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N-heterocyclic carbene complexes of Zn(II): synthesis, X-ray structures and reactivity ☆

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Abstract

The synthesis of six novel zinc (II) mono(N-heterocyclic carbene) complexes is described. 1,3-Bis(mesityl)-imidazol-2-ylidene was reacted with the zinc salts ZnX_2 (X = Cl, CH_3COO, PhCOO, and $PhCH_2COO$) to yield the corresponding monomeric Zn–NHC complex $ZnCl_2$(NHC)(THF) (**1**) and dimeric $[Zn(OOCCH_3)_2(NHC)]_2$ (**2**), $[Zn(OOCPh)_2(NHC)]_2$ (**3**), $[Zn(OOCCH_2Ph)_2(NHC)]_2$ (**4**) (NHC = 1,3-bis(mesityl)-imidazol-2-ylidene). Reaction of **1** with 2 equivalents of silver trifluoromethanesulfonate yielded monomeric $Zn(O_3SCF_3)_2$(NHC)(THF) (**5**), reaction of **1** with sodium {[R(+)-α-2-(1-phenyl-ethylimino)-methyl]-phenolate} yielded monomeric $ZnCl(OC_6H_4\text{-}2\text{-}CH{=}N(CHPhCH_3)(NHC)$ (**6**). Compounds **1**, **4–6** were structurally characterized by X-ray analysis. Selected compounds were investigated for their activity in the copolymerization of carbon dioxide with cyclohexene oxide as well as in the ring-opening polymerization of cyclohexene oxide and ε-caprolactone.

Keywords: N-heterocyclic carbenes; Zinc; Copolymerization; Ring-opening polymerization

1. Introduction

N-Heterocyclic carbenes (NHCs) [1–6] are currently among the most intensively investigated compounds since the corresponding transition metal complexes were found to possess good stabilities and high activities in various catalytic processes [7–14]. In this context, Ti- [15], Cr- [16,17], and Ni-NHC compounds [18] have been reported to be active in ethylene polymerization and oligomerization, respectively. Pd- and Ru-NHC complexes belong to the most active catalysts for C–C coupling reactions such as Heck couplings [19–21] and metathesis-based reactions [22–30] and may also be used for catalytic hydrogenation [31]. Important enough, some of these reactions can be carried out in an enantioselective way [32–34]. Quite recently, our group [35–37] and others [38] reported on Ru-NHC and Pd-NHC-catalyzed polymerization reactions such as the cyclopolymerization of 1,6-heptadiynes and the oxidative carbonylation reaction of bisphenol A, respectively.

The first NHC complexes of Zn(II), Zn(1,3-di(1-adamantyl)imidazol-2-ylidene)Et_2 and Zn(1,3-dimesityl-imidazol-2-ylidene)Et_2, were reported by Arduengo et al. [39] In this contribution, we report on the synthesis of various Zn(1,3-dimesitylimidazol-2-ylidene)-complexes and their use in ring-opening polymerization and copolymerization, respectively.

2. Results and discussion

2.1. Synthesis and X-ray structures of compounds 1–6

1,3-Dimesitylimidazol-2-ylidene was prepared from 1,3-dimesitylimidazolium chloride and potassium *t*-butanolate in THF [40]. Reaction with anhydrous $ZnCl_2$ in THF afforded $ZnCl_2$(NHC)(THF) (**1**) (NHC = 1,3-bis(mesityl)-imidazol-2-ylidene) in 80% yield (Scheme 1).

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.03.039.

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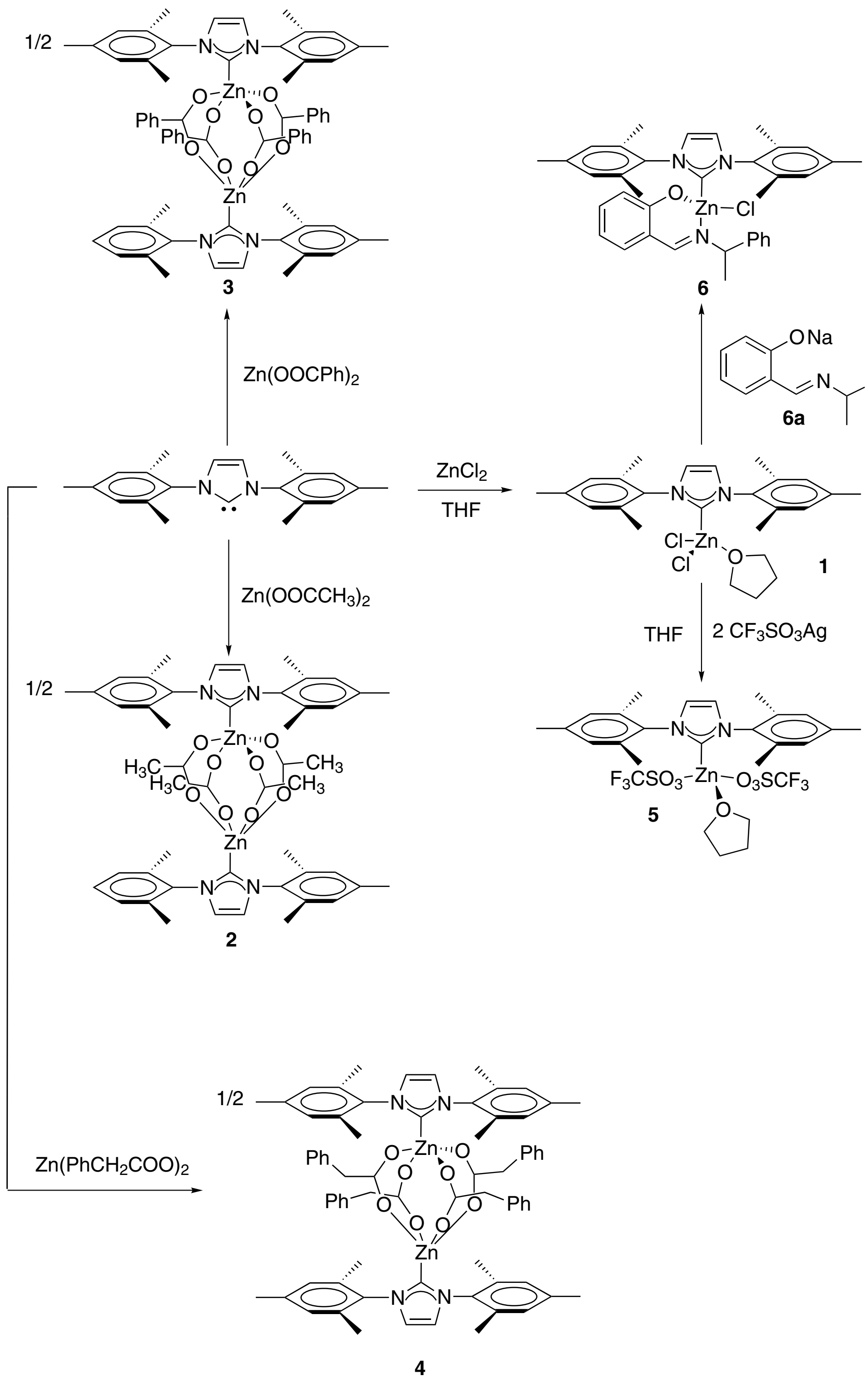

Scheme 1. Synthesis of Zn-complexes **1**–**6**.

1 (Fig. 1) crystallizes in the monoclinic space group. Relevant structural data, bond angles, and distances are summarized in Tables 1 and 2.

The distance Zn(1)–C(1) is 203.6(2) pm, the distance Zn(1)–O(1) is 210.60(15) pm, indicative for a comparably weak coordination of THF. In view of the rather poor propensity of chloride to form bridged species with Zn, a monomeric structure was obtained (see Scheme 1).

Reaction of 1,3-dimesitylimidazol-2-ylidene with anhydrous Zn(II) acetate and Zn(II) benzoate, prepared by the reaction of $ZnEt_2$ and PhCOOH in THF and used without further purification, resulted in the formation of both $[Zn(OOCCH_3)_2(NHC)]_2$ (**2**) and $[Zn(OOCPh)_2(NHC)]_2$ (**3**) in 60% yield. In analogy, $[Zn(OOCCH_2Ph)_2(NHC)]_2$ (**4**) (Fig. 2) was prepared via reaction of 1,3-dimesitylimidazol-2-ylidene with Zn(II) phenylacetate in 84% yield. Mass-spectroscopic investigations

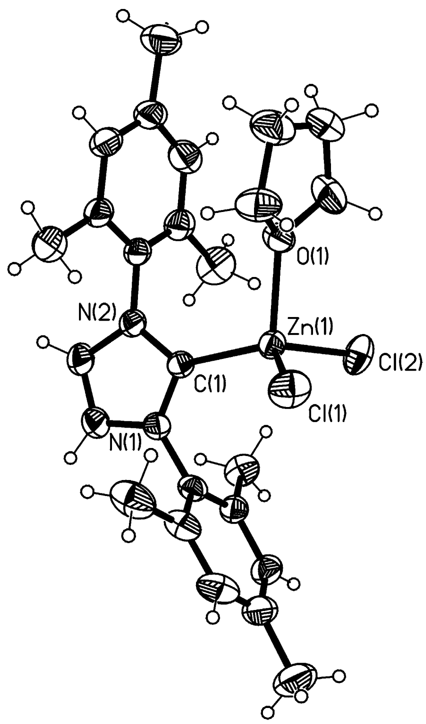

Fig. 1. X-ray structure of compound **1**.

Table 1
Crystal data and structure refinement for **1** and **4**

	1	**4**
Molecular formula	$C_{25}H_{32}Cl_2N_2OZn \times$ 0.5 THF	$C_{74}H_{76}N_4O_8Zn_2 \times$ 1.333 THF
Formula weight	548.85	1376.27
Crystal system	Monoclinic	Cubic
Space group	$C2/c$ (no. 15)	$Pn\bar{3}$ (no. 201)
a (pm)	3002.09(2)	2229.79(5)
b (pm)	1250.77(2)	2229.79(7)
c (pm)	1542.35(3)	2229.79(7)
α (°)	90	90
β (°)	98.982(1)	90
γ (°)	90	90
Volume (nm^3)	5.72039(15)	11.0864(6)
Z	8	6
Temperature (K)	233(2)	233(2)
D_{calc} (Mg/m^3)	1.275	1.237
Absorption coefficient (mm^{-1})	1.068	0.707
Color, habit	Colorless prism	Colorless prism
Number of reflections with with $I > 2\sigma(I)$	4735	1980
Goodness-of-fit on F^2	1.045	1.220
R indices $I > 2\sigma(I)$	$R_1 = 0.0354$ $\omega R_2 = 0.0955$	$R_1 = 0.0552$ $\omega R_2 = 0.1335$

confirmed the dimeric structure of these three compounds. While in the case of **4** the ion peak of the dimer minus an acetate group can be clearly identified, compounds **2** and **3** are analyzed as the corresponding dimers with one carboxylate missing and one carboxylate substituted by the matrix, i.e. 3-nitrobenzylic alcohol. Crystals suitable for X-ray analysis were obtained from

Table 2
Bond lengths (pm) and angles (°) for **1**

Zn(1)–C(1)	203.6(2)
Zn(1)–O(1)	210.60(15)
Zn(1)–Cl(2)	223.38(6)
Zn(1)–Cl(1)	223.44(7)
C(1)–Zn(1)–O(1)	108.84(7)
C(1)–Zn(1)–Cl(2)	115.13(6)
O(1)–Zn(1)–Cl(2)	99.26(5)
C(1)–Zn(1)–Cl(1)	115.32(6)
O(1)–Zn(1)–Cl(1)	100.27(5)
Cl(2)–Zn(1)–Cl(1)	115.21(3)

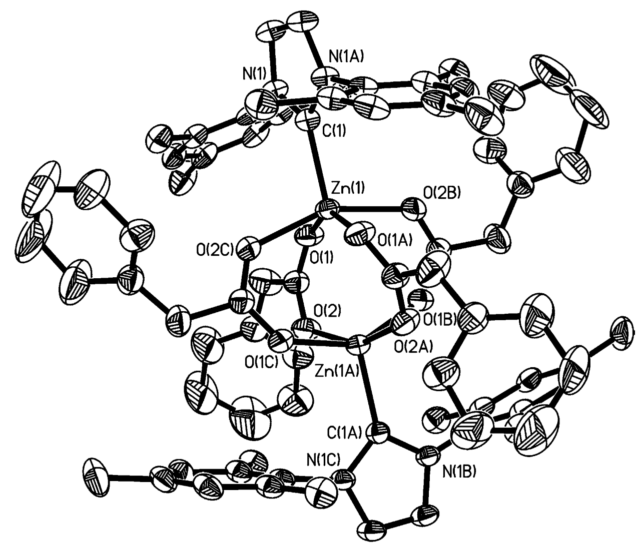

Fig. 2. X-ray structure of compound **4**.

THF. **4** crystallizes in the cubic space group $Pn\bar{3}$. Compound **4** is a dimeric Zn complex with four μ^2-bridging phenylacetates. This results in a square-pyramidal arrangement of the ligands around the 5-fold coordinated zinc. As a consequence of the reduced *trans*-effect of the carboxylates, the distance Zn(1)C(1) is slightly enlarged to 207.5(6) pm. Not unexpected, the Zn(1)–O distances to all four oxygen atoms are almost identical, i.e. 206.1(3) and 207(5) pm, respectively. Further relevant structural data, bond angles, and distances are summarized in Tables 1 and 3.

Reaction of **1** with 2 equivalents of CF_3SO_3Ag in THF afforded monomeric $Zn(O_3SCF_3)_2(NHC)(THF)$ (**5**) (Fig. 3) in 83% yield. **5** crystallizes in the triclinic space group $P\bar{1}$. Not unexpected, **5** shows the strongest *trans*-effect induced by the strongly electron-withdrawing trifluorosulfonates, resulting in a Zn(1)–C(1) distance of 199.6(3) pm. A strong binding was also observed for THF, expressed by a comparably short Zn(1)–O(7) distance of 199.83(18) pm. Further relevant structural data, bond angles, and distances are summarized in Tables 4 and 5.

Finally, $ZnCl(OC_6H_4\text{-}2\text{-}CH{=}N(CHPhCH_3)(NHC)$ (**6**) (Fig. 4) was accessible by reaction of **1** with sodium

Table 3
Bond lengths (pm) and angles (°) for **4**

Zn(1)–O(2)#1	206.1(3)
Zn(1)–O(2)#2	206.1(3)
Zn(1)–C(1)	207.5(6)
Zn(1)–O(1)	207.6(3)
Zn(1)–O(1)#3	207.6(3)
O(2)#1–Zn(1)–O(2)#2	154.46(18)
O(2)#1–Zn(1)–C(1)	102.77(9)
O(2)#2–Zn(1)–C(1)	102.77(9)
O(2)#1–Zn(1)–O(1)	86.66(14)
O(2)#2–Zn(1)–O(1)	86.07(14)
C(1)–Zn(1)–O(1)	106.67(9)
O(2)#1–Zn(1)–O(1)#3	86.07(14)
O(2)#2–Zn(1)–O(1)#3	86.66(14)
C(1)–Zn(1)–O(1)#3	106.67(9)
O(1)–Zn(1)–O(1)#3	146.66(17)

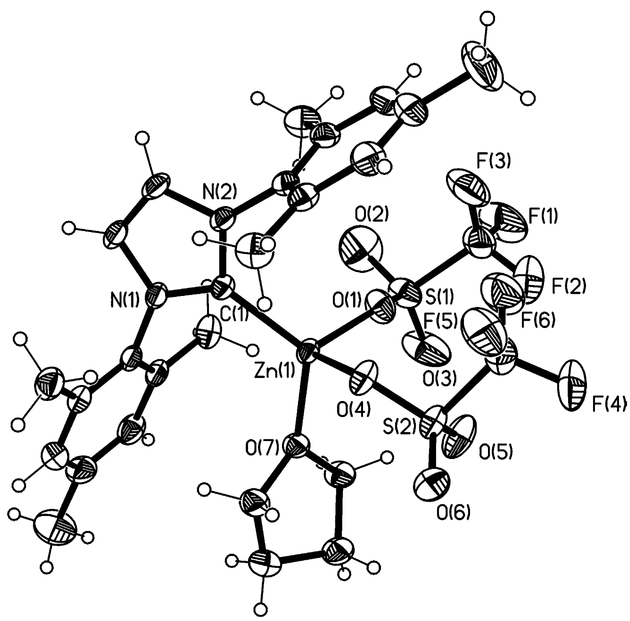

Fig. 3. X-ray structure of compound **5**.

Table 4
Crystal data and structure refinement for **5** and **6**

	5	**6**
Molecular formula	$C_{27}H_{32}F_6N_2O_7S_2Zn \times$ 0.5 THF	$C_{36}H_{38}ClN_3OZn \times CH_2Cl_2$
Formula weight	776.11	714.44
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
a (pm)	1003.5(2)	1404.18(2)
b (pm)	1345.97(3)	1577.88(4)
c (pm)	1422.84(3)	1586.03(4)
α (°)	100.200(1)	90
β (°)	94.435(1)	90
γ (°)	97.774(1)	90
Volume (nm^3)	1.8640(4)	3.51405(10)
Z	2	4
Temperature (K)	233(2)	233(2)
D_{calc} (Mg/m^3)	1.447	1.350
Absorption coefficient (mm^{-1})	0.849	0.960
Color, habit	Colorless prism	Colorless prism
Number of reflections with $I > 2\sigma(I)$	5096	3626
Goodness-of-fit on F^2	1.053	1.060
R indices $I > 2\sigma(I)$	$R_1 = 0.0393$ $\omega R_2 = 0.1022$	$R_1 = 0.0558$ $\omega R_2 = 0.1508$

Table 5
Bond lengths (pm) and angles (°) for **5**

Zn(1)–O(1)	196.6(2)
Zn(1)–O(4)	197.3(2)
Zn(1)–C(1)	199.6(3)
Zn(1)–O(7)	199.83(18)
O(1)–Zn(1)–O(4)	102.39(10)
O(1)–Zn(1)–C(1)	110.95(11)
O(4)-Zn(1)–C(1)	117.18(9)
O(1)–Zn(1)–O(7)	103.64(9)
O(4)-Zn(1)–O(7)	101.07(9)
C(1)–Zn(1)–O(7)	119.46(10)

{[R(+)-α-2-(1-phenyl-ethylimino)-methyl]-phenolate} (**6a**) in 70% yield. Again, a monomeric rather than a dimeric product was obtained. According to ^{13}C and ^{1}H NMR, **6** exists in two isomeric forms (73:27), of which one crystallizes in the orthorhombic space group $P2_12_12_1$. A comparable large Zn(1)–C(1) distance of 204.8(7) pm was found, indicative for the electron-donating character of the ligands. The Zn(1)–Cl(1) distance is almost identical to the one found in compound **1** (223.7(2)° versus 223.38(6)° and 223.44(7)°, respectively). Further relevant structural data, bond angles, and distances are summarized in Tables 4 and 6.

2.2. Catalytic activity of compounds 1,2, 4–6

Binary and ternary catalytic systems based on Zn(II) are well-known catalysts for the ring-opening polymerization (ROP) of oxiranes and for the copolymerization of oxiranes with CO_2, respectively [41–57]. In a first attempt to use the new complexes for polymerization, compounds **1**, **2**, and **5** were used in the ROP of propylene oxide. No catalytic activity was observed at all. With ε-caprolactone, **1** was found to possess extremely low activity, the turn-over number (TON) was as low as 4. An interesting finding was that of all new compounds, **5** was the only one which permitted the ROP of cyclohexene oxide in virtually quantitative yields. A TON>500 was observed. Nevertheless, the molecular weight (M_n) of poly(cyclohexene oxide) was 3300 g/mol with a polydispersity (PDI) of 1.72. These data suggest that there was some significant chain transfer during polymerization. However, these findings indicate that **5** containing the strongest electron-withdrawing substituents (trifluorosulfonates) had the strongest Lewis acidity and therefore best bonding properties for the monomer.

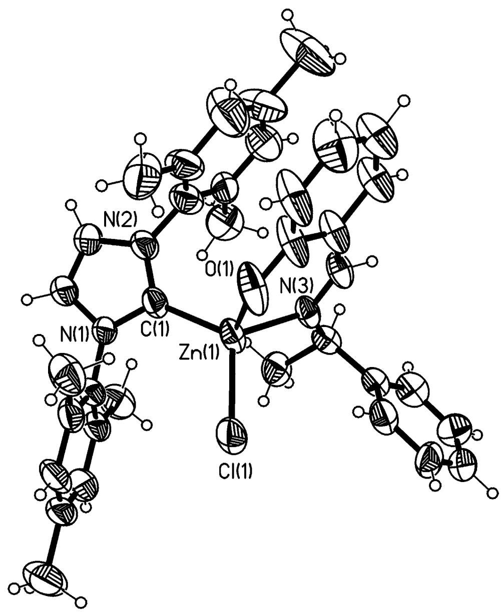

Fig. 4. X-ray structure of compound **6**.

Table 6
Bond lengths (pm) and angles (°) for **6**

Zn(1)–O(1)	196.3(5)
Zn(1)-N(3)	204.1(5)
Zn(1)–C(1)	204.8(7)
Zn(1)–Cl(1)	223.7(2)
O(1)–Zn(1)-N(3)	94.7(2)
O(1)–Zn(1)–C(1)	108.0(3)
N(3)-Zn(1)–C(1)	115.9(2)
O(1)–Zn(1)–Cl(1)	110.8(2)
N(3)–Zn(1)–Cl(1)	110.64(17)
C(1)–Zn(1)–Cl(1)	114.9(2)

In addtion, a monomeric structure appears favorable. When subject to the copolymerization of cyclohexene oxide with CO_2, a polymer ($M_n = 2700$, PDI = 1.19) was formed in quantitative yield and with high TONs = 450. Unfortunately, it consisted of only 30% of the desired copolymer and 70% of pure poly(cyclohexene oxide) (Table 7). Therefore, coordination/insertion of the epoxide into the growing polyether chain must be favored over CO_2 insertion by roughly a factor of 3.

Consequently, a more balanced reactivity was required. Substitution of both triflate groups in **5** by chlorine or better various carboxylate groups as realized in compounds **1**, **2**, **4**, and **6**, was believed to provide better conditions. Consequently, these compounds were used as catalysts in the copolymerization of cyclohexene oxide with CO_2 applying a pressure of 65–68 bar. Polymers consisting of 100% poly(carbonate) were obtained with compounds **1**, **2**, and **6**, while compound **4** was virtually inactive. With the exception of poly(carbonate) prepared by the action of **1** ($M_n = 13\,900$, PDI = 3.49), molecular weights (M_n) were in the range of 1800–2400 g/mol, with PDIs of 1.08 and 1.6, respectively. In view of the dimeric structure of **4**, its inactivity was not surprising at all, though the dimeric compound **2** showed some (low) polymerization activity indicating the presence of small amounts of monomeric species. In summary, it should be emphasized that activities of those complexes that allowed the copolymerization of oxiran with CO_2 were generally low, making this class of compounds less attractive for these purposes. Thus, typical TONs were <25, thus requiring at least 4 mol% of catalyst in order to reach full conversion.

3. Experimental

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Purchased starting materials were used without any further purification. Pentane and tetrahydrofurane (THF) were distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was distilled from calcium hydride.

NMR data were obtained at 300.13 MHz for proton and 75.74 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. IR spectra were recorded on a Bruker Vector 22 using ATR technology. Elemental analyses were carried out at the Institute of Physical Chemistry, University of Vienna and at the Mikroanalytisches Labor, Anorganisch-Chemisches Institut, TU München, Germany. MS spectra (FAB) were recorded on a Finnigan MAT 95S using FAB ionization (Cs-gun: 20 kV, 3 μA, matrix: *m*-nitrobenzylic alcohol).

Table 7
Summary of polymerization results for the copolymerization of CO_2 with cyclohexene oxide (CHO)

Category (mg)	CHO (ml)	CO_2 (bar)	Temperature (°C)	Time (h)	M_n (g/mol)	PDI	Poly(carbonate) (%)	Yield (mg)
5 (76)	5	65	80	24	2700	1.19	30	6000
5 (76)	5	55	r.t.	6	–	–	0	0
1 (45)	5	65	80	24	13 900	3.49	100	100
2 (36)	5	68	80	24	1800	1.08	100	200
4 (65)	5	65	80	24	–	–	0	0
6 (64)	5	65	80	24	2400	1.60	100	100

3.1. $ZnCl_2$(NHC) (**1**)

$ZnCl_2$ (136.3 mg, 1.000 mmol) was dissolved in 15 ml of THF and a solution of 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (303.4 mg, 1.000 mmol) in 3 ml of THF was added slowly. The mixture was stirred at room temperature for 12 h. The resulting solution was then concentrated to ~5 ml. After the addition of 20 ml of pentane, a white solid precipitated, which was filtered off and washed three times with pentane, and dried in vacuo. Yield: 350.2 mg (80%). A crystal of **1** suitable for X-ray analysis was obtained by cooling a concentrated THF solution to −40 °C for several days. FT-IR (ATR-mode, cm^{-1}): 3030m, 2920m, 1600m, 1550s, 1482w; ^1H NMR ($CDCl_3$) δ 7.02 (2H, s), 6.89 (4H, s), 2.30 (6H, s), 2.03 (12H, s). ^{13}C NMR ($CDCl_3$) δ 172.98, 139.22, 135.45, 133.79, 129.06, 122.90, 21.11, 17.76. Anal. Calc. for $C_{21}H_{24}N_2Cl_2Zn$: C, 57.23; H, 5.49; N, 6.39. Found: C, 56.99; H, 5.39; N, 6.25%.

3.2. $[Zn(OAc)_2(NHC)]_2$ (**2**)

$Zn(OAc)_2$ (183.5 mg, 1.000 mmol) was suspended in 15 ml of THF and a solution of 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (304.4 mg, 1.000 mmol) in 3 ml THF was added dropwise. Then the mixture was stirred overnight at room temperature. The solution was then concentrated to ~5 ml, ca. 10 ml of pentane were added resulting in the formation of a white precipitate. It was filtered off, washed three times with pentane, and dried in vacuo. Yield: 292 mg (60%). FT-IR (ATR-mode, cm^{-1}): 3050m, 2920m, 1580s, 1486s; ^1H NMR ($CDCl_3$) δ 7.19 (2H, s), 7.00 (4H, s), 2.35 (6H, s), 2.10 (12H, s), 1.72 (6H, br); ^{13}C NMR ($CDCl_3$) δ 179.15, 173.46, 139.66, 135.25, 134.06, 129.02, 123.17, 22.65, 21.02, 17.24. Anal. Calc. for $C_{25}H_{30}N_2O_4Zn$: C, 61.54; H, 6.20; N, 5.74. Found: C, 61.32; H, 6.01; N, 5.73%. MS (FAB): m/z calc. for $C_{25}H_{30}N_2O_4Zn$: 486.15, found $m/z = 1007.06$ ($C_{53}H_{60}N_5O_7Zn_2$, 73.4%).

3.3. $[Zn(OCOPh)_2(NHC)]_2$ (**3**)

$Zn(OCOPh)_2$ (44.0 mg, 0.298 mmol, prepared by the reaction of $ZnEt_2$ and PhCOOH in THF and used without further purification) was suspended in 10 ml of THF, then a solution of 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (43.5 mg, 0.299 mmol) in 2 ml of THF was added. After 20 min of stirring, the precipitate had dissolved. The mixture was stirred overnight, and was then concentrated to ca. 2 ml. Ten milliliters of pentane was added and the mixture was cooled to −40 °C. A white solid formed after 2 days, which was filtered off, washed with pentane, and dried in vacuo. Yield: 52.5 mg (60%). FT-IR (ATR-mode, cm^{-1}): 3025m, 2914m, 1636s, 1585w, 1367s, 850s. ^1H NMR ($CDCl_3$) δ 7.77 (4H, t, $J = 6.93$), 7.37 (2H, t, $J = 6.93$), 7.26 (4H, t, $J = 7.60$), 7.17 (2H, s), 6.65 (4H, s), 2.11 (12H, s), 1.79 (6H, s); ^{13}C NMR ($CDCl_3$) δ 177.07, 173.55, 139.85, 135.04, 133.57, 130.71, 129.06, 127.15, 123.10, 20.61, 17.40. Anal. Calc. for $C_{35}H_{34}N_2O_4Zn$: C, 68.68; H, 5.60; N, 4.58. Found: C, 68.69; H, 5.96; N, 4.33%. MS (FAB): m/z calc. for $C_{35}H_{34}N_2O_4Zn$: 610.18, found $m/z = 1130.8$ ($C_{63}H_{64}N_5O_7Zn_2$, 20%).

3.4. $[Zn(OCOCH_2Ph)_2(NHC)]_2$ (**4**)

$Zn(OCOCH_2Ph)_2$ (100.0 mg, 0.298 mmol, prepared by the reaction of $ZnEt_2$ and $PhCH_2COOH$ in THF and used without further purification) was suspended in 10 ml of THF, then a solution of 1,3-bis(2,4,6-trimethyl-phenyl)-imidazol-2-ylidene (90.5 mg, 0.299 mmol) in 2 ml of THF was added. After 20 min of stirring, the precipitate had dissolved. The mixture was stirred overnight, and was then concentrated to 5 ml. Ten milliliters of pentane was added, resulting in the formation of a white solid, which was filtered off, washed with pentane, and dried in vacuo. Yield: 160 mg (84%). Crystals of **4** were obtained by slowly cooling a concentrated THF solution of the complex. FT-IR (ATR-mode, cm^{-1}): 3025m, 2916m, 1586s, 1487m, 1366w, 850m; ^1H NMR ($CDCl_3$) δ 7.32–6.63 (16H, m), 3.15 (4H, s), 2.35–1.74 (18H, m); ^{13}C NMR (THF-d_8) δ 182.51, 143.83, 141.03, 140.38, 140.32, 134.89, 134.62, 134.06, 132.68, 130.81, 130.38, 128.66, 48.34, 25.78, 22.25; MS calc. for $C_{74}H_{76}N_4O_8Zn_2$ 1276.42, found 1162.56 ($[(M+H)-PhCH_2CO]^+$), 1145.57 ($[(M+H)-PhCH_2COOH]^+$).

3.5. $Zn(OSO_2CF_3)$(NHC) (**5**)

A solution of $AgOSO_2CF_3$ (358.3 mg, 1.394 mmol) in 3 ml of THF was added slowly to a solution of **1** (309.4 mg, 0.6973 mmol) in 7 ml of THF. A white solid precipitated immediately. The mixture was stirred for 2 h at room temperature, then it was filtered. The filtrate was concentrated to ~5 ml, after the addition of 20 ml pentane, a white solid precipitated, which was filtered off, washed three times with pentane and dried in vacuo. Yield: 430 mg (83%). Crystals of **5** were obtained by slowly diffusion of pentane to a concentrated THF solution of the complex. IR (ATR-mode, cm^{-1}): 3121m, 2921m, 1610m, 1486m, 1320s, 1201w, 1009s; ^1H NMR ($CDCl_3$) δ 7.24 (2H, s), 7.03 (4H, s), 3.63 (4H, t), 2.33 (6H, s), 2.09 (12H, s), 1.75 (4H, m); ^{13}C NMR ($CDCl_3$) δ 166.85, 140.86, 134.81, 133.00, 130.0, 129.66, 125.38, 121.16, 116.95, 112.74, 69.64, 25.19, 21.03, 17.22.

3.6. {[R(+)-α-2-(1-phenylethylimino)-methyl]-phenol} (**6a**)

Salicyaldehyde (3.05 g, 25.0 mmol) and R(+)-α-methylbenzylamine (3.03 g, 25.0 mmol) were dissolved in a mixture of ethanol and toluene (6:4). The solution was refluxed for 2 h. Upon cooling to 0 °C, a yellow solid precipitated from the reaction mixture. The solid was filtered, washed with cold pentane and then dried in vacuo. Yield: 5.00 g (90%). FT-IR (ATR-mode, cm^{-1}): 2913m, 1620s, 1493w, 1211s, 802s; ^1H NMR ($CDCl_3$) δ 13.53 (1H, s), 8.40 (1H, s), 7.40–7.2 (7H), 6.94 (1H, d, $J = 8.22$), 6.85 (1H, t, $J = 7.31$), 4.54 (1H, q, $J = 6.85$), 1.62 (3H, d, $J = 6.86$); ^{13}C NMR ($CDCl_3$) δ 163.33, 160.95, 143.70, 132.15, 131.29, 128.54, 127.12, 126.25, 118.70, 118.50, 116.82, 68.36, 24.84.

3.7. *ZnCl(NHC){[R(+)-α-2-(1-phenylethylimino)-methyl]-phenolate}* (**6**)

A solution of sodium {[R(+)-α-2-(1-phenylethylimino)-methyl]-phenolate} (108 mg, 437 mmol, obtained by the reaction of **6a** and NaH) in 3 ml of THF was added to a solution of **1** (192mg, 437mmol) in 10 ml of THF. The mixture was stirred at room temperature overnight and the precipitate that formed was removed by filtration through celite. The filtrate was concentrated to 5 ml, then pentane (20 ml) was added. A white solid precipitated, it was filtered off, washed three times with pentane and dried in vacuo. Yield: 170 mg (70%). Crystals of **6** were obtained by slowly diffusion of pentane to a concentrated CH_2Cl_2 solution of the complex. FT-IR (ATR-mode, cm^{-1}): 3050m, 2920m, 1605s, 1550w, 1483s; ^1H NMR ($CDCl_3$) δ 7.38 (H, s), 7.35–6.02 (15H, m), 3.87 (H, q, $J = 7.31$), 2.29 (6H, d, $J = 3.65$), 2.15 (6H, d, $J = 5.48$), 2.06 (6H, d, $J = 3.2$), 1.55 (3H, d, $J = 6.85$); ^{13}C NMR ($CDCl_3$) δ 176.5, 170.8, 170.3, 168.0, 143.5, 141.1, 139.5, 139.4, 135.6 135.2, 135.0, 134.5, 133.7, 133.4, 129.4, 129.3, 129.1, 129.0, 128.6, 128.3, 128.0, 127.6, 127.3, 123.4, 123.3, 123.3, 118.5, 118.3, 112.5, 112.4, 68.0, 65.5, 63.0, 25.6, 24.4, 22.1, 21.2, 17.9, 17.8, 17.5; Anal. Calc. for $C_{36}H_{38}N_3OClZn$: C, 68.68; H, 6.08; N, 6.67; Cl, 5.63. Found: C, 68.57; H, 6.27; N, 6.31; Cl, 5.37%.

3.8. *Copolymerization of cyclohexene oxide with CO_2*

A 0.10 mmol amount of active catalyst was dissolved in 5 ml (51.0 mmol) of cyclohexene oxide. The resulting solution was added through the injection port to a predried autoclave and the reactor was pressurized to 50 bar with CO_2. The reactor was then heated to 80 °C, raising the pressure to ca. 65 bar, for the time indicated in Table 1. After cooling and release of the pressure, the reaction mixture was diluted with CH_2Cl_2 and washed with 0.1 N HCl. The organic phase was separated, dried over Na_2SO_4, and then concentrated to ~3 ml. Finally, 20 ml of methanol were added to the solution to induce precipitation. ^1H NMR ($CDCl_3$) δ 4.57 (br, H–CO_2–), 3.31 (br, H–CO–), 2.04–1.17 (m, –CH_2–); ^{13}C NMR ($CDCl_3$) δ 153.69, 153.23, 153.06, 152.76, 79.22–78.15 (m), 76.13–74.85 (m), 33.08–27.30 (m), 24.38–20.76 (m).

3.9. *Ring-opening polymerization of ε-caprolactone*

1 (30 mg, 58 μmol) was dissolved in 5 ml of toluene and ε-caprolactone (1.1 ml, 9.6 mmol) was added. The resulting solution was placed inside a Schlenk tube and heated to 50 °C for 24 h. After reaction, the mixture was cooled to room temperature and added to acidic methanol. Twenty five milligrams of product (2.2 %) was obtained.

3.10. *ROP of cyclohexene oxide*

Seventy six milligrams of **5** and 5 ml of CHO were dissolved in 5 ml of toluene. The resulting solution was added to Schlenk and heated to 80 °C for 6 h. Then the mixture was cooled to room temperature and added to acidic methanol; the solid that precipitated was filtered off and dried in vacuo. Yield: 5.2 g (100%), M_n, 3300, PDI, 1.72. ^1H NMR ($CDCl_3$) δ 4.66 (br), 3.16 (br), 2.14~1.39 (m); ^{13}C NMR ($CDCl_3$) δ 79.0–77.9 (m), 76.0–74.6 (m), 33.4–18.5 (m).

3.11. *X-ray measurement and structure determination of* ***1, 4, 5*** *and* ***6***

Data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo Kα-radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK [58]. Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELX97 [59]. The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the structure of **4**, there was a 1:1 positional disorder of the C_6H_5-moiety in the benzyl group with one overlying C-atom (C16). The solvent THF is positioned near a 3-fold axis of rotation. In the structure of **5**, there was a 1:1 disorder of THF into 2 nearly overlaying positions.

4. Supporting information

The crystallographic data for **1**, **4**, **5** and **6** have been deposited with the CCDC Nos. 225967–225970, and on the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

5. Summary

A series of new NHC complexes of Zn(II) have been prepared. These compounds are accessible via straightforward synthetic routes and possess low activity yet high selectivity in the copolymerization of cyclohexene oxide with CO_2.

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