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Formation of Coordinated RZn(macrocycle)$^+$ Cations and Organozincate Anions from Reactions of Organozinc Compounds and Macrocycles

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An RZnZ compound (R = alkyl) and a macrocycle react in benzene to form RZn(macrocycle)$^+$ ions when the macrocycle is an effective coordinator for RZn$^+$ and Z$^-$ can exist as the anion or become attached to an organometallic acceptor to form an organometalate anion. R$_2$Zn and R$_3$Al form RZn(macrocycle)$^+$R$_4$Al$^-$ with 14N4 (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), 15N5 (1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane), 2,1,1-cryptand, or 2,2,1-cryptand but not with 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane, 2,2,2-cryptand, 15-crown-5, or 18-crown-6. RZnZ, R$_2$Zn, and 14N4 form RZn(14N4)$^+$R$_2$ZnZ$^-$ when Z is Cl, Br, I, or 3,5-di-*tert*-butylphenoxy but not when Z is *tert*-butoxy. Various combinations of RZnZ with Z = Cl, Br, I, 2,6-di-*tert*-butylphenoxy, or 3,5-di-*tert*-butylphenoxy and 14N4, 15N5, 2,1,1-cryptand, or 2,2,1-cryptand form RZn(macrocycle)$^+$Z$^-$ solids; solids do not form when Z is methoxy or *tert*-butoxy nor when the macrocycle is 12-crown-4, 15-crown-5, or 18-crown-6.

In contrast to formation of RMg(macrocycle)$^+$ and organomagnesate ions from a range of R$_2$Mg compounds and macrocycles (e.g., eq 1),[1] similar reactions of R$_2$Zn

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

compounds have been found with only a few macrocycles particularly effective at coordinating RZn$^+$ and R groups particularly effective at stabilizing R$_3$Zn$^-$.[2] The objective of this study was to determine if RZn(macrocycle)$^+$ and organometalate ions could be synthesized from (1) reactions in which, besides R$_2$Zn and a macrocycle, a second organometallic compound is present that might be a more effective acceptor of an anion than is R$_2$Zn or from (2) reactions of macrocycles and compounds RZnZ from which Z, a group other than alkyl or aryl, might be more easily transferred to an acceptor molecule to form an anion. Because of the many similarities of organozinc and organomagnesium compounds, it is relevant that reactions[4] of Grignard reagents (RMgX) and 14N4 (14N4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) lead to RMg(14N4)$^+$, XMg(14N4)$^+$, RMgX$_2^-$, and X$^-$, the composition depending on X (Cl, Br, or I) and the RMgX/14N4 ratio.

Results and Discussion

The solvent was benzene (or benzene-d_6), and, except where noted, equimolar amounts of reactants were used. NMR observations (at ca. 23 °C) were not dependent on time (spectra taken soon after preparation of solutions, typically 1 h, and 1−2 days later were essentially identical) nor significantly on concentration in the range (0.1−0.5 M) that was used.

R$_2$Zn, R$_3$Al, and a Macrocycle.[5] In these experiments R$_3$Al was added as a possibly more effective "R$^-$" acceptor than R$_2$Zn. Solutions prepared from R$_2$Zn and R$_3$Al (R = Me, Et, or *i*-Bu) without a macrocycle show only one set of ^{1}H NMR absorptions for R. The species in solution are R$_2$Zn and R$_3$Al, however, since (when equimolar amounts are used) the absorptions lie exactly midway between those of these compounds. As expected, exchange of all R groups is sufficiently rapid relative to the NMR time scale to lead to single sets of R absorptions. A solution of a macrocycle and either R$_2$Zn or R$_3$Al exhibits only a single set of R absorptions. Depending on the macrocycle, however, combining a macrocycle, R$_2$Zn, and R$_3$Al in benzene results (Table 1) in one of three behaviors: (1) formation of a second liquid phase that contains principally RZn(macrocycle)$^+$R$_4$Al$^-$ (eq 2);

$$\mathrm{R_2Zn} + \mathrm{R_3Al} + \text{macrocycle} \rightarrow \mathrm{RZn(macrocycle)^+} + \mathrm{R_4Al^-} \quad (2)$$

a homogeneous solution of R$_2$Zn and R$_3$Al with R groups not exchanging relative to the NMR time scale; (3) a homogeneous solution of R$_2$Zn and R$_3$Al with R groups

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[1] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432. Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510. Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660.

[2] Ref 3 and references therein.

[3] Tang, H.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **2000**, *19*, 4810.

[4] Pajerski, A. D.; Chubb, J. E.; Fabicon, R. M.; Richey, H. G., Jr. *J. Org. Chem.* **2000**, *65*, 2231.

[5] Some preliminary results were reported: Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 639.

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Table 1. Reactions in Benzene-d_6 of Two Organometallic Reactants and a Macrocycle[a]

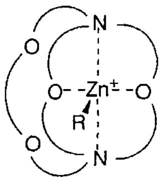
reactant 1[b]	reactant 2	macrocycle[c]	ionic products	observations[d]
Me_2Zn	Me_3Al	14N4	$MeZn(14N4)^+Me_4Al^-$	2 liquid phases
Et_2Zn	Et_3Al	14N4	$EtZn(14N4)^+Et_4Al^-$	2 liquid phases
i-Bu_2Zn	i-Bu_3Al	14N4	i-$BuZn(14N4)^+i$-Bu_4Al^-	2 liquid phases
Et_2Zn	Et_3Al	15N5	$EtZn(15N5)^+Et_4Al^-$	2 liquid phases
i-Bu_2Zn	i-Bu_3Al	15N5	i-$BuZn(15N5)^+i$-Bu_4Al^-	2 liquid phases
Et_2Zn	Et_3Al	211C	$EtZn(211C)^+Et_4Al^-$	2 liquid phases
Et_2Zn	Et_3Al	221C	$EtZn(221C)^+Et_4Al^-$	2 liquid phases
Et_2Zn	Et_3Al	18N6	none	no Et exchange
Et_2Zn	Et_3Al	222C	none	no Et exchange
Et_2Zn	Et_3Al	18C6	none	rapid Et exchange
Et_2Zn	Et_3Al	15C5	none	rapid Et exchange
EtZnCl	Et_2Zn	14N4	$EtZn(14N4)^+Et_2ZnCl^-$	solution
EtZnBr	Et_2Zn	14N4	$EtZn(14N4)^+Et_2ZnBr^-$	solution
EtZnI	Et_2Zn	14N4	$EtZn(14N4)^+Et_2ZnI^-$	2 liquid phases
EtZnOAr	Et_2Zn	14N4	$EtZn(14N4)^+Et_2ZnOAr^-$	solution
EtZnO-t-Bu	Et_2Zn	14N4	none	no Et exchange
BuZnO-t-Bu	Bu_2Zn	14N4	none	no Bu exchange

[a] The temperature is ca. 23 °C. Equimolar amounts of the macrocycle and of each organometallic reactant were used. [b] Ar = 3,5-di-*tert*-butylphenyl. [c] 14N4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, 15N5 = 1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane, 211C = 2,1,1-cryptand, 221C = 2,2,1-cryptand, 18N6 = 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane, 222C = 2,2,2-cryptand, 18C6 = 18-crown-6, 15C5 = 15-crown-5. [d] Homogeneous solutions except where noted. When two liquid phases are indicated, the ionic products are in the denser phase. Rapid exchange indicates that only one set of ^{1}H NMR absorptions is observed for R.

exchanging rapidly (as in the solutions without a macrocycle).

(1) When two phases form, NMR spectra of preparations that use equimolar amounts of reactants show most solute to be in the denser phase.[6] Formation of two phases, the denser containing the ionic species, has been noted often when RMg(macrocycle)$^+$ cations and organometalate anions form in benzene.[7] Several features of NMR spectra indicate that a dense phase contains principally RZn(macrocycle)$^+R_4Al^-$. (1) ^{1}H NMR spectra have two sets of R absorptions with 1:4 intensities, and ^{13}C NMR spectra also have two sets of R absorptions. (2) The α-H absorption of the smaller set is significantly upfield from that of R_2Zn or R_3Al alone. In fact, most[8] ^{1}H NMR absorptions assigned to the cations in $EtZn(14N4)^+Et_4Al^-$ and $EtZn(211C)^+Et_4Al^-$ are the same (within ca. 0.2 ppm) as those found for these cations with a different anion.[3] (3) The larger sets of ^{1}H and ^{13}C absorptions of R show significant effects due to coupling to ^{27}Al. The ^{13}C absorptions of the α-C's are six equally spaced lines ($J = 71-80$ Hz), as expected for interaction with the 5/2 spin of ^{27}Al. The ^{1}H NMR absorptions of both the α- and β-H's show significant broadening and some fine structure due to coupling with ^{27}Al. The ^{27}Al NMR spectrum of the lower phase from a $Et_2Zn-Et_3Al-211C$ preparation has a single broad absorption (half-height width 35 Hz) with some fine structure ($J = 5.8$ Hz) evident; ^{1}H decoupling gives a singlet (half-height width 4 Hz). The excellent resolution of the ^{27}Al couplings indicates the Al atom to be in a symmetrical environment, consistent with a R_4Al^- ion that has no interactions (not formed and broken rapidly relative to the NMR time scale) that reduce the symmetry.

^{13}C NMR spectra of solutions prepared using 14N4 and 15N5 (1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane) show the number of absorptions expected (4 for 14N4, 2 for 15N5) if the Zn atom is bonded identically to all N atoms. The spectrum of the $Et_2Zn-Et_3Al-211C$ solution, however, has seven absorptions of approximately equal intensity for the cryptand, in contrast to the five found for free 211C and expected if identical parts of the cryptand remain identical in $EtZn(211C)^+$. This observation indicates that the Zn atom is bonded not symmetrically as in **1** but less symmetrically, most probably as in **2**, a structure having seven environments for 211C carbons (the symmetries of **1** and **2** are unchanged if the Zn atom also is bonded to both oxygen atoms of the two-oxygen bridge).[9]



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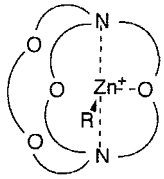

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(2) Solutions containing R_2Zn and R_3Al but with R groups not exchanging rapidly between these compounds are indicated by ^{1}H NMR spectra having two sets of R absorptions, in 2:3 ratio when equimolar amounts of reactants are used. Transient bridge-bonding of the α-carbon of an R group to both a Zn atom and Al atom must be responsible for the usually rapid exchange of R groups between R_2Zn and R_3Al. Routine[11] coordination to heteroatoms of the macrocycles must

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[6] When the macrocycle is in excess, the upper phase has macrocycle absorptions.

[7] Organometallic ions in aromatic solvents often lead to such two-phase behavior. Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., Macnicol, D., Eds.; Academic: London, 1984; Vol. 1, Chapter 9.

[8] The only absorption of $RMg(14N4)^+$ or $RZn(14N4)^+$ ions whose position varies significantly with the anion is due to four H's ($NCH\mathit{H}CH_2CH\mathit{H}N$) that lie above one face of the 14N4, projecting into the solution at a location providing the least hindered approach to the center of positive charge.

[9] The zinc atom of an organozinc compound tends to bond to N atoms rather than O atoms and to form four or five bonds rather than a larger number.[3,10]

[10] Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 4.

sufficiently lower the concentrations of free Et_2Zn and Et_3Al (or the concentration of at least one of these) that exchange becomes slow relative to the ^1H NMR time scale. As expected if some routine coordination is taking place, the ethyl absorptions of both organometallics are shifted somewhat upfield (≤ 0.3 ppm) and the macrocycle absorptions are shifted downfield (≤ 0.3 ppm). Exchange of free and coordinated macrocycles remains rapid relative to the ^1H NMR time scale, however, since 18N6 and 222C exhibit only the number of absorptions seen for the free macrocycles (although the absorptions are somewhat broad).

(3) ^1H NMR spectra of some solutions have the single sets of R absorptions seen in the absence of a macrocycle (although the absorptions are somewhat broad at ambient temperature).[12]

The macrocycles leading to $RZn(macrocycle)^+R_4Al^-$ are those particularly effective at coordinating with RZn^+.[13] Macrocycles unable to effect this transformation but able to coordinate significantly to R_2Zn and R_3Al (or to at least one of these) lead to the solutions in which R does not exchange rapidly. The macrocycles not apparently even slowing the exchange have only oxygen heteroatoms. As generally found for organozinc[10] and organoaluminum[14] compounds, O atom donors are less able than N atom donors to coordinate to R_2Zn and R_3Al and, hence, less effectively slow R exchange.

RZnX, RZnOAr, or RZnOR′ with R_2Zn and 14N4. Reactions of EtZnCl, EtZnBr, or EtZnOAr (Ar = 3,5-di-*tert*-butylphenyl) with Et_2Zn and 14N4 furnish solutions (Table 1) that contain essentially only $EtZn(14N4)^+$ and Et_2ZnX^- or Et_2ZnOAr^- (eq 3, Z = X or OAr). A similar

$$RZnZ + R_2Zn + 14N4 \rightarrow RZn(14N4)^+ + R_2ZnZ^- \quad (3)$$

reaction of EtZnI leads to separation of a small, dense liquid phase containing the corresponding (eq 3, Z = I) ions; ^1H NMR spectra indicate most solute to be in this lower phase. The structural assignments are based on features of the NMR spectra. ^1H NMR spectra of the solutions and of the lower phase of the EtZnI reaction (Figure 1) show two sets of ethyl absorptions with 2:1 intensities. The absorptions of the smaller ethyl set and of 14N4 are close to those observed[3] for $EtZn(14N4)^+$ with a different anion. Characteristic of $RZn(14N4)^+$ (and $RMg(14N4)^+$) ions are (1) a triplet-appearing 14N4 absorption[8] (δ 2.94 in Figure 1) that is at lowest field and (2) α- and β-hydrogen absorptions of R upfield from the corresponding absorptions of R_2Zn (and R_2Mg).[3,4,15] A ^{13}C NMR spectrum (Figure 1) also has two sets of ethyl absorptions.

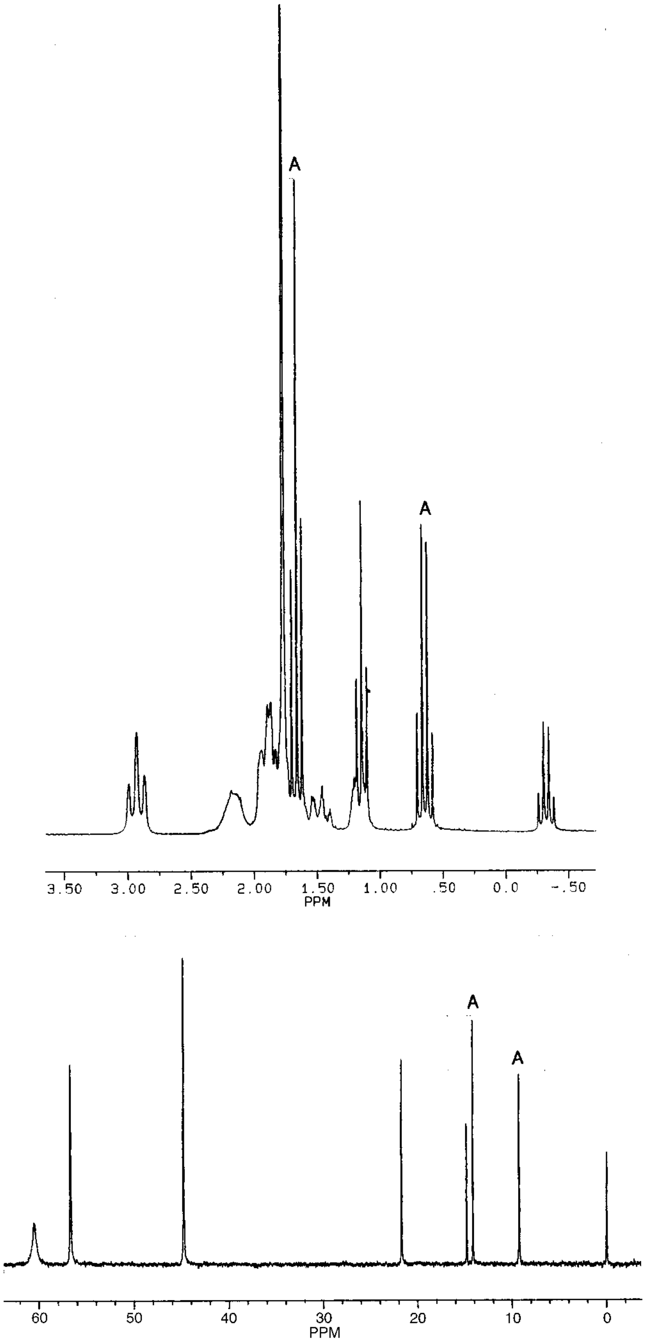

Figure 1. ^1H NMR (upper spectrum, 300 MHz) and ^{13}C (lower spectrum, 75 MHz) spectra of the lower liquid phase containing $EtZn(14N4)^+Et_2ZnI^-$ that resulted from combining equimolar amounts of Et_2Zn, EtZnI, and 14N4 in benzene-d_6. Absorptions of Et_2ZnI^- are labeled A; all other absorptions are of $EtZn(14N4)^+$.

Similar reactions of RZnO-*t*-Bu, R_2Zn, and 14N4 do not form ions. The ^1H NMR absorptions of the solutions are similar to those of the reactants. Solutions of RZnOAr and RZnO-*t*-Bu were prepared (eq 4) from reactions of R_2Zn with the appropriate alcohol or phenol.

$$R_2Zn + R'OH \rightarrow RZnOR' + RH \quad (4)$$

RZnOR′ compounds exist in solution as oligomers[10] from which monomeric RZnOR′ perhaps can be abstracted only with difficulty. RZnO-*t*-Bu therefore was generated in situ by adding excess R_2Zn to a solution containing

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[11] "Routine" is used here to refer to coordination of one or two heteroatoms of the macrocycle to the metal atom, coordination similar to that by acyclic ethers and amines. Such coordinate bonds generally form and break rapidly relative to the NMR time scale.

[12] A rotaxane of composition $Et_2Zn(18C6)$ is a component of benzene solutions of Et_2Zn and 18C6 [Chubb, J. E.; Richey, H. G., Jr. *Organometallics* **1998**, *17*, 3204]. The ethyl groups of the rotaxane must participate in the exchange.

[13] 211C and 14N4 are known to coordinate to RZn^+ more strongly than do the all-oxygen crown ethers such as 15C5;[3] 221C and 15N5 should more resemble 211C and 14N4 than 18N6, 222C, or the all-oxygen crown ethers.

[14] Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972; Chapter 4.

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

Table 2. Reactions in Benzene-d_6 of an Organozinc Reactant and a Macrocycle[a]

reactant[b]	macrocycle[c]	result
BuZnX (X = Cl, Br, or I)[d]	14N4	precipitate
HexZnX (X = Cl or Br)[d]	14N4	precipitate
EtZnOAr	14N4	precipitate
BuZnX (X = Cl, Br, or I)	15N5	precipitate
EtZnOAr′	211C	precipitate
2-EtBuZnBr[d]	221C	precipitate
EtZnOAr′	221C	precipitate
EtZnO-*t*-Bu	221C	solution
EtZnOMe	221C	solution
BuZnX (X = Cl, Br, or I)	18C6	solution
BuZnOAr′	18C6	solution
RZnO-*t*-Bu (R = Et or Bu)	18C6	solution
BuZnX (X = Cl, Br, or I)	15C5	solution
RZnOAr′ (R = Et or Bu)	15C5	solution
BuZnO-*t*-Bu	15C5	solution
RZnOAr′ (R = Et or Bu)	12C4	solution

[a] The temperature is ca. 23 °C. Except where noted, equimolar amounts of macrocycle and organozinc reactant were used. [b] Hex = hexyl, 2-EtBu = 2-ethylbutyl, Ar = 3,5-di-*tert*-butylphenyl, Ar′ = 2,6-di-*tert*-butylphenyl. [c] 14N4 = 1,4,8,11-tetramethyl-1,4,-8,11-tetraazacyclotetradecane, 15N5 = 1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane, 211C = 2,1,1-cryptand, 221C = 2,2,1-cryptand, 18C6 = 18-crown-6, 15C5 = 15-crown-5, 12C4 = 12-crown-4. [d] Organozinc/macrocycle ratios of both 1:1 and 2:1 were used.

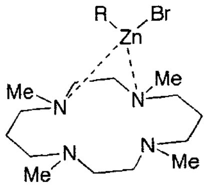
both *t*-BuOH and 14N4 so that the 14N4 might have a chance to react before oligomer formed. The potential coordination of RZn$^+$ by 14N4, however, is insufficient to transfer *t*-BuO$^-$ to R$_2$Zn from whatever form of RZnO-*t*-Bu the 14N4 encounters.

RZnX, RZnOR′, or RZnOAr and a Macrocycle. Combining one of these RZnZ compounds and a macrocycle (without R$_2$Zn) in benzene (Table 2)[16] either forms a solution containing the reactants or results in rapid formation of a precipitate that probably is RZn(macrocycle)$^+$Z$^-$ (eq 5). The alkoxy and aryloxy

$$\mathrm{RZnZ} + \text{macrocycle} \rightarrow \mathrm{RZn(macrocycle)}^{+}\ \mathrm{Z}^{-}\downarrow \quad (5)$$

reactants were prepared from reactions (eq 4) of the appropriate alcohol or phenol[17] (EtZnOMe and EtZnO-*t*-Bu were generated by adding excess Et$_2$Zn to a solution containing the alcohol and also the macrocycle).

The precipitates have 1:1 compositions since ^{1}H NMR spectra of the supernatant liquids have only weak absorptions in 1:1 (RZnZ/macrocycle) preparations but significant RZnZ absorptions in 2:1 preparations. The solids are not significantly soluble in benzene, diethyl ether, or THF. Several observations indicate that the solids are RZn(macrocycle)$^+$Z$^-$. (1) Their compositions are one RZnZ per macrocycle. (2) Precipitate formation suggests ions since most organozinc compounds are soluble in nonpolar solvents and usually remain so on addition of coordinating ethers or amines. (3) A solid phase ^{13}C NMR spectrum of the solid obtained from EtZnBr and 14N4 has just four 14N4 absorptions, the number expected for an ion having the symmetry of **4**.



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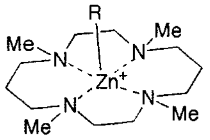

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More absorptions are expected for a structure such as **3**; rapid Zn−N bond breaking and forming that in solution could lead to averaged absorptions characteristic of the symmetry of **4** is unlikely in a solid. Moreover, the 14N4 absorptions are similar to those observed for the liquid phase containing EtZn(14N4)$^+$Et$_2$ZnI$^-$. (4) Solids result from those preparations (see Conclusions) in which coordinating ability of the macrocycle for RZn$^+$ and stability of the anion formed are greatest.[18]

The ^{1}H NMR spectra of the solutions show only one set of R (and of macrocycle) absorptions. The ^{1}H NMR absorptions of the solutions resulting from akylzinc-alkoxy or alkylzincaryloxy compounds were close (<0.1 ppm) to those of either reactant alone. The butyl and crown ether absorptions of the solutions of BuZnX with 15C5 or 18C6 were shifted more from those of the reactants: the crown ether absorption somewhat upfield (~0.1 ppm), the CH$_2$Zn absorption only slightly (<0.1 ppm) shifted, and the CH_2CH$_2$Zn and CH_2CH$_2$CH$_2$Zn absorptions generally downfield (~0.2−0.3 ppm). The small differences in positions of absorptions from those exhibited by the reactants are likely due to some routine coordination of a Zn atom to O or N atoms of a macrocycle.

Conclusions

In disproportionation of an R$_2$Zn compound to RZn(macrocycle)$^+$ and R$_3$Zn$^-$, R$_2$Zn serves as both an "R$^-$" acceptor and, in concert with the macrocycle, an "R$^-$" donor. Only rarely is the sum of donor and acceptor abilities sufficient for disproportionation to be significant. The better acceptor R$_3$Al permits more R$_2$Zn−macrocycle combinations to become donors, forming RZn(macrocycle)$^+$R$_4$Al$^-$, although not with macrocycles that are poor coordinators for RZn$^+$. Providing a leaving group more effective than "R$^-$" also favors ion formation. RZnX and RZnOAr (but not RZnOR′) compounds and 14N4 can transfer groups to R$_2$Zn to form RZn(14N4)$^+$ and R$_2$ZnX$^-$ or R$_2$ZnOAr$^-$. In the absence of R$_2$Zn, combinations of RZnX or RZnOAr and 14N4, 15N5, 211C, or 221C (though not 18C6 or 15C5, weaker coordinators[13] for RZn$^+$) form solids that must have RZn(macrocycle)$^+$ and X$^-$ or OAr$^-$ ions. Zinc counterparts of the XMg(14N4)$^+$ (X = Cl or Br) and RMgX$_2^-$ (X = Cl, Br, or I) ions observed with RMgX and 14N4 were not observed. RZnOR′ compounds did not interact significantly with any macrocycle. Solids result therefore when stabilities of RZn(macrocycle)$^{+}$ [13] and the accompanying anion[19] are greatest.

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[16] In preliminary experiments, solids formed from combinations of EtZnCl with 211C or 221C and of EtZnI with 211C, and solutions resulted from combining various ratios of EtZnBr or EtZnI and 12C4 (12-crown-4), 15C5, or 18C6 (although precipitates formed from some combinations of EtZnCl and 12C4 or 15C5).

[17] Crystalline EtZnOAr′ [Parvez, M.; BergStresser, G. L.; Richey, H. G., Jr. *Acta Crystallogr., Sect. C* **1992**, *48*, 641] was used to prepare the solutions for NMR analysis.

[18] Other factors, of course, influence formation of ionic solids from RZnZ compounds. For example, strong packing forces in a solid favor and strong aggregation of RZnZ in a solution could disfavor solid formation.

Experimental Section

Procedures involving organometallic compounds were performed under a nitrogen atmosphere using Schlenk techniques, a glovebox, and a vacuum line. Solutions for NMR analysis were prepared in the glovebox and transferred into NMR tubes to which an extension of routine glass tubing had been added to facilitate sealing with a flame. An NMR tube was capped temporarily with a septum, removed from the glovebox, immersed in liquid nitrogen, and sealed at the extension. NMR spectra were recorded at ca. 23 °C. ^1H NMR absorption positions are relative to internal C_6D_5H (δ 7.15); notations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; br, broad. ^{13}C NMR absorptions of solutions are relative to internal C_6D_6 (δ 128.0) and of solids to external hexamethylbenzene (δ 17.36). ^{27}Al spectra were taken at 78 MHz. Benzene and benzene-d_6 were distilled from CaH_2 and stored over molecular sieves (4 Å) under a nitrogen atmosphere. Diethyl ether and THF were distilled from sodium benzophenone ketyl immediately prior to use.

Dialkylzinc Compounds. The preparation procedure has been described.[20] The purification method and ^1H NMR spectrum are given for compounds for which these were not reported.

Dihexylzinc (64−69 °C, 0.1 Torr): (200 MHz) δ 0.29 (t, CH_2Zn), 0.93 (t, CH_3), 1.28−1.52 (c, $(C\mathit{H}_2)_3CH_3$), 1.56 (m, $C\mathit{H}_2CH_2Zn$).

Di(2-ethylbutyl)zinc (81−84 °C, 0.1 Torr): (300 MHz) δ 0.31 (d, CH_2Zn), 1.17 (t, CH_3), 1.52−1.88 (c, $(C\mathit{H}_2)_2C\mathit{H}$).

Alkylzinc Halides. The preparation of a butylzinc chloride solution, following a literature procedure,[21] is typical. $ZnCl_2$ (76 mg, 0.56 mmol) from a sample heated at 110 °C at reduced pressure for 24 h, Bu_2Zn (100 mg, 0.56 mmol), and benzene (1.5 mL) were sealed in a glass tube containing a magnetic stirring bar. The tube was heated at 70−75 °C and the contents were stirred until all solid dissolved.

Ethylzinc chloride: ^1H NMR (200 MHz) δ 0.65 (q, CH_3), 1.36 (t, CH_2).

Ethylzinc bromide: ^1H NMR (200 MHz) δ 0.65 (q, CH_3), 1.26 (CH_2).

Ethylzinc iodide: ^1H NMR (200 MHz) δ 0.25 (q, CH_3), 1.15 (t, CH_2).

Butylzinc chloride: ^1H NMR (200 MHz) δ 0.69 (t, CH_2Zn), 0.99 (t, CH_3), 1.36 (m, $C\mathit{H}_2CH_3$), 1.54 (m, $C\mathit{H}_2CH_2Zn$).

Butylzinc bromide: ^1H NMR (200 MHz) δ 0.58 (t, CH_2Zn), 0.98 (t, CH_3), 1.35 (m, $C\mathit{H}_2CH_3$), 1.52 (m, $C\mathit{H}_2CH_2Zn$).

Butylzinc iodide: ^1H NMR (200 MHz) δ 0.35 (t, CH_2Zn), 0.96 (t, CH_3), 1.33 (m, $C\mathit{H}_2CH_3$), 1.52 (m, $C\mathit{H}_2CH_2Zn$).

Hexylzinc chloride: ^1H NMR (200 MHz) δ 0.68 (t, CH_2Zn), 0.93 (t, CH_3), 1.28−1.39 (c, $(C\mathit{H}_2)_3CH_3$), 1.68 (m, $C\mathit{H}_2CH_2Zn$).

Hexylzinc bromide: ^1H NMR (200 MHz) δ 0.60 (t, CH_2Zn), 0.95 (t, CH_3), 1.30−1.43 (c, $(C\mathit{H}_2)_3CH_3$), 1.72 (m, $C\mathit{H}_2CH_2Zn$).

2-Ethylbutylzinc chloride: ^1H NMR (300 MHz) δ 0.70 (d, CH_2Zn), 1.32 (t, CH_3), 1.56−1.94 (c, $(C\mathit{H}_2)_2C\mathit{H}$).

2-Ethylbutylzinc bromide: ^1H NMR (300 MHz) δ 0.60 (d, CH_2Zn), 1.29 (t, CH_3), 1.48−1.54 (c, $(C\mathit{H}_2)_2C\mathit{H}$).

Alkylzinc Alkoxides and Aryloxides. Solutions of alkoxides were prepared by dropwise addition of 1 equiv of the alcohol dissolved in benzene-d_6 to a stirred benzene-d_6 solution of the dialkylzinc compound. In the preparations of ethylzinc methoxide and *tert*-butoxide, the solution of dialkylzinc compound already contained a macrocycle. The preparation and ^1H NMR spectrum of ethylzinc 2,6-di-*tert*-butylphenoxide have been described.[17] The other aryloxides were prepared by adding a solution of the dialkylzinc compound to a suspension of the phenol.

Butylzinc *tert*-butoxide: ^1H NMR (200 MHz) δ 0.47 (t, CH_2Zn), 0.98 (t, $C\mathit{H}_3CH_2$), 1.36 (s, CH_3CO), 1.45 (m, $CH_3C\mathit{H}_2$), 1.64 (m, $C\mathit{H}_2CH_2Zn$).

Butylzinc 2,6-di-*tert*-butylphenoxide: ^1H NMR (300 MHz) δ 0.52 (t, CH_2Zn), 0.99 (t, $C\mathit{H}_3CH_2$), 1.46 (m, $CH_3C\mathit{H}_2$), 1.59 (s, $(CH_3)_3C$), 1.68 (m, $C\mathit{H}_2CH_2Zn$), 6.88 (t, *p*-H), 7.29 (d, *m*-H).

Ethylzinc 3,5-di-*tert*-butylphenoxide: ^1H NMR (200 MHz) δ 0.51 (q, CH_2), 1.10 (t, $C\mathit{H}_3CH_2$), 1.42 (s, $(CH_3)_3C$), 6.88 (s, *p*-H), 7.02 (s, *o*-H).

Trialkylaluminum Compounds. The solvent was distilled at atmospheric pressure from commercial hexane solutions and the organoaluminum compounds then were distilled.

Trimethylaluminum (48−52 °C, 20 Torr): ^1H NMR (300 MHz) δ −0.37 (s, CH_3).

Triethylaluminum (60−63 °C, 5 Torr): ^1H NMR (300 MHz) δ 0.30 (q, CH_2), 1.02 (t, CH_3).

Triisobutylaluminum (93−96 °C, 1 Torr): ^1H NMR (300 MHz) δ 0.25 (d, CH_2), 0.99 (d, CH_3), 1.92 (looks like a septet, CH).

Macrocycles. 15N5 and 18N6 were synthesized as already described.[20] The other macrocycles were commercial samples.

Preparation of NMR Solutions. Preparations were done in small vials containing a magnetic stirring bar. With an alkylzinc halide, alkoxide, or aryloxide used as a solution, the macrocycle was added to the organozinc solution and the preparation was stirred. Ethylzinc halides, ethylzinc 2,6-di-*tert*-butylphenoxide, and all dialkylzinc and trialkylaluminum compounds were handled as pure solids or liquids: in a preparation using only one organozinc compound, it was added to the vial, benzene-d_6 and then the macrocycle were added, and the preparation was stirred; in a preparation using a dialkylzinc compound and another organozinc compound or a trialkylaluminum compound, the dialkylzinc compound was added to the vial, benzene-d_6 and then the macrocycle were added, the preparation was stirred, and finally the other organometallic compound was added and stirring was continued. Preparations were usually done on a 0.5 mL scale. When a second liquid phase formed, each phase was transferred to an NMR tube; because the volume of the denser phase usually was small, it was necessary to do such preparations on a larger scale. When traces of solid remained, either the preparation was filtered through a pipet fitted with glass wool into the NMR tube or, after transfer and sealing, the NMR tube was centrifuged to collect the solid at the unobserved (by the spectrometer) end. For the representative NMR spectra below, equimolar amounts of reactants were used; the concentration of each reactant (if no reaction and no phase separation occurred) was in the range 0.1−0.5 M.

$Me_2Zn-Me_3Al-14N4$: ^1H NMR (lower phase, 300 MHz) δ −1.37 (s, CH_3Zn), −0.18 (m, CH_3Al), 1.59 (br s, CH_3Zn) 2.17 (t, $C\mathit{H}HCH_2C\mathit{H}H$), 0.9−1.9 (other 14N4 H's); ^{13}C NMR (lower layer, 75 MHz) δ −15.5 (CZn), −3.2 (sextet, $J = 79.9$ Hz, CAl), 44.8 (CH_3N), 21.5 (NC*C*CN), 56.1 and 60.1 (N*CC*N and N*C*C*C*N).

$Et_2Zn-Et_3Al-14N4$: ^1H NMR (lower phase, 300 MHz) δ −0.47 (q, CH_2Zn), 0.11 (br, CH_2Al), 1.00 (t, $C\mathit{H}_3CH_2Zn$), 1.57 (br, $C\mathit{H}_3CH_2Al$), 1.62 (br s, CH_3N), 1.99 (t, $CH\mathit{H}CH_2CH\mathit{H}$), 0.9−1.8 (other 14N4 H's); ^{13}C NMR (lower phase, 75 MHz) δ −0.5 (CZn), 2.8 (sextet, $J = 72.5$ Hz, CAl), 13.1 (br, *C*CAl), 14.4 (*C*CZn), 44.3 (CH_3N), 21.3 (NC*C*CN), 56.3 and 60.3 (N*CC*N and N*C*C*C*N).

i-Bu_2Zn−*i*-$Bu_3Al-14N4$: ^1H NMR (lower phase, 300 MHz) δ −0.12 (d, CH_2Zn), 0.28 (br, CH_2Al), 0.98 (d, $(C\mathit{H}_3)_2CHCH_2Zn$), 1.42 (d, $(C\mathit{H}_3)_2CHCH_2Al$), 1.51 (m, $C\mathit{H}CH_2Al$), 1.64 (m, $C\mathit{H}CH_2Zn$), 1.27 (m, $CH_2C\mathit{H}HCH_2$), 1.60 (br s, CH_3N), 1.64 (m, $CH_2CH\mathit{H}CH_2$), 2.88 (t, $J = 12.1$ Hz, $CH\mathit{H}CH_2CH\mathit{H}$), 1.7−2.1 (other 14N4 H's).

$Et_2Zn-Et_3Al-15N5$: ^1H NMR (lower phase, 300 MHz) δ −0.24 (q, CH_2Zn), 0.12 (br, CH_2Al), 0.99 (t, $C\mathit{H}_3CH_2Zn$), 1.55

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[19] The tendency to exist as anions rather than to be bonded to zinc should be greater for halo (X) and aryloxy (OAr) than for alkoxy (OR).

[20] Fabicon, R. M.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **1999**, *18*, 5163.

[21] Boersma, J.; Noltes, J. G. *Tetrahedron Lett.* **1966**, 1521.

(br, C*H*$_3$CH$_2$Al), 1.76 (s, CH$_3$N), 1.89 (s, CH$_2$N); ^{13}C NMR (lower phase, 75 MHz) δ −0.9 (CZn), 2.8 (sextet, J = 75.7 Hz, CAl), 11.8 (*C*CZn), 13.3 (br, *C*CAl), 43.2 (br, CH$_3$N), 56.0 (br, CH$_2$N).

i-Bu$_2$Zn−*i*-Bu$_3$Al−15N5: ^{1}H NMR (lower phase, 300 MHz) δ −0.09 (d, CH$_2$Zn), 0.21 (br, CH$_2$Al), 0.93 (d, (C*H*$_3$)$_2$CHCH$_2$Zn), 1.36 (d, (C*H*$_3$)$_2$CHCH$_2$Al), 1.46 (m, C*H*CH$_2$Al), 1.60 (m, C*H*CH$_2$Zn), 1.87 (br s, CH$_3$N), 2.09 (br s, CH$_2$N); ^{13}C NMR (lower phase, 75 MHz) δ 4.1 (CZn), 3.2 (sextet, J = 73.3 Hz, CAl), 11.0 (br, *C*CAl), 14.8 (*C*CZn), 18.8 (*C*CCAl), 21.0 (*C*CCZn), 42.6 (br, CH$_3$N), 54.8 (br, CH$_2$N).

Et$_2$Zn−Et$_3$Al−2,1,1-cryptand: ^{1}H NMR (lower phase, 300 MHz) δ −0.35 (q, CH$_2$Zn), 0.09 (br, CH$_2$Al), 1.03 (t, C*H*$_3$CH$_2$Zn), 1.53 (br, C*H*$_3$CH$_2$Al), 1.7−3.5 (211C H's); ^{13}C NMR (lower phase, 75 MHz) δ 2.7 (sextet, J = 72.5 Hz, CAl), 3.3 (CZn), 13.2 (br, *C*CAl), 14.5 (*C*CZn), 55.6, 57.0, 57.3, 64.7, 65.6, 66.2, and 67.4 (211C C's).

Et$_2$Zn−Et$_3$Al−2,2,1-cryptand: ^{1}H NMR (lower phase, 300 MHz) δ −0.32 (q, CH$_2$Zn), 0.08 (br, CH$_2$Al), 1.04 (t, C*H*$_3$CH$_2$Zn), 1.55 (br, C*H*$_3$CH$_2$Al), 1.7−3.6 (221C H's).

Et$_2$Zn−Et$_3$Al−18N6: ^{1}H NMR (300 MHz) δ 0.20 (q, CH$_2$Zn), 0.22 (br, CH$_2$Al), 1.21 (t, C*H*$_3$CH$_2$Al), 1.40 (t, C*H*$_3$CH$_2$Zn), 2.09 (br s, CH$_3$N), 2.22 (br s, CH$_2$N).

Et$_2$Zn−Et$_3$Al−2,2,2-cryptand: ^{1}H NMR (300 MHz) δ 0.16 (q, CH$_2$Zn), 0.19 (br, CH$_2$Al), 1.20 (t, C*H*$_3$CH$_2$Al), 1.39 (t, C*H*$_3$CH$_2$Zn), 2.42 (br s, CH$_2$N), 3.40 (br t, OC*H*$_2$CH$_2$N), 3.52 (br s, OC*H*$_2$C*H*$_2$O).

EtZnCl−Et$_2$Zn−14N4: ^{1}H NMR (300 MHz) δ −0.24 (q, CH$_2$Zn$^+$), 0.64 (q, CH$_2$Zn$^-$), 1.20 (t, C*H*$_3$CH$_2$Zn$^+$), 1.77 (t, C*H*$_3$CH$_2$Zn$^-$), 1.79 (s, CH$_3$N); 3.24 (t, C*H*HCH$_2$C*H*H), 1.2−2.2 (other 14N4 H's).

EtZnBr−Et$_2$Zn−14N4: ^{1}H NMR (300 MHz) δ −0.27 (q, CH$_2$Zn$^+$), 0.67 (q, CH$_2$Zn$^-$), 1.19 (t, C*H*$_3$CH$_2$Zn$^+$), 1.73 (t, C*H*$_3$CH$_2$Zn$^-$), 1.77 (s, CH$_3$N), 3.18 (t, C*H*HCH$_2$C*H*H), 1.2−2.3 (other 14N4 H's).

EtZnI−Et$_2$Zn−14N4: ^{1}H NMR (lower phase, 300 MHz) δ −0.32 (q, CH$_2$Zn$^+$), 0.65 (q, CH$_2$Zn$^-$), 1.14 (t, C*H*$_3$CH$_2$Zn$^+$), 1.66 (t, C*H*$_3$CH$_2$Zn$^-$), 1.77 (s, CH$_3$N), 2.94 (t, C*H*HCH$_2$C*H*H), 1.1−2.3 (other 14N4 H's).

Ethylzinc 3,5-di-*tert*-butylphenoxide−Et$_2$Zn−14N4: ^{1}H NMR (lower phase, 300 MHz) δ −0.40 (q, CH$_2$Zn$^+$), 0.51 (br, CH$_2$Zn$^-$), 1.06 (t, C*H*$_3$CH$_2$Zn$^+$), 1.37 (s, (CH$_3$)$_3$C), 1.69 (br t, C*H*$_3$CH$_2$Zn$^-$), 1.99 (s, CH$_3$N), 7.04 (s, *p*-H), 7.27 (s, *o*-H), 0.9−2.4 (other 14N4 H's).

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