#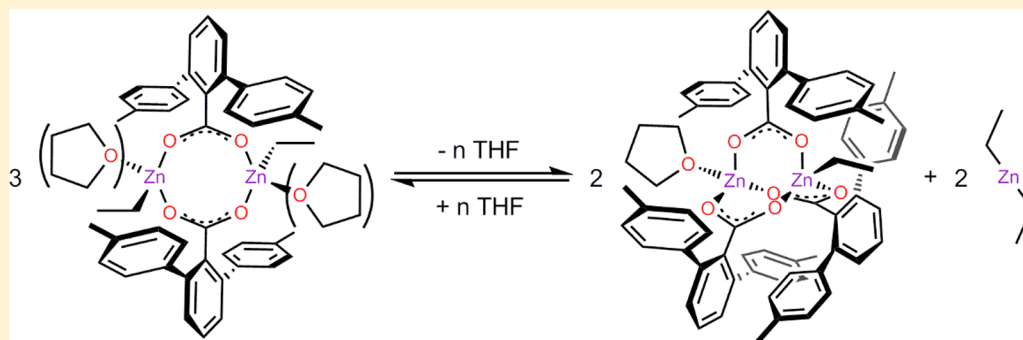 Conversion between Doubly and Triply Carboxylate Bridged Bis(ethylzinc) Complexes and Formation of the (μ-Oxo)tetrazinc Carboxylate [Zn$_4$O(Ar^{Tol}CO$_2$)$_6$]

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S *Supporting Information*

ABSTRACT: Ethylzinc 2,6-bis(*p*-tolyl)benzoate converts between two forms in solution. Through NMR spectroscopic techniques and X-ray crystallography, the species in equilibrium were identified as [Zn$_2$(Ar^{Tol}CO$_2$)$_2$(Et)$_2$(THF)$_2$] (**1**), [Zn$_2$(Ar^{Tol}CO$_2$)$_3$(Et)(THF)] (**2**), and diethylzinc (Ar^{Tol} = 2,6-bis(*p*-tolyl)phenyl). The equilibrium provides a model for understanding the speciation between doubly and triply *m*-terphenylcarboxylate bridged diiron(II) and mononuclear iron(II) complexes. Evidence is presented for the occurrence of coordinatively unsaturated trigonal zinc species in solution. Both **1** and **2** decompose in air to form the *T*-symmetric oxozinc carboxylate [Zn$_4$O(Ar^{Tol}CO$_2$)$_6$] (**3**).

The steric bulk of *m*-terphenylcarboxylates facilitates the assembly of biomimetic diiron(II) complexes that act as models for the active site of soluble methane monooxygenase.[1,2] These complexes share the general formula [Fe$_2$(RCO$_2$)$_4$(L)$_{1-2}$], where R is an *m*-terphenyl group and L is a neutral donor (Scheme 1). Within this diiron family, doubly, triply, and quadruply carboxylate bridged compounds have been isolated as solids, but the role, if any, of the neutral ligand L in modulating the number of bridging carboxylates remains unclear. In particular, the reaction of [Fe$_2$(Ar^{Tol}CO$_2$)$_4$(THF)$_2$] (**4**; Ar^{Tol} = 2,6-bis(*p*-tolyl)phenyl) with *N,N*-dimethylethylenediamine (*N,N*-Me$_2$en) produces a mixture of doubly bridged [Fe$_2$(Ar^{Tol}CO$_2$)$_4$(*N,N*-Me$_2$en)$_2$] (**5**), triply bridged [Fe$_2$(Ar^{Tol}CO$_2$)$_4$(*N,N*-Me$_2$en)] (**6**), and [Fe(Ar^{Tol}CO$_2$)$_2$(*N,N*-Me$_2$en)$_2$] (**7**), all characterized in the solid state (Scheme 1).[3] A ^{19}F NMR spectroscopic study of a fluorinated analogue of **4** revealed interconversion between doubly and quadruply bridged forms,[4] for which triply bridged intermediates were proposed.[1,3,4] The speciation of these diiron(II) complexes in solution during the oxidation of tethered substrates remains unclear, however, and is important for understanding their reactivity.

One approach to studying the solution dynamics of *m*-terphenylcarboxylate-bridged diiron(II) complexes is through parallel work on the redox-stable dizinc(II) analogues. With the use of diamagnetic zinc complexes, NMR spectroscopic

techniques can be employed to probe solution structures. An excellent candidate for such a study is the ethylzinc *m*-terphenylcarboxylate [Zn$_2$(Ar^{Tol}CO$_2$)$_2$(Et)$_2$(THF)$_2$] (**1**), which we discovered during pursuit of a dizinc analogue of the biomimetic diiron(II) carboxylate [Fe$_2$(PIM)(Ar^{Tol}CO$_2$)$_2$] (**8**) (see Figure S12 in the Supporting Information for the structure of PIM^{2-}).[5] NMR spectroscopic experiments revealed the presence of a dynamic equilibrium between doubly bridged **1** and the triply carboxylate bridged complex [Zn$_2$(Ar^{Tol}CO$_2$)$_3$(Et)(THF)] (**2**), which forms together with diethylzinc (Et$_2$Zn) in solution (Scheme 1). This equilibrium may be relevant to related diiron carboxylate complexes such as **4−7**. Compound **1** can lose its coordinated THF molecules, and evidence for a THF-free species having trigonal-planar zinc centers is also presented here. We further describe the oxozinc *m*-terphenylcarboxylate complex [Zn$_4$O(Ar^{Tol}CO$_2$)$_6$] (**3**), formed in air by decomposition of **1** or **2**, which has an interesting structure of *T* symmetry constructed by alignment of *T$_h$* and *T$_d$* local symmetries.

Ethylzinc carboxylate **1** was prepared by addition of 1 equiv of Et$_2$Zn to a solution of Ar^{Tol}CO$_2$H in THF. X-ray diffraction quality crystals of **1** formed directly from the reaction mixture, and the solid-state structure was determined (Figure 1). In **1**,

Scheme 1. (A) Diiron Ar^Tol CO_2^− Complexes and (B) Equilibrium among 1, 2, and Et_2Zn
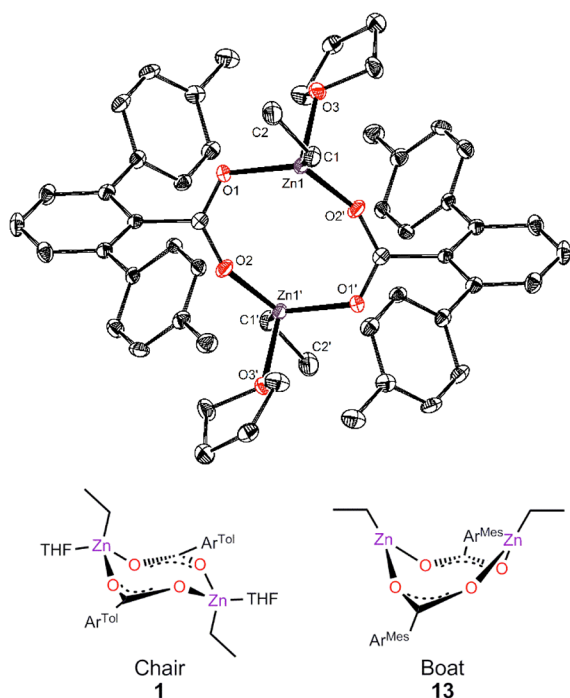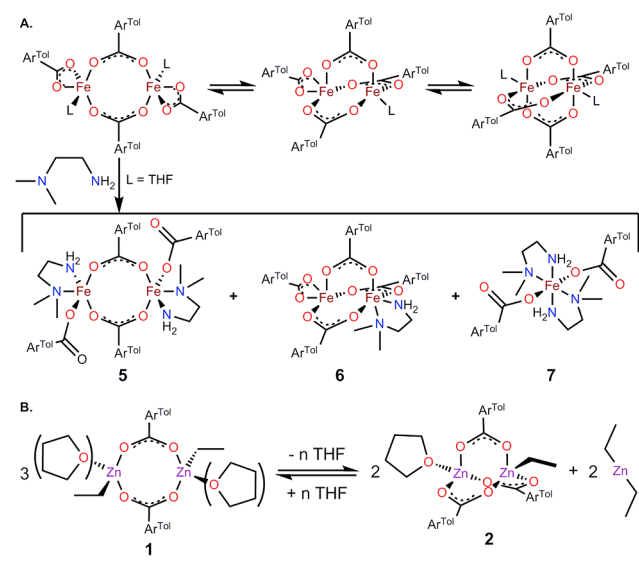

Figure 1. X-ray crystal structure of **1** (top) with thermal ellipsoids at 50% probability and the chair and boat conformations of **1** and **13** (bottom), respectively. Hydrogen atoms are omitted for clarity.

the two carboxylates bridge in a μ-1,3 mode, creating an eight-membered ring with a Zn···Zn distance of 4.06 Å. The ring adopts a chair conformation, with the ethyl groups and the THF molecules trans to each other across the ring, as required by a crystallographic inversion center in the middle (Figure 1). Further details about the crystal structure, including selected bond distances and angles, are provided in the Supporting Information (Table S4).

Compound **1** is a member of the well-known class of alkylzinc carboxylates, interest in which has increased in recent years because of their use as starting materials for oxozinc carboxylates and in polymerization catalysis.[6−9] Original work

on alkylzinc carboxylates dates back to the 1960s, and in 1974 it was demonstrated that the simple ethylzinc carboxylates of acetate, trifluoroacetate, and benzoate have increased reactivity toward methanol in comparison to Et_2Zn itself.[10] Although aggregation in solution was described, structures of the simple ethylzinc carboxylates with acetate and benzoate reported in recent years display large variations in nuclearity and overall structure. Ethylzinc acetate exists as $[Zn_5(CH_3CO_2)_6(Et)_4]$ (**9**) in C_6H_6 or toluene and as $[Zn_2(CH_3CO_2)_2(Et)_2]$ (**10**) in THF.[7,8] Additional solution studies revealed that these two motifs convert upon heating in an appropriate solvent. Ethylzinc benzoate also has two forms. From noncoordinating solvents, a hexazinc barrel-shaped compound, $[Zn_6(PhCO_2)_6(Et)_6]$ (**11**),[6] is obtained with a carboxylate-to-ethyl ratio of 1:1. From THF, a dizinc complex, $[Zn_2(PhCO_2)_3(Et)(THF)]$ (**12**),[9] crystallizes, with a ratio of 3:1. One report of an ethylzinc m-terphenyl carboxylate, $[Zn_2(Ar^{Mes}CO_2)_2(Et)_2]$ (**13**),[11] is particularly interesting because it features two trigonal zinc centers (Ar^Mes = 2,6-bis(mesityl)phenyl). The structure of **1** differs from that of **13** in that the latter has an eight-membered ring in a boat conformation (Figure 1), trigonal-planar zinc, and a Zn···Zn distance of 3.58 Å. The ¹H NMR spectrum of **13** in C_6D_6 supports the persistence of this structure in solution.[11] A summary of the carboxylate to ethyl ratios of the simple ethylzinc carboxylates is presented in Table S2 (Supporting Information).

When crystals of **1** are dissolved in C_6D_6 or toluene-d_8, more than one species is observed in the ¹H NMR spectrum (Figure 2 and the Supporting Information). In the aromatic region, two
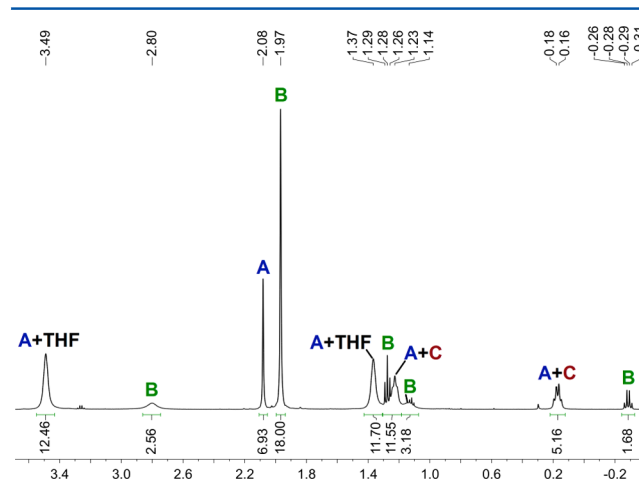
Figure 2. Upfield region of the ¹H NMR spectrum (500 MHz) of **1** dissolved in C_6D_6. Labels **A**–**C** are used to distinguish between the three species present in equilibrium. The ethyl resonances at 3.26 and 1.11 ppm correspond to a minor zinc ethoxide impurity.

sets of peaks from the 2,6-bis(p-tolyl)phenyl groups are present, but the signals are not fully resolved. Resolution is obtained for the two tolyl methyl groups (2.08 and 1.97 ppm) and two ethyl groups (−0.28/1.28 and 0.17/1.23 ppm for the CH_2/CH_3 resonances, respectively). The upfield CH_2 resonances suggest that both ethyl groups are bound to zinc. Large, broad THF resonances occur at 3.49 and 1.37 ppm. Another set of broad resonances, appearing at 2.80 and 1.14 ppm, is also assigned as THF. Because a chemical shift of 2.80 ppm is unusual for the OCH_2 resonance of THF, **1** was prepared from THF-d_8 and its ¹H NMR spectrum was acquired. The

disappearance of peaks at 3.49, 2.80, 1.37, and 1.14 ppm confirmed the THF assignments (Figure S2, Supporting Information). Heating the mixture in toluene-d_8 to 100 °C results in coalescence to a single species (Figure S3, Supporting Information), which suggests that the compounds exchange ligands, are in equilibrium, or both.

The species with methyl group resonances at 2.08 and 1.97 ppm are hereby referred to as **A** and **B,** respectively. Adding THF has an effect on the speciation of **A** and **B** (Figure S4, Supporting Information). Resonances corresponding to **B** and the ethyl group at −0.28/1.28 ppm decrease in intensity with addition of increasing amounts of THF and are most likely the same species. The THF resonances at 2.80/1.14 ppm also disappear, presumably due to increased exchange with excess THF. The methyl resonance of species **A** increases and shifts from 2.08 to 2.14 ppm upon addition of 50 equiv of THF, and the broad Et$_2$Zn ethyl group CH_2 resonance shifts from 0.17 to 0.27 ppm. The changes upon addition of THF suggest a shift in equilibrium from **B** toward **A**.

To gain a deeper insight into the nature of the species present, DOSY spectra were recorded at different concentrations of THF. In C$_6$D$_6$ or toluene-d_8 and with no extra THF added, three species are observed: *m*-terphenyl carboxylate complexes **A** and **B** and another having an ethyl group, **C** (Figure 3 and Figure S9 (Supporting Information)). Species **C**
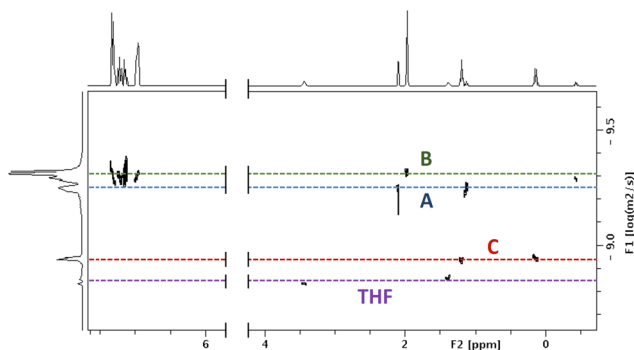

Figure 3. DOSY NMR spectrum (400 MHz) of **1** dissolved in toluene-d_8. Species **A**−**C** and THF are indicated by colored lines.

has a calculated hydrodynamic radius (R_H) of 3.31 Å, which is close to, but larger than, the X-ray-determined radius (R_{X-ray}) of Et$_2$Zn (3.14 Å), calculated from the crystal structure of Et$_2$Zn.[12] Because we expect Et$_2$Zn to coordinate THF under these conditions, an R_H value larger than R_{X-ray} is reasonable. Isolated Et$_2$Zn in C$_6$D$_6$ resonates at 0.10 and 1.08 ppm. The slight deviation of the resonances in our system from the values for Et$_2$Zn, 0.17 and 1.23 ppm, may indicate a conversion to the THF adduct or an exchange process. As the amount of THF is increased, the diffusion coefficient of **C** decreases (Table S1 and Figures S9 and S10, Supporting Information). This observation implies that Et$_2$Zn is in equilibrium with larger species in solution, such as **A** and/or **B**. The possibility that Et$_2$Zn self-associates into oligomers cannot be ruled out. Because Et$_2$Zn is on the same side of the equilibrium as **B** (see the following paragraphs), and the proportion of **B** decreases with increasing amounts of THF, there must be an ethyl group associated with **A**. Thus, the observed ethyl group resonance of **C** is a mixture of species **A** and Et$_2$Zn. As **A** becomes the dominant species in solution with increasing THF, the calculated hydrodynamic

radius of 6.38 Å is consistent with the formulation of **1** (R_{X-ray} = 6.47 Å), supporting the assignment of **A** as **1**.

The equilibrium described above shifts upon removal of Et$_2$Zn from solution under vacuum. When crystals of **1** are dissolved in toluene, stripped to dryness, and redissolved in deuterated solvent, the ¹H NMR spectrum in C$_6$D$_6$ reveals the presence of species **B**, for which the THF and ethyl group resonances can now be confidently assigned. The carboxylate/ethyl/THF ratio in **B** is 3:1:1. This ratio is the same for **12** (Table S2, Supporting Information) and supports the formulation of **B** as [Zn$_2$(Ar^{Tol}CO$_2$)$_3$(Et)(THF)] (**2**). Preparation of **2** in bulk quantities and its subsequent crystal growth by slow diffusion of pentane into a benzene solution of the compound produces colorless plates suitable for X-ray diffraction. The structure confirms the assigned formula (Figure 4). The molecule is a triply *m*-terphenylcarboxylate bridged
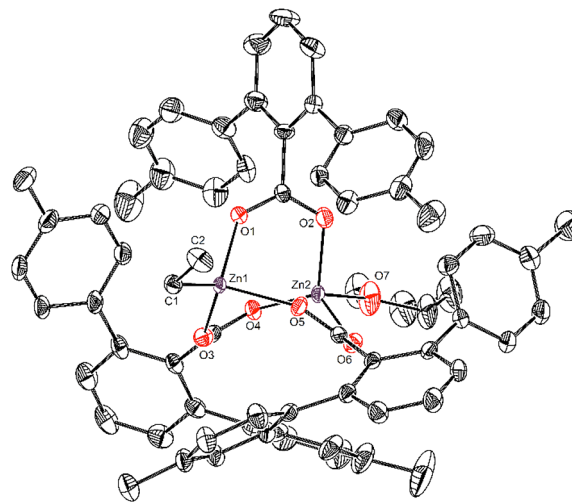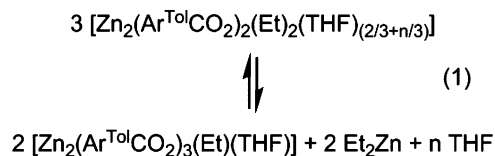

Figure 4. Structure of a single isomer of **2** with 50% thermal ellipsoids. Hydrogen and disordered atoms are omitted for clarity.

dizinc compound with a Zn⋯Zn distance of 3.32 Å. This value is smaller than that in **1**, as expected following the addition of a third bridging carboxylate. A pseudo-C_3 symmetry axis exists along the Zn−Zn vector, which, in conjunction with the lack of a collinear improper axis of rotation, produces Λ and Δ isomers, both of which occur in the crystal structure (Figure S13, Supporting Information). The DOSY NMR spectrum of **2** was also obtained, and the calculated hydrodynamic radius of 7.81 Å is larger than R_{X-ray} (7.20 Å) but still consistent with retention of this structure in solution. With the formula of the species in solution now in hand, a balanced equation (eq 1) describing the solution equilibrium can be written.

$$3\ [\text{Zn}_2(\text{Ar}^{Tol}\text{CO}_2)_2(\text{Et})_2(\text{THF})_{(2/3+n/3)}]$$

$$\updownarrow \qquad\qquad (1)$$

$$2\ [\text{Zn}_2(\text{Ar}^{Tol}\text{CO}_2)_3(\text{Et})(\text{THF})] + 2\ \text{Et}_2\text{Zn} + n\ \text{THF}$$

To further test the presence of this equilibrium in solution as well as its reversibility, Et$_2$Zn and THF were added to isolated **2** in an attempt to produce **1**. Addition of THF to a sample of **2** in C$_6$D$_6$ does not afford any **1**, and the only observable change in the ¹H NMR spectrum is a broadening of the THF resonance of **2** owing to exchange with free THF (Figure S8,

Supporting Information). When Et_2Zn is added to a solution of **2** in C_6D_6, however, **1** is clearly detectable along with a THF OCH_2 resonance at 3.30 ppm (Figure 5 and Figure S8). This
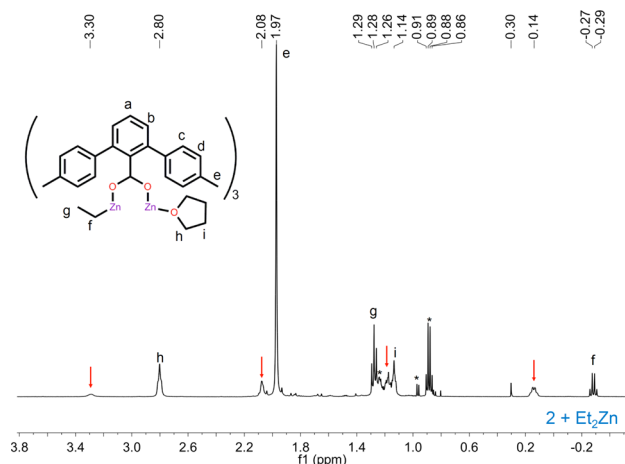

Figure 5. Upfield region of the ^1H NMR spectrum (500 MHz) of **2** in C_6D_6 upon addition of Et_2Zn. The red arrows indicate the presence of **1**. The peaks between 0.8 and 1.0 ppm and an underlying multiplet at 1.19−1.23 ppm correspond to hexane and methylcyclopentane impurities in the Et_2Zn solution.

experiment proves that extra THF is not required for the conversion of **2** to **1**. Integration of the methyl and THF OCH_2 resonances in **2** reveals that **2** retains all its bound THF. On the basis of the stoichiometry of the balanced equation between **1** and **2**, only two-thirds of a THF molecule is available per molecule of **1**. It therefore appears that THF-free **1**, $[Zn_2(Ar^{Tol}CO_2)_2(Et)_2]$ (**1′**), may exist in solution. In combination with DOSY experiments that confirm the dinuclearity of these species in solution and the crystal structure of **13**, **1′** most likely contains two coordinatively unsaturated trigonal-planar zinc centers. Generation of such potentially reactive zinc centers suggests that zinc *m*-terphenylcarboxylates might be good catalysts. Addition of both THF and Et_2Zn to a sample of **2** in C_6D_6 restores the ^1H NMR spectrum to that of a mixture of **1** and **2** similar to that obtained upon dissolution of crystals of **1** in C_6D_6 or toluene-d_8 (Figure S8). Again, THF is not required for the conversion of **2** to **1**, although it promotes the conversion between **1′** and **1**.

The conversion between solvated species of **1**, $[Zn_2(Ar^{Tol}CO_2)_2(Et)_2(THF)_{0−2}]$, probably occurs through simple association and dissociation of THF molecules. However, the mechanism of conversion of **1** to **2** is still unclear and more than one pathway may be involved. The demonstrated conversion between doubly and triply carboxylate bridged species **1** and **2** depends on the amount of THF present. The diiron complexes **5**−**7** represent analogues of **1**, **2**, and Et_2Zn, respectively, where the ethyl groups are replaced by $Ar^{Tol}CO_2^-$ and THF is replaced by *N,N*-Me$_2$en. Thus, the equilibrium among **1**, **2**, and Et_2Zn provides insight into why iron complexes **5**−**7** could be isolated from the same reaction mixture. These equilibria are crucial when considering oxidation reactions supported by diiron complexes in solution, because a species different from that observed in the solid-state structure may be responsible for the reactivity.

Unlike the interconversion between ethylzinc carboxylate compounds **9** and **10**, which occurs at elevated temperatures,[8] interconversion between **1** and **2** occurs readily at room

temperature. The reason for this difference may be a higher energy barrier associated with formation and disassembly of **9**, owing to its tightly packed pentazinc cluster core. Thus, modification of the carboxylate R group in ethylzinc carboxylates may change the kinetics of structure interconversion as well as the nuclearity of the corresponding complex. Understanding these simple zinc compounds can provide insight into the manner by which carboxylates can be used effectively for producing well-defined metal complexes.

Upon exposure to air, compounds **1** and **2** decompose into the oxozinc carboxylate $[Zn_4O(Ar^{Tol}CO_2)_6]$ (**3**). Colorless crystals of **3** were obtained by allowing an NMR spectroscopic sample of **1/2** in C_6D_6 to slowly react with air over the course of 1 week. Compound **3** crystallizes in the rhombohedral space group $R\bar{3}$ with one-sixth of a molecule in the asymmetric unit. The six *m*-terphenyl wings align with T_h symmetry (Figure 6).
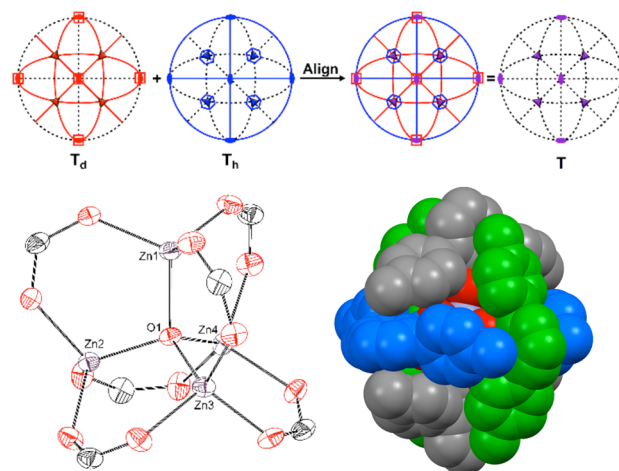

Figure 6. (top) Stereographic projections of T_d (red) and T_h (blue) symmetry and their superposition which preserves the elements of T symmetry (purple). (bottom) T_d core structure of **3** with the Ar^{Tol} groups removed for clarity (left) and space-filling diagram of **3** showing the T_h shell created by the Ar^{Tol} groups (right). Disordered atoms are removed for clarity.

The Zn_4O core has T_d symmetry, however, and the alignment of T_h and T_d symmetries limits the symmetry of **3** to T. This concept can be visualized with stereographic projections shown in Figure 6. The superposition of T_h and T_d symmetries to produce T symmetry in a molecule is interesting. None of the 60 T-symmetric molecules contained in the CSDSymmetry database[13] provide similar examples. The two enantiomers in the crystal lattice are related by the crystallographic inversion center. Variations of the orientation of the tolyl groups show that the symmetry in the solid state is only pseudo-T-symmetric. In the ^1H NMR spectrum of **3** in CD_2Cl_2, the tolyl CH_3 resonance is observed at 1.43 ppm, which is 1 ppm upfield from that of the free carboxylate. The large shift is attributed to positioning of the methyl groups above a neighboring *m*-terphenyl benzene ring and is consistent with the crystal structure. Because a single set of resonances is observed in the NMR spectrum, the molecule must have T symmetry on average in solution at 25 °C.

This report reveals that that two formulations of ethylzinc 2,6-bis(*p*-tolyl)benzoate, **1** and **2**, readily convert in solution. This behavior differs from that of the ethylzinc acetate complexes, which require heat to convert them between **9** and **10**. With the knowledge of the solution equilibrium among

1, **2**, and Et$_2$Zn, we can now propose conversion of doubly and triply carboxylate bridged diiron(II) and mononuclear iron(II) complexes, such as those observed in discrete solid-state complexes **5**−**7**. Furthermore, the use of sterically demanding *m*-terphenyl substituents provides access to coordinatively unsaturated zinc centers, offering a possible strategy for use in zinc-catalyzed reactions.

■ EXPERIMENTAL SECTION

General Considerations. Diethylzinc (1 M in heptane or hexanes) was purchased from Aldrich and used as received. A solution of Et$_2$Zn in toluene-d_8 for NMR spectroscopic experiments was prepared by adding toluene-d_8 to Et$_2$Zn in hexanes and distilling off the hexanes. Solvents were saturated with argon, passed through two columns of activated alumina, and stored over activated 3 or 4 Å molecular sieves. The compound 2,6-bis(*p*-tolyl)benzoic acid (Ar^{Tol}CO$_2$H) was prepared by a literature procedure.[14] All manipulations of compounds **1** and **2** were performed under a nitrogen atmosphere in an MBraun drybox. IR spectra were obtained on a ThermoNicolet Avatar 360 spectrometer using the OMNIC software. Details about NMR spectroscopy and X-ray data collection and refinement are provided in the Supporting Information.

Synthesis. *[Zn$_2$(Ar^{Tol}CO$_2$)$_2$(Et)$_2$(THF)$_2$] (1).* Ar^{Tol}CO$_2$H (50.8 mg, 168 μmol) was dissolved in 1 mL of THF. Diethylzinc (170 μL, 1 M in heptane) was injected into the reaction mixture with stirring. After 20 s, stirring was stopped and the solution allowed to sit overnight, forming colorless crystals of **1**. The solution was decanted, and the crystals were washed twice with 1 mL of pentane before drying under vacuum to yield 67.1 mg (71.7 μmol, 85.4%) of **1**. NMR: *compound 1 does not exist as the only species in solution; see text for discussion.* IR (KBr): 3055, 3025, 2980, 2924, 2881, 2850, 2808, 1917, 1597, 1515, 1453, 1410, 1381, 1111, 1037, 986, 883, 842, 819, 802, 784, 768, 734, 703, 605, 583, 544, 517 cm^{-1}. Anal. Calcd for C$_{54}$H$_{60}$O$_6$Zn$_2$: C, 69.31; H, 6.46. Found: C, 68.88; H, 6.32. Decomposes above 136 °C (turns yellow-brown).

[Zn$_2$(Ar^{Tol}CO$_2$)$_2$(Et)$_2$(THF-d_8)$_2$] (1·THF-d_8). The same procedure was used for the synthesis of **1**, except that THF-d_8 was used as the solvent. Yield: 46.2 mg (48.5 μmol, 57.8%).

[Zn$_2$(Ar^{Tol}CO$_2$)$_3$(Et)(THF)] (2). A sample of **1** (48.0 mg, 51.3 μmol) was dissolved in 2.5 mL of toluene, and the solvent was removed under vacuum. The crude material was dissolved in 800 μL of benzene, and pentane was allowed to slowly diffuse into the solution slowly. After 5 days, colorless plates of **2** (31.5 mg, 81.2%) were obtained. ^{1}H NMR (C$_6$D$_6$): δ 7.40 (d, $^3J_{HH}$ = 8.1 Hz, 12H), 7.27 (d, $^3J_{HH}$ = 7.7 Hz, 6H), 7.12 (t, $^3J_{HH}$ = 7.7 Hz, 3H), 7.02 (d, $^3J_{HH}$ = 7.7 Hz, 12H), 2.80 (t, $^3J_{HH}$ = 6.4 Hz, 4H), 1.97 (s, 18H), 1.28 (t, $^3J_{HH}$ = 8.1 Hz, 3H), 1.13 (t, $^3J_{HH}$ = 6.6 Hz, 4H), −0.28 (q, $^3J_{HH}$ = 8.1 Hz, 2H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 178.2, 140.8, 139.3, 136.7, 136.1, 129.7, 129.4, 128.8, 128.6, 69.55, 25.0, 21.0, 13.1, −2.4. IR (KBr): 3054, 3022, 2920, 2849, 2807, 1727, 1604, 1544, 1515, 1454, 1408, 1385, 1151, 1109, 1033, 1028, 845, 817, 801, 789, 767, 733, 706, 585, 540 cm^{-1}. Anal. Calcd for C$_{69}$H$_{64}$O$_7$Zn$_2$: C, 72.95; H, 5.68. Found: C, 73.33; H, 5.96; N, 0.05. Decomposes above 246 °C (turns yellow-brown).

Reactivity. *Exposure of 1 and 2 to Air.* An NMR solution of **1** dissolved in C$_6$D$_6$ was allowed to slowly react with air through a plastic cap over 1 week. Colorless prisms of [Zn$_4$O(Ar^{Tol}CO$_2$)$_6$] (**3**) were obtained. NMR was used to confirm that the crystals correspond to a single species in solution. No further attempts were made to isolate the compound in bulk quantities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, text, and CIF files giving experimental details, NMR spectra, and X-ray crystallographic data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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