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Notes

Synthesis and Characterization of NHC-Stabilized Zinc Aryloxide and Zinc Hydroxyaryloxide†

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*Summary: The reaction of (NHC)ZnEt$_2$ (**1**) with 2,6-diisopropylphenol in the molar ratio 1:2 at room temperature resulted in the formation of NHC-stabilized monomeric tricoordinated zinc aryloxide (**2**), whereas the reaction of (NHC)ZnEt$_2$ (**1**) with 2,4,6-trimethylphenol either in the presence of moisture or with deliberate addition of an equivalent amount of water in the molar ratio 1:2:1 afforded an unprecedented zinc hydroxyaryloxide (**3**). In this contribution we describe the syntheses and the structural characterization of **2** and **3** as well as the importance of the sterically encumbered phenols in the isolation of the final products.*

Introduction

Sol−gel processes have been widely used for the preparation of metal oxides, which have potential applications in the areas of material science and catalysis. In this method the metal alkoxides have been used as precursors, which on hydrolysis yield metal oxides. It has been presumed that the first step of the hydrolysis proceeds through an unstable monomeric metal hydroxyalkoxide intermediate. This subsequently condenses to form metal oxoalkoxides (eqs 1−3).[1] Although various metal oxoalkoxides have been reported in the last few decades, only a few examples of the metal hydroxyalkoxides (aryloxides) have been isolated to date and structurally characterized.[1,2] Moreover, in recent years there is a widespread interest in the synthesis of metal hydroxides containing Brønsted acidic protons due to their exciting potential in several areas. To name a few, these can serve as (a) starting materials to study the condensation reactions that occur in the sol−gel process, (b) precursors for the synthesis of heterometallic oxides, and (c) supports for the catalytically active metal centers.[3] Therefore we have been interested in studying the controlled hydrolysis of metal alkoxides/aryloxides and in isolating the soluble monomeric metal hydroxo compounds.

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

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

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

The hydrolysis of metal alkoxides depends upon various experimental parameters such as the nature of the metal, oxidation state, coordination number, nature of the R group, stoichiometry of water, solvent, and rate. In almost all the cases known so far, the hydrolysis of metal alkoxides, even on varying the different experimental parameters, afforded metal oxoalkoxides.[1a] Therefore in our studies we have made two changes with respect to the choice of the precursors, in order to prevent the condensation and/or oligomerization of the final product. First, instead of metal alkoxides, we have chosen sterically encumbered metal aryloxides as precursors, since compared to the former, the latter are more resistant to hydrolysis. Second, we have decided to “block” some of the coordination sites with a Lewis base. The choice of N-heterocyclic carbene (NHC) ligands as the Lewis bases is due to their strong σ-donating character to the metal center and also due to the hydrolytic durability of the NHC−metal bonds in complexes.[4] Moreover it is also possible to vary the steric bulk on both the nitrogen centers of the NHC, which would help to study their role in preventing oligomerization/condensation reactions. By keeping the above assumption, we report herein the syntheses and the structural characterization of a zinc aryloxide (**2**) and a zinc hydroxyaryloxide (**3**). Moreover, we have also discussed the importance of the sterically encumbered phenols in the isolation of the final products.

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† Dedicated to Professor H. W. Roesky.

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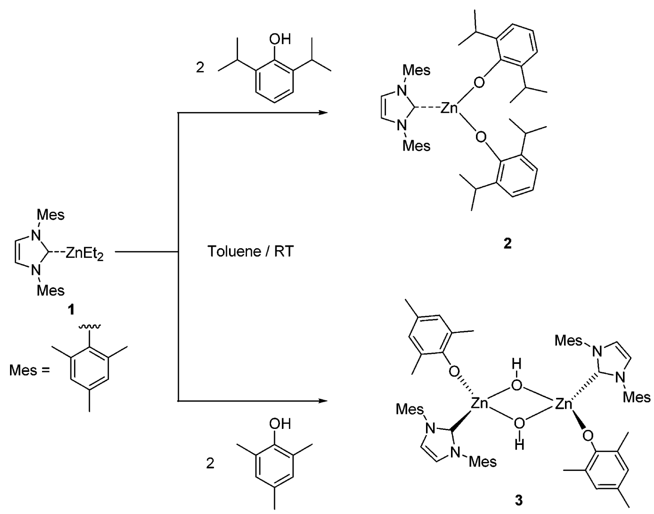
10.1021/om060867r CCC: $37.00

Scheme 1. Synthesis of Complexes 2 and 3



Results and Discussion

Addition of 2 equiv of 2,6-diisopropyl phenol to a toluene solution of *in situ* generated **1**^{5} afforded colorless crystals of zinc aryloxide (**2**) in nearly quantitative yield (Scheme 1). Surprisingly, compound **2** is remarkably stable under ambient atmosphere conditions, both in the solid and in the solution state. It may be noted that the ^{1}H NMR of **2** in $CDCl_3$, *used as-obtained*, does not indicate decomposition. The ^{1}H NMR spectrum shows resonances for the methyl protons of mesityl groups of NHC (of both ortho and para position) and 2,6-diisopropyl phenoxide ions in the expected ratio of 3:4. Further the single-crystal X-ray diffraction reveals that the molecular structure of **2** (Figure 1) contains a tricoordinated zinc that is attached to a carbene carbon atom along with two oxygen atoms of 2,6-diisopropyl phenoxide ion.^{6} The bond distance of Zn−C is found to be 1.983 Å, which is shorter than the Zn−C (1.994 Å) reported in the case of tricoordinated NHC−$ZnEt_2$ [NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene].^{5} A longer Zn−O bond distance (1.872 Å) is observed in **2** as compared to the reported value for $Zn(O\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)_2\cdot 2THF$ (av Zn−O: 1.851 Å).^{7a} It is interesting to note that among the adducts of zinc diaryloxide known in the literature,^{7} there are only two structurally characterized examples where the zinc is in a tricoordination mode.^{7b,c}

In contrast to the situation found in the formation of **2**, the addition of 2 equiv of 2,4,6-trimethylphenol to **1** in toluene afforded an unprecedented zinc hydroxyaryloxide (**3**) in low yield (method A; Scheme 1; see Experimental Section). The stretching frequency at 3688 cm^{-1} in the IR spectrum suggests that there could be a presence of a hydroxyl group at the zinc center. In order to confirm the product formation (**3**), a single-crystal X-ray diffraction analysis was carried out (Figure 2).^{6} Single crystals of **3** were grown in toluene solution at −20 °C, and a suitable one was subjected to X-ray structural analysis. The molecular structure reveals the formation of zinc hydroxyaryloxide (**3**) (Figure 2). It consists of two zinc atoms that are bridged by two hydroxyl groups, forming a Zn_2O_2 four-membered ring. In **3**, each zinc atom is in a tetrahedral geometry,

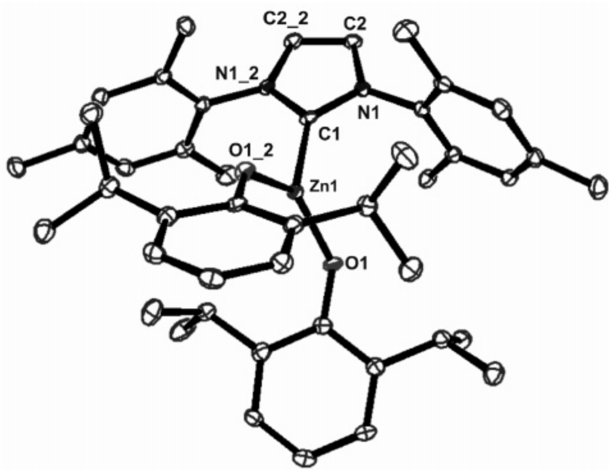


Figure 1. ORTEP drawing of the molecular structure of **2**. The thermal displacement ellipsoids are drawn at 30% probability, and the hydrogen atoms were omitted for clarity. Important bond lengths (Å) and bond angles (deg): Zn1−O1 1.872(2), Zn1−O1_2 1.872(2), Zn1−C1 1.983(4), O1_2−Zn1−O1 135.47(14), O1_2−Zn1−C1 112.26(7), O1−Zn1−C1 112.26(7).

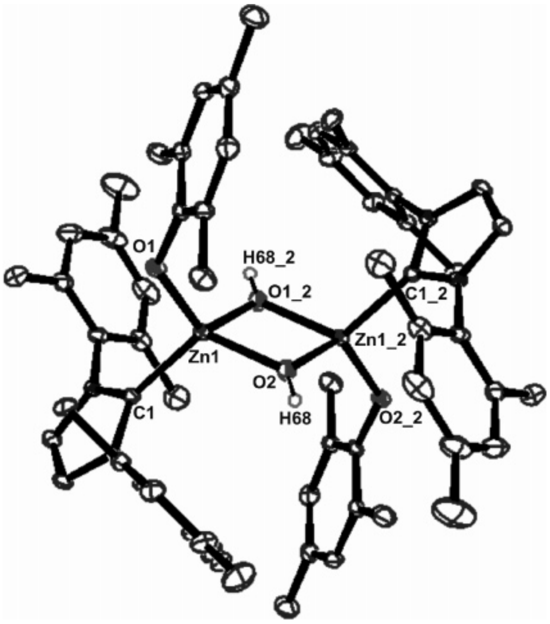


Figure 2. ORTEP drawing of the molecular structure of **3**. The thermal displacement ellipsoids are drawn at 30% probability, and the hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg): Zn1−O1 1.933(3), Zn1−O1_2 1.973(3), Zn1−O2 1.982(3), Zn1−C1 2.039(4), Zn1---Zn1_2 2.9732(8), O1−Zn1−O2_2118.61(11), O1−Zn1−O2 119.10(12), O2_2−Zn1−O2 82.53(13), O1−Zn1−C1104.56(12), O2_2−Zn1−C1 116.59(14), O2−Zn1−C1 115.18(13), Zn1_2−O2−Zn1 97.47(13).

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(6) $[(NHC)Zn(O\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)_2]$ (**2**): $C_{45}H_{58}N_2O_2Zn$, monoclinic, space group *C*2/*c*, $a = 24.015(5)$ Å, $b = 9.998(2)$ Å, $c = 18.294(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 115.14(3)°$, $V = 3976.5(14)$ Å^{3}, $Z = 4$, $\rho = 1.210$ mg/m^{3}, $T = 100(2)$ K, 13 023 collected reflections, 4943 crystallographically independent refections ($R(\mathrm{int}) = 0.0420$), GooF = 1.162, $R_1 = 0.0506$, $wR_2 = 0.0975$. $[(NHC)\underline{Z}n(\mu\text{-}OH)(OC_6H_2\text{-}2,4,6\text{-}Me_3)]_2$ (**3**): $C_{67}H_{80}N_4O_4Zn_2$, triclinic, space group $P\bar{1}$, $a = 13.1223(12)$ Å, $b = 15.0004(13)$ Å, $c = 17.2102(15)$ Å, $\alpha = 78.166(2)°$, $\beta = 68.737(2)°$, $\gamma = 78.164(2)°$, $V = 3058.0(5)$ Å^{3}, $Z = 2$, $\rho = 1.234$ mg/m^{3}, $T = 100(2)$ K, 16 204 collected reflections, 10 633 crystallographically independent refections ($R(\mathrm{int}) = 0.0381$), GooF = 1.017, $R_1 = 0.0590$, $wR_2 = 0.1260$.

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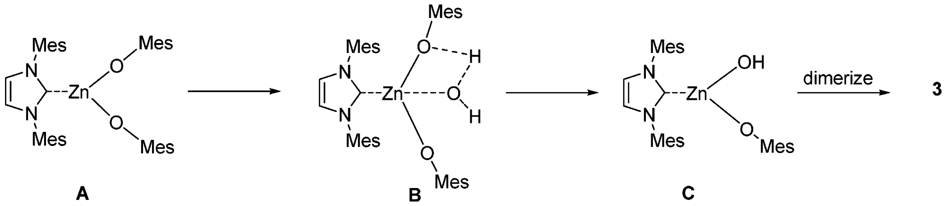
Scheme 2. Probable Mechanism for the Formation of 3



each being coordinated to a carbene carbon of NHC, to an oxygen atom of the 2,4,6-trimethylphenoxide ion, and also to the two bridging hydroxyl groups. The Zn−O of the hydroxyl groups show two different bond distances, 1.972 and 1.983 Å, respectively, which are comparable with the reported value for similar compounds.[8] The Zn−C bond distance (2.039 Å) is shorter than the observed value for $[(NHC)Zn(OCH_2Ph)_2]_2$ [Zn−C = 2.054 Å; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene].[9] The Zn−O bond distance (1.933 Å) in **3** is found to be longer than the Zn−O of monomeric $Zn(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2(Py)_2$ (Zn−O: 1.885 Å).[7a]

Compound **3** can be synthesized deliberately (method B) in 68% yield by the addition of 1 equiv of water to the 1:2 reaction mixture of **1** and 2,4,6-trimethylphenol. Similar to **2**, compound **3** is also stable toward air and moisture both in the solid state and in solution.[10] The formation of **3** (Scheme 2) can be understood if we compare it with the detailed general mechanism proposed for the hydrolysis of metal alkoxides.[1j] Based on this, a tentative mechanism for the formation of **3** is shown in Scheme 2. Accordingly, in the initial steps (**A**−**C**) an *in situ* tricoordinated product **A**, similar to **2**, is likely to be formed after the addition of 2 equiv of 2,4,6-trimehylphenol. Further in the presence of water, either adventitiously or by deliberate addition, **A** would undergo hydrolysis to first yield the monomeric monohydroxy zinc derivative, which on dimerization affords **3**. Although the zinc-containing monomeric Zn−OH as well as dimeric four-membered $Zn(OH)_2Zn$ compounds are known using chelating tris(pyrazolyl)borate or other sterically encumbered ligands, it may be noted that there are no reports on their stabilization using the simple alkoxides/aryloxide ligands.[11]

Conclusion

We have reported the first example of NHC-supported zinc aryloxide (**2**) and zinc hydroxyaryloxide (**3**). Compound **3** represents an intermediate on the way to the formation of Zn−O−Zn bonds that have been proposed in the sol−gel processes, in general, involving the hydrolysis of metal alkoxides (aryloxides). The formation of **3** also shows the remarkable stability of the zinc−carbene carbon bond, which is another example of the hydrolytic durability of NHC metal complexes. We are continuing our efforts to isolate the monomeric zinc hydroxyaryloxides by further modulation of ligand design.

Experimental Section

General Information. 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 a dry nitrogen atmosphere using standard Schlenk line technique. Glassware was dried in an oven at 140 °C overnight. Chemicals such as 2,4,6-trimethylaniline, diethylzinc (1 M in hexane), 2,6-diisopropylphenol, and 2,4,6-trimethylphenol were purchased from Aldrich Chemicals and used as received. Glyoxal, HCl (37% in H_2O), and paraformaldehyde were purchased from S.D. Fine-Chem, India, and used as received. Compounds 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride[12] and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene zinc diethyl[5] (**1**) were prepared by literature procedures.

Instrumentation. ^{1}H NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer operating at 400.0 MHz. 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 using a Thermoquest CE Instruments model EA-1110 CHNS-O elemental analyzer.

X-ray Crystallography. The crystal data for compounds **3** and **4** were collected on a Bruker SMART APEX CCD diffractometer. SMART (version 6.45) was used for integration of the intensity of reflections and scaling, and SADABS was used for absorption correction. The crystal structures were solved and refined by full matrix least-squares methods against F^2 using SHELXTL (version 6.14).[13] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were fixed at calculated positions and refined isotropically.

Synthesis of $[(NHC)Zn(O2,6\text{-}i Pr_2C_6H_3)_2]$ (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) (2). 2,6-Diisopropylphenol (0.8 mL, 4 mmol) was slowly added to a solution of **1** [generated *in situ* by the addition of diethylzinc (2.0 mL of a 1.0 M solution in hexane, 2.0 mmol) to the NHC (0.6 g, 2 mmol) in toluene (50 mL)][5] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred for 12 h and heated to 60 °C for 1 h. The solution was then cooled to room temperature and then concentrated to one-third of its volume. Colorless crystals of **2** were formed at −20 °C within a day. Yield: 1.30 g, 90%. Anal. Calcd for **2**: C, 74.61; H, 8.07; N, 3.87. Found: C, 74.11; H, 8.21; N, 3.66. (KBr): $\tilde{\nu}$ = 3134(m), 1586(m), 1537(m), 1439(vs), 1379(m), 1267(s), 1235(m), 1204(m), 1106(m), 1041(m), 931-

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[10] The ^{1}H NMR spectrum is recorded in $CDCl_3$ *used as received* as solvent. However it may be pointed out that such solutions of **2** and **3** are not stable after half an hour.

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(m), 883(s), 852(m), 750(s), 692(m), 507(w), 449(w) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ 1.20 (d, 24H, CH(CH_3)$_2$), 2.13 (s, 12H, *o*-CH_3), 2.28(s, 6H, *p*-CH_3), 3.12(m, 4H, CH(CH$_3$)$_2$), 6.84(t, 2H, *p*-OC$_6$H$_3$), 6.97(d, 4H, *m*-OC$_6$H$_3$), 6.99(s, 2H, N(CH)$_2$N), 7.11(s, 4H, *m*-C$_6$H$_2$).

Synthesis of [(NHC)Zn(μ-OH)(OC$_6$H$_2$-2,4,6-Me$_3$)]$_2$ (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) (3). Method A: 2,4,6-Trimethylphenol (0.52 g, 4 mmol) was slowly added to a solution of **1** [generated *in situ* by the addition of diethylzinc (2.0 mL of a 1.0 M solution in hexane, 2.0 mmol) to the NHC (0.6 g, 2 mmol) in toluene (50 mL)][5] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred for 14 h and heated to 60 °C for 1 h. The solution was then cooled to room temperature and then concentrated to one-third of its volume. Colorless crystals were formed at −20 °C within 2 days.

Method B: 2,4,6-Trimethylphenol (0.52 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 (0.6 g, 2 mmol) in toluene (50 mL)][5] at room temperature. After the evolution of ethane gas ceased, the reaction mixture was stirred for 10 h. To this clear solution was added double-distilled water (0.036 mL, 2 mmol) 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 refluxed for 1 h and then filtered in hot conditions using Celite. The filtrate was kept at −20 °C. Colorless crystals of **3** were formed after 4 days. Yield: 0.72 g, 68%. Anal. Calcd for **3**: C, 70.83; H, 7.10; N, 4.93. Found: C, 70.40; H, 7.43; N, 4.66. IR (KBr): $\tilde{\nu}$ = 3688(w), 3153(w), 3113(m), 1604(m), 1481(vs), 1453(s), 1310(s), 1266(s), 1290(s), 1154(m), 1108(w), 1034(m), 932(w), 852(s), 804(m), 733(s), 697(s), 571(w), 2500(m), 465(w), 426(m) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ 2.13 (m, 36H, *o*-CH_3), 2.27 (m, 18H, *p*-CH_3), 6.63 (s, 4H, N(CH)$_2$N), 6.96 (s, 8H, *m*-OC$_6$H$_2$), 7.11 (s, 4H, *m*-C$_6$H$_2$).

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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