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# Bulky bis-guanidine ligand-based neutral and cationic zinc alkyl, halide, and hydride complexes: synthesis, characterization, and catalytic application

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The tetra-aryl substituted bis-guanidine ligand L(3H) (L(3H) = {(ArHN)(ArNH)–C=N–C=(NAr)(NHAr)}; Ar = 2,6-$^{i}Pr_2$-$C_6H_3$) was used for the synthesis of mononuclear zinc(II) alkyl [L(2H)ZnR, R = Me (**Zn-1**), Et (**Zn-2**)], iodide [L(2H)ZnI, (**Zn-3**)], and hydride [L(2H)ZnH, (**Zn-4**)] complexes. Moreover, the reactions of **Zn-1**, **Zn-2**, and **Zn-3** with $[PhNMe_2H]^+$ $[B(C_6F_5)_4]^-$ yielded the biguanide zinc alkyl $[L(3H)ZnR]^+$ $[B(C_6F_5)_4]^-$ (R = Me (**Zn-5**), Et (**Zn-6**)) and iodide $[L(3H)ZnI]^+$ $[B(C_6F_5)_4]^-$ (**Zn-7**) cationic compounds in good yields. All newly isolated and thermally stable zinc complexes (**Zn-1–Zn-7**) were well characterized by multinuclear NMR ($^1H$, $^{13}C\{^1H\}$, with additional $^{11}B$ and $^{19}F\{^1H\}$ for **Zn-5–Zn-7**), HRMS, and single crystal X-ray diffraction studies. Moreover, the well-defined zinc iodide cation (**Zn-7**) $[L(3H)ZnI]^+$ $[B(C_6F_5)_4]^-$ was further used as a catalyst for the synthesis of cyanohydrin enol ether products (RCR'CNOSiMe$_3$) by TMSCN addition to carbonyl compounds (RCOR', R' = alkyl/aryl) under mild reaction conditions.

## Introduction

Over the last few years, zinc complexes have been used as catalysts for various organic transformations in homogeneous and heterogeneous catalytic processes.[1] Although neutral zinc complexes can also be used as catalysts, cationic zinc complexes are more effective than the corresponding neutral species due to their enhanced Lewis acidity of the metal centers caused by nucleophilic counter-anions.[2] In this context, it should be noted that various molecular zinc cations have been synthesized using N-, O-, and P-based ligands.[2,3] Concerning molecular zinc cations, only a few examples were introduced for catalysis applications.[4] In an earlier report, Dagorne and coworkers utilized N-heterocyclic carbene (NHC) zinc cations $[NHC\text{-}ZnMe(THF)_x]^+$ $[Me(B_6F_5)_3]^-$ (where $x$ = 1, 2; NHC = 1,3-(2,6-$^{i}Pr_2Ph$)$_2$-imidazol-2-ylidene or 1,3-(2,4,6-$Me_3Ph$)$_2$-imidazol-2-ylidene) for ring-opening polymerization of trimethylene carbonate and cyclic esters (β-butyrolactone and lactide) under mild conditions.[5] Furthermore, in 2015, Roesky, Braun, and coworkers introduced a hydroamination reaction by using a structurally characterized zinc organyl compound, $[Zn_2Cp^*_3]^+$ $[BAr^F_4]^-$ (where $BAr^F_4$ = B(3,5-$(CF_3)_2C_6H_3)_4$), as a precatalyst to obtain the C–N coupled products.[6] Later, the Parkin and Dagorne groups independently described zinc cations as effective catalysts for the hydrosilylation of carbon dioxide.[4,7] Additionally, zinc hydride cations were reported for catalytic hydrosilylation of carbonyls, including carbon dioxide and nitrile functionalities.[8]

In the past few years, the cyanosilylation reaction was used to prepare various organic compounds for the chemical industry and agriculture.[9] For this, trimethylsilyl cyanide (TMSCN) is used as a cyanating reagent compared to HCN (hydrogen cyanide) with carbonyl compounds to afford the cyanohydrin products in high yield.[10] Transition and main group molecular metal complexes have been discovered for Si–CN addition to carbonyls.[9a,11] Leung and co-workers reported catalyst-free cyanosilylation of aldehydes in 2019.[12] Notably, cyanosilylation of ketones is difficult compared to that of aldehydes due to the lower electrophilicity of the carbonyl group in ketones than that in aldehydes, which creates a larger energy barrier. Moreover, there are only three reports on zinc-based cyanosilylation of carbonyl groups.[10,13] In 1978, the Talley group established the first zinc-based cyanosilylation of carbonyls.[13] Recently, Pombeiro and co-workers reported multinuclear zinc(II)–arylhydrazone used as catalysts for the cyanosilylation of aldehydes.[10] However, in main group catalysis, only a handful of cationic complexes have been reported for TMSCN addition to aldehydes and ketones.[14] Surprisingly, concerning

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the literature study, we found that no cationic zinc complex was reported for the cyanosilylation of ketones.

We recently established bis-guanidine stabilized dinuclear Zn(I) and Zn(II) complexes and used them to catalyze the hydrofunctionalization of various challenging organic unsaturated functional groups under mild conditions.[15]

Therefore, herein we report the preparation and characterization of bis-guanidinate coordinated mononuclear zinc alkyl (**Zn-1** and **Zn-2**), iodide (**Zn-3**), and hydride (**Zn-4**) compounds. Moreover, we established the cationic biguanide supported zinc alkyl and halide complexes (**Zn-5**–**Zn-7**) for the first time. All synthesized zinc compounds were thoroughly characterized by multinuclear NMR, HRMS, and single crystal X-ray diffraction studies. Furthermore, we employed a well-defined cationic zinc iodide complex, $[L(3H)ZnI]^+$ $[B(C_6F_5)_4]^-$ (**Zn-7**), as a catalyst for the cyanosilylation of a broad range of ketones to cyanohydrin enol ether products.

## Results and discussion

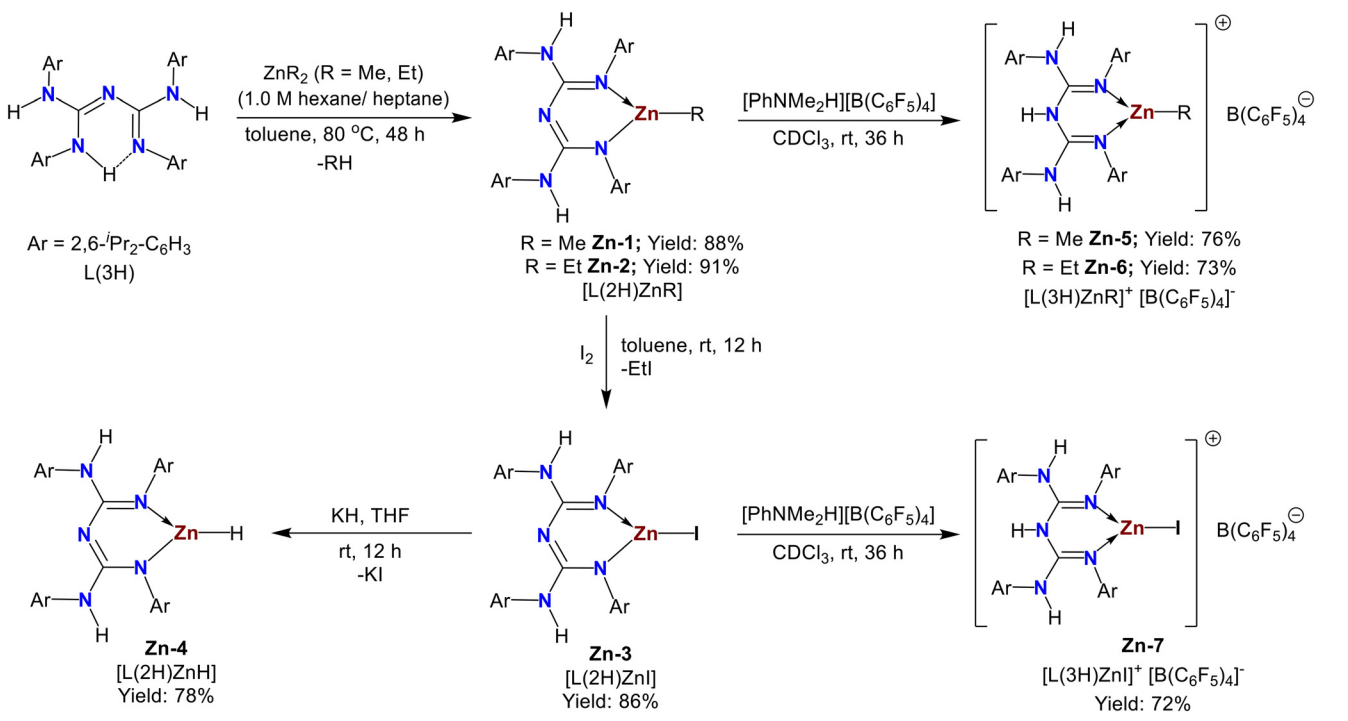
### Synthesis and characterization of bis-guanidine supported neutral zinc(II) alkyl, halide, hydride, and cationic zinc(II) alkyl and halide complexes

In the previous report, we described the synthesis of the bulky bis-guanidine ligand L(3H) (where L(3H) = {(ArHN)(ArNH)–C=N–C=(NAr)(NHAr)}; Ar = 2,6-$^i$Pr$_2$-C$_6$H$_3$) by the reaction of 2.0 equiv. of $^{Dipp}$CDI {(Dipp)NCN(Dipp); Dipp = 2,6-$^i$Pr$_2$-C$_6$H$_3$} with 1.0 equiv. of ammonium chloride in ethanol at 80 °C.[15e,16] Our group recently introduced tetra-aryl substituted bis-guanidinate stabilized main group and transition metal complexes, including cationic complexes, and studied their catalytic applications.[11a,15f,17] In this work, we have synthesized monomeric neutral and cationic zinc alkyl and iodide compounds (**Zn-1**–**Zn-7**) coordinated by bulky bis-guanidine anions in good yields.

The neutral organozinc compounds [L(2H)ZnR, R = Me (**Zn-1**), Et (**Zn-2**)] were synthesized by deprotonation of the ligand (L3H) with an equimolar solution of a dialkylzinc reagent ($ZnR_2$, R = Me, Et, 1.0 M hexane/heptane) in toluene, with 88–91% isolated yields (Scheme 1). Furthermore, the reaction of compound **Zn-2** with an equivalent amount of $I_2$ in toluene at room temperature was conducted, which yielded the bis-guanidinate zinc iodide complex (**Zn-3**) [L(2H)ZnI] in an 86% isolated yield. Furthermore, compound **Zn-3**, upon treatment with KH in toluene, resulted in the formation of compound **Zn-4** in a 78% yield (Scheme 1).

Unsubstituted/substituted biguanide supported zinc complexes are reported in the literature.[18] Recently, Kretschmer and co-workers synthesized 3,4-ethylene-bridged 1,1,2,5-tetra-substituted biguanide-stabilized zinc complexes.[19] Our group reported tetra-aryl substituted bis-guanidine Zn(II) complexes.[15d,f] However, tetra-aryl substituted biguanidine zinc cations are not known.

As already stated, examples of *N*,*N*′ chelated molecular zinc organyl and halide cations remain scarce. To our knowledge, there have been no reports on biguanide chelated zinc alkyl and iodide cations. Therefore, we targeted the biguanide organozinc and halide cations in an additional experiment. Accordingly, the reaction of neutral zinc complexes (**Zn-1** to




**Scheme 1** Synthesis of bis-guanidine supported neutral and cationic zinc compounds (**Zn-1**–**Zn-7**).

**Zn-3**) with an equivalent quantity of the $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ reagent in chloroform-d ($CDCl_3$) at rt yielded the three coordinate monomeric zinc alkyl cations $[L(3H)ZnR]^+[B(C_6F_5)_4]^-$ (R = Me (**Zn-5**), Et (**Zn-6**)) and zinc halide cation $[L(3H)ZnI]^+[B(C_6F_5)_4]^-$ (**Zn-7**) in 72–76% yields (Scheme 1).

All compounds (**Zn-1**–**Zn-7**) were characterized by multinuclear NMR ($^1H$, $^{13}C\{^1H\}$, with additional $^{11}B$ and $^{19}F\{^1H\}$ for **Zn-5**–**Zn-7**) and HRMS, and structurally characterized by the single crystal X-ray diffraction technique (Fig. 1 and 2).

The $^1H$ NMR spectra of compounds **Zn-1** and **Zn-5** exhibit singlet resonances for the methyl group attached to the zinc atom (Zn–*Me*) at −1.12 and −0.81 ppm, respectively. For compounds **Zn-2** and **Zn-6**, the $^1H$ NMR spectra show triplet (at 0.99 ppm for **Zn-2** and **0.47** ppm for **Zn-6**) and quartet (at 0.42 ppm for **Zn-2** and 0.13 ppm for **Zn-6**) resonances, corresponding to the $CH_3$ and $CH_2$ protons of the ethyl groups attached to the zinc atom. The complete disappearance of $ZnCH_2CH_3$ and $ZnCH_2CH_3$ proton resonances in $^1H$ NMR spectra indicates the formation of compounds **Zn-3** and **Zn-7**. More importantly, the $^1H$ NMR spectra of compounds **Zn-3** and **Zn-7** exhibit singlet resonances for the side arm ArN–*H* at 5.59 and 6.23 ppm, respectively. The $^1H$ NMR spectrum of compound **Zn-4** shows the characteristic Zn–*H* resonance at 4.42 ppm, which is in good agreement with the monomeric $^{Dipp}$NacNac(L′) zinc hydride complex (L′ZnH; L′ = $HC[C(Me)N(2,6\text{-}^iPr_2C_6H_3)]_2$) with the terminal Zn–H moiety (4.39 ppm) reported by the Harder group.[20]

The $^{13}C\{^1H\}$ NMR resonances for the Zn–*C* carbon atom ($\delta$ = −13.43 and −0.01 ppm for **Zn-5** and **Zn-6**, respectively) are downfield relative to the corresponding neutral compounds **Zn-1** and **Zn-2** ($\delta$ = −14.98 and −0.79 ppm, respectively). However, the $^{13}C\{^1H\}$ NMR spectrum of compound **Zn-3** reveals the complete disappearance of the ZnEt peak, which suggests the alkyl halide exchange in compound **Zn-3**. Moreover, the $^{11}B$ NMR spectra of compounds **Zn-6** and **Zn-7** show singlets at −16.64 and −16.67 ppm, respectively, corresponding to the counter anion part, $B(C_6F_5)_4$. The single crystals suitable for X-ray diffraction of the compounds **Zn-1**, **Zn-2**, **Zn-3**, and **Zn-4** were grown from a concentrated toluene solution at −10 °C, while for compounds **Zn-5**, **Zn-6**, and **Zn-7**, the crystals were grown from chloroform-d solutions.

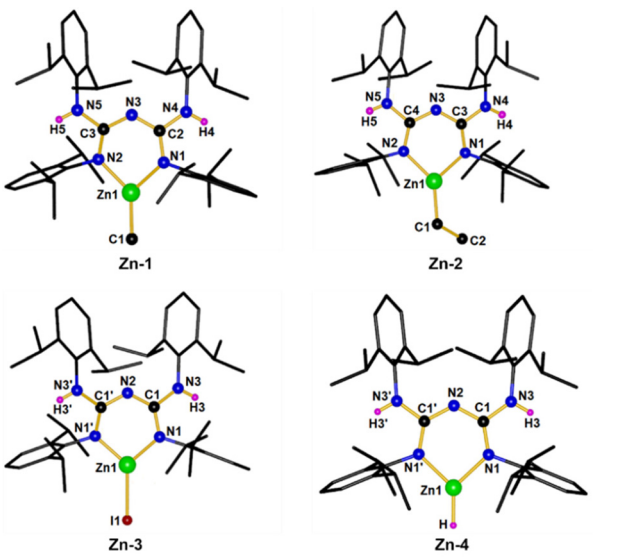



**Fig. 1** Molecular structures of **Zn-1** (upper left), **Zn-2** (upper right), **Zn-3** (lower left), and **Zn-4** (lower right). All the hydrogen atoms (except H(4), H(5), H(3′) and H) are removed for clarity. Selected bond lengths (Å) and angles (°): for **Zn-1** (upper left): Zn1–C1 1.9475(17), Zn1–N1 1.9513(11), Zn1–N2 1.9505(11), N2–C3 1.3380(16), N3–C3 1.3390(16), N3–C2 1.3372(16), N1–C2 1.3385(16), N5–C3 1.3705(16), N4–C2 1.3676(16); N1–Zn1–N2 93.89(5), N1–Zn1–C1 131.67(6), N2–Zn1–C1 134.43(6); for **Zn-2** (upper right): Zn1–C1 1.962(4), Zn1–N1 1.955(3), Zn1–N2 1.958(3), C1–C2 1.538(5), N2–C4 1.348(4), N5–C4 1.368(4), N3–C4 1.326(4), N3–C3 1.339(4), N1–C3 1.341(4); N1–Zn1–N2 94.56(11), N1–Zn1–C1 137.23(13), N2–Zn1–C1 128.03(13), Zn1–C1–C2 115.6(2); for **Zn-3** (lower left): Zn1–I1 2.4427(5), Zn1–N1 1.9111(19), Zn1–N1′ 1.9112(19), N1–C1 1.346(3), N2–C1 1.338(2), N3–C1 1.367(3); N1–Zn1–N1′ 97.88(11), N1–Zn1–I1 131.07(6), N1′–Zn1–I1 131.06(6); and for **Zn-4** (lower right): Zn1–N1 1.9404(13), Zn1–N1′ 1.9404(13), N1–C1 1.342(2), N2–C1 1.3438(17), N3–C1 1.3706(19); N1–Zn1–N1′ 93.97(7).

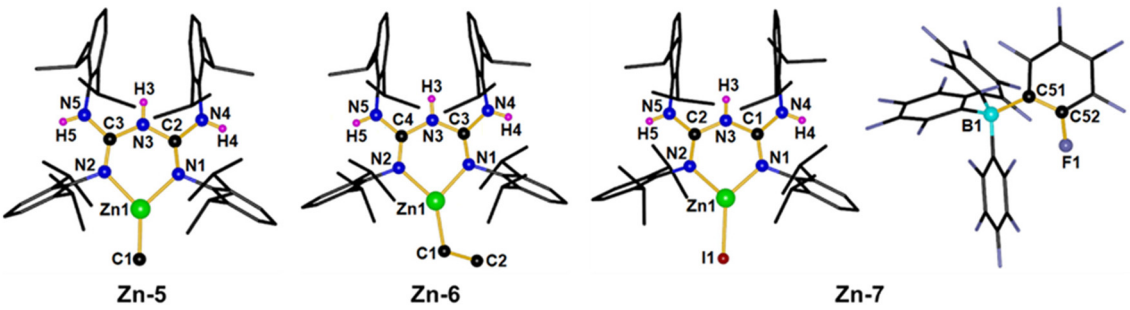



**Fig. 2** Molecular structures of **Zn-5** (left), **Zn-6** (middle), and **Zn-7** (right). All the hydrogen atoms (except H(3), H(4), H(5), and anion $B(C_6F_5)_4$ (except **Zn-7**)) are removed for clarity. Selected bond lengths (Å) and angles (°): for **Zn-5** (upper left): Zn1–C1 1.924(7), Zn1–N1 1.988(4), Zn1–N2 1.987(4), N1–C2 1.281(7), N4–C2 1.353(6), N3–C2 1.392(6), N3–C3 1.395(6), N5–C3 1.356(6), N2–C3 1.280(7); N1–Zn1–N2 91.21(18), N1–Zn1–C1 133.8(2), N2–Zn1–C1 134.9(2); for **Zn-6** (upper right): Zn1–C1 2.038(7), Zn1–N2 2.005(4), Zn1–N2 1.994(5), C1–C2 1.425(11), N1–C3 1.257(7), N4–C3 1.361(5), N3–C3 1.395(6), N3–C4 1.361(5), N5–C4 1.351(7), N2–C4 1.276(7), N1–Zn1–N2 90.48(18), N1–Zn1–C1 127.4(2), N2–Zn1–C1 142.1(2); and for **Zn-7** (lower): Zn1–I1 2.4317(14), Zn1–N1 1.945(8), Zn1–N2 1.957(8), N1–C1 1.299(12), N4–C1 1.343(11), N3–C1 1.390(11), N3–C2 1.361(12), N5–C2 1.370(12), N2–C2 1.299(12), B1–C51 1.658(15), C51–C52 1.397(18), C52–F1 1.319(13); N1–Zn1–N2 95.6(3), N1–Zn1–I1 135.1(2), N2–Zn1–I1 129.2(2), B1–C51–C52 120.7(9), C51–C52–F1 119.6(9).

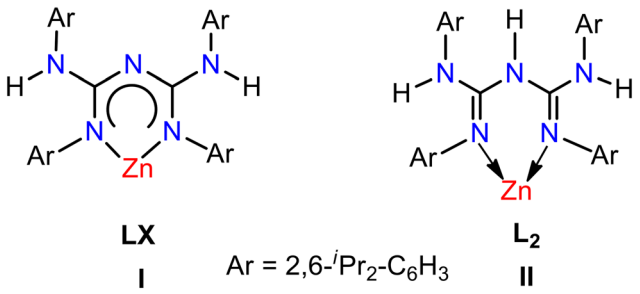
Compounds **Zn-1**, **Zn-3**, and **Zn-4** were crystallized in the monoclinic system with the *P*2(1)/*c* (for **Zn-1**) and *C*2/*c* (for **Zn-3** and **Zn-4**) space groups, whereas compound **Zn-2** crystallized in the triclinic system with the space group $P\bar{1}$. The selected data collection parameters and structural refinement details of compounds **Zn-1** to **Zn-7** are summarized in Tables S2 and S3 in the SI. The zinc atom adopts a distorted trigonal planar environment with three coordination sites in all cases. The solid state structures of compounds **Zn-1** to **Zn-7** show that the zinc atom is connected to the bis-guanidine ligand in the *N*,*N*′-chelate fashion, and the other site is occupied by an alkyl (**Zn-1**, **Zn-2**, **Zn-5**, and **Zn-6**) or an iodide (**Zn-3** and **Zn-7**) or a hydride (**Zn-4**) group.

Furthermore, solid-state structures confirmed that all compounds **Zn-1**–**Zn-7** are monomeric and exhibit six-membered metallacycles containing a $C_2N_3Zn$ ring.

The Zn–C bond lengths in compounds **Zn-1**, **Zn-2**, **Zn-5**, and **Zn-6** lie in the range of 1.924(7) Å to 2.038(7) Å and are similar to those reported for N-donor ligand stabilized neutral and cationic zinc complexes (**A**–**D**). **A:** L′ZnMe (L′ = HC[C(Me)N(2,6-$^{i}Pr_2C_6H_3$)]$_2$)[21] (Zn(1)–C(6) 1.941(3) Å). **B:** [L′ZnEt][22] (Zn(1)–C(1) 1.963(5) Å). **C:** [(*a*IDipp)(*n*IDipp)ZnMe]$^+$ (Dipp = 2,6-$^{i}Pr_2C_6H_3$)[4a,7] (Zn(1)–C(55) 1.997(4) Å). **D:** (IDipp)Zn-Et$^+$ [IDipp = 1,3-bis-(2,6-$^{i}Pr_2C_6H_3$)imidazolin-2-ylidene][4a] (Zn–Et 1.909(5) Å). Also, Zn–N bond distances are comparable to those of the reported zinc alkyl complexes (**A** and **B**).[21,22]

The Zn–I bond lengths for compounds **Zn-3** and **Zn-7**, *i.e.*, Zn1–I1, are 2.4427(5) Å and 2.4317(14) Å, respectively. These values are close to some of the Zn–I bond lengths of a previously reported *N*,*N*′-chelated $^{Diethyl}$bis-guanidine supported zinc iodide complex, **E:** [L$^{I}$ZnI]$_2$ [L$^1$ = {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar = 2,6-Et$_2$-C$_6$H$_3$] [Zn1–I1: 2.5819(15) Å, Zn1–I1′: 2.7702(16) Å].[15f] Similarly, for compound **Zn-4**, the Zn1–N1 bond distance is 1.9404 (13) Å, comparable with that of the previously reported $^{Dipp}$NacNac zinc hydride complex, *i.e.*, 1.950(1) Å.[20] The N–Zn–N bite angles in compounds **Zn-1**–**Zn-7** are in the range of 90.48(18)–97.88(11)°, which are similar to the N–Zn–N bite angles in six-membered zinc heterocyclic compounds **A**, **B**, and **E**: 97.00(8)° (**A**), 97.07(12)° (**B**), and 95.7(3)° (E).

The bonding mode **I** has been observed for the neutral zinc alkyl (**Zn-1** and **Zn-2**), halide (**Zn-3**), and hydride (**Zn-4**) complexes, while **II** is noticed for the cationic zinc alkyl (**Zn-5** and **Zn-6**) and halide (**Zn-7**) complexes. In bonding mode **I**, the *N*,*N*′-chelating scaffold exhibits an LX-type ligand consisting of one σ- and one π-donor. However, cationic zinc complexes are characterized as L$_2$-type ligands consisting of two π-donors (Scheme 2). The above study suggests that in the case of neutral compounds, the ligand behaves as monoanionic, whereas in the cationic complexes, the ligand acts as neutral.

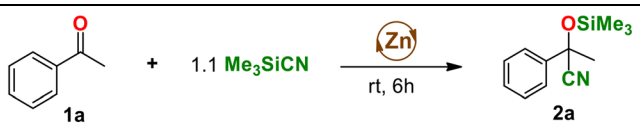



**Scheme 2** Two bonding modes.

### Catalysis: zinc catalyzed TMSCN addition to ketones

In the literature, we observed that, unlike the B–H addition to carbonyls, only a few main-group molecular metal complexes have been employed for cyanosilylation reactions, which encouraged us to explore trimethylsilyl cyanide (TMSCN) addition across the carbonyl bonds to synthesize the cyanohydrin silyl ether products using a biguanide stabilized zinc iodide cationic complex (**Zn-7**). In the initial investigation, acetophenone (**1a**) reacted with 1.1 equiv. of TMSCN under solvent-free and catalyst-free conditions and afforded only 12% of cyanohydrin product **2a** (Table 1, entry 1). We noticed that 0.5 mol% of the zinc iodide cationic complex **Zn-7** is the lowest catalyst load for complete conversion of acetophenone into the respective silylated product **2a**, both under neat conditions and in solvents such as toluene, benzene, and THF (Table 1, entries 6–9). Additionally, reagent $ZnI_2$ also promotes complete conversion for the reaction under the same conditions; however, other zinc complexes as well as the [PhNMe$_2$H]$^+$ [B(C$_6$F$_5$)$_4$]$^-$ reagent exhibit lower catalytic per-

**Table 1** Optimization of cyanosilylation of acetophenone[a]




| Entries | Catalysts | mol% | Solvent | Conv.[b] (%) |
|---|---|---|---|---|
| 1 | — | — | Neat | 12% |
| 2 | **Zn-7** | 5.0 | Neat | >99% |
| 3 | **Zn-7** | 3.0 | Neat | >99% |
| 4 | **Zn-7** | 2.0 | Neat | >99% |
| 5 | **Zn-7** | 1.0 | Neat | >99% |
| **6** | **Zn-7** | **0.5** | **Neat** | **>99%** |
| 7 | **Zn-7** | 0.5 | Toluene | >99% |
| 8 | **Zn-7** | 0.5 | Benzene | >99% |
| 9 | **Zn-7** | 0.5 | THF | >99% |
| 10 | **Zn-1** | 0.5 | Neat | 15 |
| 11 | **Zn-2** | 0.5 | Neat | 16 |
| 12 | **Zn-3** | 0.5 | Neat | 18 |
| 13 | **Zn-4** | 0.5 | Neat | 16 |
| 14 | **Zn-5** | 0.5 | Neat | 98 |
| 15 | **Zn-6** | 0.5 | Neat | 98 |
| 16 | [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] | 0.5 | Neat | 60 |
| 17 | **ZnI$_2$** | 0.5 | Neat | >99% |

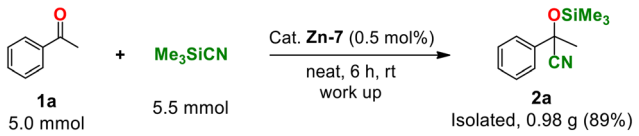
[a] Reaction conditions: acetophenone (0.3 mmol, 1.0 equiv.), TMSCN (0.33 mmol, 1.1 equiv.) and catalyst (**Zn-7**) (*x* mol%) were stirred in a 10 mL sealed vial for 6 h at rt under an inert $N_2$ atmosphere. [b] Conversion for Si–CN addition in acetophenone was confirmed by NMR ($^1$H and $^{13}$C{$^1$H}) spectroscopy based on the disappearance of the starting material and formation of the characteristic proton signal for PhCMeCNOSiMe$_3$, with respect to the internal standard $CH_2Cl_2$.

formance for TMSCN addition in acetophenone (Table 1, entries 10–17). In line with the Gutmann–Becket method, compound **Zn-7** exhibits a slightly greater Lewis acidity compared to compound **Zn-3** and other cationic complexes (**Zn-5** and **Zn-6**) (Table S1).

With the optimized conditions in hand for Si–CN addition in acetophenone, next, we widen the substrate scope for TMSCN addition to various aryl and alkyl ketones using a zinc catalyst (**Zn-7**). As shown in Table 2, complex **Zn-7** catalyzed the complete formation of cyanohydrin products of selected ketones (**2a–2r**, >99%) and showed excellent tolerance towards ester ($CO_2R$) functional groups under solvent-free conditions. In the initial investigation, all aryl electron rich (Me, OMe, and MeS; **1b–1f**) and electron poor (F, Cl, and Br; **1g–1j**) ketones yielded the corresponding cyanohydrin enol ether products (**2b–2j**) under neat conditions. Additionally, for 4-acetylbenzonitrile (**1k**) and 4-acetylphenylacetate (**1l**), we established an intramolecular chemoselective Si–CN addition to the carbonyl bond with undisturbed nitrile and ester moieties to afford the quantitative formation of cyanohydrin products (**2k** and **2l**). In addition, the TMSCN addition to fused, heterocyclic, alkyl, and long chain ketones **1m–1r** led to the complete formation of cyanohydrin silyl ether products **2m–2r** in excellent yields similar to literature reports.

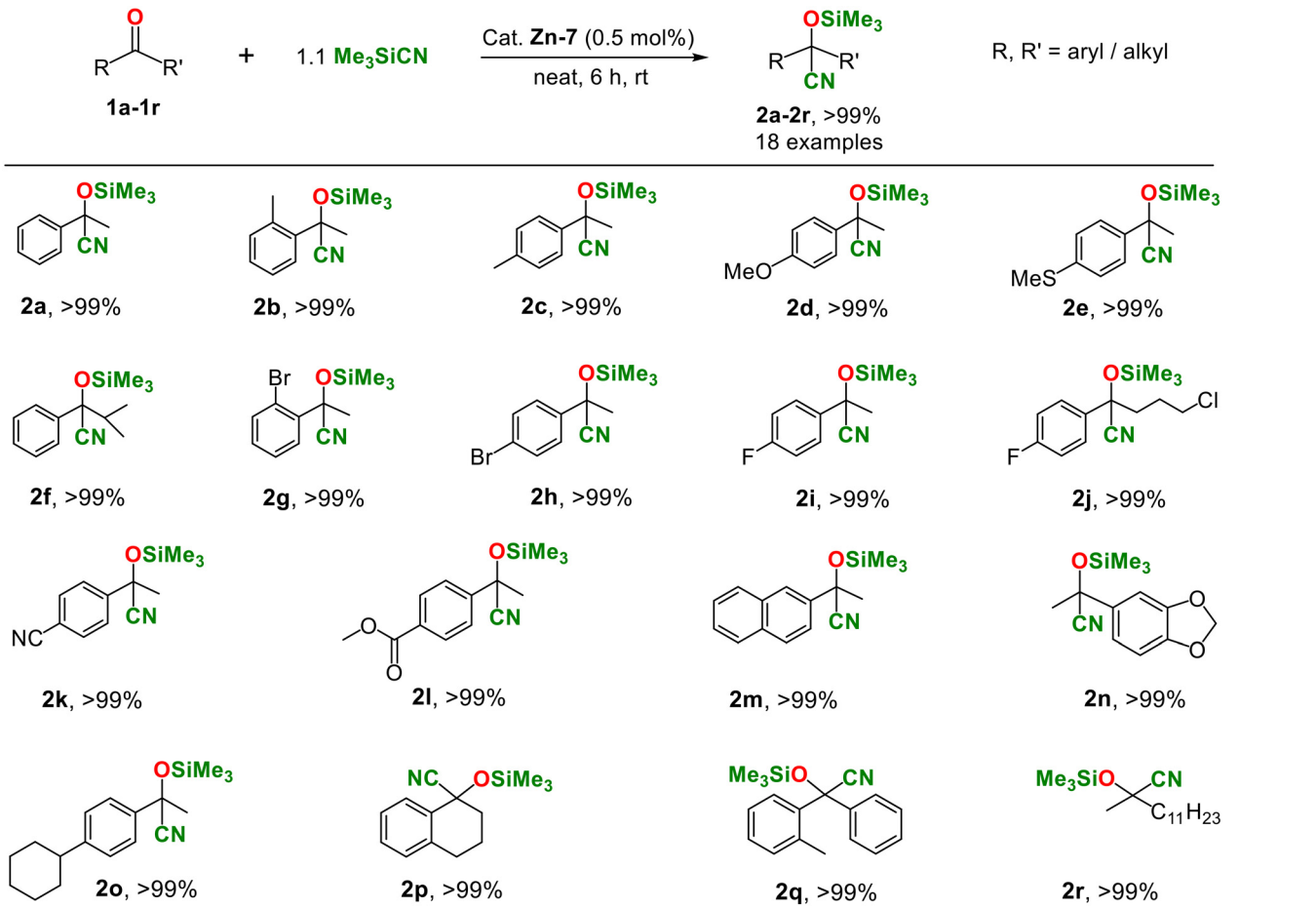
### Scale-up reaction

In additional experiments, the cyanosilylation reaction was conducted on a larger scale under mild conditions to confirm the practical application of the above catalytic reaction (Scheme 3). Interestingly, on a 5.0 mmol scale, the cyanosilyla-

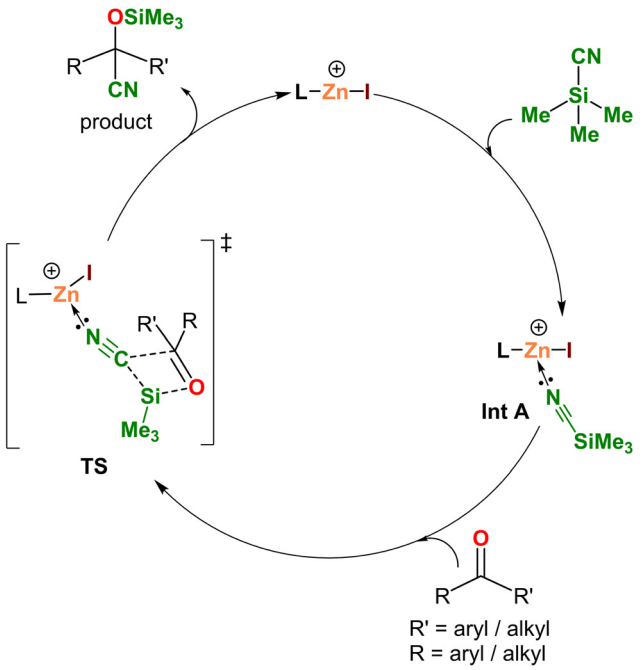



**Scheme 3** Scale-up reaction.

**Table 2** Substrate scope for cyanosilylation of ketones catalyzed by the cationic zinc complex **Zn-7**[a]




[a] Reactions were conducted with ketones (0.3 mmol, 1.0 equivalent), trimethylsilylcyanide (0.33 mmol, 1.1 equivalent), and cat. **Zn-7** (0.5 mol%) in a 10 mL reaction vial under $N_2$ and stirred at rt for 6 h. Conversion for Si–CN addition to ketones was confirmed by NMR ($^1H$ and $^{13}C\{^1H\}$) spectroscopy based on the disappearance of the starting material and formation of the characteristic proton signal for RCR′CNOSi$Me_3$, with respect to the internal standard $CH_2Cl_2$.




**Scheme 4** Proposed mechanism for cyanosilylation of ketones catalyzed by **Zn-7**.

tion of acetophenone with trimethylsilyl cyanide (1.1 equiv.) yielded the respective air-stable cyanohydrin product (**2a**, 0.98 g (89%), isolated).

### Catalytic cycle for cyanosilylation of ketones

Based on literature reports of main group metal catalyzed cyanosilylation of carbonyls, we demonstrate the proposed catalytic cycle of the zinc iodide cation (**Zn-7**) catalyzed addition of TMSCN to ketones in Scheme 4. In the initial catalytic cycle, TMSCN coordinates with the Lewis acidic zinc center in **Zn-7** to yield the labile adduct (Int A). After that, the reaction of the carbonyl with Int A resulted in the corresponding cyanohydrin products and regenerated the catalyst **Zn-7**.

## Conclusion

In summary, we have described the synthesis and structural characterization of N-donor bis-guanidinate chelated mononuclear zinc(II) alkyl, halide, and hydride complexes (**Zn-1** to **Zn-4**). In addition, we have demonstrated the first-time synthesis of cationic zinc methyl, ethyl, and iodide compounds (**Zn-5** to **Zn-7**) coordinated by a tetra-substituted biguanidine ligand in good yields. Moreover, the zinc iodide cation $[L(3H)ZnI]^+$ $[B(C_6F_5)_4]^-$ (**Zn-7**) was employed for cyanosilylation of a wide range of ketones using TMSCN as a cyanide precursor to synthesize cyanohydrin enol ether products in excellent yields under solvent-free conditions. The notable Lewis acidity of the cationic zinc complex opens a new gateway to other challenging organic transformations in main group metal catalysis.

## Conflicts of interest

The authors declare no competing financial interest.

## Data availability

Supplementary information: $^1$H and $^{13}C\{^1H\}$ NMR spectra of all compounds and catalysis products. See DOI: **https://doi.org/10.1039/d4dt02907k**.

CCDC 2292532, 2292533, 2292534, 2292535, 2292536, 2292537 and 2292539 contain the supplementary crystallographic data for this paper.[23a–g]

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