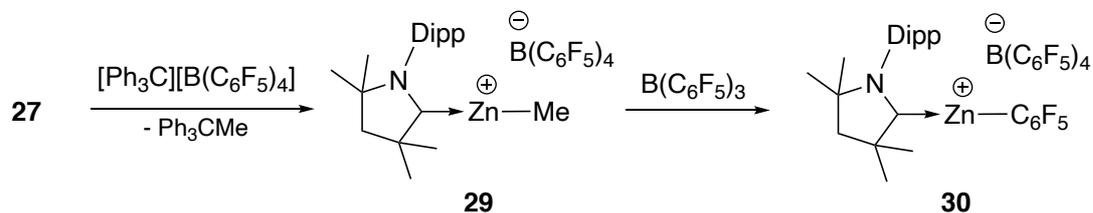


Figure 6. Molecular structure (ORTEP view) of insertion product **28**.

Despite the thermal instability of neutral adduct **27**, it may nevertheless be converted to robust two-coordinate CAAC-supported Zn(II) organocations of the type [(CAAC)Zn–R]⁺ (R = alkyl, aryl; **29** and **30**, Scheme 21).



Scheme 21. Synthesis of CAAC-supported two-coordinate Zn(II) cations **29** and **30**.

As estimated from DFT calculations, the LUMO energy level of [(CAAC)Zn–C₆F₅]⁺ species is significantly lower than that of cation [(IDipp)Zn–C₆F₅]⁺ (Figure 7), which is due to

the higher π -accepting properties of the CAAC carbene. The latter may in principle lead to more reactive $[(\text{CAAC})\text{Zn-R}]^+$ electrophiles provided the reactivity of such Zn(II) cations is, at least to some extent, under orbital control. Yet, both $[(\text{CAAC})\text{Zn-C}_6\text{F}_5]^+$ and $[(\text{IDipp})\text{Zn-C}_6\text{F}_5]^+$ cations display similar activity in alkene and CO_2 hydrosilylation catalysis, strongly suggesting that the reactivity of these cationic systems is only under charge control.

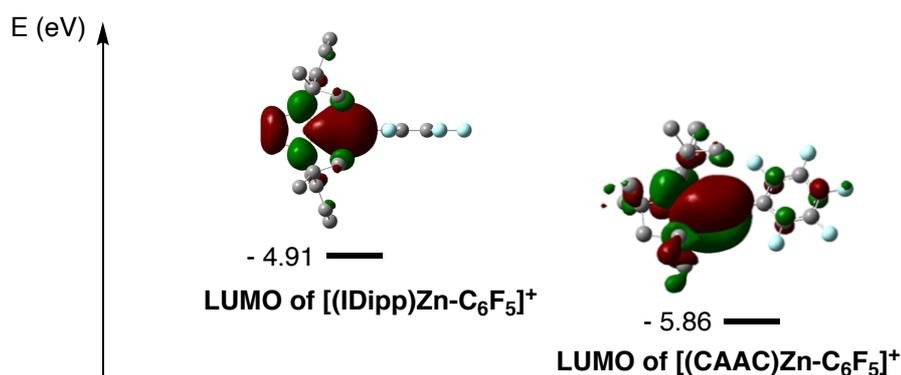
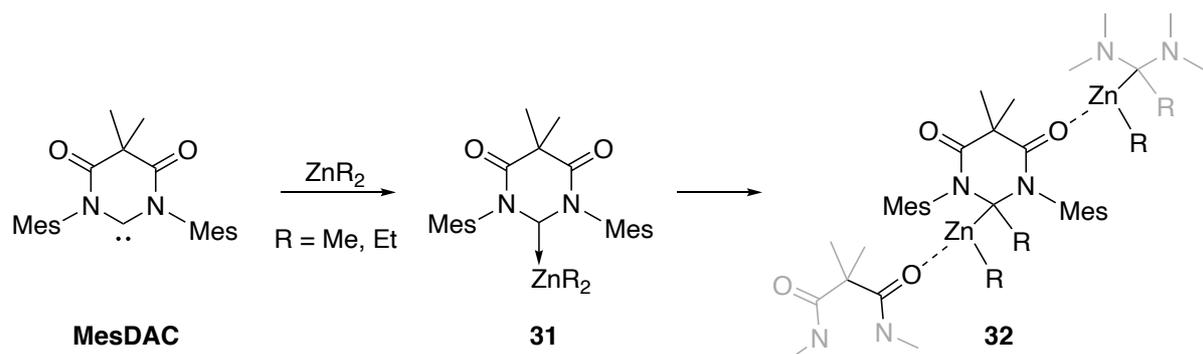


Figure 7. DFT-estimated LUMOs of $[(\text{IDipp})\text{Zn-C}_6\text{F}_5]^+$ (**12**) and $[(\text{CAAC})\text{Zn-C}_6\text{F}_5]^+$ (**30**) cations

Due to the presence of carbonyl groups adjacent to the ring nitrogen atoms, diamido carbenes (DACs, see for instance MesDAC in Scheme 22; MesDAC = 1,3-bis(2,4,6-trimethylphenyl), tetrahydro-5,5-dimethyl-4,6-dioxo-pyrimidin-2-ylidene) constitute a recently developed class of NHCs also displaying enhanced π -accepting properties and a more electrophilic carbene center when compared to classical diamino NHCs.⁵³ DACs have primarily been used as ligands for the stabilization of various late transition metal centers.⁵⁴ One example of DAC-supported Zn(II) species is known to date, $[(\text{MesDAC})\text{ZnR}_2]$ (**31**, Scheme 22).⁵⁵ Akin to CAAC-Zn chemistry discussed above, adduct **31** is unstable at RT (in solution) and undergoes carbene insertion into one the Zn-alkyl bond to yield product **32**, as unambiguously confirmed by X-ray crystallographic analysis. Such reactivity clearly arises from the electrophilic character of the $\text{C}_{\text{carbene}}$ center in **31**.



Scheme 22. Di-amido-carbene-supported Zn(II) species and derived carbene insertion reactivity.

Conclusion

Over the past five to ten years, NHC-stabilized Zn complexes have undoubtedly contributed to fundamental progress and applications of Zn organometallics. The extra-ordinary ability of NHCs to stabilize Zn(II) has permitted the stabilization and characterization of unprecedented Zn(II) structural motifs, most notably two-coordinated Zn(II) organocations and molecularly well-defined Zn hydrides. In addition to their fundamental interest, these two classes of compounds have led to novel catalytic applications, in particular hydrosilylation catalysis of small molecules of interest (CO_2 , carbonyls, alkenes, alkynes, imines, nitriles) under mild conditions. Further, thanks to their straightforward and superior stability *vs.* most adducts of the type $[(L)ZnX_2]$, more classical $[(NHC)ZnX_2]$ species have also demonstrated their suitability for various catalytic processes ranging from CO_2 reductive amination, cross-coupling catalysis, alkyne dehydroboration, alkynyl boronic ester hydroboration, imine hydrogenation to enantioselective alkylation reactions. Given the readily synthetic availability of numerous NHC scaffolds with tailored electronic and steric properties, NHC-Zn species hold great potential in the coming years for fundamental developments in organometallic chemistry and the mediation of various catalytic processes.

Acknowledgments. The authors thank the CNRS and the University of Strasbourg for financial support.

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