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Insertion Reactions of Carbon Dioxide into Zn–N Bonds: Syntheses and Structures of Tetrameric and Dimeric Alkylzinc Carbamato Complexes

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The formal insertions of carbon dioxide into a series of methylzinc dialkylamide complexes ($MeZnNR_2$) initially form solvent-free, tetrameric zinc carbamato complexes [$Me_4Zn_4(O_2CNR_2)_4$] (NR_2 = N(*i*-Pr)$_2$ (**1**), N(*i*-Bu)$_2$ (**2**), and piperidinyl (**3**)). These compounds have been characterized by traditional techniques as well as by single-crystal X-ray diffraction analyses. The tetrameric backbones seen in the solid state for **1**–**3** were structurally similar to each other. Addition of excess pyridine (py) to **1**–**3** breaks apart the tetramers and converts them into solvated dimeric species [$Me_2Zn_2(O_2CNR_2)_2(py)_2$] ($NR_2$ = N(*i*-Pr)$_2$ (**4**), N(*i*-Bu)$_2$ (**5**), and piperidinyl (**6**)). X-ray crystallographic analyses of **4** and **5** confirmed the dimeric structure in the solid state. This study significantly increases the number of well-characterized zinc carbamates prepared via CO_2 insertion into zinc amides.

Introduction

Increasing attention to the insertion reactions of carbon dioxide into metal−nitrogen bonds to form carbamates has been evident over the past several years. This interest has been due to a wide range of reasons, most notably the efforts to use these materials as catalysts or useful intermediates in the synthesis of other, more-valuable chemicals.[1,2] As well, the transformation of CO_2, an abundant natural source of carbon, into more useful organic materials is desired. The chemical nature of CO_2, with an electrophilic center at carbon and nucleophilic centers at oxygen, allows a diverse number of reactions to occur, thus leading to a wide variety of potential transition metal CO_2 complexes.[3] Even though many of the studies of the activation of CO_2 involve the use of early transition metal compounds,[4−8] main group metal and post transition metals species also play important roles in the conversion of CO_2 into carbamates or carboxylates.[9−15]

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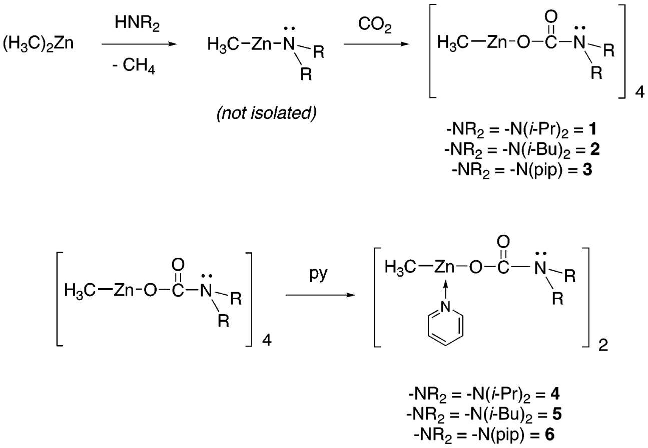
Scheme 1



In recent related work, the reactions of CO_2 with Mg amides by Chang[16] and Zn amides by Caudle[17] to form metal carbamates were studied and reported in several papers from each group. We are interested in the reactions of CO_2 with main group amides to form organic carbamates or diimines that might eventually prove useful in organic synthesis. O'Brien has previously studied the insertion chemistry of CO_2 into mixed alkylzinc diethylamides ["$R-Zn-NEt_2$"] prepared in situ to generate tetranuclear Zn complexes of formula $[R_2Zn_4(O_2CNEt_2)_6]$ (R = Me, Et).[18] He further treated this methylated complex formed with an excess of Me_2Zn to yield $[Me_4Zn_4(O_2CNEt_2)_4]$ after methyl/carbamate exchange had occurred (mechanism unknown).[19] It is not immediately apparent to us why the initial products obtained by O'Brien are of stoichiometry $[R_2Zn_4(O_2CNEt_2)_6]$; it seems that the CO_2 insertion into an "$R-Zn-NEt_2$" species should generate a compound with overall stoichiometry "$R-Zn-O_2CNEt_2$" as was seen by O'Brien in the related insertion chemistry of CS_2 into "$R-Zn-NEt_2$" complexes.[20] In this paper we now report quite different initial reaction products from the reaction of CO_2 with a series of related methylzinc diamides, $MeZnNR_2$ (NR_2 = N(*i*-Pr)$_2$, N(*i*-Bu)$_2$, and piperidinyl). While we obtain tetrameric carbamates as did O'Brien, the ratio of alkyl to carbamate formed in our compounds is *different* from the ratio observed by O'Brien using the diethylamides.[18] As such, we have directly isolated solvent-free $[Me_4Zn_4(O_2CNR_2)_4]$ (NR_2 = N(*i*-Pr)$_2$ (**1**), N(*i*-Bu)$_2$ (**2**), and piperidinyl (**3**)) derived from the formal insertion of CO_2 into each Zn−N bond (Scheme 1). The highly symmetrical cage structures in the solid state exhibited by these tetramers were shown by single-crystal X-ray diffraction analyses. Further, we show that upon addition of an excess of a coordinating solvent such as pyridine (py) the tetrameric carbamates can be converted into solvated dimers of the general formula $[Me_2Zn_2(O_2CNR_2)_2(py)_2]$ (NR_2 = N(*i*-Pr)$_2$ (**4**), N(*i*-Bu)$_2$ (**5**), and piperidinyl (**6**)). Single-crystal X-ray structures of **4** and **5** confirm the dimeric nature of the structure in the solid state.

Experimental Section

General Considerations. All manipulations were carried out in an Ar-filled glovebox or by using standard Schlenk techniques.[21] Anhydrous solvents were purchased from Aldrich or Fisher Scientific Co. and stored in the glovebox over 4 Å molecular sieves. Dimethylzinc as a 2 M solution in toluene, diisopropylamine, diisobutylamine, piperidine, and carbon dioxide were purchased from Aldrich and used without further purification. **Caution!** *Dimethylzinc is pyrophoric and should be handled with care under inert atmosphere.* The amines were stored over 4 Å molecular sieves in a drybox. Benzene-d_6 was obtained from Aldrich and dried and stored over 4 Å molecular sieves. ^{1}H and ^{13}C spectra were obtained on a Bruker AMX 250 spectrometer using C_6D_6 as a solvent. Elemental analyses for carbon, hydrogen, and nitrogen were measured in sealed volatile sample pans using a Perkin-Elmer series II CHNS/O 2400 analyzer.

$[MeZn(O_2CN(\textit{i}\text{-}Pr)_2)]_4$ (1). Dimethylzinc (30 mL, 60 mmol) was reacted with 1 equiv of diisopropylamine (6.07 g, 60 mmol) in 100 mL toluene for 10 h at 70 °C under argon. The resulting solution was cooled to room temperature and dry CO_2 gas bubbled through for 30 min. The solution was then evaporated to dryness and the solid product recrystallized from toluene/hexane (6:1) at −20 °C to give colorless cubic crystals of **1** (9.43 g, 70%). ^{1}H NMR (C_6D_6): δ −0.23 (s, 3H, *Me*Zn), 1.11 (d, 12H, *Me$_2$*CH, $^3J_{H-H} = 6.4$ Hz), 3.86 (m, 4H, −C*H*Me$_2$). ^{13}C NMR (C_6D_6): δ −17.24 (*Me*Zn), 20.64 (*Me$_2$*CH), 46.06 (−*C*HMe$_2$), 163.50 (*C*O$_2$). Anal. Calcd for $C_{32}H_{68}N_4O_8Zn_4$: C, 42.78; H, 7.63; N, 6.24. Found: C, 42.48; H, 7.17; N, 6.81.

$[MeZn(O_2CN(\textit{i}\text{-}Bu)_2)]_4$ (2). The procedure to prepare **2** was analogous to the procedure used in the preparation of **1** with the following quantities used: dimethylzinc (30 mL, 60 mmol); diisobutylamine (7.83 g, 60 mmol). The solid product was recrystallized from hexane at −20 °C to give colorless cubic crystals of **2** (10.91 g, 72%). ^{1}H NMR (C_6D_6): δ −0.41 (s, 3H, *Me*Zn), 0.79 (d, 12H, *Me$_2$*CH, $^3J_{H-H} = 6.4$ Hz), 1.83 (m, 2H, −C*H*Me$_2$). 3.08 (d, 4H, −C*H$_2$*N, $^3J_{H-H} = 7.0$ Hz). ^{13}C NMR (C_6D_6): δ −14.94 (*Me*Zn), 20.38 (*Me$_2$*CH), 27.23 (−*C*HMe$_2$−), 55.81 (−*C*H$_2$N), 164.68 (*C*O$_2$). Anal. Calcd for $C_{40}H_{84}N_4O_8Zn_4$: C, 47.54; H, 8.38; N, 5.54. Found: C, 47.94; H, 8.15; N, 5.53.

$[MeZn(O_2C\text{-}pip)]_4$ (3). The procedure to prepare **3** was analogous to the procedure used in the preparation of **1** with the following quantities used: dimethylzinc (30 mL, 60 mmol); piperidine (5.11 g, 60 mmol). The solid product was recrystallized from toluene/hexane (5:1) at −20 °C to give colorless cubic crystals of **3** (9.38 g, 75%). ^{1}H NMR (C_6D_6): δ −0.23 (s, 3H, *Me*Zn), 1.13 (m, 2H, −C*H$_2$*− (4 position)), 1.23 (m, 4H, −C*H$_2$*− (3,5 positions)), 3.34 (m, 4H, −C*H$_2$*N). ^{13}C NMR (C_6D_6): δ −16.44 (*Me*Zn), 24.35 (−*C*H$_2$− (4 position)), 25.97 (−*C*H$_2$− (3,5 positions)), 45.88 (−*C*H$_2$N), 162.81 (*C*O$_2$). Anal. Calcd for $C_{28}H_{52}N_4O_8Zn_4$: C, 40.31; H, 6.28; N, 6.72. Found: C, 40.51; H, 6.21; N, 6.53.

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Table 1. Crystallographic Data and Parameters for Complexes **1**−**5**

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{32}H_{68}N_4O_8Zn_4$	$C_{40}H_{84}N_4O_8Zn_4$	$C_{28}H_{52}N_4O_8Zn_4$	$C_{26}H_{44}N_4O_4Zn_2$	$C_{30}H_{52}N_4O_4Zn_2$
fw	898.38	1010.59	834.22	607.4	663.50
cryst size (mm)	0.50 × 0.50 × 0.40	0.35 × 0.30 × 0.25	0.35 × 0.20 × 0.10	0.35 × 0.25 × 0.20	0.35 × 0.25 × 0.20
cryst syst	tetragonal	tetragonal	tetragonal	monoclinic	triclinic
space group	$P4_1$	$I\bar{4}$	$P4_2/n$	$P2_1/c$	$P\bar{1}$
a, Å	13.0143(4)	13.3038(11)	14.3865(4)	8.9062(5)	9.2058(10)
b, Å	13.0143(4)	13.3038(11)	14.3865(4)	9.3491(5)	9.4827(10)
c, Å	26.6298(16)	15.006(2)	8.8462(5)	18.4682(10)	10.5975(11)
α, deg					93.746(2)
β, deg				91.3370(10)	114.231(2)
γ, deg					95.017(2)
V, Å^3	4510.3(3)	2655.9(5)	1830.91(13)	1537.34(15)	835.15(15)
Z, Z'	4, 1	2, 0.25	2, 0.25	2, 0.5	1, 0.5
calcd density, g/cm^3	1.323	1.264	1.513	1.312	1.319
μ(Mo Kα), mm^{-1}	2.145	1.829	2.636	1.594	1.473
measd reflcns	32 881	9522	12 928	10 883	5270
indep reflcns	10 465	3102	2201	3615	3684
R_{int}	0.0284	0.0296	0.0285	0.0290	0.0120
obsd reflcns	9735	2777	1934	3210	3550
data/restraints/params	10 465/1/433	3102/0/124	2201/0/152	3615/0/251	3684/0/181
T, K	213(2)	100(2)	213(2)	213(2)	100(2)
R1,[a] wR2[b] (all data)	0.0292, 0.0617	0.0411, 0.1121	0.0303, 0.0685	0.0407, 0.0866	0.0280, 0.0770
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0262, 0.0607	0.0394, 0.1102	0.0256, 0.0660	0.0349, 0.0836	0.0273, 0.0766
GOF on F^2	0.997	1.004	1.007	1.041	1.050

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R(\omega F^2) = \{\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$ (a, b: 0.0336, 0.00 (**1**); 0.0885, 0.5346 (**2**); 0.0366, 0.7597 (**3**); 0.0454, 0.4823 (**4**), 0.0508, 0.3295 (**5**), respectively).

$[MeZn(O_2CN(\textit{i}\text{-}Pr)_2)(py)]_2$ (4). **1** (4.24 g, 4.71 mmol) was dissolved in 50 mL of toluene and treated with excess pyridine (10 mL) and stirred for 2 h. The solution was then evaporated to dryness and the solid product recrystallized from toluene/hexane (5:1) at −20 °C to give colorless cubic crystals of **4** (4.64 g, 81%). ^{1}H NMR (C_6D_6): δ −0.17 (s, 3H, *Me*Zn), 1.12 (d, 12H, *Me*$_2$CH, $^3J_{H-H} = 6.8$ Hz), 3.87 (m, 2H, −C*H*Me$_2$), 6.69 (m, 1H, py), 6.96 (m, 2H, py), 8.62 (m, 2H, py). ^{13}C NMR (C_6D_6): δ −16.36 (*Me*Zn), 21.22 (*Me*$_2$CH), 46.01 (−*C*HMe$_2$), 124.06 (py), 137.15 (py), 149.53 (py), 163.21 (*C*O$_2$). Anal. Calcd for $C_{26}H_{44}N_4O_4Zn_2$: C, 51.41; H, 7.30; N, 9.22. Found: C, 51.48; H, 7.49; N, 9.02.

$[MeZn(O_2CN(\textit{i}\text{-}Bu)_2)(py)]_2$ (5). **2** (2.12 g, 2.10 mmol) was dissolved in 50 mL of toluene, and the solution was treated with an excess of pyridine (10 mL) and stirred for 2 h. The solution was then evaporated to dryness and the solid product recrystallized from toluene/hexane (5:1) at −20 °C to give colorless cubic crystals of **5** (2.37 g, 85%). ^{1}H NMR (C_6D_6): δ −0.15 (s, 3H, *Me*Zn), 0.84 (d, 12H, *Me*$_2$CH, $^3J_{H-H} = 6.6$ Hz), 1.89 (m, 2H, −C*H*Me$_2$), 3.12 (d, 4H, −C*H*$_2$N, $^3J_{H-H} = 7.4$ Hz), 6.67 (m, 1H, py), 6.92 (m, 2H, py), 8.64 (m, 2H, py). ^{13}C NMR (C_6D_6): δ −15.87 (*Me*Zn), 20.50 (*Me*$_2$CH), 27.74 (−*C*HMe$_2$), 55.90 (−*C*H$_2$N), 124.07 (py), 137.31 (py), 149.38 (py), 164.78 (*C*O$_2$). Anal. Calcd for $C_{30}H_{52}N_4O_4Zn_2$: C, 54.31; H, 7.90; N, 8.44. Found: C, 54.49; H, 7.77; N, 8.48.

$[MeZn(O_2C\text{-}pip)(py)]_2$ (6). **3** (2.56 g, 3.07 mmol) was dissolved in 50 mL of toluene and treated with excess pyridine (10 mL). The resulting solution was stirred for 2 h and then evaporated to dryness and the solid product recrystallized from toluene/hexane (6:1) at −20 °C to give colorless cubic crystals of **6** (2.65 g, 75%). ^{1}H NMR (C_6D_6): δ −0.12 (s, 3H, *Me*Zn), 1.20 (m, 4H, −C*H*$_2$− (3,5 position)), 2.10 (m, 2H, −C*H*$_2$− (4 position)), 3.40 (m, 4H, −C*H*$_2$N), 6.73 (m, 1H, py), 7.00 (m, 2H, py), 8.66 (m, 2H, py). ^{13}C NMR (C_6D_6): δ −16.16 (*Me*Zn), 24.79 (−*C*H$_2$− (3,5 position)), 26.12 (−*C*H$_2$− (4 position)), 45.45 (−*C*H$_2$N), 124.26 (py), 137.60 (py), 149.32 (py), 163.17 (*C*O$_2$). Anal. Calcd for $C_{24}H_{36}N_4O_4Zn_2$: C, 50.10; H, 6.31; N, 9.74. Found: C, 49.47; H, 6.36; N, 9.08.

X-ray Crystallography. X-ray-quality crystals of **1**−**5** were grown from either hexane or a mixture of toluene and hexane. Data for **1**, **3**, and **4** were collected on a Bruker P4/CCD diffractometer at 223 K while data for **2** and **5** were collected on a Smart Apex CCD diffractometer at 100 K, both using λ(Mo Kα) = 0.710 73 Å radiation. Crystallographic data and details of the X-ray studies are given in Table 1. As all of the compounds are extremely air-sensitive, the crystals were always handled under inert atmosphere. They were covered with oil and immediately transferred to the N_2 stream of the diffractometer prior to data collection. SADABS absorption corrections were applied in all cases ($T_{min}/T_{max} = 0.776$ (**1**), 0.711 (**2**), 0.716 (**3**), 0.772 (**4**), and 0.837 (**5**)). Non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms in **3** and **4** were found from the difference *F*-maps and refined with isotropic thermal parameters. Hydrogen atoms in other structures were treated as idealized contributions. The $-CH_2CH(CH_3)_2$ groups in **2** are disordered over two positions in the ratio 1/1. The Flack parameters in **1** and **2** are 0.009(6) and 0.01(2), respectively. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).[22]

Results and Discussion

Each of the starting $MeZnNR_2$ complexes was generated in situ by the stoichiometric (1:1) reaction of the respective dialkylamine with Me_2Zn in toluene for 10 h at 70 °C under inert atmosphere.[18,19] In each case after cooling of the solution to room temperature, dry CO_2 gas was bubbled through the solution for 30 min. The solid products remaining after solvent removal were recrystallized from hexane or a toluene/hexane mixture at −20 °C to produce high yields (>70%) of **1**−**3** as analytically pure, colorless cubic crystals. The

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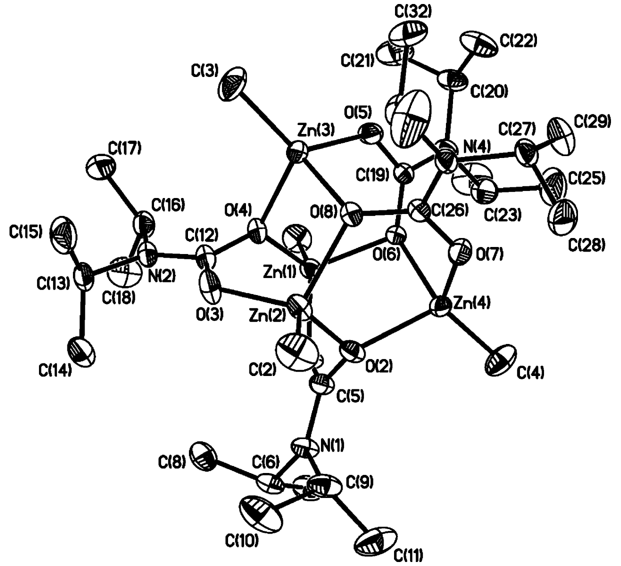

Figure 1. Molecular structure of **1** (30% ellipsoids). The H atoms are omitted for clarity. Important bond lengths (Å) and angles (deg) are as follows: Zn(2)−C(2) 1.950(3), Zn(2)−O(2) 2.088(2), Zn(2)−O(3) 1.992(2), Zn(2)−O(8) 2.055(2), O(3)−C(12) 1.259(3), C(12)−O(4) 1.308(3), C(12)−N(2) 1.339(3); O(3)−Zn(2)−O(8) 101.98(7), O(2)−Zn(2)−O(3) 100.54(7), O(2)−Zn(2)−O(8) 93.45(6), O(3)−C(12)−O(4) 121.0(2).

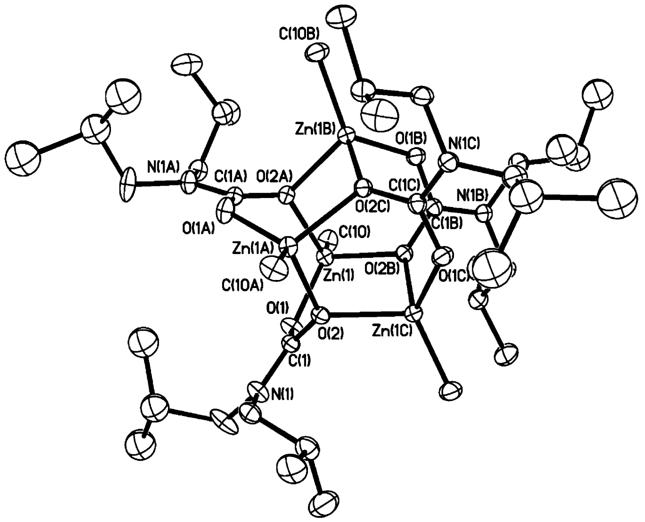

Figure 2. Molecular structure of **2** (30% ellipsoids). The H atoms are omitted, and only one position of the disordered $-CH_2CH(CH_3)_2$ groups is shown for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)−C(10) 1.960(3), Zn(1)−O(1) 1.974(2), Zn(1)−O(2A) 2.078(2), Zn(1)−O(2B) 2.085(2), C(1)−O(1) 1.273(4), C(1)−O(2) 1.296(4), C(1)−N(1) 1.336(4); O(1)−Zn(1)−O(2B) 99.69(9), O(1)−Zn(1)−O(2A) 100.1(1), O(2A)−Zn(1)−O(2B) 93.5(1), C(10)−Zn(1)−O(1) 124.1(2), C(10)−Zn(1)−O(2A) 115.7(2), C(10)−Zn(1)−O(2B) 118.1(2), O(1)−C(1)−O(2) 122.4(3).

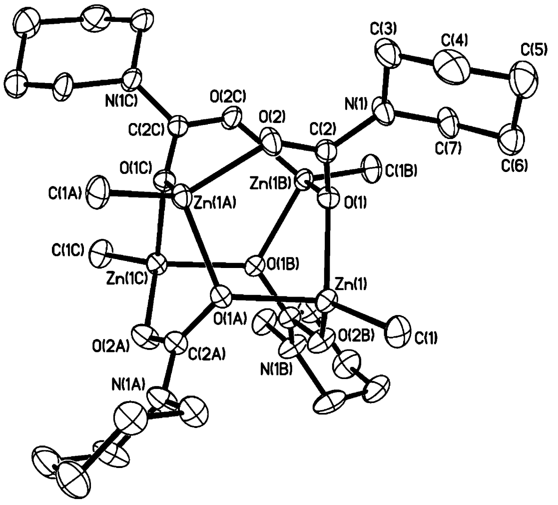

Figure 3. Molecular structure of **3** (30% ellipsoids). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)−C(1) 1.951(2), Zn(1)−O(1) 2.069(1), Zn(1)−O(1A) 2.067(1), Zn(1)−O(2B) 1.969(1), C(2)−O(1) 1.299(2), C(2)−O(2) 1.259(2), C(2)−N(1) 1.331(2); O(1)−Zn(1)−O(2B) 101.30(5), O(1)−Zn(1)−O(1A) 92.15(6), O(1A)−Zn(1)−O(2B) 101.64(5), C(1)−Zn(1)−O(1) 114.89(8), C(1)−Zn(1)−O(2B) 122.61(9), O(1)−C(2)−O(2) 122.19(16).

crystals are soluble in toluene and dissolved only slightly in hexane. The crystals proved suitable for X-ray diffraction and were subjected to crystallographic analysis (Table 1).

The X-ray single-crystal analyses of **1**−**3** indicated relatively similar solid-state structures with tetrameric molecular units. As was seen with $[Me_4Zn_4(O_2CNEt_2)_4]$ previously prepared by O'Brien,[19] their solid-state structures were based on four zinc atoms in an approximately tetrahedral arrangement. The four zinc atoms in each tetramer are connected with bridging carbamates to form two puckered, six-membered Zn_2O_3C rings, which are linked together by bridging oxygen atoms to afford a cage structure. The planes of the two Zn_2O_3C rings in **1** (Figure 1) and **2** (Figure 2) were essentially centrosymmetrically parallel to each other; however, the case is different in complex **3** (Figure 3). In **3**, although the general connectivity of the backbone is the same as in **1** and **2**, the two planes of the Zn_2O_3C rings are now twisted and significantly more distorted relative to each other. In all cases, the oxygens of the carbamato ligands were coordinated to zinc atoms via two different bonding modes. One of the oxygen atoms in the carbamate was bound only to one zinc atom and one carbon atom (O dicoordinate mode, μ_2), while the other oxygen atom bridged two different zinc atoms in addition to the bond to carbon (O tricoordinate mode, μ_3). In **1**−**3**, each zinc atom is essentially in a roughly tetrahedral coordination environment, binding to three oxygen atoms (two μ_3 O's and one μ_2 O) in addition to the carbon atom of the attached methyl group. In **1**, the Zn−O(μ_3) bond distances of Zn(1)−O(6) (2.073(2) Å) and Zn(1)−O(4) (2.069(2) Å) are comparable. However, these were found to be slightly longer than the Zn−O(μ_2) distance of Zn(1)−O(1) (1.970(2) Å), presumably due to the different Zn−O bonding modes. The same situation with Zn−O bond lengths was seen with both **2** and **3**. These bond lengths are consistent with those seen by O'Brien.[19] The O−C−O angles of the carbamato ligands in **1**−**3** were almost identical with bond angles of 121.0(2)−122.19(19), 122.4(3), and 122.2(2)°, respectively.

As expected, ^1H and ^{13}C NMR spectra of **1**−**3** could not reveal the exact oligomeric structures in solution as was possible using X-ray diffraction in the solid state. However, NMR did indicate the presence of the basic structural backbones of the carbamates $-O_2CN(i\text{-}Pr)_2$ for **1**, $-O_2CN(i\text{-}Bu)_2$ for **2**, and $-O_2C$(piperidinyl) for **3** (see Experimental Section for detailed assignments). The high-field resonances of the methylzinc moiety are particularly noteworthy—in the

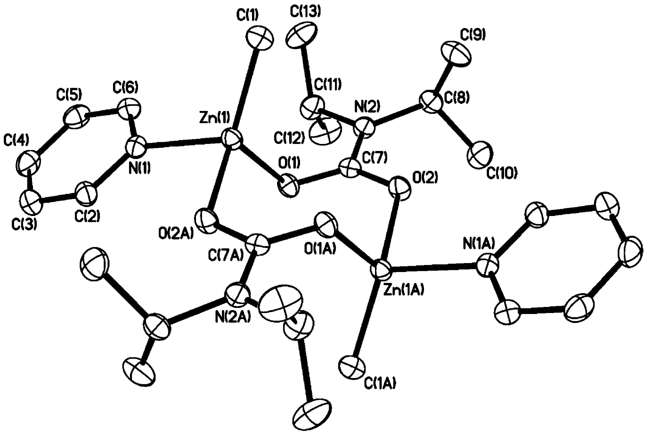

Figure 4. Molecular structure of **4** (30% ellipsoids). The H atoms are omitted for clarity. Important bond lengths (Å) and angles (deg) are as follows: Zn(1)−C(1) 1.973(2), Zn(1)−O(1) 2.042(2), Zn(1)−O(2A) 1.984(2), Zn(1)−N(1) 2.118(2), C(7)−O(1) 1.272(2), C(7)−O(2) 1.269(2), C(7)−N(2) 1.335(2); O(1)−Zn(1)−O(2A) 103.38(6), N(1)−Zn(1)−O(2A) 92.85(6), N(1)−Zn(1)−O(1) 95.16(6), C(1)−Zn(1)−N(1) 113.07(3), C(1)−Zn(1)−O(1) 114.65(9), C(1)−Zn(1)−O(2A) 130.50(9), O(1)−C(7)−O(2) 122.3(2).

^{1}H NMR the proton resonances are near 0 ppm while in the ^{13}C NMR the carbon peak falls far upfield near −16 ppm. For **1**−**3**, the signals in the 163−165 ppm range were assigned to the quaternary carbon of the carbamato groups, which fall into the range of previously known compounds of $[Me_4Zn_4(O_2CNEt_2)_4]$ and $[Me_2Zn_4(O_2CNEt_2)_6]$.[18,19]

The tetramers **1**−**3** were each treated with excess pyridine at room temperature over a 2 h period to afford the solvated complexes **4**−**6**. The pyridine adducts were then dissolved in a toluene/hexane mixture and upon recrystallization at −20 °C gave transparent cubic crystals. The presence of pyridine in the complexes was established initially by ^{1}H and ^{13}C NMR in addition to elemental analysis. While NMR and elemental analysis indicated to us the overall molecular formulas of the new compounds, to determine exact connectivities we needed to turn to X-ray analysis. Fortunately, crystals of **4** and **5** proved suitable for diffraction analyses.

X-ray diffraction analyses of **4** and **5** demonstrated that the preferred structure in the solid state for each was a centrosymmetric dimer. The core of the each dimeric unit was an eight-membered puckered ring $[Zn_2O_4C_2]$ in which each of the two zinc atoms was found to be bound to a methyl group, a pyridine solvent molecule, and two oxygens from the carbamato ligand. Each zinc atom can be considered to be in a distorted tetrahedral coordination environment (Figures 4 and 5). The pyridines in each were located on opposing faces of the eight-membered ring, each pointed away from the ring.

The C−O bond distances 1.272(2) and 1.269(2) Å in the carbamato groups in **4** are consistent with those in compound **5**, 1.276(2) Å. The two Zn−O bonds in either **4** or **5** were not equivalent. In compound **4**, the Zn−O(1) bond distance of 2.042(2) Å was slightly longer than that of Zn−O(2), 1.984(2) Å. This is similar to the corresponding Zn−O distances in compound **5**, 2.040(1) and 1.974(1) Å. The Zn−N bond distances of the pyridine adducts are 2.118(2) and 2.123(1) Å in **4** and **5**, respectively, and these were slightly greater than those observed in $[(C_5H_5N)Zn_2CH_3(O_2CNEt_2)_3]$ (2.057(6) Å)[23] and $[(C_5H_5N)Zn[S_2CNMe_2]_2]$ (2.079 Å)[24] but considerably shorter than those in the chelating complexes $[Me_2Zn(Me_2N(CH_2)_2NMe_2)_2]$ (2.260(8) Å),[23] $[Me_2N(CH_2)_3]_2Zn$ (2.307(4) Å),[25] or $[(Me_3CCH_2)_2Zn(Me_2N(CH_2)_2NMe_2)]$ (2.411(4) Å).[26] The Zn−C bond distances in compounds **4** and **5** are both approximately 1.98 Å, typical for the Zn−C bonds seen in methylated Zn compounds. The O−C−O angles of the carbamato groups found in **4** and **5** are 122.3(2) and 122.9(2)°, respectively, consistent with those found above in compounds **1**−**3**.

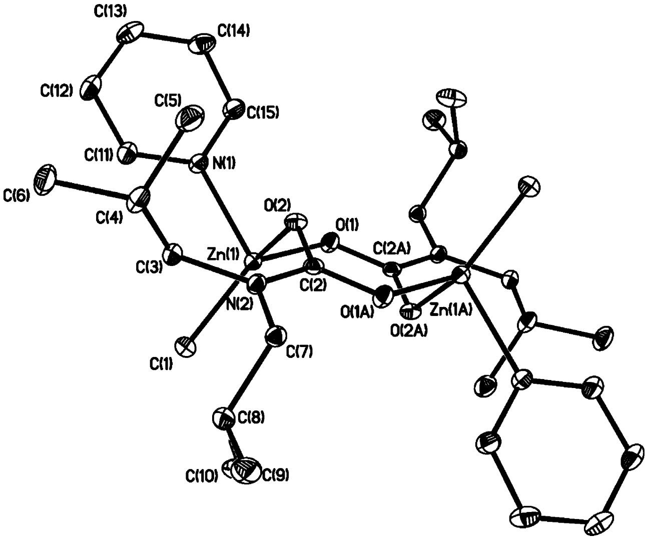

Figure 5. Molecular structure of **5** (30% ellipsoids). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)−C(1) 1.982(2), Zn(1)−O(1) 1.974(1), Zn(1)−O(2) 2.040(1), Zn(1)−N(1) 2.123(1), C(2)−O(2) 1.276(2), C(2)−O(1A) 1.276(2), C(2)−N(2) 1.365(2); O(1)−Zn(1)−O(2) 104.15(5), N(1)−Zn(1)−O(1) 92.23(5), N(1)−Zn(1)−O(2) 95.02(5), C(1)−Zn(1)−O(1) 130.92(6), C(1)−Zn(1)−O(2) 113.74(6), C(1)−Zn(1)−N(1) 113.39(6), O(1A)−C(2)−O(2) 122.9(2).

Compounds **4**−**6** have also been further characterized by ^{1}H and ^{13}C NMR spectroscopies. In the ^{1}H NMR spectrum of **4** the $-N(i\text{-}Pr)_2$ group appeared as expected, and the $Zn-CH_3$ protons again could be characterized by appearance at high field, −0.17 ppm. The pyridine groups appeared as three multiplets at lower field. The ^{13}C NMR spectrum consisted of a high-field resonance for the $Zn-CH_3$ moiety at −16.36 ppm, two signals for $-N(i\text{-}Pr)_2$ carbons, three peaks for pyridine, and the carbamato $(-O_2CNR_2)$ resonance at 163.20 ppm. Similarly, the ^{1}H and ^{13}C NMR spectra for **5** and **6** also reveal the basic backbone structure of the carbamato groups (see Experimental Section for detailed assignments). Interestingly, the ^{13}C chemical shifts for the CO_2 carbon in the carbamato ligands of **1**−**6** vary by at most by ~2 ppm, all lying in the range of 163−165 ppm. It appears that this peak can be a useful diagnostic for identification of Zn carbamates.

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We failed to obtain X-ray-quality crystals for **6**, a compound which is highly moisture and air sensitive. However, we feel it is reasonable to assume the solid-state structure of **6** is dimeric and similar to **4** and **5**. While elemental analysis along with ^{1}H NMR and ^{13}C NMR spectroscopies can indicate the general formula for **6**, as stated above any oligomeric nature of **6** in the solid-state cannot be said for certain in the absence of an X-ray structure.

In summary, we have synthesized and structurally characterized several new tetrameric, solvent-free zinc carbamates by the direct insertion of CO_2 into alkylzinc dialkylamides. We have additionally shown that reaction of a strongly coordinating solvent with the tetramers can convert the tetramers into solvated dimers. With the compounds reported herein we expand significantly upon the number of known and structurally well-characterized Zn carbamato complexes.

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Supporting Information Available: Crystallographic data in CIF format for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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