# Structural Diversity of Ethylzinc Carboxylates

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Ⓢ *Supporting Information*

**ABSTRACT:** The synthesis and structural characterization of a new series of ethylzinc carboxylates are reported. Structurally diverse complexes were derived from three monofunctional carboxylic acids with different numbers of phenyl groups on the $\alpha$-carbon, and two bifunctional carboxylic acids with a neutral donor terminus, namely, methoxyacetic and diethylphosphonoacetic acids. Donor solvents are commonly used in various transformations of alkylzinc carboxylates; therefore, the effect of THF as a donor solvent on the reaction outcome was also investigated. Reactions of equimolar amounts of $Et_2Zn$ and the selected carboxylic acid in THF solutions gave ethylzinc carboxylates with a large variety of structures. In the cases of triphenylacetic and diphenylacetic acids, THF solvated products of stoichiometry $[EtZn(O_2CR)(THF)]$ were isolated as a dimer and a 1D coordination polymer, respectively, whereas, with methoxyacetic acid, a novel solvent-free hexanuclear structural motif with a butterfly-like framework was formed, ($[EtZnO_2CCH_2OCH_3]_6$). The corresponding reaction with diethylphosphonoacetic acid produced a rare example of a nonanuclear organozinc oxo carboxylate cluster, $[(EtZn)_8Zn(\mu_3\text{-}O)_2(O_2CCH_2(O)P(OEt)_6)]$.
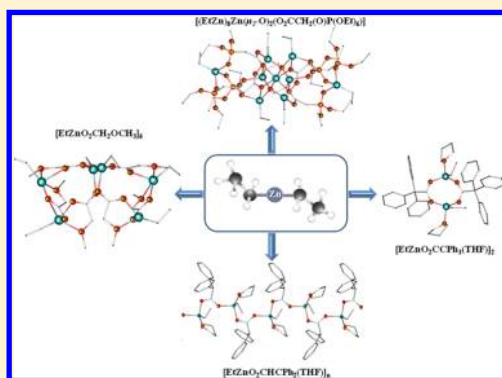
## ■ INTRODUCTION

The origins of organozinc carboxylates chemistry dates back to the 60s to the pioneering work on methylzinc acetate.[1] Nevertheless, only in recent years, this group of compounds has become an area of extensive studies and found application in various research areas. For example, alkylzinc carboxylate compounds have been shown to act as efficient catalysts in the alternating copolymerization of epoxides and carbon dioxide[2] and reagents for organic synthesis.[3] Compounds of general formula $[RZn(O_2CR')]$ were also exploited as model compounds for the activation of dioxygen and elemental sulfur,[4] and very recently, they turned out to be excellent and easy to prepare reagents, which, in combination with molecular oxygen, create free radicals that efficiently initiate organic reactions.[5] In the course of our extensive investigations on organometallic approaches to various metal oxo carboxylates,[4,6] we also elaborated a mild and efficacious route for the coversion of alkylzinc complexes to zinc oxo carboxylate clusters, which, in turn, can be further utilized as molecular building blocks for noncovalent porous materials.[7] A new area in which organozinc carboxylates have shown a significant promise is as intriguing precursors of nanostructured ZnO-based functional materials.[8]

Surprisingly, despite the increasing role of alkylzinc carboxylates in various fields, there are only a few examples of structurally well-defined complexes to date. For example, the reaction of $Et_2Zn$ and $m$-terphenyl carboxylic acid afforded a dimeric complex with the three-coordinated metal center.[9] In the analogues reaction with less spatially hindered, benzoic and acetic acids, a hexameric aggregate $[EtZn(O_2CPh)]_6$ was isolated,[4] while the reaction of $Et_2Zn$ and zinc bis(acetate) afforded a pentanuclear cluster.[10] In turn, application of $(C_6F_5)_2Zn$ and a functionalized benzoic acid leads to the formation of two pentanuclear carboxylates, $[(C_6F_5Zn)_4Zn(Ar^1)_6]$ and $[(C_6F_5Zn)_4Zn(Ar^2)_6]$ ($Ar^1$ = 2-chlorobenzoic acid, $Ar^2$ = 2,4,6-trimethylbenzoic acid).[11] All of these structurally characterized organozinc carboxylates occurred as molecular complexes, and only recently, 1D polymeric structures based on solvent-free mononuclear basic units $[EtZnO_2CC_2F_5]$ or dinuclear units $[EtZn(\mu_3\text{-}OAc)]_2$ were reported.[10,12]

Unceasing investigations on alkylzinc complexes indicate that the stability and structural diversity of the resulting carboxylate derivatives are strongly affected by the character of carboxylate ligand substituents. The structure is also influenced by the presence of a donor solvent in the reaction medium. For example, Minier and Lippard reported on a dynamic conversion in solution between $[Zn_2(Ar^{Tol}CO_2)_2(Et)_2(THF)_2]$ and $[Zn_2(Ar^{Tol}CO_2)_3(Et)(THF)]$ with doubly and triply bridged carboxylates.[13] However, thorough inspection of the data implies inconsistencies in presented equilibrium and does not clearly prove the interconversion between the two species. The importance of a donor solvent is particularly evident in the ethylzinc acetate derivative.[2b] For example, the presence of
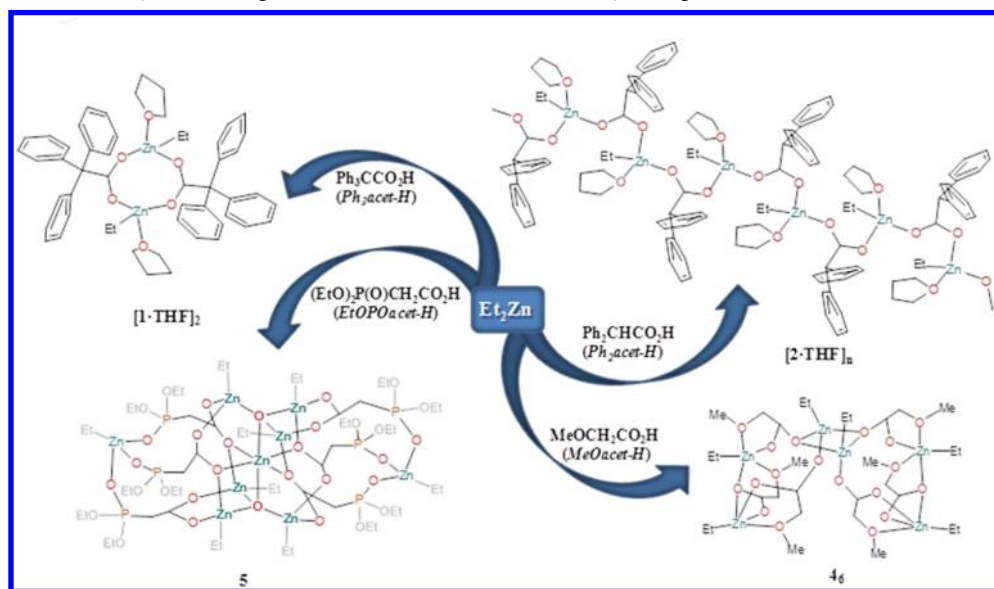
**Scheme 1. Selected Carboxylic Acids: (*a*) Triphenylacetic, (*b*) Diphenylacetic, (*c*) Phenylacetic, (*d*) Methoxyacetic, (*e*) Diethylphosphonoacetic**
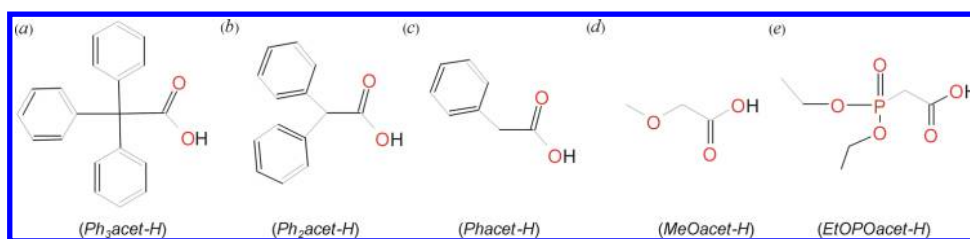


**Scheme 2. Synthetic Pathways Involving Et₂Zn and the Selected Carboxylic Ligands**



noncoordinating aromatic solvents in the reaction medium leads to formation of the pentanuclear cluster $[Zn_5(\mu_3\text{-}OAc)_6(Et)_4]$ independently from reagents stoichiometry, while introduction of even 1 equiv of THF to the solution resulted in formation of coordination polymer $[EtZn(OAc)]_n$ with nonsolvated dimeric basic units $[EtZn(\mu_3\text{-}OAc)]_2$.[2b,10] Similarly, the presence of pyridine enabled the isolation of a polymeric structure constructed of $[EtZn(\mu_2\text{-}OAc)(py)]_2$ units. Another example highlighting the importance of donor species in a reaction medium was the introduction of a strong base into the polymeric system $[EtZnO_2CC_2F_5]_n$. The addition of TMEDA to the latter compound leads to isolation of a monomeric adduct $[EtZn(O_2CC_2F_5)]\cdot TMEDA$.[12] Recently, our group developed an effective procedure for the synthesis of a solvent-ligated dinuclear aggregate $[\{EtZn(O_2CPh)\}\{Zn(O_2CPh)_2\}\cdot THF]$ by a proper choice of reagents stoichiometry.[5a]

All of the above-mentioned organozinc complexes form structures based on monofunctional carboxylate ligands. Examples of organozinc derivatives of carboxylic acids supported by other functionalities, such as −NH₂, −SH, and −OH groups, are scant. For instance, in the reaction of Ph₂C(NH₂)CO₂H and Et₂Zn, a cyclic tetranuclear ethylzinc cluster was obtained, where not deprotonated −NH₂ groups are involved in intramolecular hydrogen bonding interactions. In the case of benzilic acid, a more robust hexanuclear complex was isolated.[14] An alkylzinc derivative with a bifunctional carboxylate acid with thiol termini forms a linear polymeric

chain $[(EtZn(py))_2L]_n$ (L = mercaptopropionic acid, py = pyridine).[15]

The above analysis of the literature data revealed significant voids in structurally characterized organozinc carboxylates. Without more in-depth fundamental knowledge of the factors affecting their structures and reactivities, limited progress can be made in terms of molecular control of the desired reagents or precursors of functional materials based on this group of organometallics. These observations prompted us to explore the impact of carboxylate ligand characteristics on the structures of alkylzinc carboxylates. Herein, we report the synthesis and structural characterization of a series of structurally diverse ethylzinc carboxylates derived from monofunctional carboxylic acids and bifunctional carboxylic acids with a neutral donor terminus. THF is one of the most commonly used solvents in various transformations of alkylzinc carboxylates;[2b,4,5,6a,7,9,13] therefore, the effect of THF as a donor solvent on resulting products was also investigated.

■ **RESULTS AND DISCUSSION**

**Synthesis.** To gain insight into the factors determining the structures and stabilities of alkylzinc carboxylates, five carboxylic acids were selected as proligands, i.e., monofunctional triphenylacetic (*Ph₃acet-H*), diphenylacetic (*Ph₂acet-H*), and phenylacetic (*Phacet-H*) acids differing in the number of phenyl groups on the α-carbon, and bifunctional methoxyacetic (*MeOacet-H*) and diethylphosphonoacetic (*EtOPOacet-H*) acids with neutral oxygen donor termini (Scheme 1). The methoxy group in *MeOacet-H* and the P=O group in

*EtOPOacet-H* were thought to act as donor groups competing with THF in the reaction systems. All the reactions between carboxylic acids and commercially available Et₂Zn in an inert gas atmosphere proceed according to the following general scheme (Scheme 2). The addition of 1 equiv of Et₂Zn to a toluene or THF solution of an appropriate carboxylic acid was followed by ethane evolution and homogenization of the reaction mixture. The reactions with *Ph₃acet-H*, *Ph₂acet-H*, *Phacet-H*, and *MeOacet-H* lead to the formation of ethylzinc complexes supported by monoanionic carboxylates of general stoichiometry ["EtZnO₂CR"], i.e., ([EtZn(*acetPh₃*)] (**1**), [EtZn(*acetPh₂*)] (**2**), [EtZn(*acetPh*)] (**3**), and [EtZn-(*acetOMe*)] (**4**), and the Schlenk-type redistribution processes were not encountered. In the case of diethylphosphonoacetic acid, an oxo zinc cluster [(EtZn)₈Zn(μ₃-O)₂(O₂CCH₂(O)P-(OEt)₆)] (**5**) was isolated. All the reactions were performed using the standard Schlenk technique with the same batches of solvents; therefore, the oxo cluster **5** was probably formed as a result of trace amounts of water in the liquid proligand *EtOPOacet-H* used in the synthesis.[16] Complexes **1**−**5** were almost quantitatively isolated from the postreaction mixtures. Single crystals of **1** and **2** suitable for X-ray diffraction analyses were isolated from a THF solution, and those of **4** and **5** were crystallized from toluene (we were not able to isolate single crystals of **4** and **5** from a THF solution). Despite numerous attempts, the isolation of single crystals of the phenylacetic derivative **3** from toluene or THF solutions was unsuccessful.

**Single-Crystal X-ray Diffraction Study.** The triphenyl-acetic acid derivative **1** crystallizes from a THF solution as a solvated dimer [EtZn(*acetPh₃*)(THF)]₂ (**1·THF**)₂ in triclinic space group *P*1̄ (Figure 1). The central six-membered ring of
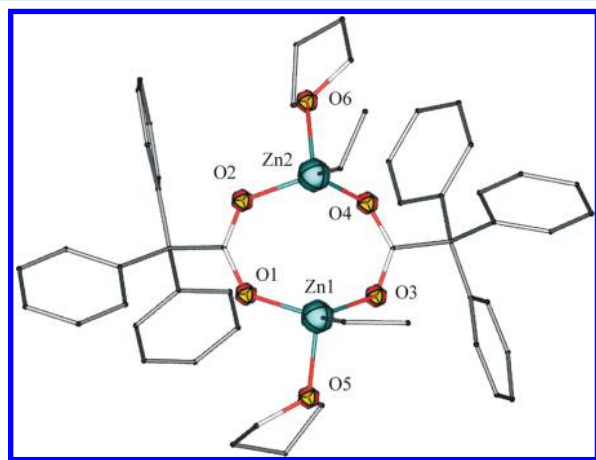
**Figure 1.** Molecular structure of (**1·THF**)₂. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−O1 2.001 (1), Zn1−O3 2.028(1), Zn2−O2 1.965 (1), Zn2−O4 2.018(1), Zn1−O5 2.137(1), Zn2−O6 2.118(3), O1−Zn1−O5 88.2(5), O1−Zn1−O3 102.9(6), O2−Zn2−O4 100.7(6), O4−Zn2−O6 86.4 (6).

(**1·THF**)₂ consists of two four-coordinated zinc atoms bridged by oxygen donor atoms from two carboxylate μ₂:η₁:η₁-bridging ligands. The coordination geometry of the zinc atoms is completed by THF molecules. The Zn−O_carboxylate bond lengths are in the range 1.965−2.028 Å. The use of diphenylacetic acid as the ligand precursor gave an ethylzinc carboxylate that favors an open-chain structure in the solid state. Compound **2** crystallizes in the monoclinic space group *P*2₁/*c* as a 1D

coordination polymer [EtZn(*acetPh₂*)(THF)]ₙ (**2·THF**)ₙ based on the mononuclear zinc diphenylacetate solvated units (Figure 2). The carboxylate groups act as bidentate μ₂:μ₁:μ₁ bridging
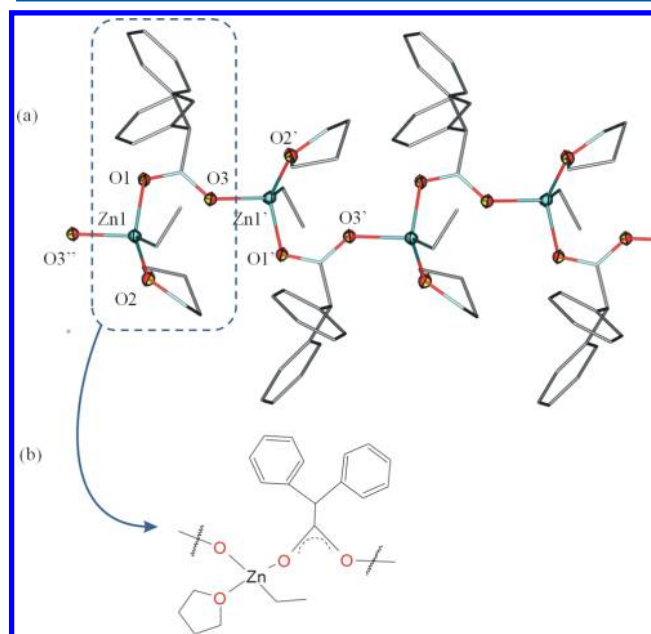
**Figure 2.** (a) Molecular structure of (**2·THF**)ₙ. (b) Representation of the molecular building block. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−O1 2.010(1), Zn1−O2 2.110(1), Zn1′−O3 2.019(1), O1−Zn1−O2 102.00(5), O1−Zn1−O3″ 90.3(5), O3−Zn1′−O2″ 92.0(5).

ligands and are bonded to ethylzinc units in a *syn−anti* fashion. The coordination environment of the ethylzinc units is completed by THF molecules. The Zn−O_carboxylate bond lengths are 2.010(1) and 2.019(1) Å for *syn* and *anti* positions, respectively, while, for Zn−O_THF, the distance is slightly longer, 2.110(1) Å. This difference in bond distances suggests that, for zinc carboxylates, the Zn−O bond in the *syn* position is stronger than that in the *anti* position, which is in contrast, for example, to the related data for organoaluminum carbox-ylates.[17]

The ethylzinc derivative of methoxyacetic acid **4** crystallizes from a toluene solution in the monoclinic *P*1̄ space group as a novel hexameric structural motif for alkylzinc carboxylates. The molecular structure of the ethylzinc derivative of methoxyacetic acid **4₆** is shown in Figure 3. The framework of **4₆** resembles a butterfly-like structure composed of two 12-membered rings joined by a central 4-membered ring, through which the 2-fold symmetry axis passes. The central four-membered ring links another two five-membered rings, creating a planar unit. In the two units, two zinc atoms are five-coordinated, and one is four-coordinated. In this intricate structure, carboxylate groups coordinate with zinc centers via two different modes. Two of them display a μ₃:μ₂:κ₂ coordination mode, and four carboxylate groups present both chelating (μ₂:κ₂:κ₂) and bridging coordination in *syn*- and *syn−anti* fashion. Each of the zinc centers is terminally coordinated with an ethyl group.

Compound **5** crystallizes in the triclinic *P*1̄ space group as light yellow rhombic crystals; its molecular structure is shown in Figure 4. Formally, the nonanuclear cluster **5** can be viewed as a dianionic aggregate composed of a central seven-nuclear (EtZn)₆(μ₄-O)₂Zn core supported by six carboxylate ligands
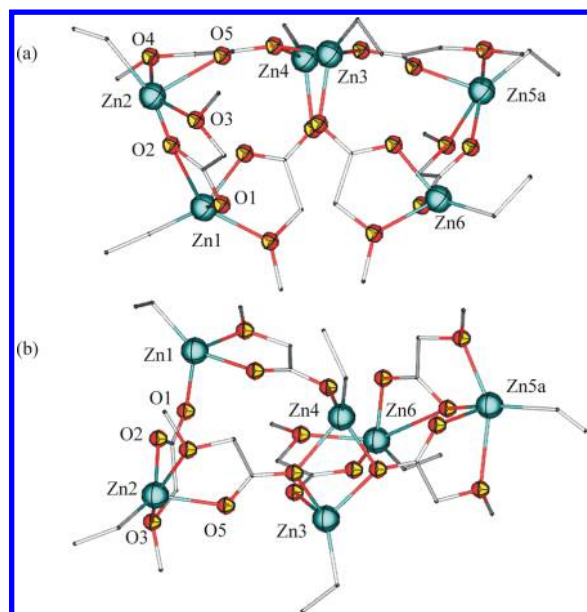
**Figure 3.** Molecular structure of $4_6$: (a) Representation of butterfly-like structural motif. (b) Projection through the planar three-membered fragment. Hydrogen atoms are omitted for clarity. Although the structure is fully refined, due to a limited quality of the crystallographic data, the geometric parameters are not taken into consideration in the discussion.
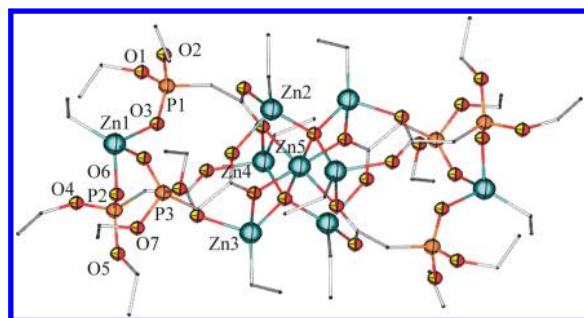


**Figure 4.** Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): O3−P1 1.493(3), Zn1−O3 2.026(3), P3−O7 1.567(3), Zn1−O6 2.022(2), P2−O6 1.478(3), O1−P1−O3 114.9(1), O3−Zn1−O6 92.7(1), O4−P2−O6 114.5(2).

and flanked by two cationic EtZn moieties, each stabilized by three P=O residues. The central six-coordinated metal center is a vertex linking two $Zn_4(\mu_4\text{-O})_2$ units, and eight EtZn moieties have a tetrahedral $CZnO_4$ environment. The bridging carboxylate groups show two different coordination modes: $\mu_3{:}\mu_2{:}\eta_1$ and $\mu_2{:}\eta_1{:}\eta_1$, and the terminal P=O moieties display an $\eta_1$ coordination mode.

**Spectroscopic Characterization.** The $^1$H NMR spectra of **1**−**5** are consistent with the structures found in the solid state (see the Experimental Section). Compound $(\mathbf{2{\cdot}THF})_n$ crystallizes as the 1D polymer, $[EtZn(acetPh_2)(THF)]_n$; therefore, we examined its aggregation state in solution. The corresponding DOSY experiment indicated that, in a THF solution, the compound $(\mathbf{2{\cdot}THF})_n$ occurs as an equilibrating solvated trimer and tetramer, $[EtZn(acetPh_2)(THF)]_3$ and $[EtZn(acetPh_2)(THF)]_4$, respectively. In the IR spectra of all the complexes, the strong C=O absorptions are red-shifted compared with the corresponding vibrations distinctive for the

free acids. For **1**−**3**, the asymmetric and symmetric vibrational stretches ($\nu_{as}$ and $\nu_s$) appear as bands of strong or medium intensities at 1590, 1560, 1564 cm$^{-1}$ and 1443, 1410, 1412 cm$^{-1}$, respectively. The magnitude of the difference between the signals corresponding to the C=O asymmetric and symmetric stretches, the main criterion used in the spectroscopic analysis of carboxylate ligand coordination modes in metal complexes,[18] indicates bidentate bridging of monocarboxylate ligands to the metal centers. For cluster $4_6$, signals corresponding to $\nu_{as}$ and $\nu_s$ $CO_2$ stretches appear at 1584 and 1426 cm$^{-1}$, respectively. Moreover, an additional band is present at 1415 cm$^{-1}$ as a result of the two different coordination modes of the carboxylate groups, $\mu_3{:}\mu_2{:}\kappa_2$ bridging or both $\mu_3{:}\mu_2{:}\kappa_2$ bridging and $\mu_2{:}\kappa_2{:}\kappa_2$ chelating. In the IR spectrum of **5**, the characteristic P=O stretching band appears at 1008 cm$^{-1}$, and signals corresponding to $\nu_{as}$ and $\nu_s$ $CO_2$ stretches are present at 1580 and 1395 cm$^{-1}$.

## ■ CONCLUSIONS

In summary, the present studies provide an enhanced understanding of factors controlling the structure of alkylzinc carboxylates. We synthesized and structurally characterized several new ethylzinc carboxylates derived from monofunctional $Ph_{3-x}CH_xCO_2H$ acids ($x$ = 0, 1, or 2) differing in the number of phenyl groups on the $\alpha$-carbon, and methoxyacetic and diethylphosphonoacetic acids containing a second coordinating functionality. Strikingly, although all of the resulting ethylzinc complexes supported by monoanionic carboxylates (except the diethylphosphonoacetic acid derivative) have the same $[EtZnO_2CR]$ stoichiometry, their skeletal structures vary significantly depending on the character of the supporting carboxylate ligand. The most spatially hindered triphenylacetate ligand favors a classical solvated dimer, whereas diphenylacetate gives the 1D coordination polymer. The introduction of a neutral oxygen donor terminus into the acetate group resulted in a novel solvent-free hexanuclear structural motif with a butterfly-like framework. We were unable to isolate a product with analogous stoichiometry for the reaction involving diethylphosphonoacetic acid likely due to contamination by water of the proligand used; in this case, a new nonanuclear organozinc oxo cluster was isolated. Further studies on the chemistry of various organozinc carboxylates, including their controlled transformations into molecular building blocks of inorganic−organic porous materials and carboxylate-coated ZnO nanocrystals, are in progress.

## ■ EXPERIMENTAL SECTION

**General Considerations.** All manipulations were conducted in a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled from sodium−potassium alloy and benzophenone prior to use. All reagents were purchased from commercial vendors and used in a dry nitrogen atmosphere. $^1$H NMR spectra were acquired on a Varian Mercury 400 MHz spectrometer at 298 K, and chemical shifts are internally referenced to THF-$d_8$ or $C_6D_6$ and calculated relative to TMS. Chemical shifts are expressed in $\delta$ (ppm). The infrared spectra were recorded on an FT-IR PerkinElmer Sytem 2000 spectrometer.

**Synthesis of $(\mathbf{1{\cdot}THF})_2$.** An appropriate amount of triphenylacetic acid (288 mg, 1 mmol) was dissolved in a THF (4 mL) and cooled to −78 °C in a $N_2$ atmosphere. Then, $Et_2Zn$ (0.5 mL of a 2 M solution in hexane, 1 mmol) was added dropwise under vigorous stirring. The reaction after a few minutes was gradually warmed up to room temperature. After 1 h, volatiles were removed under vacuum, and white solid material was crystallized from THF solution at −18 °C

with a yield of 59% (268 mg). $^1H$ NMR ($\delta$, THF-$d_8$, RT, 400 MHz): 0.27 (q, 2 H, CH$_2$CH$_3$), 1.21 (t, 3H, CH$_2$CH$_3$), 1.78 (m, THF$_{coord}$), 3.63 (m, THF$_{coord}$), 6.96−7.26 (m, 15H, Ph$_3$); $^{13}C$ NMR: −1.51, 13.21, 26.36, 68.27, 126.82, 127.89, 131.63, 145.49, 146.15, 180.43; IR (ATR) cm$^{-1}$: 3065 (vw), 2981 (w), 2941 (w), 2895 (w), 2857 (w), 1618 (m), 1590 (m), 1493 (m), 1446 (m), 1384 (s), 1194 (w), 1160 (w), 1037 (m), 886 (m), 744 (s), 696 (vs), 673 (m), 648 (m), 604 (s). Elemental analysis: calcd. for C$_{22}$H$_{20}$O$_2$Zn: % C 69.21, % H 5.28, found % C 68.99, % H 5.14.

**Synthesis of (2·THF)$_n$.** A similar procedure as that for [1·THF]$_2$, using 1 mmol of Et$_2$Zn (0.5 mL of a 2 M solution in hexane) and 212 mg (1 mmol) of diphenylacetic acid. Yield 69% (260 mg). $^1H$ NMR ($\delta$, THF-$d_8$, RT, 400 MHz): 0.35 (q, 2 H, CH$_2$CH$_3$), 1.31 (t, 3H, CH$_2$CH$_3$), 1.78 (m, THF$_{coord}$), 3.68 (m, THF$_{coord}$), 5.15 (s, 1H, CH), 7.23−7.40 (m, 10H, Ph$_2$); $^{13}C$ NMR: −1.43, 13.28, 61.28, 127.22, 128.89, 129.88, 142.12, 180.20; IR (nujol) cm$^{-1}$: 2950 (s), 2920 (vs), 2850 (s), 1940 (vw), 1870 (vw), 1800 (vw), 1650 (vw), 1580 (s), 1560 (s), 1490 (s), 1450 (s), 1410 (s), 1400 (s), 1370 (s), 1260 (w), 1070 (w), 1030 (w), 908 (vw), 876 (vw), 795 (w), 739 (m), 692 (m), 645 (m). Elemental analysis: calcd. for C$_{20}$H$_{24}$O$_3$Zn: % C 63.55, % H 6.40, found % C 63.45, % H 6.33. DOSY experiment. For details, see the Supporting Information. Diffusion coefficient of [2·THF]$_n$ and its estimated molecular weight (MW) in THF-$d_8$: MW$_{calcd.}$ = 377,28 g/mol, $D$ = 4.1 × 10$^{-10}$ m$^2$·s$^{-1}$, MW$_{exp.}$ = 1249 g/mol.

**Synthesis of 3.** A similar procedure as that for [1·THF]$_2$, using 1 mmol of Et$_2$Zn (0.5 mL of a 2 M solution in hexane) and 136 mg of phenylacetic acid (1 mmol). The postreaction mixture was reduced in vacuum to dryness, and the amorphous residue was characterized spectroscopically. Yield 89% (204 mg). $^1H$ NMR ($\delta$, THF-$d_8$, RT, 400 MHz): 0.22 (q, 2 H, CH$_2$CH$_3$), 1.22 (t, 3H, CH$_2$CH$_3$), 3.58 (s, 2H, CH$_2$), 7.19 and 7.25 (m and d, 5H, Ph); $^{13}C$ NMR: −1.48, 13.15, 44.63, 126.95, 128.81, 130.27, 137.71, 180.00; IR (ATR) cm$^{-1}$: 2961 (w), 2910 (vw), 2902 (vw), 1564 (s), 1409 (s), 1385 (s), 1286 (m), 704 (vs), 611 (m), 515 (m). Elemental analysis: calcd. for C$_{10}$H$_{12}$O$_2$Zn: % C 52.12, % H 5.27, found % C 52.03, % H 5.13.

**Synthesis of 4$_6$.** An appropriate amount of methoxyacetic acid (91 mg, 1 mmol) was dissolved in toluene (4 mL) and cooled to −78 °C in a N$_2$ atmosphere. Then, Et$_2$Zn (0.5 mL of a 2 M solution in hexane, 1 mmol) was added dropwise under vigorous stirring. The reaction after a few minutes was gradually warmed up to room temperature. After 3 h, volatiles were removed in vacuum, and the final product was crystallized from a toluene solution at −18 °C with a yield of 95% (174 mg). $^1H$ NMR ($\delta$, C$_6$D$_6$, RT, 400 MHz): 0.73 (q, 2H, CH$_3$CH$_2$), 1.63 (t, 3H, CH$_3$CH$_2$), 3.03 (s, 3H, CH$_3$O), 3.82 (s, 2H, O-CH$_2$-COO); $^{13}C$ NMR: −2.07, 12.91, 59.35, 69.33; IR (ATR) cm$^{-1}$: 2934 (vw), 2889 (vw), 2853 (vw), 2834 (vw), 1597 (vs), 1584 (vs), 1441 (s), 1426 (s), 1415 (m), 1334 (m), 1323 (m), 1262 (vw), 1233 (vw), 1201 (m), 1103 (s), 1020 (w), 976 (s), 947 (m), 919 (w), 804 (w), 725 (m), 602 (m), 537 (m), 514 (s), 419 (s). Elemental analysis: calcd. for C$_5$H$_{10}$O$_2$Zn: % C 35.85, % H 6.02, found % C 35.31, % H 5.89. We note that, in this case, the data of the DOSY experiment were inconsistent, likely due to a lack of a sufficient model for the molecule in question.

**Synthesis of 5.** A similar procedure as that for 4$_6$, using 1 mmol of diethylphosphonoacetic acid (206 mg, 95% solution) and 1 mmol of Et$_2$Zn (0.5 mL of a 2 M solution in hexane). Yield 74% (167 mg). $^1H$ NMR ($\delta$, C$_6$D$_6$, RT, 400 MHz): 0.64 (m, 2H, CH$_3$CH$_2$), 1.06 (s$_{br}$, 3H, CH$_3$CH$_2$(O)P), 1.66 (m, 3H, CH$_3$CH$_2$), 3.16 (s$_{br}$, 2H, P-CH$_2$-COO), 3.99 (s$_{br}$, P(O)CH$_2$CH$_3$); $^{13}C$ NMR: 1.65, 13.32, 16.22, 21.36, 63.80; IR (ATR) cm$^{-1}$: 2957 (w), 2909 (vw), 2849 (vw), 2162 (w), 1613 (m), 1580 (m), 1395 (m), 1257 (s), 1183 (m), 1082 (s), 1008 (vs), 937 (s), 872 (m), 795 (s), 707 (m), 600 (m), 512 (m). Elemental analysis: calcd. for C$_{20}$H$_{24}$O$_3$Zn: % C 24.29, % H 4.92, found % C 24.14, % H 4.84.

**Crystallographic Data.** The crystals were selected under Paratone-N oil, mounted on the nylon loops, and positioned in the cold stream on the diffractometer. The selected crystallographic data, the parameters of data collections and refinement procedures are presented in Table S1 in Supporting Information.

The X-ray data for complexes **1**, **2**, and **4** were collected at 100(2) K on a Nonius Kappa CCD diffractometer using graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å).[19] The unit cell parameters were determined from 10 frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package).[20] The X-ray data for complex **5** were collected at 100(2) K on a SuperNova Agilent diffractometer using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The data were processed with CrysAlisPro.[21] The structure was solved by direct methods using the SHELXS-97 program and was refined by full matrix least-squares on $F^2$ using the program SHELXL-97.[22,23] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. For compound **4**, some residual electron densities are observed; therefore, the initial data set was subjected to the SQUEEZE function of PLATON.[24] To improve the geometrical parameters in **4**, ultimately restrained instructions DFIX and SIMU were applied in the refinement. Compound **5** formed a twinned crystal with partially superimposed reciprocal lattices. The transformation matrix of indices of the twin components for crystals was determined roughly as 1 1.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 1.0000; 2 1.0001 −0.0003 −0.0002 0.1205 −0.9997 0.0000 0.1195 0.0004 −0.9998.

## ■ ASSOCIATED CONTENT

### ⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00557.

> Crystallograhic data (CIF)
> $^1H$ and $^{13}C$ NMR spectra and crystallographic data (PDF)
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## ■ AUTHOR INFORMATION

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### Notes
The authors declare no competing financial interest.

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