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Hydrolysis of NHC stabilized zinc diaryloxide [(NHC)Zn(OAr)$_2$]: Impact of stoichiometric quantity of water and base

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Dedicated to Professor V. Chandrasekhar on the occasion of his 60th birthday

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ABSTRACT

The reaction of (NHC)ZnEt$_2$ (**1**) with 2,6-dimethylphenol in the molar ratio 1:2 at room temperature resulted in a monomeric zinc dimethylphenoxide [(NHC)Zn(OC$_6$H$_3$-2,6-Me$_2$)$_2$] (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) **(2)**. Whereas, the reaction of **1** with 2,6-dimethylphenol in the presence of water in the molar ratios 1:2:0.5 or 1:2:1 afforded [(NHC)$_2$Zn$_2$(μ-OH)(μ-OC$_6$H$_3$-2,6-Me$_2$)(OC$_6$H$_3$-2,6-Me$_2$)$_2$] (**3**) and [(NHC)Zn(μ-OH)(OC$_6$H$_3$-2,6-Me$_2$)]$_2$ (**4**) respectively. Moreover, reaction of **1** with 2,6-diisopropylphenol in the presence of a base led to the isolation of [(NHC)Zn(μ-OH)(OC$_6$H$_3$-2,6-^{i}Pr$_2$)]$_2$ (**5**). Compounds **2**–**5** have been fully characterized by spectroscopic and single crystal X-ray diffraction studies. In this paper, we have discussed the synthesis, structural characterizations of **2**–**5** and the mechanism for the formation of compounds **3**–**5** from **2**.

1. Introduction

The synthesis of novel molecular compounds containing main group elements has been a challenge and also of great interest over the past few decades. Many molecular compounds once thought to be inaccessible were made possible with the help of judicious choice of the ligands based on their electronic and steric properties. Some of the path breaking compounds include the multiple bonds between the main group elements, low valent compounds of main group elements, frustrated Lewis pairs and so on [1]. Besides the earlier contributions on multiple bonds by West, Sekiguchi, Power and others, notable contributions were made in the preparation of boron-boron triple bond, silicon-silicon double bonds with zerovalent silicon atom, monovalent boron hydride, and divalent silicon(II) species in recent times [1,2]. Most of these achievements have occurred with the use of one of the strong sigma donating Lewis base, *N*-heterocyclic carbenes like imidazole-2-ylidene, and cyclic alkyl amino carbenes (CAAC) which culminated on these developments [3]. In this context, the use of 1,3-dimesitylimidazol-2-ylidene (IMes) in stabilizing novel molecular zinc hydroxyaryloxide, an unstable intermediate normally observed during the hydrolysis of metal alkoxides through sol-gel process (eqn 1) was reported by our group a decade ago [4].

$$\mathrm{M(OR)_n + H_2O \rightarrow (RO)_{n-1}MOH + ROH} \quad (1)$$

$$\mathrm{MOH + ROH + M(OR)_n \rightarrow (RO)_{n-1}MOM(OR)_{n-1} + ROH} \quad (2)$$

$$\mathrm{2(RO)_{n-1}MOH \rightarrow (RO)_{n-1}MOM(OR)_{n-1} + H_2O} \quad (3)$$

Bradley and others have carried out systematic studies on hydrolysis of metal alkoxides (eqn 1–3) [5a]. They have observed that the reaction depends on a number of experimental factors, such as the nature of metal, its oxidation state and coordination number, nature of R group, stoichiometry of water, solvent, and rate of the reaction. Although in some cases the metal hydroxyalkoxide have been observed *in situ*, only the metal oxyalkoxides/metal oxides have been isolated (eqn. 2 and 3). Even the use of sterically hindered alkyl substituents on alcoholic groups were found to be ineffective to isolate the metal hydroxyalkoxide [5]. Instead, terminal metal/non-metal (E) hydroxide compounds have been made

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by the hydrolysis of LEX_n, wherein L and X are mono/multidentate ligand and X varies from halides, alkoxides or carboxylates bound to the central atom [5f,6,7]. Alternatively, the metal phenoxides have been a good choice for the study on hydrolysis, as they are less prone to hydrolysis than the corresponding metal alkoxides, and thereby enhancing the possibility of isolation of metal hydroxyaryloxide. However, they are resistant to hydrolysis due to the oligomeric structures of metal phenoxide [5a,5f]. Earlier, Caulton and others reported the synthesis of monomeric Lewis base adduct of zinc diaryloxides containing sterically encumbered phenols and some of them such as phosphine adducts of zinc aryloxides have been studied for its catalytic activity for copolymerization reactions of epoxides with CO_2 [8]. In addition, the zinc alkoxides and other main group metal alkoxides, have also been used as catalyst for ring opening polymerization (ROP) of cyclic esters [9]. However, the studies on hydrolysis of zinc alkoxides(aryloxides) or organozinc are very limited [10, 11].

Earlier, we have reported the preparation of unsaturated soluble NHC (IMes) adduct of zinc diaryloxides by utilizing the sterically encumbered ortho-substituted phenols (2,6-diisopropyl phenol) [4]. The modification of sterics on phenols from 2,6-diisopropyl phenoxide to 2,4,6-trimethyl phenoxide resulted in a hydrolyzed product **B** (Scheme 1) [4]. In order to understand better the role of steric with respect to the hydrolyzed product formation, 2,6-dimethyl phenol which is closely related to 2,4,6-trimethyl phenol has been used as aryloxide source to isolate the monomeric zinc diaryloxide $[(NHC)Zn(OC_6H_3\text{-}2,6\text{-}Me_2)]$ (**2**). Further, hydrolysis of **2** was carried out under different stoichiometric ratios of water which led to isolation of two different products such as $[(NHC)_2Zn_2(\mu\text{-}OH)(\mu\text{-}OC_6H_3\text{-}2,6\text{-}Me_2)(OC_6H_3\text{-}2,6\text{-}Me_2)_2]$ (**3**) and $[(NHC)Zn(\mu\text{-}OH)(OC_6H_3\text{-}2,6\text{-}Me_2)]_2$ (**4**). In addition, hydrolysis of zinc diaryloxide (**A**) in the presence of a base afforded $[(NHC)Zn(\mu\text{-}OH)(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2$ (**5**). In this paper, we report synthesis, spectroscopic characterizations, and the single crystal x-ray diffraction studies of **2**–**5**.

2. Results and discussion

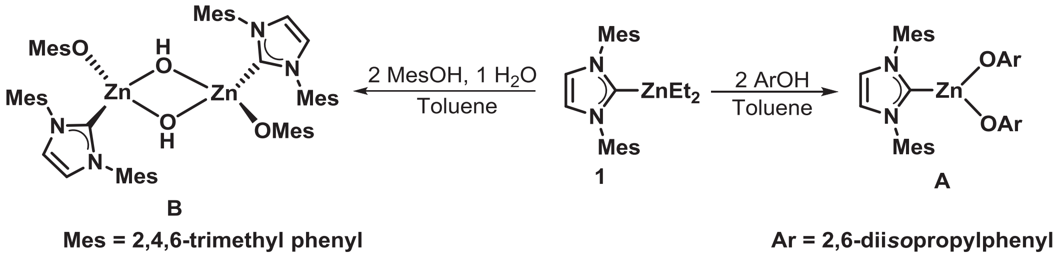
2.1. Synthesis of Zn–NHC complexes 2–5

Addition of two equivalents of 2,6-dimethylphenol to a toluene solution of *in situ* generated **1** [12c], afforded colorless crystals of NHC supported zinc bis(2,6-dimethylphenoxide) (**2**) in nearly quantitative yield (Scheme 2). Compound **2** is hygroscopic in solid and quite stable in solution. Like **A**, the ^{1}H NMR of **2** in $CDCl_3$, used as obtained, does not indicate decomposition [13]. The ^{1}H NMR spectrum shows two distinct singlet peaks at 1.91 ppm and 2.33 ppm for the presence of both *ortho* and *para* methyl protons of *N*-substituted mesityl groups in NHC and a singlet peak at 2.00 ppm for *ortho* methyl group of 2,6-dimethylphenoxide ions. In addition, three distinct peaks for aromatic protons of dimethylphenoxide (*para*) at 6.32 ppm, dimethylphenoxide (*meta*) at 6.68 ppm, and mesityl group (*meta*) at 6.94 ppm in the ratio of 1:2:2 respectively, authenticated the presence of **2** in solution. Further, the molecular structure of **2** was confirmed through the single crystal X-ray diffraction studies.

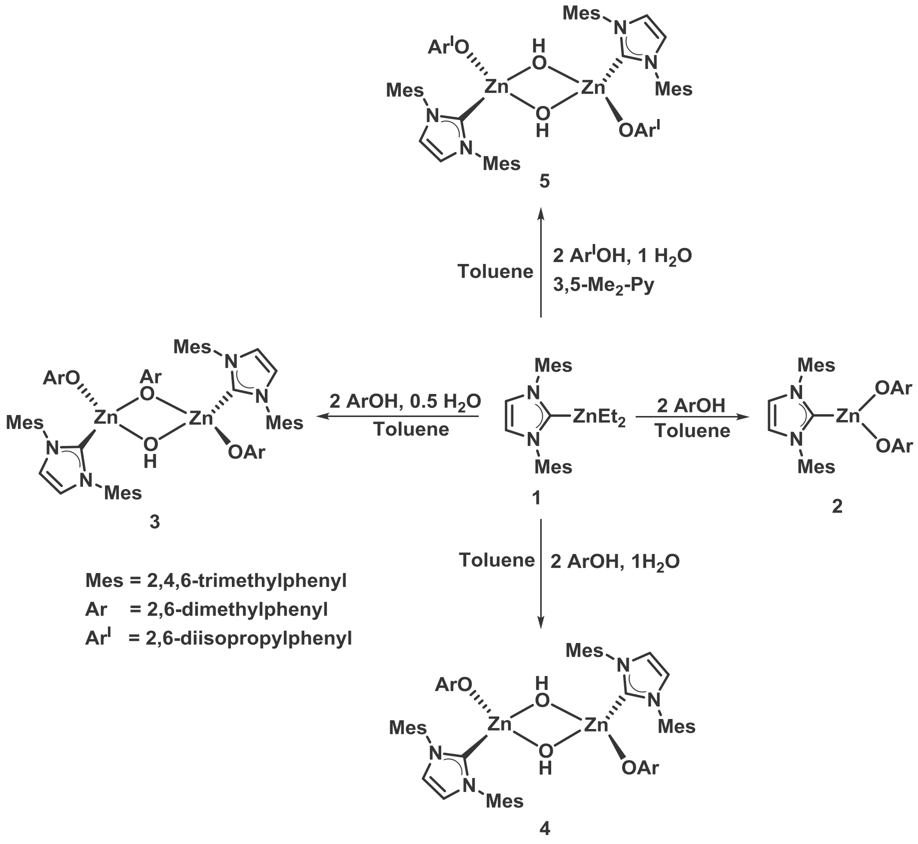
The above reaction is very sensitive towards moisture during the experimental conditions which indeed affects the overall reaction products. Thus, the reaction of 1 with two equivalents of 2,6-dimethylphenol in toluene resulted in colorless crystals of an unexpected partially hydrolyzed zinc hydroxyaryloxide (3) which may be due to the absorption of adventitious moisture. The same product was also isolated with the deliberate addition of stoichiometric quantities of water (0.5 equivalents) to the above reaction mixture (Scheme 2). The ^{1}H NMR of **3** shows the presence of methyl protons of mesityl group in NHC as well as the 2,6-dimethyl phenoxide ions between 2.12–2.28 ppm region. Also, the presence of a multiplet for *para* protons of dimethylphenoxide at 6.68 ppm, a doublet for *meta* protons of dimethyl phenoxide ions at 6.91 ppm and multiplet for meta protons of mesityl group and one of the 4,5 CH of imidzol-2-ylidene from 6.97-7.21 ppm and a singlet for the another backbone proton of imidazol-2-ylidene at 7.52 ppm respectively indicates the presence of partially hydrolyzed product **3**. Further, the IR spectrum of **3** shows a peak at 3672 cm^{-1} indicates the presence of OH group attached to the zinc center. To further authenticate the formation of **3**, a single crystal X-ray diffraction analysis was carried out.

The formation of **3** has prompted us to attempt and to isolate the monomeric zinc hydroxyaryloxide or hydroxy bridged product similar to the previously reported compound **B** (Scheme 1) by the addition of an equivalent amount of water to the reaction mixture. Thus, the reaction between **1**, 2,6-dimethylphenol and water in the stoichiometric ratio of 1:2:1 was carried out (Scheme 2). The ^{1}H NMR spectrum of **4** shows resonances for the methyl protons of mesityl groups of NHC and 2,6-dimethylphenoxide ions at 2.12–2.28 ppm and the *p*-CH proton of 2,6-dimethylphenoxide ion at 6.66 ppm which indicates the presence of 1:1 ratios of NHC ligand and 2,6-dimethylphenoxide ion. The IR spectrum of **4** shows a peak at 3671 cm^{-1} for the presence of hydroxyl group at zinc center. Based on the above characterization, it is clear that the structure of **4** could be similar to that of **B** (Scheme 1), and it was confirmed by single crystal X-ray diffraction study.

As it was noted earlier by us, **2** was hygroscopic and thus it is expected to form the hydrolyzed product under the experimental conditions of **3** or **4**. To our surprise, the hydrolysis of **A** under the same conditions for the preparation of **4**, yielded multiple products and it was difficult to purify to get one single compound. Alternatively, the reaction of **1** and 2,6-diisopropylphenol in the presence of 3,5-dimethylpyridine and water in the molar ratio 1:2:2:1 in toluene afforded **5** with good yield. The stretching frequency (3700 cm^{-1}) in IR spectrum suggests the presence of a hydroxyl group at the zinc center. The ^{1}H NMR spectrum of **5** shows



Scheme 1. Synthesis of complexes **A** and **B**.



Scheme 2. Synthesis of complexes **2**–**5**.

resonates for the methyl protons of mesityl groups of NHC at 2.18 ppm (*ortho*) and 2.31 ppm (*para*) as well as $-CH_3$ and $-CH$ of *iso*propyl groups of 2,6-diisopropylphenoxide ion at 1.28 and 3.17 ppm respectively in the ratio of 6:3:6:1. Also, aromatic protons of mesityl group and *para* protons of 2,6-diisopropylphenoxide group resonance around 6.92 ppm, whereas *meta* protons of 2,6-diisopropylphenoxide group and 4,5-C*H* of imidazole-2-ylidene shows resonance at 7.10 and 8.13 ppm respectively, indicating the presence of **5** in solution. Based on the above characterization, it was clear that the structure of **5** could be similar to that of **B** and **4** (Scheme 1) which was also confirmed by single crystal X-ray diffraction study. It is worthy to point out that in the sol-gel process, addition of base helps to form the condensed product i.e. metal oxoalkoxides or metal oxide [5a,14]. However, in the present case, the addition of base facilitates the hydrolysis of zinc aryloxides to form **5**.

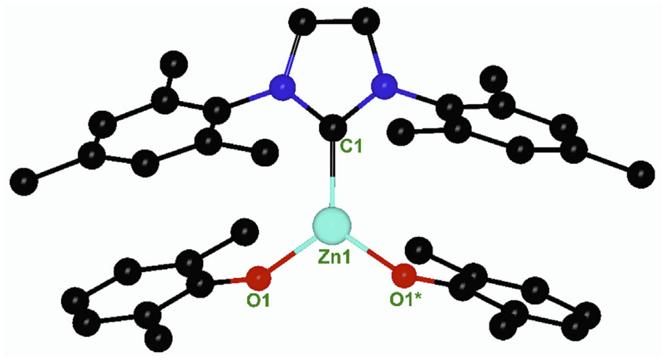


Fig. 1. Diamond drawing molecular structure of **2**. All the hydrogen atoms were omitted for clarity. The important bond lengths (Å) and angles (°): Zn1–O1 1.886(2), Zn1–O1* 1.886(2), Zn1–C1 1.989(4); O1–Zn1–O1* 113.15(13), O1–Zn1–C1 123.43(6), O1*-Zn1-C1 123.43(6).

2.2. *Solid state structures for compounds* **2**–**5**

Structures of **2**–**5** were unambiguously confirmed by single crystal X-ray diffraction studies. The crystallographic data and structure refinements are given in Table S1 in supplementary data. Single crystals of **2** were obtained in toluene solution at 0 °C and a suitable one was subjected to the single crystal x-ray diffraction study. The molecular structure of **2** is shown in Fig. 1 and the selected bond lengths and angles are provided in the legend. The molecular structure of **2** contains a tri-coordinated zinc surrounded by a carbene carbon atom of NHC along with two oxygen atoms of 2,6-dimethylphenoxide ions to form a $CZnO_2$ trigonal planar geometry. The imidazole ring of the NHC is lying along with the planar $CZnO_2$, whereas the phenyl ring of the 2,6-dimethylphenoxide ions are lying above and below the plane (Fig. 2a). The bond distance of Zn–C (1.989(4) Å) is comparable to the previously reported compound (**A**), whereas, the Zn–O (1.886(2) Å) bond distance is slightly longer than Zn–O (1.872(4) Å) in **A** (Fig. 2a). Overall, the bond distances and angles in **2** and **A** define an imperfect equilateral triangle [4]. It is to be pointed out that there is a shorter distance between hydrogen of one of the methyl carbon of the 2,6-dimethylphenoxide ion with the zinc center indicating the formation of agostic interaction [Zn–H = 2.430 Å [5]; bond angle Zn–H–C = 105.59 (18)°]. Also, compound **2** shows intermolecular C*H*···O interaction between oxygen of 2,6-dimethylphenoxide and the backbone 4,5-CH of NHC

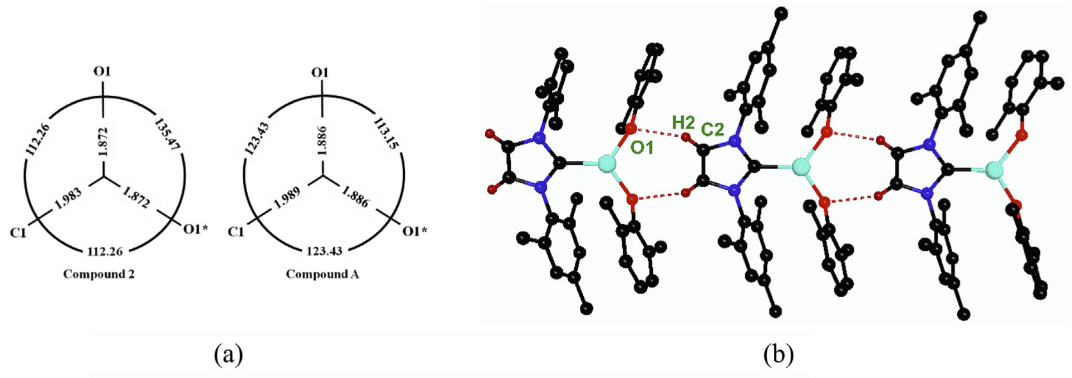


Fig. 2. (a) Bond angles and distances in trigonal planar compounds **2** and **A**. (b) C*H*···O interaction in **2.** A view down to *a*-axis.

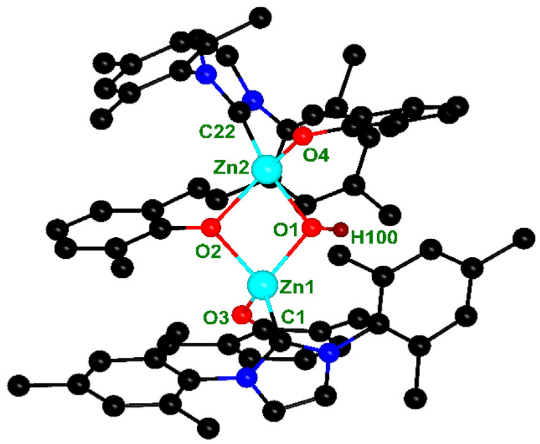


Fig. 3. Diamond drawing molecular structure of **3.** Except hydroxyl hydrogen (H100), all the hydrogen atoms were omitted for clarity. The important bond lengths (Å) and angles (°): Zn1–C1 2.060(4), Zn1–O3 1.932(2), Zn1–O1 1.953(3), Zn1–O2 2.054(2), Zn2–O4 1.928(2), Zn2–O1 1.945(3), Zn2–C22 2.048(3), Zn2–O2 2.083(2), Zn1–Zn2 3.0304(8); O1–Zn2–O2 81.58(10), O1–Zn1–O2 84.07(14), O3–Zn1–O1 109.94(11), O3–Zn1–C1 102.65(15), O4–Zn2–C22 103.88(14), N2–C1–N1 104.3(4), N4–C22–N3 103.9(4).

that results in supramolecular 1D chain along *b*-axis [*C*2–H2 0.930 Å, H2···*O*1 2.312(2) Å, *C*2···*O*1 3.165(4) Å, *C*2-H···*O*1 152.25(20)°] (Fig. 2b).

Single crystals of **3** were grown in toluene solution at -20 °C and a suitable one was subjected to the X-ray structural analysis. Compound **3** crystallizes in the centrosymmetric space group $P2_1/c$. The structure of zinc hydroxyaryloxide (**3**) is shown in Fig. 3 along with important bond length and bond angles. It consists of two zinc atoms which are bridged by a hydroxy group and the 2,6-dimethyl phenoxide ions forming a Zn_2O_2 four membered ring. Further, each zinc atom is coordinated to a carbene carbon of NHC and an oxygen atom of the 2,6- dimethylphenoxide ion to complete the four coordination number around zinc atoms. The NHCs and the terminal 2,6-dimethyl phenoxide ions attached to the zinc atoms are *trans* to each other. The average Zn–O bond distance of the hydroxyl group to zinc atoms is 1.949 Å, which is shorter than the reported values as well as for compound **B** [4, 8f]. The average Zn–O bond distances of bridged and the terminal 2,6-dimethyl phenoxide ion was found to be 1.983(3) Å and 1.930(3) Å respectively and the Zn–O bond distances between Zn and terminal 2,6-dimethylphenoxide is found to be longer than the Zn–O of monomeric $Zn(OC_6H_3\text{-}2,6\text{-}Me_2)_2(Py)_2$ (Zn–O: 1.903(4) Å) and $Zn(OC_6H_3\text{-}2,6\text{-}Me_2)_2(MeIm)_2$ (Zn–O: 1.918(2) Å) [14]. The Zn–C bond distance (2.0385(4) Å) is almost comparable to the value observed for Zn–C in **B** (Zn–C: 2.039(4) Å) [4].

Single crystals of **4** and **5** were grown in toluene solution at low temperatures and suitable crystals were subjected to the X-ray structural analysis. Both **4** and **5** are isostructural (Fig. 4), but crystallized in different space group *C* 2/*c* and $P\bar{1}$ respectively. The solid state structures of **4** and **5** are shown in Fig. 4 along with selected bond lengths and bond angles. It consists of two zinc atoms which are bridged by two hydroxy groups forming a planar four membered Zn_2O_2 ring. Each zinc atom is in tetrahedral geometry and are coordinated by a carbene carbon of NHC, an oxygen atom of the phenoxide ion as well the bridging hydroxy groups. The Zn-O of the hydroxy groups show two different bond distances, [1.977(3) Å and 1.983(3) Å (**4**) as well as 1.987(5) Å and 1.971(4) Å (**5**)], which are comparable with the reported value for the similar compounds [4]. The Zn-C bond distances [2.038(4) Å and 2.019(4) Å (**4**) and 2.046(6) Å and 2.033(5) Å (**5**)] are shorter than the observed value for $[(NHC)Zn(OCH_2Ph)_2]_2$ [Zn-C = 2.054(3) Å; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] [8g] and almost similar to **B** [4].

2.3. Mechanism for the formation of 3, 4 and 5

The formation of **3, 4** and **5** (Scheme 2) can be understood if we compare with the detailed general mechanism proposed for the hydrolysis of metal alkoxides [2]. Based on this, a tentative mechanism is shown in Scheme 3. Accordingly, the first step is the formation of water adduct with zinc aryloxides (**II**), followed by the elimination of an equivalent amount of substituted phenol to form a *in situ* monomeric zinchydroxyaryloxide (**III**). The tri-coordinated zinc in **III**, due to lack of steric stability, combines either with an equivalent of zincaryloxide (**I**) to give **3** or dimerizes to **4** or **5** or **B** whereby zinc attains four coordination.

3. Conclusion

In conclusion, we have synthesized the NHC supported zinc aryloxide (**2**) and its hydrolyzed products zinc hydroxyaryloxides (**3** and **4**). The presence of these compounds (**2–4**) in solution has been identified by ^1H NMR. Compound **3** represents an intermediate formed on the way to the formation of **4**. In fact, the isolation of these two compounds suggests that the intermediate metal hydroxyalkoxides may have various possible structures before they undergo condensation reactions in the sol-gel processes. Further, zinc dihydroxyaryloxide **5** could be isolated in presence of a 3,5-

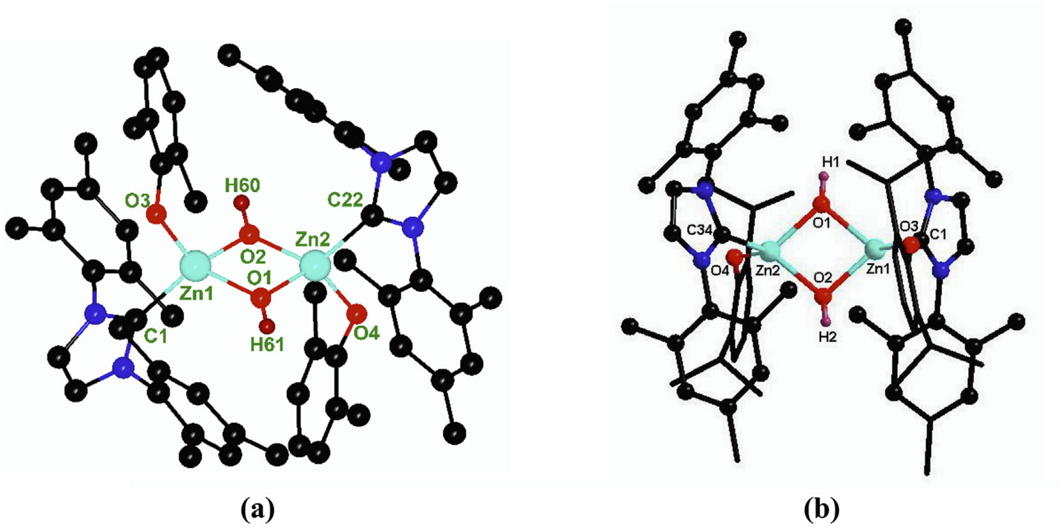
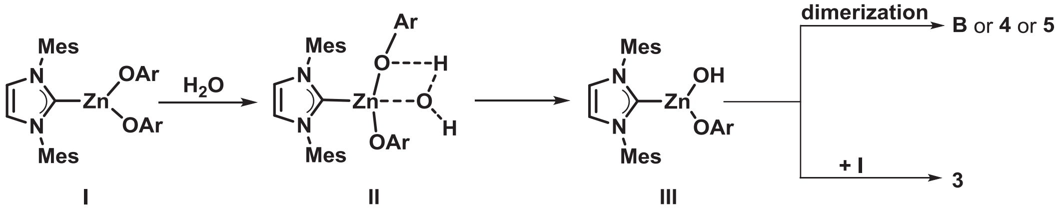


Fig. 4. (**a**) Diamond drawing molecular structure of **4**. Except H60and H61, all the hydrogen atoms were omitted for clarity. The important bond lengths (Å) and angles (°): Zn1–C1 2.038(4), Zn1–O3 1.931(3), Zn1–O1 1.986(3), Zn1–O2 2.054(2), Zn2–O4 1.929(3), Zn2–O1 1.980(3), Zn2–C22 2.019(4), Zn2–O2 1.987(3), Zn1–Zn2 2.9454(7); Zn1–O2–Zn2 96.28(15), Zn2–O1–Zn1 95.92(15), O3–Zn1–O1 114.07(14), O1–Zn1–C1 115.94(17), O2–Zn1–C1 124.45(15), O3–Zn1–C1 102.65(15), N2–C1–N1 104.3(4), N4–C22–N3 103.9(4). (**b**) Diamond drawing molecular structure of **5**. Except H394, H398, all hydrogen atoms and toluene were removed for clarity. The important bond lengths (Å) and angles (°): Zn(1)–C(1) 2.046(6), Zn(2)–C(34) 2.033(5), Zn(1)–O(1) 1.987(5), Zn(1)–O(2) 1.971(4), Zn(1)–O(3), 1.915(4), Zn(2)–O(1) 1.979(5), Zn(2)–O(2) 1.979(4), Zn(2)–O(4) 1.914(4). Zn(1)–Zn(2) 2.9827(11); Zn(1)-O(1)-Zn(2) 97.6(2), Zn(1)-O(2)-Zn(2) 98.0(2), O(1)-Zn(1)-O(2) 82.19(19), O(1)-Zn(2)-O(2) 82.20(19), O(2)-Zn(1)-C(1) 121.1(2), O(2)-Zn(2)-C(34) 123.2(2), N(1)-C(1)-N(2) 104.3(5), N(3)-C(34)-N(4) 103.7(5).



Mes = 2,4,6-trimethylphenyl
Ar = 2,4,6-trimethylphenyl (**B**)
2,6-dimethylphenyl (**3** and **4**)
2,6-diisopropylphenyl (**5**)

Scheme 3. Probable mechanism for the formation of **3**, **4** and **5**.

dimethylpyridine. Also **3**, **4** and **5** shows the remarkable stability of zinc-carbene carbon bond which adds up as an example for the hydrolytic durability in NHC metal complexes. We are continuing our efforts to isolate the monomeric zinc hydroxyaryloxide by further modulation of aryloxides and coordinating ligands.

4. Experimental section

4.1. Materials and method

Tetrahydrofuran and toluene were dried and freshly distilled prior to use from sodium/benzophenone under nitrogen. All the reactions and manipulations were carried out under dry nitrogen atmosphere using standard Schlenk line technique. Glassware were dried in oven at 120 °C overnight. Chemicals such as 2,4,6-trimethylaniline, diethylzinc (1 M in hexane) and 2,6-dimethyl phenol were purchased from Aldrich Chemicals and used as received. Glyoxal, HCl (37% in H_2O) and paraformaldehyde were purchased from sd fine chemicals, India and used as received. Compounds 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride [12a,b] and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene zinc diethyl (**1**) [12c] were prepared by literature procedures. ^{1}H NMR spectra were obtained on JEOL (400 or 500 MHz) spectrometers. The spectra were recorded in $CDCl_3$ solution, and the chemical shifts were referenced with respect to TMS. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FTIR spectrophotometer operating from 400 to 4000 cm^{-1}. Elemental analyses were carried out by using a Thermo quest CE instrument model CE440 CHNS–O elemental analyzer.

4.2. X-ray crystallography

Intensity data of compounds **2** to **5** were collected on a Bruker Smart Diffractometer and Bruker Smart Diffractometer/CCD area detector fitted with graphite monochromatised MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). No decomposition of the crystal occurred during data collection. All calculations for data reduction were done using Bruker SADABS program. Structure solution and refinement were done using the programs incorporated in WINGX 1.70.1 crystallographic collective package and SHELXTL program. The structures were first solved by direct methods (SIR-92 or SIR-97) and successive Fourier synthesis and refined (SHELXL 97) by full matrix least squares procedures methods based on F^2, minimizing the function $\Sigma w(|F_o| - |F_c|)$ [2], where F_o and F_c are the observed and calculated structure amplitudes, and the weight $w = 1$. Anisotropic refinements were performed by full-matrix least-squares procedure on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in idealized positions, and a riding model was used [15]. The crystal structure of **5** was solved through Olex2 [16]. The details of the individual crystals are summarized in tables. In the crystal **3,** the disordered toluene solvent molecule was squeezed with program SQUEEZE in PLATON [17a]. The crystallographic figures were generated by using *Diamond 3.1f* programme [17b].

4.3. Synthesis and characterization

4.3.1. Synthesis of [(NHC)Zn(OC$_6$H$_3$-2,6-Me$_2$)$_2$] (**2**)

2,6-Dimethyl phenol (0.49 g, 4 mmol) was slowly added to a solution of **1** [generated *in situ* by the addition of zinc diethyl (2.0 mL of a 1.0 M solution in hexane, 2.0 mmol) to the NHC (0.62 g, 2 mmol) in toluene (50 mL)] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred overnight and filtered using celite. Colorless small crystals were formed at 0 °C after a month. **2**: Yield (based on NHC): 1.08 g, 87%. Anal.Calcd. for $C_{37}H_{42}N_2O_2Zn$ (612.11) [18]: C, 72.60; H, 6.92; N, 4.58. Found: C, 68.74; H, 7.97; N, 4.14. IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3436(w), 3151(w), 3070(w), 3007(w), 2914(m), 2850(w), 1763(w), 1593(m), 1548(w), 1480(vs), 1427(vs), 1370(m), 1283(vs), 1237(s), 1109(m), 1089(s), 1030(m), 979(w), 915(w), 853(vs), 780(m), 754(vs), 700(m), 590(w), 571(w), 495(w), 468(w) cm^{-1}.^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ 1.91 (s, 12H, *o*-C*H*$_3$ (mesityl)), 2.00 (s, 12H, *o*-C*H*$_3$ (dimethylphenol)), 2.33 (s, 6H, *p*- C*H*$_3$ (mesityl)), 6.32 (m, 2H, *p*-OC$_6$*H*$_3$-(CH$_3$)$_2$), 6.68 (m, 4H, *m*-OC$_6$*H*$_3$-(CH$_3$)$_2$), 6.94 (s, 4H, *m*-C$_6$*H*$_2$-(CH$_3$)$_3$). The proton of N(C*H*)$_2$N) is merged with residual proton of CDCl$_3$.

4.3.2. Synthesis of [(NHC)$_2$Zn$_2$(μ-OH)(μ-OC$_6$H$_3$-2,6-Me$_2$)(OC$_6$H$_3$-2,6-Me$_2$)$_2$] (**3**)

Method A: 2,6-Dimethyl phenol (0.49 g, 4 mmol) was slowly added to a solution of **1** [generated *in situ* by the addition of zinc diethyl (2.0 mL of a 1.0 M solution in hexane, 2.0 mmol) to the NHC (0.62 g, 2 mmol) in toluene (50 mL)] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred for overnight. The solution was concentrated to one-third of its volume and then filtered using celite. Colorless crystals were formed from the filtrate at −20 °C within two days.

Method B: 2,6-Dimethyl phenol (0.25 g, 2 mmol) was slowly added to a solution of **1** [generated *in situ* by the addition of zinc diethyl (1.0 mL of a 1.0 M solution in hexane, 1.0 mmol) to the NHC (0.31 g, 1 mmol) in toluene (50 mL)] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred for 3 h. To this clear solution, double distilled water (0.009 mL, 0.5 mmol) was added in one shot. The resulting mixture was stirred for 14 h and during this period a small amount of white solid was formed. The reaction mixture was heated for 1 h and then filtered in hot condition using celite. The filtrate was kept at −20 °C. Colorless crystals were formed after few days. **3**: Yield (based on NHC): 0.72 g, 63%. Anal.Calcd. for $C_{66}H_{76}N_4O_4Zn_2$ (1120.09): C, 70.77; H, 6.84; N, 5.00. Found: C, 69.34; H, 7.42; N, 4.75. IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3672(w), 3159(w), 3122(w), 3028(m), 2999(m), 2919(s), 2857(s), 1675(s), 1589(m), 1466(vs), 1423(vs), 1378(m), 1330(w), 1292(vs), 1239(s), 1161(w), 1088(s), 1033(m), 965(w), 931(w), 851(vs), 802(w), 744(vs), 697(m), 572(w), 427(m). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ 2.12 (s, 24H, *o*-C*H*$_3$(carbene)), 2.17 (s, 18H, *o*-C*H*$_3$ (phenol)), 2.28 (s, 12H, *p*-C*H*$_3$ (carbene)), 6.68 (m, 3H, *p*-OC$_6$H$_3$), 6.91 (d, 6H, *m*-OC$_6$H$_3$), 6.97–7.21 (m, 11H, *m*-C$_6$H$_2$, partially N(C*H*–C*H*)$_2$N), 7.52 (s, 1H, NC*H*–C*H*N).

4.3.3. Synthesis of [(NHC)Zn(μ-OH)(OC$_6$H$_3$-2,6-Me$_2$)]$_2$ (**4**)

2,6-Dimethyl phenol (0.25 g, 2 mmol) was slowly added to a solution of **1** [generated *in situ* by the addition of zinc diethyl (1.0 mL of a 1.0 M solution in hexane, 1.0 mmol) to the NHC (0.31 g, 1 mmol) in toluene (30 mL)] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred for 8 h. To this clear solution, double distilled water (0.018 mL, 1 mmol) was added in one shot. The resulting mixture was stirred for 12 h and during this period a small amount of white solid was formed and then filtered using celite. The filtrate was kept at −20 °C. Colorless crystals were formed after one week. **4**: Yield (based on NHC): 0.82 g, 78%. Anal.Calcd. for $C_{58}H_{68}N_4O_4Zn_2$ (1015.94): C, 68.57; H, 6.75; N, 5.51. Found: C, 65.64; H, 6.66; N, 4.97. IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3671(w), 3159(w), 3123(m), 2921(s), 1588(m), 1465(vs), 1422(s), 1378(s), 1292(vs), 1238(m), 1104(m), 1088(m), 1032(m), 965(w), 932(m), 850(s), 744(s), 698(s), 571(w), 519(m), 464(w) 427(m). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ 2.12–2.28 (m, 48H, *o,p*-C*H*$_3$(carbene), *o*-C*H*$_3$ (phenol)), 6.66 (t, 2H, *p*-OC$_6$H$_3$), 6.89 (d, 4H, *m*-OC$_6$H$_3$), 6.96–7.01 (m, 8H, *m*-C$_6$*H*$_2$). The proton of N(C*H*)$_2$N) is merged with residual proton of CDCl$_3$.

4.3.4. Synthesis of [(NHC)Zn(μ-OH)(OC$_6$H$_3$-2,6-^{i}Pr$_2$)]$_2$ (**5**)

2,6-Diisopropyl phenol (0.40 mL, 2 mmol) was slowly added to a solution of **1** [generated *in situ* by the addition of zinc diethyl (1.0 mL of a 1.0 M solution in hexane, 1.0 mmol) to the NHC (0.31 g, 1 mmol) in toluene (30 mL)] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred for overnight. To this reaction mixture, 3,5-dimethylpyridine (0.2 mL, 2 mmol) and double distilled water (0.018 mL, 1 mmol) were added in one shot. The resulting mixture was stirred for 12 h and during this period a small amount of white solid was formed. The solution was reduced to one-third of its volume by vacuum and then filtered using celite. The filtrate was kept at −25 °C. Colorless crystals were formed after 20 days. **5**: Yield (based on NHC): 0.485 g, 84%. Anal. Calcd. for $C_{66}H_{84}N_4O_4Zn_2$ (1015.94): C, 70.26; H, 7.50; N, 4.97. Found: C, 70.20; H, 7.71; N, 4.81. IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3700(w), 2953(s), 2923(m), 2860(w), 1587(w), 1489(m), 1429(vs), 1379(w), 1343(m), 1279(m), 1239(w), 1141(w), 1106(w), 849(m), 749(s), 697(w), 571(w), 547(w), 422(w) cm^{-1}.^{1}H NMR (500 MHz, CDCl$_3$, 19.7 °C, TMS): δ 1.28 (d, 24H, CH(C*H*$_3$)$_2$), 2.18 (s, 24H, *o*-C*H*$_3$), 2.31 (s, 12H, *p*-C*H*$_3$), 3.17 (m, 4H, C*H*(CH$_3$)$_2$), 6.92 (m, 10H, *p*-OC$_6$H$_3$ and *m*-C$_6$H$_2$), 7.10 (d, 4H, *m*-OC$_6$H$_3$), 8.13 (s, 4H, N(C*H)*$_2$N).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.05.001. It contains crystallographic data, and NMR of reported complexes **2**-**5**. CCDC entries 654628, and 1886799-1886801 contains supplementary crystallographic data of the structures reported in this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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[13] The ^{1}H NMR spectrum is recorded in $CDCl_3$ used as received as solvent. However it may be noted that the solutions of **2** - **5** are not stable after half an hour and hence the ^{13}C NMR spectra were not provided.

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[18] In solid, compound **2** is stable under ambient atmosphere conditions for few minutes however for exposure of this compound for prolonged period of time shows absorption of moisture followed by decomposition. Hence our effort to obtain the elemental analysis of the compound was not successful.