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Interactions of Organozinc Compounds with Crown Ethers and Cryptands: Formation of R_2Zn(18-crown-6) Rotaxanes

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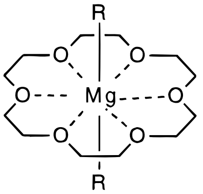
Several pieces of evidence indicate that R_2Zn(18-crown-6) rotaxanes are components of solutions prepared from some R_2Zn (R = alkyl or aryl) compounds and 18-crown-6, and crystal structures show that Et_2Zn(18-crown-6) and Ph_2Zn(18-crown-6) solids that precipitate from such solutions have rotaxane structures. By contrast, the R_2Zn compounds do not form rotaxanes with 15-crown-5 or its nitrogen equivalent, 1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane. Disproportionation of R_2Zn by macrocycles to form coordinated RZn^+ cations and R_3Zn^- anions is less favorable than the corresponding reaction with R_2Mg, although Tol_2Zn (Tol = *p*-methylphenyl) and 2,1,1-cryptand do form TolZn(2,1,1-cryptand)$^+Tol_3Zn^-$.

Addition of some cryptands to solutions of diorganomagnesium compounds leads to disproportionation that results in solids and solutions containing RMg^+ cations coordinated by the cryptand and organomagnesate ions, such as R_3Mg^- (e.g., eq 1).[2−4]

$$2R_2Mg + \text{cryptand} \rightarrow RMg(\text{cryptand})^+ + R_3Mg^- \quad (1)$$

$$nR_2Mg + \text{crown} \rightarrow RMg(\text{crown})^+ + \text{“}R_{2n+1}Mg_n^{\ -}\text{”} \quad (2)$$

Some crown ethers lead to a similar disproportionation, although conversion of R_2Mg to $RMg(crown)^+$ by crown ethers containing only oxygens (eq 2) never has been as complete as in eq 1.[4,5] R_2Mg and crown ethers also form neutral species of composition R_2Mg(crown) having rotaxane or “threaded” structures (e.g., **1**).[5,6] An X-ray diffraction study[6] established a rotaxane structure for a solid obtained from Et_2Mg and 18C6 (18-crown-6), and Bickelhaupt and co-workers[2,7] have provided related examples. Some rotaxanes of diarylmagnesium compounds have been demonstrated to be present in solution.[4] Rotaxanes of dialkylmagnesium compounds also may exist in some solutions,[5] but rapid exchanges between components in the solutions often preclude observation of discrete NMR absorptions for them.



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The metal atoms of organozinc[8] and organomagnesium compounds bond similarly to donors, such as O or N, and form bonds of similar length to atoms such as C, N, or O. Zn is less electropositive than Mg, however, and R_2Zn is less prone than R_2Mg to form additional bonds. The purpose of this work was to determine if R_2Zn compounds form R_2Zn(crown) rotaxanes, coordinated RZn^+ cations, and organozincate anions. We hoped that R_2Zn analogues of R_2Mg rotaxanes (**1**) would be more readily observed and characterized. An earlier paper[9] reported a study of the mechanism of formation of Tol_2Zn(18C6) rotaxane. This paper presents evidence for rotaxane structures and the abilities of various macrocycles to form rotaxanes and ions.

Results and Discussion

Results with 18-Crown-6; Formation of R_2Zn(18-crown-6) Rotaxanes. Observations with this crown ether differ qualitatively from those with the other macrocyclic compounds that were studied. One difference is that some R_2Zn compounds formed precipitates of composition R_2Zn(18C6). When an equimolar amount of 18C6 was added to a solution (~0.4 M) of R_2Zn (benzene-d_6 was the usual solvent), a precipitate formed

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[1] Much of this work is taken from the following, although some was done later: Fabicon, R. M., Ph.D. Dissertation, The Pennsylvania State University, 1991.

[2] For a review of interactions of organomagnesium and organozinc compounds with macrocyclic compounds see: Richey, H. G., Jr. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 1 (G. W. Gokel, Ed.), Chapter 21.

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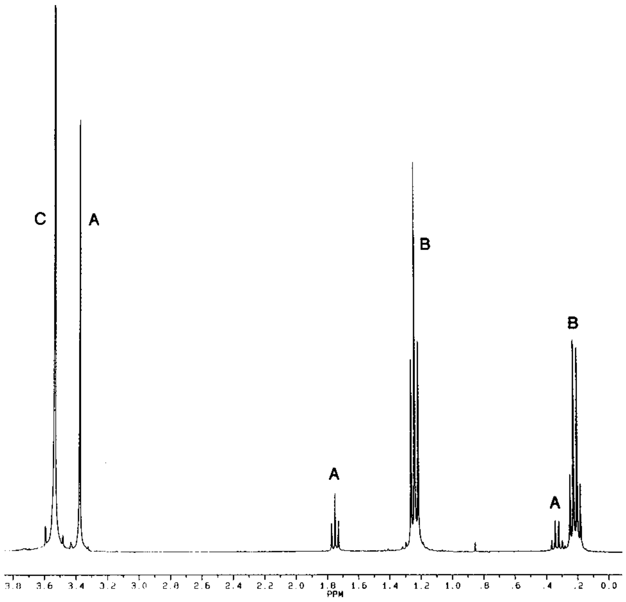

Figure 1. ^{1}H NMR spectrum (200 MHz) of a benzene-d_6 solution prepared from Et_2Zn (ca. 0.15 M) and 18-crown-6 (ca. 0.13 M). The spectrum was taken before much rotaxane precipitated. Absorptions assigned to the Et_2Zn(18-crown-6) rotaxane are labeled A. Absorptions of Et_2Zn and 18-crown-6 not incorporated into the rotaxane are labeled B and C, respectively.

rapidly with Me_2Zn, Et_2Zn, and (methallyl)$_2$Zn (methallyl is $CH_2{=}C(CH_3)CH_2^-$), and after 2−3 weeks with Pr_2Zn and Bu_2Zn. Tol_2Zn and Ph_2Zn are less soluble. Tol_2Zn (Tol is *p*-methylphenyl) appeared to dissolve in the presence of 18C6, but a precipitate soon began to appear. Ph_2Zn dissolved but eventually gave a precipitate if its initial concentration was not significantly less than 0.1 M. $(PhC{\equiv}C)_2Zn$ is insoluble in benzene and did not appear to dissolve when 18C6 was present. Precipitates were not observed with *i*-Bu_2Zn, *s*-Bu_2Zn, *t*-Bu_2Zn, $(Me_3SiCH_2)_2Zn$, or $(Me_2C{=}CH)_2Zn$.

A second difference between results with 18C6 and with other macrocycles is that ^{1}H NMR spectra of some solutions show two sets of absorptions, as seen in Figure 1 for a solution prepared from Et_2Zn.[10] The areas of one set of R absorptions and one 18C6 absorption correspond to an R to 18C6 ratio of 2 and must be due to a species of composition R_2Zn(18C6). When a precipitate is dissolved, using sufficient solvent that no solid remains, ^{1}H NMR absorption areas show the total R to total 18C6 ratio to be 2.

Crystal Structures of R_2Zn(18-crown-6) Solids. Recrystallization of solids that precipitated from solutions of 18C6 and Et_2Mg or Ph_2Zn provided crystals suitable for X-ray structure determination. The Ph_2Zn(18C6) crystals are surprisingly stable in air: the first crystals obtained were inadvertently left out of the glovebox for a day and since they suffered no obvious decomposition nearly were discarded as being an artifact. A description of the rotaxane structure of Et_2Zn(18C6) has appeared.[6] Ph_2Zn(18C6) also has a rotaxane structure (Figure 2). The Zn is located approximately at the center of the crown ether. The Zn−O distances (Table 1), all different, range from 2.674(3) to 3.024(3) Å; the average (2.812 Å) is somewhat shorter than the average (2.867(3) Å) in the more symmetrical (centrosymmetric) Et_2Zn(18C6). These Zn−O distances are very much longer than bonds ordinarily resulting from

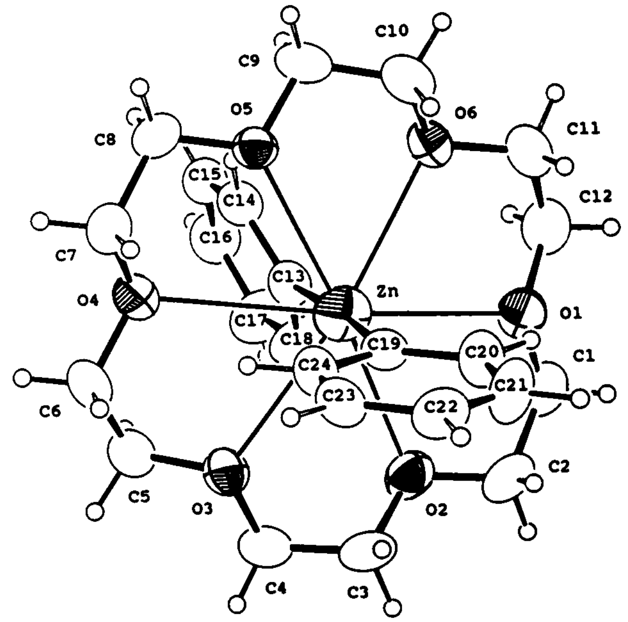

Figure 2. ORTEP drawing of rotaxane Ph_2Zn(18-crown-6). Atoms are shown with 50% probability ellipsoids.

Table 1. Bond Lengths (Å) and Angles (deg) (esd's in parentheses) of Rotaxane Ph_2Zn(18-crown-6)

Bond Distances

Zn−O(1)	2.674(3)	Zn−O(4)	3.024(3)
Zn−O(2)	2.696(3)	Zn−O(5)	2.950(3)
Zn−O(3)	2.803(3)	Zn−O(6)	2.735(2)
Zn−C(13)	1.981(3)	C(5)−C(6)	1.489(6)
Zn−C(19)	1.988(3)	C(7)−C(8)	1.506(5)
O(1)−C(1)	1.418(5)	C(9)−C(10)	1.474(5)
O(1)−C(12)	1.416(4)	C(11)−C(12)	1.494(6)
O(2)−C(2)	1.394(4)	C(13)−C(14)	1.402(5)
O(2)−C(3)	1.417(4)	C(13)−C(18)	1.396(5)
O(3)−C(4)	1.430(4)	C(14)−C(15)	1.375(5)
O(3)−C(5)	1.405(4)	C(15)−C(16)	1.379(5)
O(4)−C(6)	1.411(4)	C(16)−C(17)	1.381(6)
O(4)−C(7)	1.422(4)	C(17)−C(18)	1.405(5)
O(5)−C(8)	1.402(4)	C(19)−C(20)	1.375(4)
O(5)−C(9)	1.420(4)	C(19)−C(24)	1.393(4)
O(6)−C(10)	1.441(4)	C(20)−C(21)	1.397(4)
O(6)−C(11)	1.417(4)	C(21)−C(22)	1.373(5)
C(1)−C(2)	1.497(5)	C(22)−C(23)	1.374(5)
C(3)−C(4)	1.473(6)	C(23)−C(24)	1.396(4)

Bond Angles

C(13)−Zn−C(19)	174.5(1)	O(1)−C(12)−C(11)	108.9(3)
C(1)−O(1)−C(12)	113.9(3)	Zn−C(13)−C(14)	120.6(3)
C(2)−O(2)−C(3)	114.9(3)	Zn−C(13)−C(18)	123.9(2)
C(4)−O(3)−C(5)	113.8(3)	C(14)−C(13)−C(18)	115.4(3)
C(6)−O(4)−C(7)	113.1(3)	C(13)−C(14)−C(15)	122.9(3)
C(8)−O(5)−C(9)	112.2(3)	C(14)−C(15)−C(6)	120.9(3)
C(10)−O(6)−C(11)	112.5(3)	C(15)−C(16)−C(17)	118.2(3)
O(1)−C(1)−C(2)	108.8(3)	C(16)−C(17)−C(18)	120.7(4)
O(2)−C(2)−C(1)	109.0(3)	C(13)−C(18)−C(17)	121.7(3)
O(2)−C(3)−C(4)	109.5(3)	Zn−C(19)−C(20)	124.6(2)
O(3)−C(4)−C(3)	110.0(3)	Zn−C(19)−C(24)	120.0(2)
O(3)−C(5)−C(6)	109.7(3)	C(20)−C(19)−C(24)	115.4(3)
O(4)−C(6)−C(5)	109.1(3)	C(19)−C(20)−C(21)	122.6(3)
O(4)−C(7)−C(8)	108.3(3)	C(20)−C(21)−C(22)	120.6(3)
O(5)−C(8)−C(7)	109.2(3)	C(21)−C(22)−C(23)	118.8(3)
O(5)−C(9)−C(10)	110.0(3)	C(22)−C(23)−C(24)	119.7(3)
O(6)−C(10)−C(9)	110.7(3)	C(19)−C(24)−C(23)	123.1(3)
O(6)−C(11)−C(12)	109.7(3)		

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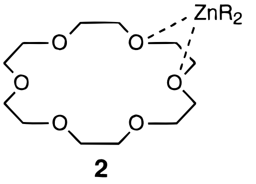
[10] The rates at which equilibrium was achieved in these solutions were not determined. By the time that NMR observations were made (usually several hours after preparation of a solution), however, no subsequent changes ever were noted with solutions in which R was alkyl. When R is aryl, approach to equilibrium can be slow.[9]

dative[11] bonding of oxygens to Zn.[12] Not all Zn(18C6) compounds have such relatively similar Zn−O distances; $[Zn(H_2O)Cl(18C6)^+]_2[Zn_2Cl_6{}^{2-}]$ has three much shorter Zn−O distances (average 2.28 Å) in the range typical for Zn−O dative bonds and three even longer distances.[13] It is noteworthy that the Zn−C bonds in Ph_2Zn(18C6) (1.981(3) and 1.988(3) Å) are longer than in Et_2Zn(18C6) (1.957(5) Å), even though bonds to aryl C's normally are shorter than to saturated carbons. The C−Zn−C bond angle is 174.5(1)°, and the dihedral angle between the phenyl least-squares planes is 111.96(13)°. The phenyl rings are nearly planar; the greatest deviation from a least-squares plane is 0.0103(39) Å.

Evidence for R_2Zn(18-crown-6) Rotaxanes in Solution. Non-rotaxane structures, such as **2**, having



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"peripheral" or "side-on"[7] complexing of Zn with crown ether oxygens are possible for species of composition R_2Zn(18C6). Several considerations, however, indicate that the R_2Zn(18C6) species observed in some solutions are rotaxanes.

1. It is those R_2Zn solutions with NMR absorptions for R_2Zn(18C6) species that form precipitates of that composition; the two solids investigated by X-ray diffraction have rotaxane structures.

2. When the Ph_2Zn(18C6) precipitate is carefully recrystallized before redissolving, the resulting solution exhibits only the ^1H NMR absorptions attributed to the rotaxane.[9]

3. One ^1H or ^{13}C NMR absorption is observed for the crown ether of R_2Zn(18C6) and a second for the other 18C6's in the solution. Exchange of oxygens involved in dative[11] bonds to R_2Zn, even those of dicoordinate DME (dimethoxyethane), generally is rapid.[14] Yet exchange of the 18C6 of R_2Zn(18C6) with other 18C6 is slow on the NMR time scale.

4. The ^1H and ^{13}C NMR absorptions of the 18C6 of the R_2Zn(18C6) species are singlets. Even if Zn−O bonds in a rotaxane in solution vary somewhat in length, they probably interchange sufficiently rapidly on the NMR time scale to lead to observation of a singlet. Of course, a singlet also would be seen for a much less symmetrical structure, such as **2**, if breaking and making of Zn−O bonds were sufficiently rapid. The experimental observations, however, require that any rapid interchange of Zn−O bonds must occur *without exchange of the 18C6 of R_2Zn(18C6) with other 18C6's in the solution*. Rapid interchange of oxygens that would lead to the Zn moving around one face of the 18C6 is reasonable. Rapid jumping of Zn from one face of the 18C6 to the other also would be required, however, and seems less likely, particularly since this jumping could not be accompanied by exchange with other 18C6's in the solution.

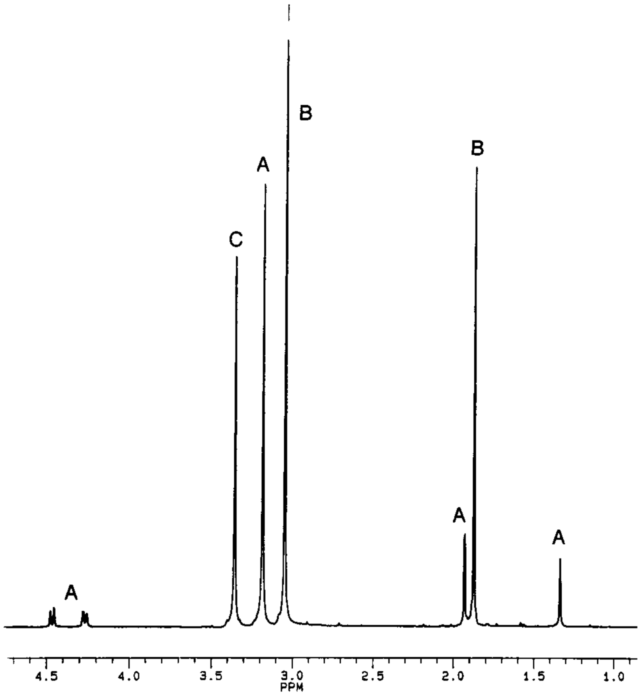
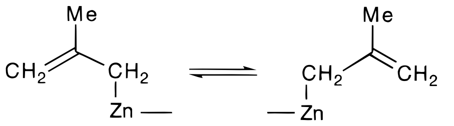


Figure 3. ^1H NMR spectrum (300 MHz) of a benzene-d_6 solution prepared from $(CH_2{=}C(CH_3)CH_2)_2Zn$ and 18-crown-6. Some precipitation occurred, and the solution has about a 1:1.2 ratio of these reactants. Absorptions assigned to the $(CH_2{=}C(CH_3)CH_2)_2Zn$(18-crown-6) rotaxane are labeled A. Absorptions of the organozinc compound and 18-crown-6 not incorporated into the rotaxane are labeled B and C, respectively.

5. The two sets of ^1H (Figure 3) and ^{13}C NMR absorptions for the methallyl group in solutions prepared from (methallyl)$_2$zinc and 18C6 differ qualitatively. Only two ^1H or ^{13}C absorptions are seen for the methallyl groups not in the rotaxane: one for the methyl group, the other for the two methylene groups. This is expected, since equilibration of the Zn between the ends of allylic zinc compounds (eq 3) ordinarily is rapid.[15] By contrast, for the methallyl groups associated with 18C6, discrete ^1H absorptions are seen for CH_2Zn and for the cis and trans hydrogens of $=CH_2$, and discrete ^{13}C absorptions are seen for CH_2Zn and $=CH_2$. Lack of rapid equilibration is more consistent with a rotaxane than a peripheral structure; to similarly resolve the ^{13}C NMR spectrum of (methallyl)$_2$zinc in THF, a strongly coordinating solvent that must slow equilibration, required lowering the temperature to −100 °C.[16]



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6. Significant ^1H nuclear Overhauser enhancements[17] were observed between the 18C6 H's and the *o*-H's of Tol_2Zn(18C6) and the CH_2Zn H's of (methallyl)$_2$Zn(18C6) or Et_2Zn(18C6) but not between H's of non-rotaxane 18C6 and R_2Zn in these solutions. Neither were significant enhancements observed with solutions of Et_2Zn and 15C5 or of Tol_2Zn and 15C5, 12C4, or TMEDA (tetramethylethylenediamine). These results suggest that the R_2Zn(18C6) species differ from the coordinated species that form between R_2Zn and most O and N donors. In rotaxane structures, the *o*-H's of Tol_2Zn and the CH_2Zn H's of methallyl or ethyl are held in close proximity to some of the 18C6 H's.

Extent of R_2Zn(18-crown-6) Rotaxane Formation. With equimolar Tol_2Zn and 18C6 at various concentrations (<0.1 M for each component to avoid precipitation), about 40% of the material was incorporated into the Tol_2Zn(18C6) species.[18] The extent of R_2Zn(18C6) formation (each component ca. 0.5 M) was similar when R was Me or methallyl, somewhat less when R was Et, and <5% when R was Pr or Bu.[10] R_2Zn(18C6) absorptions were not detected when R was *i*-Pr, *s*-Bu, *t*-Bu, Me_3SiCH_2, or $Me_2C{=}CH$. Et_2Zn(18C6) was formed in toluene-d_8, $CDCl_3$, and CD_2Cl_2 to about the same extent as in benzene.

Besides the NMR absorptions of the R_2Zn(18C6) species, the solutions show an additional 18C6 absorption and set of R absorptions. The positions of these absorptions vary with reactant ratio. A study with Tol_2Zn and 18C6 indicated that most of the limiting reactant (whichever has the lower initial concentration) not in the rotaxane is in a peripheral Tol_2Zn(18C6) complex which equilibrates rapidly on the NMR time scale with free R_2Zn and free 18C6.[9] Peripheral complexes also must be present in the solutions of other R_2Zn compounds. The effect of adding TMEDA provides evidence for such complexation. After TMEDA addition to 18C6-Et_2Zn or 18C6-Tol_2Zn solutions, the ^1H NMR absorptions of non-rotaxane R_2Zn and of TMEDA are characteristic of R_2Zn(TMEDA) and the absorption of non-rotaxane 18C6 is that of free 18C6. Coordination of R_2Zn with TMEDA must replace coordination with 18C6 (coordination[19] of R_2Zn by N generally is stronger than by O). TMEDA, however, does not alter the absorptions of the Et_2Zn(18C6) and Tol_2Zn(18C6) rotaxanes. The extent of rotaxane formation, therefore, is related to the electronic and steric effects of the organic groups of R_2Zn on both rotaxane and peripheral complexes and may not reflect accurately the strength of interaction between R_2Zn and 18C6 in the rotaxane.[20]

Results with 12-Crown-4, 15-Crown-5, and Azacrown Ethers. 15C5 was studied with Me_2Zn, Et_2Zn, Pr_2Zn, *i*-Pr_2Zn, Bu_2Zn, *s*-Bu_2Zn, *t*-Bu_2Zn, $(Me_3SiCH_2)_2Zn$, (methallyl)$_2$Zn, and Tol_2Zn; 12C4 was studied with Et_2Zn and Tol_2Zn. Equimolar amounts of R_2Zn and crown ether usually were used, each 0.2−0.3 M, although additional ratios and concentration levels also were sometimes used. Tol_2Zn concentration was lower, although this relatively insoluble compound often was more soluble in the presence of a macrocycle. ^1H NMR spectra of all solutions showed only one set of R absorptions and one crown ether absorption. The crown ether absorption generally was upfield and the R absorptions, particularly of H's α or β to the Zn, downfield from the absorptions of the crown ether and R_2Zn compound when each was alone. Shifts ordinarily did not exceed 0.1 ppm, though were somewhat larger for Tol_2Zn or (methallyl)$_2$Zn with 15C5: the δ 7.73 (*o*-H), 7.10 (*m*-H), and 2.20 (CH_3) absorptions of Tol were at δ 7.78, 7.30, and 2.33; the δ 1.69 (Me) and 2.91 (CH_2's) absorptions of methallyl were at δ 2.02 and 3.13. Results of studies of Et_2Zn, $(Me_3SiCH_2)_2Zn$, and Tol_2Zn[21] with 14N4 (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and of these organozinc compounds and *i*-Bu_2Zn with 15N5 (1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane) were similar to those with 15C5 and 12C4, although, particularly with 15N5, some downfield chemical shifts of the organic group absorptions were somewhat larger. The small changes in absorption positions probably are due to peripheral coordination, forming and breaking rapidly on the NMR time scale, rather than to rotaxane formation.[22] Addition of an equimolar amount of DME to Et_2Zn, for example, results in downfield shifts of ^1H NMR absorptions (CH_2Zn 0.09 ppm, $C\mathbf{H}_3CH_2Zn$ 0.15 ppm) of the magnitude caused by crown ethers and no increase in number of absorptions.

Precipitates formed from 18N6 (1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane) and Et_2Zn or Tol_2Zn. ^1H NMR spectra of the solution obtained by dissolving the Et_2Zn precipitate (recrystallized from toluene, mp 42−44 °C) showed it to have a 2:1 ratio of Et_2Zn to 18N6. The shifts of absorptions from those of the free components were similar to shifts in the spectra with 15N5. Because of the insolubility of the Tol_2Zn precipitate (mp 88−94 °C), no solution NMR spectrum was obtained. Its composition must be $(Tol_2Zn)_2$(18N6), however, since the ^1H NMR spectrum of the supernatant liquid remaining after its formation had only weak absorptions when the Tol_2Zn to 18N6 ratio was 2:1 but strong 18N6 absorptions when the ratio was

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(18) The extent of formation of Tol_2Zn(18C6) is almost independent of the initial concentrations of Tol_2Zn and 18C6.[9]

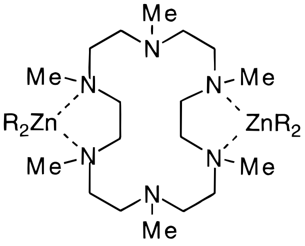
(19) Many equilibrium data are available for coordination to Zn^{2+} in water and methanol. Coordination to macrocycles: Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271. Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721. Coordination to macrocyclic and acyclic coordinating agents: Christensen, J. J.; Izatt, R. M. *Handbook of Metal Ligand Heats and Related Thermodynamic Quantities*, 3rd ed.; Dekker: New York, l983. Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York; 1975; Vol. 2; 1982; Vol. 5; 1989; Vol. 6. The absolute values are influenced by the large hydration energies of the ions in water and methanol, but nitrogen is clearly more effective than oxygen in increasing the equilibrium constant.

(20) For the same reason, the abilities of coordinating agents to react with R_2Mg to form $RMg(coord)^+R_3Mg^-$ do not parallel their abilities to coordinate to RMg^+ to form $RMg(coord)^+$: Tang, H.; Richey, H. G., Jr. *Organometallics* **1997**, *15*, 4891.

(21) Tang, H. Ph.D. Dissertation, The Pennsylvania State University, 1997.

(22) The changes in absorption position might conceivably be due to at least partial disproportionation to ions or, with 15C5 or 15N5, which can form sufficiently large cavities, to rotaxane formation. If either $RZn(crown)^+$ or rotaxane R_2Zn(crown) is formed in significant amounts, however, then equilibration of its components with other species in the solution must be rapid on the NMR time scale. Yet exchange with other solution components of coordinated $EtZn(crown)^+$ cations prepared with other anions[23] and of the species assigned rotaxane R_2Zn(18-crown-6) structures are slow on the NMR time scale.

1:1. Probably the solids have structures such as **3**, and the interaction between 18N6 and Et_2Zn in solution involves similar peripheral coordination.



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Species in Solutions of R_2Zn with 15C5 or 15N5. In contrast to the behavior with 18C6, neither precipitates nor two sets of NMR absorptions were ever observed with 15C5. Could R_2Zn(15C5) rotaxanes be present (or even the dominant species) but not exhibit discrete NMR absorptions because equilibration with other components in the solutions is rapid on the NMR time scale? Several observations make this possibility unlikely.

1. Addition of 15C5 to a solution prepared by dissolving solid Et_2Zn(18C6) did not alter the proportion of absorptions of Et_2Zn(18C6) rotaxane. 15C5, if more effective than 18C6, should eventually displace 18C6 from Et_2Zn(18C6), and the absorptions of that rotaxane should diminish. Although Et_2Zn−15C5 solutions do not form precipitates, adding 15C5 to a stirred suspension of solid Et_2Zn(18C6) in benzene did not dissolve significantly more of the solid; when solid Et_2Zn(18C6) was completely dissolved in such a 15C5-containing solution by heating and then the solution was cooled, the ^1H NMR spectrum after precipitation was as before heating.

2. The positions of ^1H NMR absorptions of solutions prepared from R_2Zn with 15C5 were similar to those prepared with 12C4, which has a cavity too small to form a rotaxane, and also similar to those of the non-rotaxane absorptions of solutions prepared with 18C6.

3. Except for slight broadening of all absorptions below −60 °C, no significant changes were noted when ^1H NMR spectra of toluene-d_8 solutions prepared from 1:1 and 2:1 ratios of Et_2Zn and 15C5 were taken at temperatures as low as −80 °C. If a rotaxane is present, its equilibration with non-rotaxane Et_2Zn and 15C5 must be extremely rapid.

4. In contrast to significant nuclear Overhauser enhancements observed with R_2Zn(18C6), enhancements were negligible in solutions prepared from 15C5 and Et_2Zn or Tol_2Zn.

The 15N5 preparations also did not form precipitates and exhibited only single sets of R and macrocycle ^1H NMR absorptions; that R absorptions were similar to those with the smaller 14N4 suggests that rotaxanes are not involved. In contrast to results with 15C5 or TMEDA, however, ^1H nuclear Overhauser enhancements were observed between 15N5 and Et. Moreover, ^1H NMR spectra of a solution prepared from $(Me_3SiCH_2)_2Zn$ (0.4 M) and 15N5 (0.2 M) showed at −30 °C some broadening and at −80 °C a very broad absorption for 15N5 and two approximately equal sets of Me_3SiCH_2 absorptions. Given the broadness of the 15N5 absorptions, however, it is more likely that the absorptions are of peripheral $(Me_3SiCH_2)_2Zn$−15N5 complexes (and perhaps also of some free $(Me_3SiCH_2)_2Zn$) than of a rotaxane and free $(Me_3SiCH_2)_2Zn$.

Results with Cryptands. Solutions were prepared from Et_2Zn or Tol_2Zn and 2,1,1-, 2,2,1-, or 2,2,2-cryptand. Et_2Zn concentrations were in the range 0.08−0.16 M and the Et_2Zn-to-cryptand ratios in the range 0.7−4.[24] The ^1H NMR absorptions of each component in these solutions were essentially the same (no change > 0.1 ppm) as in the absence of the other component. Similarly, in solutions prepared from Tol_2Zn (~0.1 M) and 2,2,1- or 2,2,2-cryptand (Tol_2Zn-to-cryptand ratio ~2), only single, unbroadened sets of absorptions were seen for each component, although changes in absorption position were somewhat greater.

By contrast, the ^1H NMR spectrum[21] of a solution prepared from Tol_2Zn (~0.2 M) and 2,1,1-cryptand (~0.1 M) resembles that[4] of $TolMg(cryptand)^+Tol_3Mg^-$. It exhibits (1) two sets of *p*-tolyl absorptions in 3:1 ratio, (2) the absorption (δ 8.14) of two aryl hydrogens (ortho to Zn) of the larger set considerably downfield from the corresponding Tol_2Zn absorption (δ 7.23), and (3) cryptand absorptions more complex than those of the free cryptand and some shifted considerably upfield. The solution most probably contains $TolZn(cryptand)^+Tol_3Zn^-$.[25]

Conclusions and Summary

Solids that precipitate from solutions prepared from some R_2Zn compounds and 18C6 have rotaxane structures. Because of the extremely long Zn−O distances and hence only weak Zn−O bonding, the rotaxanes might be regarded almost as clathrates, having a linear or nearly linear R_2Zn encapsulated within 18C6 but bonded only weakly to its oxygens. The weight of evidence indicates that the NMR absorptions seen for R_2Zn(18C6) species in solutions also are of rotaxanes. In no R_2Zn−18C6 solution studied was incorporation of R_2Zn into a rotaxane more favorable than into a peripheral complex. Although all Zn−O distances in the solids are not identical, the single 18C6 NMR absorption of the rotaxanes suggests that in solutions they are identical on the NMR time scale. Alternation of unequal Zn−O bonds probably would be rapid, and the Zn−O distances in solutions could be similar to those in the solids.

Rotaxanes probably do not form with 15C5 or 15N5 even though they might have ordinary Zn−O or Zn−N bond lengths. In fact, 15C5 and 18C6 have almost equal abilities to form rotaxanes with Tol_2Mg,[4] and 15C5 generally is more effective[26] than 18C6 in coordinating with RMg^+ cations.[27] Although understanding is clouded by the observation that the extent of formation of a rotaxane is related not only to its stability but also to that of a peripheral complex, the lesser ability of Zn than of Mg to coordinate to O and N donors may be crucial. Formation of a rotaxane with 15C5 would

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[23] Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 6680.

[24] These experiments were performed by Gretchen BergStresser.

[25] Formation of $TolZn(cryptand)^+Tol_3Zn^-$ is an exception to the generalization[23] that reactions of diorganozinc compounds and cryptands do not produce such ions.

[26] Pajerski, A. D. Ph.D. Dissertation, The Pennsylvania State University, 1990.

require distortion of the 15C5. Strong Mg−O coordination may exceed the distortion energy; weaker Zn−O coordination may be insufficient to pay for the requisite distortion.

Disproportionation by macrocycles of R_2Zn to R_3Zn^- anions and coordinated RZn^+ cations is less favorable than the corresponding reaction (eq 1) with R_2Mg, but is observed with a diarylzinc compound and 2,1,1-cryptand.

Experimental Section

^{1}H NMR absorption positions are reported in parts per million (δ) downfield from internal C_6H_5D (δ 7.15) for benzene-d_6 solutions, internal $CHCl_3$ (δ 7.26) for $CDCl_3$ solutions, and internal $PhCD_2H$ (δ 2.09) for toluene-d_8 solutions; the following notations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; br, broad. ^{13}C NMR spectra were proton decoupled; absorption positions are reported in parts per million (δ) downfield from internal C_6D_6 (δ 128.0). Procedures involving organometallic compounds were performed under a nitrogen atmosphere using Schlenk techniques, a glovebox, and a vacuum line. Hydrocarbon solvents, including the deuterated solvents, were distilled from CaH_2 and stored over molecular sieves (4 Å) under a nitrogen atmosphere.

Preparation of 15N5 and 18N6. A synthesis of 15N5 apparently has not previously been described. A solution of NaOMe was prepared by cautious addition of Na pieces (4.4 g, 0.19 mol) to methanol (80 mL) that had been dried by reaction with Mg followed by distillation. This solution was added dropwise over 1 h to a stirred suspension of the tetra-*p*-toluenesulfonate of triethylenetetramine[28] (63.8 g, 0.0833 mol) in methanol (200 mL) that was maintained under nitrogen. The mixture was heated to the reflux temperature, which dissolved all solid, and maintained at that temperature for 1 h. White crystals formed on cooling. The liquid was decanted and the solid washed with cold methanol (two 100-mL portions) and then heated at 50 °C at reduced pressure for 12 h to give the disodium salt of the tetra-*p*-toluenesulfonate of triethyenetetramine (64.3 g, 0.0794 mol, 95%). 1,4,7,10,13-Pentaazacyclopentadecane was prepared from this salt and the tri-*p*-toluenesulfonate of diethanolamine[29] closely following a literature procedure.[30] Following in part a procedure used for methylation of another azacrown ether,[31] a solution prepared from 1,4,7,10,13-pentaazacyclopentadecane (10.4 g, 0.0483 mol), an aqueous formic acid solution (88%, 50 mL), and an aqueous formaldehyde solution (35%, 10 mL) was heated at 100 °C for 12 h. Aqueous HCl (36%, 50 mL) was added, and the resulting solution was subjected to reduced pressure, to leave a white solid, which was recrystallized from a 3:1 (v/v) solution of ethanol and aqueous HCl (2 M). The resulting pentahydrochloride was dissolved in an aqueous NaOH solution (6 M, 30 mL) and extracted with chloroform (10 30-mL portions). The chloroform solution was dried (Na_2SO_4) and filtered. The solvent was removed at reduced pressure to leave a yellow viscous liquid, which was distilled over NaOH using a Kugelrohr apparatus. 15N5 was collected at 100−110 °C at 0.1 Torr (11.0 g, 0.0386 mol, 80%): ^{1}H NMR (benzene-d_6) δ 2.16 (s, 3 H, CH_3), 2.50 (s, 4 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 43.87 (CH_3), 55.27 (CH_2); MS *m*/*z*: calcd for $C_{15}H_{35}N_5$ 285.2892; found, 285.2883.

18N6 was prepared using similar procedures except that tetraethylenepentamine was one of the reactants: ^{1}H NMR (benzene-d_6) δ 2.16 (s, 3 H, CH_3), 2.49 (s, 4 H, CH_2).

Preparation of R_2Zn Compounds. To prepare di(phenylethynyl)zinc,[32] Et_2Zn (1.0 g, 8 mmol) and phenylacetylene (1.24 g, 12 mmol) were mixed and heated gradually to 100 °C. Gas was evolved, and a white solid formed. The solid was stirred with benzene, solids were allowed to settle, and liquid was removed with a syringe. The remainder was left for 12 h at 60 °C and ~0.1 Torr. Not enough of the solid dissolved in benzene-d_6 to give observable ^{1}H NMR absorptions. The other diorganozinc compounds were synthesized from organic halides using standard procedures. Thermally unstable compounds were used immediately after purification.

Preparation of NMR Samples. The organozinc compound was weighed into a vial equipped with a magnetic stirring bar. Benzene-d_6 (generally 0.5 mL) was added with stirring. The macrocycle was weighed in and the mixture or solution stirred for an additional 5−10 min. In a few instances DME or TMEDA (each was refluxed over and distilled from CaH_2 prior to use) was added before or after the crown ether. If the preparation was homogeneous, it was transferred with a pipet into an NMR tube to which had been added an extension of ordinary glass tubing to facilitate sealing with a flame. The tube was sealed temporarily with a septum, removed from the glovebox, immersed in liquid nitrogen, and sealed at the extension with a flame. When solid was present, either the slurry was filtered through a pipet fitted with glass wool into the NMR tube or the sealed NMR tube containing solid was centrifuged to place the solid in its upper end.

R_2Zn−18C6 Preparations. Solutions generally were prepared using R_2Zn to 18C6 ratios of 2.0, 1.0, and 0.75 and an initial R_2Zn concentration in the range 0.2−0.4 M. NMR spectra (benzene-d_6 except in the instance noted) of the 1:1 preparations are given below. "Rot" (rotaxane) refers to an absorption of the R_2Zn(18C6) species and "free" to other absorptions; no designation is given when only absorptions assigned to "free" components were observed. The ratio of free to rotaxane species obtained by comparing absorption areas is indicated. In all instances the areas of absorptions assigned to R_2Zn(18C6) indicated an R to 18C6 ratio of 2. Any unusual features associated with the preparation are noted. For comparison, positions of NMR absorptions of solutions (benzene-d_6) of the diorganozinc compounds alone are listed in brackets.

Dimethylzinc. A large precipitate formed rapidly. A sample of the white precipitate was recrystallized from toluene and washed with benzene (mp 66−71 °C). Recrystallized solid (5 mg) heated with benzene-d_6 (0.5 mL) gave a homogeneous solution (0.03 M): ^{1}H NMR, δ −0.66 (s, free CH_3), −0.49 (s, rot CH_3), 3.30 (s, rot 18C6), 3.41 (s, free 18C6) [δ −0.67]. The ratio of total Me to total 18C6 was 2 and of Me_2Zn(18C6) to free Me_2Zn and 18C6 was 0.38.

Diethylzinc. A precipitate formed between 2 and 10 min after mixing. The precipitate was recrystallized from a 3:1 toluene−pentane mixture (mp 92−96 °C). Dissolving the crystals (6 mg) in benzene-d_6 (0.5 mL) gave a homogeneous solution (0.03 M): ^{1}H NMR δ 0.16 (q, free CH_2), 0.30 (q, rot CH_2), 1.23 (t, free CH_3), 1.71 (t, rot CH_3), 3.31 (s, rot 18C6), 3.48 (s, free 18C6) [δ 0.12, 1.11]; ^{13}C NMR δ 6.4 (free CH_2), 7.0 (rot CH_2), 10.7 (free CH_3), 14.5 (rot CH_3), 70.2 (rot 18C6),

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[27] Mg−O and Zn−O bonds generally have relatively similar lengths. Compared to similar bonds involving Mg, data from X-ray structures show covalent[11] C−Zn, N−Zn, and O−Zn bonds usually to be slightly shorter and dative[11] N−Zn and O−Zn bonds often to be slightly longer. References to X-ray structures of organozinc compounds: Bruce, M. I. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, l995; Vol. 13. Melnik, M.; Skorsepa, J.; Györyová, K.; Holloway, C. E. *J. Organomet. Chem*. **1995**, *503*, 1. Reviews of crystal structures of organomagnesium compounds: Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem*. **1991**, *32*, 147. Holloway, C. E.; Melnik, M. *J. Organomet. Chem*. **1994**, *465*, 1.

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71.0 (free 18C6) [δ 6.7, 10.3]. The ^{1}H NMR spectrum showed the ratio of total Et to total 18C6 to be 2 and of Et_2Zn(18C6) to free Et_2Zn and 18C6 to be 0.16.

Dipropylzinc. ^{1}H NMR δ 0.29 (t, free CH_2Zn), 1.04 (t, free CH_3), 1.61 (m, free CH_3CH_2), 3.30 (s, rot 18C6), 3.44 (s, free 18C6) [δ 0.25, 0.95, 1.53]. The absorptions of the coordinated propyl group were too weak to characterize accurately. The ratio of rotaxane to free 18C6 was less than 0.05. A white crystalline precipitate formed after 2 weeks. Positions of ^{1}H NMR absorptions of a benzene-d_6 solution (~0.03 M) were similar to those above and indicated that the ratio of total Pr to total 18C6 was 2.

Diisopropylzinc. ^{1}H NMR δ 0.66 (septet, CH), 1.19 (d, CH_3), 3.44 (s, 18C6) [δ 0.64, 1.20].

Dibutylzinc. ^{1}H NMR δ 0.33 (t, free CH_2Zn), 0.99 (t, free CH_3), 1.39 (m, free CH_3CH_2), 1.62 (m, free CH_2CH_2Zn), 3.30 (s, coor 18C6), 3.49 (s, free 18C6) [δ 0.26, 0.95, 1.35, 1.52]. The absorptions of the coordinated butyl group were too weak to characterize accurately. The ratio of coordinated to free 18C6 was less than 0.05. A white crystalline precipitate formed after 3 weeks.

Diisobutylzinc. ^{1}H NMR δ 0.42 (d, CH_2Zn), 0.98 (d, CH_3), 2.04 (m, CH), 3.45 (s, 18C6) [δ 0.39, 0.96, 2.01].

Di-*s*-butylzinc. ^{1}H NMR δ 0.37 (m, CH), 1.08 (t, CH_3CH_2), 1.29 (d, CH_3CH), 1.69 (m, CH_2), 3.44 (s, 18C6) [δ 0.31, 1.04, 1.20, 1.50 (CH*H*), 1.64 (C*H*H)].

Di-*tert*-butylzinc. ^{1}H NMR δ 1.20 (s, CH_3), 3.44 (s, 18C6) [δ 1.07].

Dimethallylzinc. A yellow solid precipitated immediately and was recrystallized from benzene (mp 102−106 °C with decomposition); if the recrystallization temperature exceeded 60 °C, a gray solid, presumably Zn metal, formed. Crystals (5 mg) were dissolved in benzene-d_6 (0.5 mL) to give a homogeneous solution (0.02 M), from which no precipitation was observed on cooling: ^{1}H NMR δ 1.41 (s, rot CH_2Zn), 1.90 (s, free CH_3), 2.08 (s, rot CH_3), 3.08 (s, free CH_2═ and CH_2Zn), 3.22 (s, rot 18C6), 3.40 (s, free 18C6), 4.48 (m, rot ═CH*H*), 4.62 (m, rot ═C*H*H) [δ 1.69, 2.91]; ^{13}C NMR δ 26.3 (free CH_3), 27.5 (rot CH_3), 30.0 (rot CH_2Zn), 63.6 (free CH_2═ and CH_2-Zn), 68.8 (rot crown), 70.8 (free crown), 94.8 (rot CH_2═), 151.6 (free *C*═CH_2), 163.1 (rot *C*═CH_2) [δ 26.3, 63.3, 151.0]. The ^{1}H NMR spectrum indicated the ratio of total methallyl to total 18C6 to be 2 and of (methallyl)$_2$Zn(18C6) to free (methallyl)$_2$Zn and 18C6 to be 0.36.

Di(2-methyl-1-propenyl)zinc. ^{1}H NMR δ 2.05 (s, one CH_3), 2.06 (s, other CH_3), 3.50 (s, 18C6), 5.72 (br s, CH) [δ 1.83, 1.92, 5.47].

Di(trimethylsilylmethyl)zinc. ^{1}H NMR δ −0.58 (s, CH_2-Zn), 0.14 (s, CH_3), 3.46 (s, 18C6) [δ −0.64, 0.12].

Diphenylzinc. Ph_2Zn initially was 0.15 M. ^{1}H NMR ($CDCl_3$, referencing somewhat imprecise because of overlap of the $CHCl_3$ and Ph absorptions) δ 3.20 (s, rot 18C6), 3.40 (s, free 18C6), 7.1−7.4 (c, rot and free *m*-H and *p*-H), 7.70 (d, free *o*-CH), 8.12 (d, rot *o*-H) [(benzene-d_6) δ 7.30−7.55 (*m*-H and *p*-H), 7.72 (*o*-H)].

Di(*p*-methylphenyl)zinc. There was immediate precipitation on mixing. The mixture was transferred to an NMR tube, which then was heated to dissolve the precipitate. Solids that formed on cooling were centrifuged to the upper end of the NMR tube leaving a clear solution: ^{1}H NMR δ 2.28 (s, free CH_3), 2.43 (s, rot CH_3), 3.17 (s, rot 18C6), 3.34 (s, free 18C6), 7.22 (d, free *m*-H), 7.39 (d, rot *m*-H), 7.81 (d, free *o*-H), 8.19 (d, rot o−H) [δ 2.20, 7.10, 7.73]; ^{13}C NMR δ 21.2 (free CH_3), 24.3 (rot CH_3), 69.3 (rot 18C6), 70.6 (free 18C6), 127.5 (rot *m*-C), 128.1 (free *m*-C), 132.0 (rot *p*-C), 135.7 (free *p*-C), 138.9 (free *o*-C), 140.4 (rot *o*-C), 149.4 (free CZn), 156.2 (rot CZn) [δ 21.3, 128.1, 135.7, 138.9, 149.4]. The ^{1}H NMR spectrum indicated the ratio of total Tol to total 18C6 to be 2 and of Tol_2Zn(18C6) to free Tol_2Zn and 18C6 to be 0.4.

X-ray Crystal Structure Determination. Ph_2Zn (200 mg, 0.91 mmol) and 18C6 (238 mg, 0.90 mmol) were added to stirred toluene (2.0 mL). A white solid formed rapidly. The suspension was heated (80 °C) until the solids dissolved. Slow cooling resulted in formation of colorless, rectangular crystals (mp 122−124 °C). A crystal (0.32 mm × 0.41 mm × 0.65 mm) was sealed in an X-ray capillary tube under a nitrogen atmosphere.

Crystal data for $C_{24}H_{34}O_6Zn$: monoclinic, space group $P2_1/n$, $a = 10.109(2)$ Å, $b = 14.365(1)$ Å, $c = 16.549(6)$ Å, $\beta = 98.78(2)°$, $V = 2375.2$ Å^3, $Z = 4$, $D_{calcd} = 1.238$ g/cm^3, $F(000) = 1024$. The intensities of 4516 reflections were collected at 20 °C using Cu Kα radiation (1.5418 Å) by the $\omega/2\theta$ scan technique (scan width $0.60 + 0.14 \tan\theta$) using variable scan speed (1.37−8.24° min^{-1}) in the range $5° < \theta < 65°$. Three standard reflections were measured every hour of X-ray exposure time and indicated a decay of 0.8%; the data were corrected for decay by appropriate scaling. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms. The final cycle of refinement was to $R = 0.0503$ and $R_w = 0.0819$ for 2858 reflections with $I > 3\sigma(I)$. The largest peak in the difference Fourier map corresponded to 0.37 e/Å^3.

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Supporting Information Available: Nuclear Overhauser data; tables for the X-ray study of atomic coordinates and *B* values, anisotropic displacement parameters, and least-squares planes. This material is available free of charge via the Internet at http://pubs.acs.org.

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