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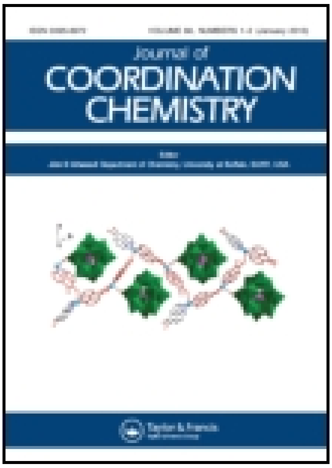

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Reaction of sterically congested NHC-Zn(CH_2CH_3)$_2$ with substituted phenols leading to zincate complexes

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Reaction of sterically congested NHC–$Zn(CH_2CH_3)_2$ with substituted phenols leading to zincate complexes

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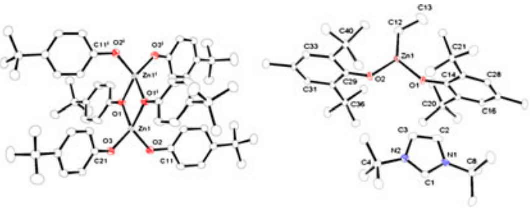

The treatment of a sterically congested NHC–$Zn(CH_2CH_3)_2$ Lewis adduct (**1**) obtained from 1,3-di-tert-butylimidazol-2-ylidene and diethyl zinc, with various substituted phenols (4-tert-butylphenol,2,6-di-tert-butyl-4-methyl phenol and 1-bromo-4,6-di-tert-butyl phenol) are described.

We report the reaction of a sterically congested NHC–$Zn(CH_2CH_3)_2$ Lewis adduct (**1**) prepared through reaction of an equimolar ratio of 1,3-di-tert-butylimidazol-2-ylidene and diethyl zinc, with various substituted phenols (4-tert-butyl-phenol, 2,6-di-tert-butyl-4-methyl phenol, and 1-bromo-4,6-di-tert-butyl phenol). The NHC–Zn dative bond was cleaved in each of the reactions with the substituted phenols to afford the corresponding ionic complexes of imidazolium cation and aryloxo-zincate, $[\{(4\text{-}CMe_3C_6H_4O)_2Zn(\mu\text{-}OC_6H_4\text{-}4\text{-}CMe_3)\}_2\{(1,3\text{-}(CMe_3)_2\text{-}ImCH\}_2]$ (**2**), $[\{(2,6\text{-}(CMe_3)_2\text{-}4\text{-}Me\text{-}C_6H_3O)_2\}Zn\{(1,3\text{-}(CMe_3)_2\text{-}ImCH\}]$ (**3**), and $[\{(1\text{-}Br\text{-}3,5\text{-}(CMe_3)_2C_6H_2O)_2\}_2\text{-}Zn\{(1,3\text{-}(CMe_3)_2\text{-}ImCH\}]$ (**4**), where 1,3-$(CMe_3)_2$-ImCH) is imidazolium carbocation. The molecular structures of **1**–**4** were established by X-ray diffraction analyses and from the solid-state structures of **2**–**4**, it was confirmed that, in all the compounds, zinc ions are coordinated through substituted phenolate groups.

Keywords: *N*-heterocyclic carbene; Imidazolium cation; Aryloxo-zincate; Metallacycle

1. Introduction

Biologically, one of the most important metals is zinc and an adult human body contains approximately 2 g of zinc [1]. The remarkable discovery of the first organometallic

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*Corresponding author. Email: tpanda@iith.ac.in compound, diethyl zinc from ethyl iodide and zinc metal by Frankland unearthed the potential of applications of organo-zinc compounds in the development of synthetic organic chemistry [2, 3]. There has been significant interest in zinc alkoxides and carboxylates, as these compounds are efficient catalysts for copolymerization of epoxides such as cyclohexene oxide, propene oxide, and CO_2 under ambient conditions [4–7]. In particular, zinc alkoxides, stabilized by bulky β-diiminate ligands in the coordination sphere, exhibit excellent rates for the living copolymerization of cyclohexene oxide and CO_2 to make polycarbonates, the synthesis of poly (lactic acid) by stereoselective ring-opening polymerization (ROP) of lactide [8, 9], and the ROP of β-butyrolactone and γ-valerolactone [10] reported by Coates *et al.* [11–14]. Rieger *et al.* [15, 16] also showed that the ethyl-sulfinate ligand could be a highly efficient initiating group for zinc β-di-iminate-catalyzed copolymerization reaction of CO_2 and epoxides. Chisholm *et al.* [17] reported that hydroxyl end groups in polycarbonates could be prepared by zinc gluterate catalysts. Inoue's [18] discovery of a heterogeneous $ZnEt_2/H_2O$ mixture for copolymerization of CO_2 and propene oxide paved the way for the development of a number of additional heterogeneous systems. *N*-heterocyclic carbenes (NHCs) have become ubiquitous and ligands derived from the 1*H*-imidazole heterocycle currently play a major role in organo-transition metal and coordination chemistry [19]; they are also capable of stabilizing highly reactive main group molecules [20–25]. Arduengo *et al.* first reported NHC-zinc compounds using 1,3-dimesitylimidazol-2-ylidene and 1,3-di(1-adamentyl)-imidazol-2-ylidine and diethyl zinc [26]. Jensen *et al.* also reported a series of zinc complexes of monodentate sterically bulky pyridyl-substituted NHC and used them as catalysts in lactide polymerization [27]. In each case, the NHC–Zn dative bond is retained in the zinc aryloxide complexes. Very recently, Robinson *et al.* demonstrated NHC-stabilized triorganozincates and transformation to unusual carbine-zinc complexes [28]. Dagorne *et al.* also reported neutral and cationic NHC–Zn complexes to use in ring-opening polymerization of β-butyrolactone, lactide, and trimethylene carbonate [29]. We were interested in exploring the reactivity of the NHC–Zn dative bond with sterically more hindered substituted phenols.

Here, we describe the syntheses of $[\{(1,3\text{-}(CMe_3)_2ImCH\}Zn(CH_2CH_3)_2]$ (**1**), $[\{(4\text{-}CMe_3\text{-}C_6H_4O)_2Zn(m\text{-}OC_6H_4\text{-}4\text{-}CMe_3)\}_2\{(1,3\text{-}(CMe_3)_2ImCH\}_2]$ (**2**), $[\{(2,6\text{-}(CMe_3)_2\text{-}4\text{-}MeC_6H_3O)_2\}Zn\{(1,3\text{-}(CMe_3)_2ImCH\}]$ (**3**) and $[\{(1\text{-}Br\text{-}3,5\text{-}(CMe_3)_2C_6H_2O)_2\}_2Zn\{(1,3\text{-}(CMe_3)_2ImCH\}]$ (**4**). Full characterization and structural studies of all the compounds have been carried out.

2. Experimental

2.1. *General information*

All manipulations of air-sensitive materials were performed by rigorously excluding oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced with a high-vacuum (10^{-4} torr) line, or in an argon-filled M. Braun glove box. THF was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. *n*-Pentane was distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ (100 MHz), and $^{31}P\{^1H\}$ NMR (161.9 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. A BRUKER ALPHA FT-IR was used for FT-IR measurements. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad.

1,3-Di-tert-butylimidazol-2-ylidene was prepared according to the procedure in the literature [30]. Diethyl zinc, 4-tert-butyl-phenol, 2,6-di-tert-butyl-4-methyl phenol, and 1-bromo-4,6-di-tert-butyl phenol were purchased from Sigma Aldrich and used without purification. The NMR solvents C_6D_6 and DMSO-d_6 were purchased from Sigma Aldrich and dried by either Na/K alloy (C_6D_6) or molecular sieves (DMSO-d_6) prior to use.

2.2. *Synthesis of* $[NHC–Zn(CH_2CH_3)_2]$ *(1)*

To solution of 1.4 g of (7.76 mM) 1,3-di-tert-butylimidazol-2-ylidene, in hexane (30 mL), diethyl zinc (7.76 mL, 1 M solution in hexane, 7.76 mM) was added at room temperature. A white precipitate formed after 3 h of stirring and the precipitate was filtered. Colorless crystals appeared after recrystallization from toluene–pentane (1 : 1) solution. Yield: 1.75 g (74%). ^1H NMR (400 MHz, C_6D_6): δ 6.45 (s, 2H, NHC), 1.30 (s, 18H, ^{t}Bu), 1.80 (t, $^3J = 8.1$ Hz, 6H, Me), 0.75 (q, $^3J = 8.1$ Hz, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 166.9 (N*C*N), 119.6 (N*CC*N), 55.6 (*C*CH_3), 32.3 (C*C*H_3), 29.3 (*C*H_3), 14.9 (*C*H_2) ppm. IR, (selected peaks): $\upsilon = 2944$(s), 1581(w), 1354(s), 1191(s), 1051(w), 751(w) cm^{-1}. Elemental analysis: $C_{15}H_{30}N_2Zn$ (303.79); Calcd: C, 59.30; H, 9.95; N, 9.22. Found: C, 58.99; H, 9.73; N, 8.89.

2.3. *Synthesis of* $[\{(4\text{-}CMe_3C_6H_4O)_2Zn(\mu\text{-}OC_6H_4\text{-}4\text{-}CMe_3)\}_2\{(1,3\text{-}(CMe_3)_2ImCH\}_2]$ *(2)*

In a dry Schlenk flask, 100 mg (0.33 mM) of **1**, 150 mg (1 mM) of 4-tert-butyl-phenol and 4 mL of dry THF were added. After 12 h of stirring, the solvent was partially evaporated to reduce the volume to 2 mL. Pentane was layered onto the reaction mixture and kept in the freezer. Colorless crystals were obtained at –35 °C. Yield: 294 mg (61%). ^1H NMR (400 MHz, DMSO-d_6): δ 9.20 (s, 2H, N*H*CN), 8.10 [s, 4H, N(C*H*)$_2$ N), 6.80 (d, $^3J = 6.6$ Hz, 6H, ArH), 6.52 (d, $^3J = 6.6$ Hz, 6H, ArH), 1.63 (s, 36H, CH_3), 1.20 (s, 54H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 166.9 (Ar), 132.4 (N*C*N), 131.6 (Ar), 124.5 (Ar), 120.5 (Ar), 118.4 (Ar), 59.6 (*C*CH_3), 33.1 (*C*CH_3), 31.9 (CH_3), 29.1 (CH_3) ppm. IR, (selected peaks): $\upsilon = 2959$(s), 1502(s), 1463(w), 1015(s), 794(s) cm^{-1}. Elemental analysis: $C_{114}H_{184}N_4O_{14}Zn_2$ (1965.5); Calcd: C, 69.66; H, 9.44; N, 2.85. Found: C, 68.88; H, 9.04; N, 2.11.

2.4. *Synthesis of* $[\{(2,6\text{-}(CMe_3)_2\text{-}4\text{-}Me\text{-}C_6H_3O)_2\}Zn\{(1,3\text{-}(CMe_3)_2ImCH\}]$ *(3)*

Complex **3** was prepared using a procedure similar to that which produced **2**. Yield: 243 mg (86%). ^1H NMR (400 MHz, DMSO-d_6): δ 9.17 (s, 1H, N*H*CN), 8.13 [s, 2H, N(C*H*)$_2$ N], 6.69 (s, 4H, ArH), 2.14 (s, 6H, ArCH_3), 1.66 (s, 18H, CCH_3), 1.38, (s, 36H, CCH_3), 0.78 (t, $^3J = 8.0$ Hz, 3H, CH_3), –0.16 (q, $^3J = 8.04$ Hz, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 164.4 (Ar), 136.8 (Ar), 132.3 (NCN), 124.1 (Ar), 120.5 (Ar), 117.6 (Ar), 59.6 (*C*CH_3), 34.5 (*C*CH_3), 31.1 (CH_3), 30.2 (C*C*H_3), 29.1 (C*CH$_3$*), 21.3 (CH_3), 12.7 (CH_2) ppm. IR (selected peaks): $\upsilon = 3146$(w), 2945(m), 1456(s), 1028(s), 793(s) cm^{-1}. Elemental analysis: $C_{51}H_{88}N_2O_4Zn$ (858.6); Calcd: C, 71.34; H, 10.33; N, 3.26; Found: C, 70.93; H, 9.89; N, 3.03.

2.5. *Synthesis of* $[\{(1\text{-}Br\text{-}3,5\text{-}(CMe_3)_2C_6H_2O)_2\}_2Zn\{(1,3\text{-}(CMe_3)_2ImCH\}]$ *(4)*

Complex **4** was prepared using a procedure similar to that which produced **2**. Yield: 222 mg (80%). ^1H NMR (400 MHz, DMSO-d_6): δ 9.28 (s, 1H, NHCN), 8.15 (s, 2H, N(CH)$_2$ N), 7.21 (s, 4H, Ar), 7.06 (s, 4H, Ar), 1.69 (s, 18H, CCH_3), 1.45 (s, 18H, CCH_3), 1.28, (s, 18H, CCH_3), 1.08 (t, $^3J = 8.04$ Hz, 3H, CH_3), –0.01 (q, $^3J = 8.04$ Hz, 2H, CH_2) ppm. ^{13}C {1H} NMR (100 MHz, DMSO-d_6): 131.7 (NCN), 128.1 (Ar), 127.3 (Ar), 127.0 (Ar), 126.8 (Ar), 124.5 (Ar), 119.7 (Ar), 58.9 (*C*CH_3), 34.7 (*C*CH_3), 32.7 (*C*CH_3), 31.0 (C*C*H_3), 28.7 (CH_3), 28.4 (C*C*H_3), 12.5 (CH_2) ppm. IR (selected peaks): $\upsilon = 3027$(w), 2954(m), 1492(m), 1079(s), 725 (s) cm^{-1}. Elemental analysis: $C_{47}H_{66}Br_2N_2O_4Zn$ (948.21); Calcd: C, 59.53; H, 7.02; N, 2.95; Found: C, 58.87; H, 6.85; N, 2.65.

2.6. *Single-crystal X-ray structure determinations*

Single crystals of **1** were obtained from a toluene–pentane mixture and **2–4** were grown from a solution of a mixture of THF and pentane under inert atmosphere at a temperature of –35 °C. In each case, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromated CuKα (1.54184 Å) radiation. The structures were solved by direct methods (SIR92) [31] and refined on F^2 by full-matrix least-squares using SHELXL-97 [32]. Non-hydrogen atoms were anisotropically refined except one solvent THF (in **4**), which was highly disordered, and all the carbons were treated isotropically. Hydrogens were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (a\mathrm{P})^2 + b\mathrm{P}]$), where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions $R1$ and $wR2$ were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$, respectively. ORTEP-3 was used to draw the molecule (Supplementry material see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.886688).

3. Results and discussion

3.1. *Spectroscopy of 1*

Compound **1** was prepared in good yield by straightforward reaction involving 1,3-di-tert-butylimidazol-2-ylidene with diethyl zinc in a 1:1 M ratio at ambient temperature in hexane (see scheme 1). Colorless crystals were obtained from toluene–pentane mixture (1:1) at –4 °C. Compound **1** was characterized using standard analytical/spectroscopic techniques and the solid-state structure was established by single crystal X-ray diffraction.

The conversion of the 1,3-di-tert-butylimidazol-2-ylidene-bearing hydrogens at 4,5 positions can be easily monitored by ^1H NMR spectroscopy because a pronounced high field shift of −0.70 ppm was observed for resonances of the NCH hydrogens upon formation of **1**. In ^1H NMR spectra, the resonances of 18 hydrogens attached to the *tert*-butyl group appear as a singlet at 1.30 ppm. A triplet at 1.80 ppm and a quartet at 0.75 ppm can be assigned to four methylene protons and six methyl protons attached to zinc. A coupling constant of 8.06 Hz ($^3J_{HH}$) was observed due to coupling between methylene protons and methyl protons positioned three sigma bonds away from each other. In the ^{13}C {^1H} NMR spectra of **1**, the resonance of the N*C*N carbon is at 166.9 ppm, approximately 46 ppm high field shifted from the corresponding resonance observed in the free carbene (213.2 ppm) [30]. From ^1H and ^{13}C{^1H}NMR spectra, **1** exhibits pseudo-C_{2v} symmetry in solution, implying that rotation around the $C_{carbene}$–Zn1 axis is fast on the NMR time scale.

Table 1. Structural refinement parameters for **1–4.**

Compounds	**1**	**2**	**3**	**4**
CCDC no.	957175	957178	957176	957177
Empirical formula	$C_{15}H_{30}N_2Zn$	$C_{114}H_{184}N_4O_{14}Zn_2$	$C_{51}H_{88}N_2O_4Zn$	$C_{47}H_{66}Br_2N_2O_4Zn$
Formula weight	303.78	1965.39	858.62	948.21
Temperature	150(2) K	150(2) K	150(2) K	150(2) K
Wavelength	1.54184 A	1.54184 A	1.54184 A	1.54184 A
Crystal system, space group	Monoclinic, *P2₁/m*	Monoclinic, *P2₁/c*	Monoclinic, *Cc*	Orthorhombic, *Pbca*
Unit cell dimensions	$a = 8.2497(8)$ Å, $b = 10.8740(7)$ Å, $c = 10.2210(10)$ Å, $\alpha = 90^\circ$, $\beta = 112.401(12)^\circ$, $\gamma = 90^\circ$	$a = 11.8754(2)$ Å, $b = 28.8514(3)$ Å, $c = 18.2870(3)$ Å, $\alpha = 90^\circ$, $\beta = 116.5910(10)^\circ$, $\gamma = 90^\circ$	$a = 17.7663(4)$ Å, $b = 22.0902(5)$ Å, $c = 14.0446(4)$ Å, $\alpha = 90^\circ$, $\beta = 109.477(3)^\circ$, $\gamma = 90^\circ$	$a = 18.6267(8)$ Å, $b = 18.9103(7)$ Å, $c = 28.0146(10)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$
Volume	847.71(13) Å^3	5602.79(14) Å^3	5196.5(2) Å^3	9867.8(7) Å^3
Z, Calcd density	2, 1.190 Mg/m^3	2, 1.165 Mg/m^3	4, 1.097 Mg/m^3	8, 1.228 Mg/m^3
Absorption coefficient	1.888 mm^{-1}	0.996 mm^{-1}	0.962 mm^{-1}	2.857 mm^{-1}
F (0 0 0)	328	2136	1880	3824
Theta range for data collection	4.68°–70.70°	4.09°–70.75°	3.31°–70.78°	3.69°–70.84°
Limiting indices	$-8 \le h \le 10$, $-9 \le k \le 13$, $-11 \le l \le 12$	$-14 \le h \le 11$, $-35 \le k \le 33$, $-22 \le l \le 22$	$-16 \le h \le 19$, $-22 \le k \le 16$, $-8 \le l \le 12$	$-22 \le h \le 12$, $-22 \le k \le 13$, $-34 \le l \le 33$
Reflections collected/ unique	3093/1663 [*R*(int) = 0.0544]	24,738/10,606 [*R*(int) = 0.0266]	4475/2763 [*R*(int) = 0.0223]	24,817/9308 [*R*(int) = 0.0343]
Completeness to theta = 71.25	(70.70) 96.5%	(70.75) 98.3%	(70.78) 97.5%	(70.84) 97.9%
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan

Max. and min. transmission	1.00000 and 0.42637	1.00000 and 0.803	1.00000 and 0.71965	1.000 and 0.521
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	1663/0/100	10,606/0/707	2763/2/544	9308/0/495
Goodness-of-fit on F^2	1.029	1.023	1.017	1.023
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0526$, $wR2 = 0.1315$	$R1 = 0.0428$, $wR2 = 0.1080$	$R1 = 0.0301$, $wR2 = 0.0796$	$R1 = 0.0573$, $wR2 = 0.1587$
R indices (all data)	$R1 = 0.0626$, $wR2 = 0.1429$	$R1 = 0.0506$, $wR2 = 0.1143$	$R1 = 0.0306$, $wR2 = 0.0804$	$R1 = 0.0679$, $wR2 = 0.1705$
Largest diff. peak and hole	0.645 and −0.644 e A^{-3}	0.320 and −0.516 e A^{-3}	0.312 and −0.258 e A^{-3}	0.972 and −0.898 e A^{-3}

Similar spectral behavior was observed for NHC-MR_2 (NHC = 1,3-di-adamentylimidazol-2-ylidene and 1,3-di-mesitylimidazol-2-ylidene, M = Mg, Zn) [26]. The solid-state structure of **1** was established by X-ray diffraction analysis.

3.2. *Crystal structure of 1*

Compound **1** crystallizes in the monoclinic space group *P2₁/m* and has one molecule in the unit cell. The structural parameters of the crystal structure of **1** are given in table 1. The molecular structure of **1** is shown in figure 1. A crystallographic mirror plane passes through the C7–Zn1 bond and the planar imidazole ring which are coplanar to each other. The zinc and the carbine–carbon distance Zn1–C7 2.124(4) Å is slightly greater compared to the distances (1.994(4) and 2.009(4) Å) observed in NHC–ZnEt_2 (NHC = 1,3-di-adamentylimidazol-2-ylidene) reported by Arduengo *et al.* [26], presumably due to the presence of two *tert*-butyl groups on the nitrogens. The ring internal angle at C7 is 103.7°, very similar to 104.2° found in NHC–ZnEt_2 (NHC = 1,3-di-adamentylimidazol-2-ylidene), indicating that substitution at imidazolium nitrogen does not affect the ring internal angle at the former carbene carbon [26]. The C–N bond distances (1.366(5) and 1.369(6) Å) are in agreement with the C–N distance (1.358 Å) reported in the literature. Due to coordination of two ethyl groups and NHC, the zinc adopted trigonal planar geometry and the plane containing Zn1, C13, and C12 is orthogonal with respect to the imidazole plane containing N1, C7, N2, C6, and C5. This kind of geometry of zinc is rare but known [26, 33, 34].

3.3. *Reactivity study with bulky substituted phenols*

Reactivity studies of **1** were made with various substituted phenols. We chose three different substituted phenols, 4-tert-butyl-phenol, 2,6-di-tert-butyl-4-methyl phenol, and 1-bromo-4,6-di-tert-butyl phenol, having different substitution to verify the stability of the NHC–Zn bond. Reaction between **1** and 4-tert-butyl-phenol in THF at ambient temperature afforded dissociation of the NHC–Zn bond to form ion-pair complex **2**, which was isolated in good yield. In a similar reaction between **1** and 2,6-di-tert-butyl-4-methyl phenol, **3**, with aryloxo-zincate as the anioinc part, was obtained in good yield (scheme 2). When 1-bromo-4,6-di-tert-butyl phenol containing a bromide side group was treated with **1** at ambient temperature, the corresponding ionic complex **4** was isolated in quantitative yield (scheme 2). Even in cases where a slight excess of substituted phenols was used with **1** and the phenols being used in the 1 : 1 M ratio, corresponding aryloxo-zincate complexes **2–4** were the major products. The characteristics of **2–4** were determined by spectroscopic and analytical techniques, and the molecular structures of **2–4** were established by X-ray diffraction analyses.

3.4. *Spectroscopy of 2–4*

In ^{1}H NMR spectra of **2–4**, a sharp singlet for the proton attached to imidazolium cation is at 9.20 ppm (**2**), 9.17 ppm (**3**) and 9.28 ppm (**4**), whereas the olefinic protons attached to the imidazolium ring show resonances at 8.10 ppm (**2**), 8.13 ppm (**3**) and 8.15 ppm (**4**). The methyl protons of the *tert*-butyl groups attached to nitrogen appear at 1.63 ppm (**2**), 1.66 ppm (**3**) and 1.69 ppm (**4**). In **2**, a sharp singlet at 1.23 ppm can be assigned to the 27 hydrogens of *tert*-butyl groups attached to 4-tert-butyl-phenolate. The phenyl protons are in the expected range. In $^{13}C\{^1H\}$ NMR spectra of **2**, resonance of the NCN carbon is at 132.3 ppm, approxi-

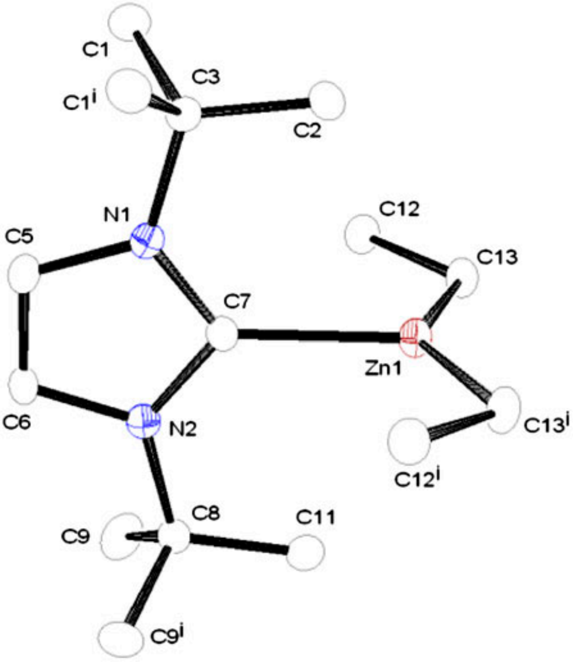


Figure 1. ORTEP drawing of **1** at 30% thermal probability. Selected bond lengths [Å] and angles [°] are: Zn1–C7 2.124(4), Zn1–C13 2.014(3), Zn1–C13^{i} 2.014(3), C7–N2 1.366(5), C7–N1 1.369(6), N2–C6 1.389(6), N1–C5 1.386 (6), C5–C6 1.321(7), C13–C12 1.536(5), N1–C3 1.489(6), N2–C8 1.478(6), C7–Zn1–C13 111.20(10), C13–Zn1–C13^{i} 137.6(2), C7–Zn1–C13^{i} 111.20(10), N1–C7–N2 103.7(4), C7–N2–C8 127.2(4), C7–N1–C3 127.8(4).

mately 81 ppm high field shifted from the corresponding resonances in the free carbene and 35 ppm high field shifted from **1**, but in the same range as that of the corresponding imidazolium chloride (135.5 ppm) [30].

3.5. *Crystal structures of 2 and 3*

Compound **2** crystallizes in the monoclinic space group $P2_1/c$, with one molecule of **2** and four THF molecules in the unit cell. Details of the structural parameters for **2** are given in table 1. The molecular structure of the anionic part of **2** is shown in figure 2. The molecular structure of **2** consists of an ion pair composed of an imidazolium carbocation and a centrosymmetric dimeric zinc aryloxide $[Zn_2(OAr)_6]$ (Ar = 4-tert-butyl-phenyl) as anion, clearly indicating rupture of the NHC–Zn dative bond to generate the imidazolium carbocation and a formal negative charge on zinc complex. The ethyl groups attached to zinc in diethyl zinc were substituted by phenolate groups by elimination of ethane gas. Thus, in the anionic part of **2**, two zinc ions are connected by two bridging μ_2–OAr groups to generate a Zn_2O_2 square with a Zn–O distance of 2.0046(12) Å, together with Zn–O17–Zn^{i} and O1–Zn–O1^{i} angles of 100.69(5)° and 79.31(5)°, respectively. The Zn_2O_2 cores share C_2 symmetry in the bridging O–O inter-atomic axis. The coordination sphere of each Zn ion is completed by two terminal aryloxide groups, affording a distorted tetrahedral geometry. The terminal metal–oxygen distances are shorter (Zn–O2, 1.9050(13) Å and Zn–O3, 1.9182(13) Å) than those to the bridging oxygens. However, the zinc–zinc distance (3.0824

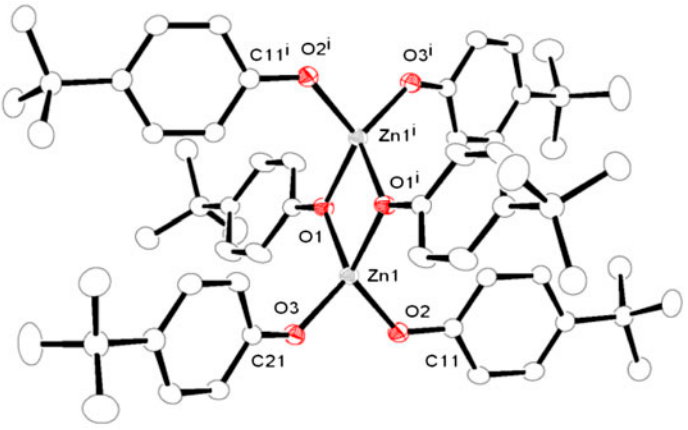


Figure 2. Molecular structure of anionic part of **2** at 30% thermal probability. Hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are: Zn1–O1 2.0046(12), Zn1–O2 1.9050(13), Zn1–O3 1.9182(13), Zn1–O1$^{\text{i}}$ 1.9990(12), Zn1$^{\text{i}}$–Zn1$^{\text{i}}$ 3.0824(4), O2–Zn1–O3 94.16(6), O1–Zn1–O1$^{\text{i}}$ 79.31(5), O1–Zn1–O2 116.44(6), O3–Zn1–O1$^{\text{i}}$ 124.87(5), O3–Zn1–O1 123.63(6), Zn1$^{\text{i}}$–O1–Zn1 100.69(5).

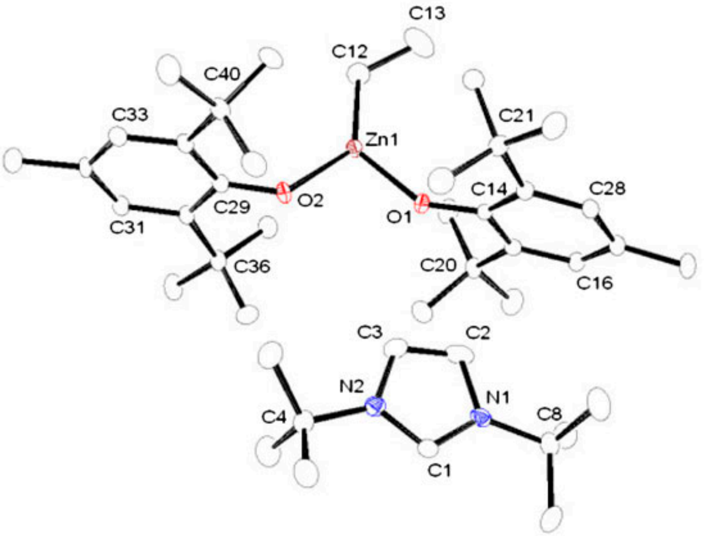


Figure 3. Molecular structure of **3** omitting hydrogens for clarity. Selected bond lengths [Å] and angles [°] are: Zn1–O2 1.908(3), Zn1–O1 1.919(3), Zn1–C12 1.976(5), C12–C13 1.486(8), O2–C29 1.336(5), O1–C14 1.325(5), C1–N1 1.331(6), C1–N2 1.336(6), C2–C3 1.357(6), N1–C2 1.391(7), N2–C3 1.357(6), N1–C8 1.494(6), N2–C4 1.505(6), O1–Zn1–O2 98.29(13), O1–Zn1–C12 129.55(19), O2–Zn1–C12 132.12(19), Zn1–O1–C14 144.5(3), Zn1–O2–C29 132.0(3), N1–C1–N2 106.6(5), C1–N1–C2 106.6(5), C1–N2–C3 107.5(4).

(4) Å) is in the range (2.935 Å) and (3.021 Å) similar to that reported by Jensen *et al.*, indicating a more tightly coupled dimeric structure of **2** [27].

Compound **3** crystallizes in the monoclinic space group *Cc* having four molecules of **3** and two THF molecules in the unit cell. The structural parameters for **3** are given in table 1. The molecular structure of **3** is shown in figure 3. Similar to **2**, in the presence of bulkier

2,6-di-tert-butyl-4-methyl phenol, the NHC–Zn bond underwent dissociation to produce imidazolium carbocation and an aryloxo-zincate counter anion.

However unlike **2**, only one ethyl is substituted by the 2,6-di-tert-butyl-4-methyl phenolate moiety. Thus, in the anionic part of the molecule, zinc is ligated by two aryloxide moieties along with one ethyl to give an unusual three-coordinate zinc with trigonal planar geometry. Bond distances Zn–O1 and Zn–O2 (1.919(3) and 1.908(3) Å , respectively) are in the range similar to the Zn–O terminal bonds observed for **2**. The plane containing Zn1, O1, and O2 is almost orthogonal (85.28°) with respect to the aryl plane containing C14, C15, C16, C17 and C18. However, this kind of geometry of zinc was observed for **1** as well. The ^{1}H NMR spectra of **3** also complies with the solid-state structure of the compound. The sharp singlet at 1.39 ppm can be assigned to the *tert*-butyl group attached to the aryl group. The methyl protons at the *p*-position of the aryl ring appear at 1.50 ppm as a singlet. One triplet at 0.78 ppm and one quintet at –0.16 ppm were assigned to the methyl and methylene group, respectively, for the ethyl attached to zinc. Similar spectral behavior was observed for **2** also.

3.6. *Reactivity study with bulkier substituted phenols*

To investigate whether the introduction of a more sterically demanding 1-bromo-4,6-di-tert-butyl phenolate would affect the nuclearity of the resulting zinc complexes, a THF solution of **1** was treated with two equivalents of 1-bromo-4,6-di-tert-butyl phenol, and re-crystalli-

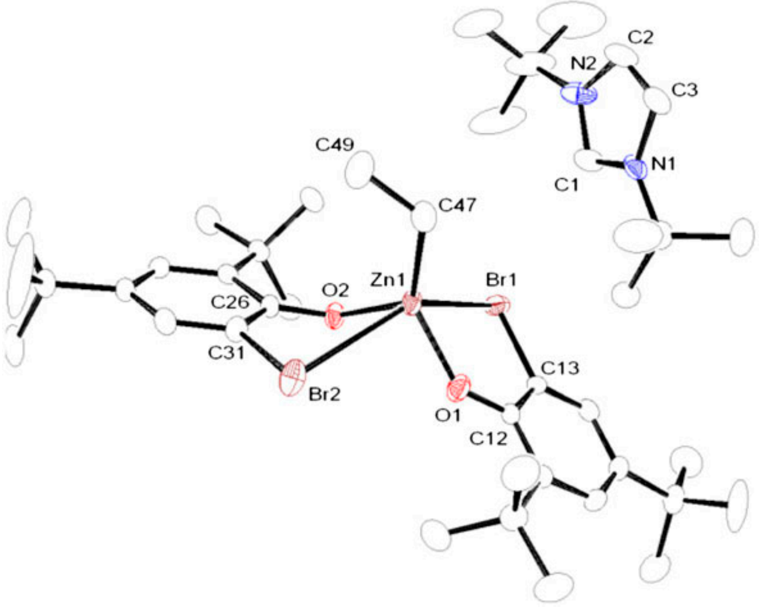
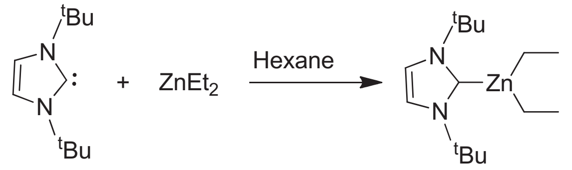
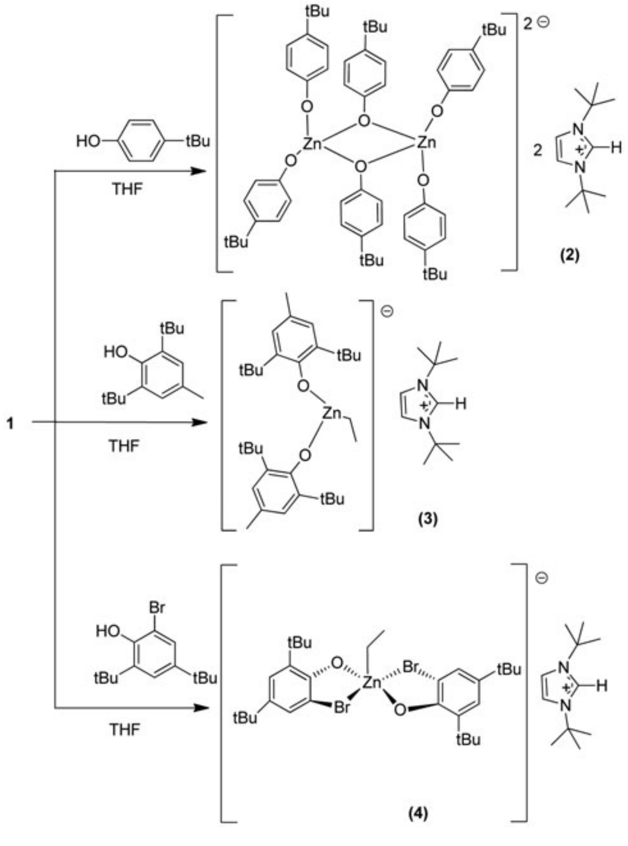


Figure 4. Molecular structure of **4** and hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are: O1–Zn1 1.904(3), O2–Zn1 1.927(2), Zn1–Br1 3.084(3), Zn1–Br2 3.093(3), Zn1–C47 1.972(4), C47–C49a 1.44(3), C13–Br1 1.918(3), C1–N1 1.328(6), C1–N2 1.333(5), N1–C4 1.494(6), N2–C8 1.501(7), C2–C3 1.314(8), O1–Zn1–O2 103.48(12), O1-Zn1–C47 133.83(18), O2–Zn1–C47 133.83(18), Zn1–Br1–C13 86.68, Zn1–Br2–C31 82.74, Br1–Zn1–Br2 145.74.



(**1**)

Scheme 1. Synthesis of **1**.



(2)

(3)

(4)

Scheme 2. Reaction of **1** with various substituted phenols.

zation of the resulting yellowish residue from THF and pentane mixture afforded **4** as a colorless, crystalline solid in almost quantitative yield. The ^{1}H NMR spectrum of **4** shows one set of signals for the imidazolium cation, as discussed above. One set of signals was also observed for the 1-bromo-4,6-di-tert-butyl phenolate at 1.45 and 1.28 ppm for the protons of each *tert*-butyl group present in the aromatic ring as they are chemically non-symmetric due to the presence of the bromine. In addition, one triplet at 1.08 ppm and one quintet at –0.01 ppm were observed, which can be assigned to methyl and methylene, respectively, of the ethyl attached to zinc.

Single crystals of the THF solvate **4** THF were subjected to an X-ray diffraction analysis; it crystallizes in the orthorhombic space group *Pbca* with one molecule of **4** in the asymmetric unit. The molecular structure of **4** is shown in figure 4, revealing that in the anionic aryloxo-zincate complex, zinc attains a coordination number of five by chelation of two oxygens and two bromines from two 1-bromo-4,6-di-tert-butyl phenolates along with one ethyl. The geometry around zinc can be described as either distorted trigonal–bipyramidal with both Br1 and Br2 in apical positions, or as square–pyramidal with the methylene carbon C47 adopting the apical position, with two oxygens and two bromines in basal positions. Two five-member metallacycles Zn1–O1–C12–C13–Br1 and Zn1–O2–C26–C31–Br2 are formed in the coordination sphere. The Zn–O distances (1.904(3) and 1.927(2) Å) are similar to our previous observations for **2** and **3**. The Zn–Br distances (3.084 and 3.093 (3) Å) are slightly shorter compared to that of diamino zinc bromide ($ZnBr_2$(TEEDA); TEEDA = *N,N,N′,N′*-tetraethylethylenediamine) (3.49(1) Å) [35]. The Zn–C47 distance (1.972(4) Å) is in agreement with that of **1** (2.014(3) Å) and **3** (1.976(5) Å).

4. Conclusion

We have presented the synthesis and structure of sterically congested NHC–$Zn(CH_2CH_3)_2$ Lewis adduct **1**, which reacted with various substituted phenols, 4-tert-butyl-phenol, 2, 6-di-tert-butyl-4-methyl phenol, and 1-bromo-4,6-di-tert-butyl phenol to produce the imidazolium cation and aryloxo-zincate complexes where zinc has flexible coordination numbers, three (**3**), four (**2**), and five (**4**). These results clearly show that the NHC–Zn bond is kinetically unstable in the presence of substituted aryl phenols. Application of **1–4** as initiators for ROP of lactones and lactides are in progress in our laboratory.

Supplementary material

Supplementary data for ^{1}H, $^{13}\{^1$H$\}$ NMR spectra of **1–4** can be found online. Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC 957175 (1), 957178 (2), 957176 (3) and 957177 (4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + (44) 1223-336-033; E-mail: deposit@ccdc.-cam.ac.uk).

Acknowledgments

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