

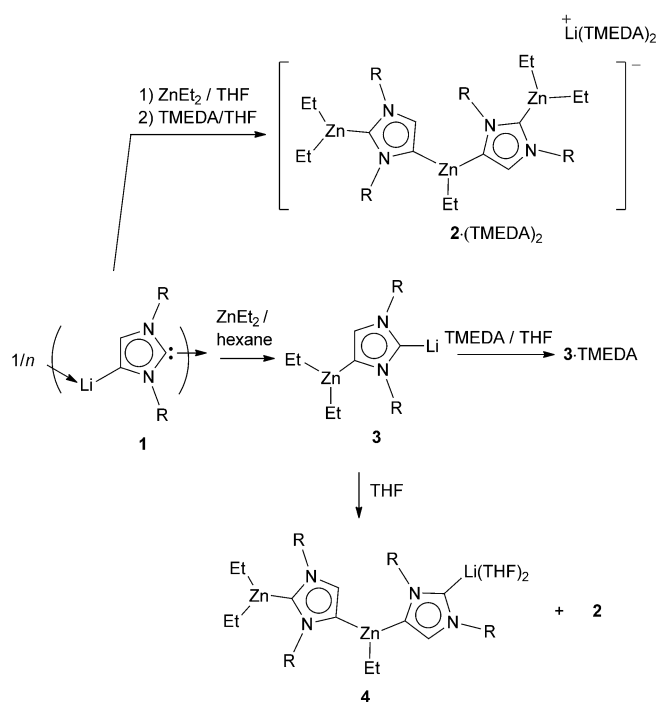
NHC-Stabilized Triorganozincates: Syntheses, Structures, and Transformation to Abnormal Carbene–Zinc Complexes**

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The chemistry of organozinc compounds has been inextricably entwined with the development of organic synthetic methods since Frankland's seminal discovery of zinc alkyls in 1849.^[1,2] Compared to diorganozinc reagents, the corresponding anionic zincate derivatives are considerably better nucleophiles.^[3–8] Consequently, triorganozincates $[R_3Zn]M$ ($M =$ alkali metals) and tetraorganozincates $[R_4Zn]M_n$ ($M =$ alkali metals, $n = 2$; $M =$ alkali earth metals, $n = 1$) have been extensively utilized in organic transformations such as halogen–metal exchanges,^[9–12] nucleophilic additions,^[1,2] deprotonative metalations,^[6–8] and epoxide ring-openings.^[9,10] Recently, Mulvey et al. employed TMP-zincates (TMP = 2,2,6,6-tetramethylpiperidide) in developing a zincation–anion trapping strategy^[13] and in realizing the unusual transformation of a diamine into an unsaturated diazaethene through a lithium/zinc bimetallic system.^[14,15] The advantages of organozincates may be attributed to their intrinsic “bimetallic” character. Indeed, due to their synergic reactivity, bimetallic systems often outperform their monometallic components and have shown greater potential in organic transformations.^[6] Lithium zincate investigations reveal that not only the Li/Zn ratio^[3,4,9] but also the substituents^[5] may have remarkable effects on their reactivity. Thus, the TMP ligand has contributed to the renaissance of metallation chemistry involving organozincate compounds.^[6–8] We show here that extensions of the ligand systems can result in organozincates with novel reactivity.

While N-heterocyclic carbenes (NHCs) have become ubiquitous ligands for organic^[16] and transition-metal^[16] catalysis, they are also capable of stabilizing highly reactive main group molecules.^[17–22] NHC-zinc complexes may act as polymerization catalysts.^[23–26] However, all the reported NHC-based zinc compounds are neutral and C2-bound. Considering the unique application of C4-bound NHC [i.e.,

abnormal carbene^[27] (*a*NHC)] complexes in catalysis,^[28] synthesis of NHC-based anionic zincates, especially those involving C4 carbene center, is intriguing. A common synthetic route to zincates involves the reaction of organolithium reagents with either diorganozinc or zinc halides.^[5] We recently synthesized the first anionic N-heterocyclic dicarbene [NHDC; **1**, $R = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$; Scheme 1] through C4-lithiation of the NHC ligand.^[29–31] Significantly, ligand **1** provides a convenient platform to access the unexplored NHC-based zincate chemistry. Herein, we report the syntheses,^[32]



Scheme 1. Synthesis of NHC-stabilized triorganozincates **2** and **3**.

structures,^[32] and computations^[33] of the first NHC-based 1:3 (the lithium/zinc ratio) (**2**) and 1:1 (**3**) triorganozincates. Moreover, **2** can be efficiently converted into *a*NHC-Zn-(Et)OTf dimer, **5**, by reaction with methyl triflate (MeOTf). Notably, compound **5** represents the first *a*NHC-stabilized Group 12 compound.

Compound $2 \cdot (TMEDA)_2$ was isolated as colorless crystals (72.7% yield) by crystallization (in TMEDA/THF) of the viscous residue from the reaction of **1** with excessive $ZnEt_2$ in THF (Scheme 1). $2 \cdot (DME)_2$ was isolated through the same procedure. **3** was prepared in almost quantitative yield

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(96.2%) by combining ligand **1** with ZnEt_2 in hexane (Scheme 1). The formation of **3** may be related to the poor solubility of both **1** (reactant) and **3** (product) in hexane. Recrystallization of **3** in TMEDA/THF mixed solvent results in the isolation of **3**-TMEDA as colorless crystals. The ^1H NMR measurements (in $[\text{D}_8]\text{THF}$) show that **2** is stable in THF while **3** gradually dissociates in THF and converts into a final mixture, mainly consisting of THF-solvated **2** and **4** (Scheme 1). **4**, as one of the dissociation products of **3** in THF, can be crystallized out in the THF/hexane mixed solvent system.^[32] The dissociation of **3** in THF indicates the (thermal) lability of Zn–C4 bond in **3**. When compared to **3**, the increased stability of **2**·(solvent)₂ (solvent = TMEDA or DME) may be partially ascribed to the increased steric shielding of the C4-bound zinc atom. While C2-bound NHC zinc complexes are usually prone to dissociate,^[24] the Zn–C2 bond in an NHC zinc aryloxide exhibits significant stability, rendering the “hydrolytic durability” of this complex.^[34] Based on the 7.46 ppm ^1H NMR signal of neutral C2-bound NHC- ZnEt_2 complex $\{\text{NHC} = \text{:C}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}]_2\}$,^[32] the high field-shifted imidazole ^1H NMR resonances of **2** and **3** (6.16 and 6.38 ppm, respectively) indicate their anionic character.^[29]

Compound **2** exists in the solid state as an ion-separated 1:3 triorganozincate involving the coordination of TMEDA (or DME) to the lithium cation (Figure 1).^[32] While binding to ZnEt_2 moieties at the C2 carbene centers [i.e., C(1) and C(28)], the two NHC ligands are bridged by one ZnEt fragment through their C4 sites [i.e., C(3) and C(29)]. Each three-coordinate zinc atom adopts a trigonal planar geometry. The Zn–C distances in **2**-DME [1.994(10)–2.105(9) Å] are comparable to those of typical Zn–C single bonds in NHC-zinc complexes.^[23–26,35] NBO analysis^[33] suggests considerable dicationic character of each zinc atom. The zinc natural charges range from +1.39 to +1.44 in the simplified model **2a** $[\text{NHC} = \text{:C}(\text{NHCH})_2]$. The Wiberg bond indices (WBIs) of the Zn–C bonds in **2a** range from 0.17 to 0.38. Notably, in **2** the Zn–C4 bonds [i.e., Zn(1)–C(3), 2.022(9) Å; Zn(1)–C(29), 2.009(8) Å] are somewhat shorter than the Zn–C2 bonds [i.e., Zn(2)–C(1), 2.105(9) Å; Zn(3)–C(28), 2.072(8) Å], which is in accord with computational results for **2a** [Zn–C4 bonds, 2.05 Å (av), WBIs = 0.23–0.25; Zn–C2 bonds, 2.14 Å (av), WBIs = 0.17].

In contrast to **2**, both **3** (Figure 1) and **4** (Figure S1 in the Supporting Information) are ion-associated, where solvated lithium cations coordinate to the C2 site [i.e., C(1)] of the imidazole ring. The Li–C bond distances in **3** [2.093(4) Å] and in **4** [2.019(11) Å] compare to those (2.09 Å) of the anionic NHDC-borate or aluminate adducts.^[29] It is noteworthy that the Zn–C4 bond in **3** [Zn(1)–C(3), 2.049(2) Å] is marginally longer than in **2** [2.009(8)–2.022(9) Å]. Similar to **2**, the three-coordinated zinc atoms in both **3** and **4** also adopt trigonal planar geometries. The Zn–C4 bonds in **4** [Zn(1)–C(2), 1.999(5) Å; Zn(1)–C(29), 2.018(5) Å] are about 0.09 Å shorter than the Zn–C2 bond [Zn(2)–C(28), 2.094(6) Å].

Abnormal N-heterocyclic carbene (*a*NHC) chemistry has experienced rapid growth^[27,28,36] in the decade since Crabtree’s discovery of the first transition metal-*a*NHC complex.^[37] Bertrand’s recent isolation of the first metal-free

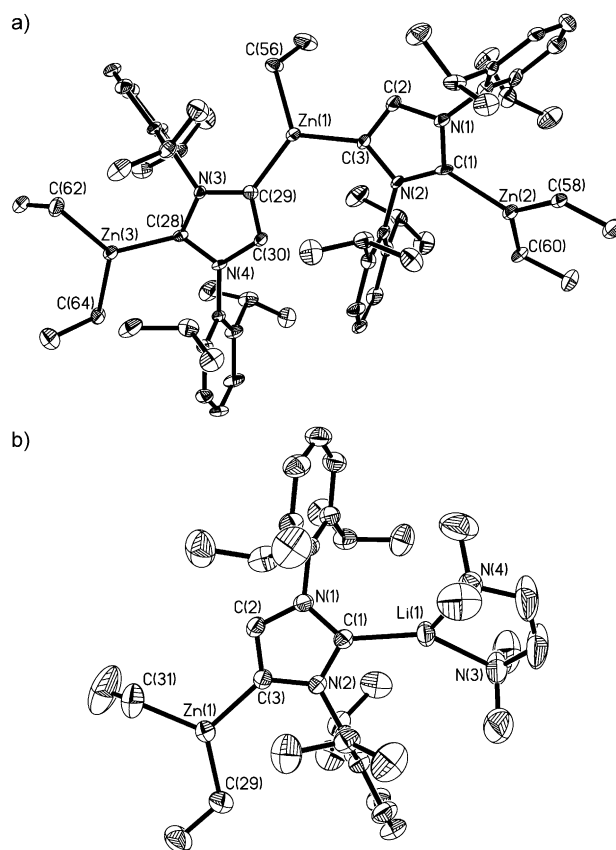
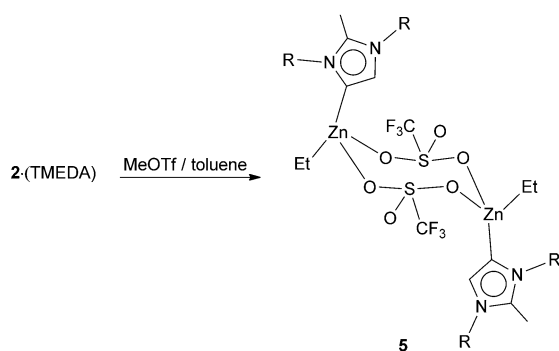


Figure 1. Molecular structures of a) **2** (anion only) and b) **3**-TMEDA. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: For **2** (anion only): Zn(1)–C(3) 2.022(9), Zn(1)–C(29) 2.009(8), Zn(1)–C(56) 2.030(9), Zn(2)–C(1) 2.105(9), Zn(2)–C(58) 1.994(10), Zn(2)–C(60) 2.032(10), Zn(3)–C(28) 2.072(8), Zn(3)–C(62) 2.021(10), Zn(3)–C(64) 2.02(2); C(3)–Zn(1)–C(29) 120.7(4), C(3)–Zn(1)–C(56) 113.2(4), C(29)–Zn(1)–C(56) 126.0(4); for **3**-TMEDA: Zn(1)–C(29) 1.993(3), Zn(1)–C(31) 2.034(4), Zn(1)–C(3) 2.049(2), Li(1)–C(1) 2.093(4); C(3)–Zn(1)–C(31) 111.13(14), C(3)–Zn(1)–C(29) 122.49(10), C(29)–Zn(1)–C(31) 126.28(16).

*a*NHC set a new benchmark.^[38–40] The *a*NHC ligands have stronger electron-donating capabilities^[27,28,36] than their normal NHC counterparts. The catalytic utility^[28] of transition metal-*a*NHC complexes makes these C4-bound carbenes especially intriguing.

While *a*NHC complexes mainly involve transition metals,^[27,28,36] the literature reveals a paucity of main group element *a*NHC complexes.^[31,41–43] Indeed, the chemistry of Group 12 metal-*a*NHC complexes is unexplored.^[27,28,36] We synthesized the first *a*NHC-zinc complex **5** (Scheme 2) by reaction of 1:3 triorganozincate **2** with excess MeOTf. Reaction of **3** with MeOTf also gives **5**, however, with a much lower yield. The transformation of **2** (and **3**) into **5** illustrates two points: 1) In NHC-based zincates, the imidazole ring C2 carbon is more prone to be methylated than the C4 carbon; 2) MeOTf acts not only as an electrophile (its well-known role) to methylate the C2 carbon, but also as a nucleophile (the OTf[−] anion attacks the C4-bound zinc atom^[44]) to give the Zn(Et)OTf units in **5**.



Scheme 2. Synthesis of *a*NHC-stabilized eight-membered $[\text{Zn}(\text{Et})\text{OTf}]_2$ ring (**5**).

The X-ray structural analysis reveals that **5** involves crystallographic “whole molecule disorder”.^[32] Compound **5** resides about a center of symmetry (Figure 2). While the C2 carbon atoms of the two NHC ligands are capped by methyl groups, the corresponding C4 carbene sites bind to the zinc

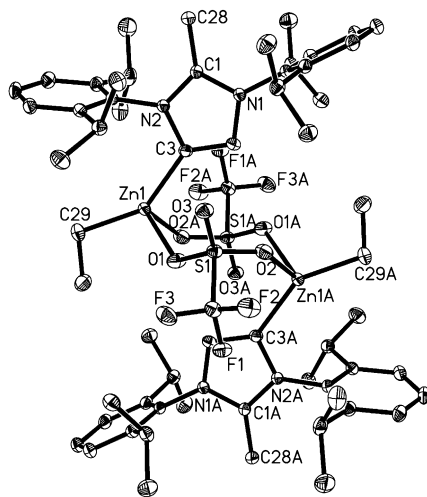


Figure 2. Molecular structure of **5**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zn(1)–C(3) 2.031(2), Zn(1)–C(29) 1.986(3), Zn(1)–O(1) 2.2299(19), Zn(1)–O(2A) 2.215(2), S(1)–O(1) 1.4473(19), S(1)–O(2) 1.448(2), S(1)–O(3) 1.4298(19); C(3)–Zn(1)–C(29) 144.00(11), C(3)–Zn(1)–O(1) 98.57(8), C(3)–Zn(1)–O(2A) 100.43(9), O(1)–Zn(1)–O(2A) 95.76(8), O(1)–Zn(1)–C(29) 101.16(10), C(29)–Zn(1)–O(2A) 107.15(10), Zn(1)–O(1)–S(1) 127.67(12), O(1)–S(1)–O(2) 113.59(12).

atoms of an eight-membered $\text{Zn}_2\text{S}_2\text{O}_4$ ring in a twist-chair conformation. Each four-coordinate zinc atom adopts a distorted tetrahedral geometry. The Zn–C bond [2.031(2) Å] in **5** is very similar to that in **3** [2.049(2) Å], but is marginally shorter than the Zn–C2 bonds in **2** and **4** (2.07–2.11 Å) and in normal NHC–ZnEt₂ complexes (2.09–2.10 Å).^[23–26,35] The Zn–O bonds in dimeric **5** [2.2299(19) and 2.215(2) Å] are considerably longer than in monomeric NHC:Zn(THF)(OTf)₂ (NHC = 1,3-bis(mesityl)-imidazol-2-ylidene) [1.966(2)–1.973(2) Å]. The same trend of Zn–O bond dis-

tances [1.8878(16) (monomer) vs. 2.0565(9) Å (dimer)] has also been observed in other functionalized NHC-zinc complexes.^[26]

Anionic NHDC (**1**) has been utilized in the synthesis of unique NHC-stabilized triorganozincates **2–4**. These syntheses suggest the feasibility of direct metalation of the unsaturated backbones of the NHC ligands with various “ate”^[8] compounds. The 1:3 triorganozincate **2** provides a convenient and effective route to access the first *a*NHC-based zinc complex **5**. Considering the readily tunable electronic and steric properties of NHC ligands, syntheses of zincates **2–4** and the *a*NHC-zinc complex **5** may lead to novel synthetic and catalytic applications.

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