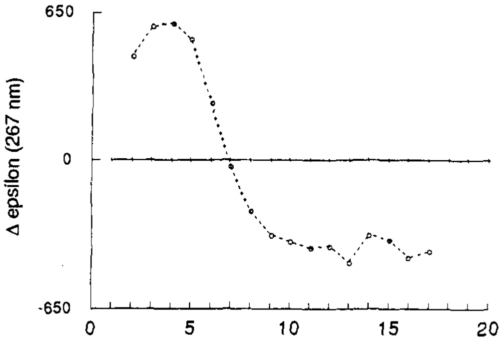

Figure 2. $\Delta\epsilon$(267nm) of fractions of Ru(phen)$_3^{2+}$ eluted from DNA-hydroxylapatite column.

equilibrium dialysis binding studies, to bind more strongly to double-stranded DNA. The column results, then, paralleled the results obtained in equilibrium dialysis experiments. A plot of the $\Delta\epsilon$(267nm) versus column fraction is presented in Figure 2. The published value[8] of $\Delta\epsilon$(267nm) is +540 for the Λ isomer. Clearly, the leading fractions are significantly enriched in the Λ isomer and the tailing fractions in the Δ isomer.

We then attempted resolution of Ru(bpy)$_2$·**1**$^{2+}$ on the same column. A 1.0-mL sample of the complex (0.7 mM) was eluted through the column and was observed to separate into two distinct bands, separated by several centimeters just before final elution from the column. Again, peak ratios for ultraviolet absorption bands were checked to eliminate the possibility of DNA coelution. The circular dichroism spectra of the bands indicated that they were indeed enriched in the two enantiomers. The first band eluted gave $\Delta\epsilon$(289nm) = (−)120 and $\Delta\epsilon$(273nm) = (+)38 while the second band gave $\Delta\epsilon$(289nm) = (+)115 and $\Delta\epsilon$(273nm) = (−)32. A second pass of pooled and concentrated fractions from each band through the column was performed. CD spectra of these samples showed the same $\Delta\epsilon$ values within a few percent, indicating that the first pass through the column gave approximately 95% enantiomerically pure fractions. Equilibrium dialysis experiments performed in our laboratory with this complex qualitatively paralleled the column results. That is, the same isomer whose flow through the column is retarded is found to bind more strongly to DNA in solution. It seems reasonable, then, that the previously described preferred steric fit of the Δ isomer as it intercalates within the major groove of the adsorbed DNA retards its flow through the column relative to the Λ isomer, resulting in the observed separation. Because of the analogy with the Ru(phen)$_3^{2+}$ results,[9] we propose to tentatively assign the leading fractions as the Λ isomer and the tailing fractions as the Δ isomer. The maximal CD values for the Λ isomer are as follows: $\Delta\epsilon$(289nm) = (−)130; $\Delta\epsilon$(273nm) = (+)40; $\Delta\epsilon$(393nm) = (+)15.8; $\Delta\epsilon$(503nm) = (−)4.0. The Δ isomer has the same values with opposite signs.

Additional trials with several other complexes, including Ru(bpy)$_2$phen^{2+}, have indicated that this method is generally useful in accomplishing significant enantiomeric fractionation for complexes of this type, when at least one of the ligands shows evidence of potential intercalation with DNA (i.e., several fused aromatic rings). At present this is only a strong correlation and does not provide definitive evidence of the basis for the resolving power of DNA–hydroxylapatite columns. However, with the ability to separate enantiomers of such complexes, we look forward to studying, via a variety of spectroscopic methods, the effect of binding individual isomers to DNA and contributing to the resolution of this question.

Acknowledgment. We gratefully acknowledge the Queens College Biomedical Research Support Grant Program (NIH) and the PSC-BHE Award program of The City University of New York for partial support of this work.

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Formation of Organozincate Ions from Diorganozinc Compounds and Potassium Alkoxides

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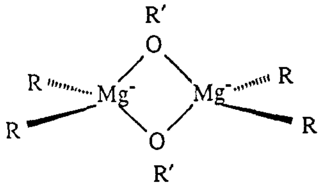
The objective of this work is to determine what species form upon mixing diorganozinc compounds and alkali-metal alkoxides. In related work, addition of alkali-metal alkoxides and some other salts to diorganomagnesium compounds was found to prepare solutions and mixtures that generally are more reactive than conventional organomagnesium compounds.[1] These preparations often are similar in reaction behavior to those obtained from diorganomagnesium compounds and crown ethers or cryptands, in which magnesiate ions (such as R_3Mg^-) are known to be significant species.[2,3] In fact, **1** was recently shown to be the probable structure for a prominent species in solutions prepared from R_2Mg and R′OK or R′ONa.[4] It seemed likely that addition of alkali-metal alkoxides to diorganozinc compounds might also form more reactive solutions that would contain species structurally similar to those formed in the Mg systems.



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Except for investigations of compositions and structures of zincates involving hydride as the added anion,[5] we could find only a few related, prior studies of R_2Zn–salt combinations. One publication[6] reported that diorganozinc compounds react with carbon monxide after, but not before, addition of *t*-BuOK. Tetraalkylammonium halides are reported[7] to somewhat increase the rate of reaction of Pr_2Zn and benzaldehyde and to significantly increase the ratio of addition to reduction product, and salts[8] of composition $Pr_4N^+RZnX_2^-$ have been isolated. There have also been a few physical studies of zincate species, prepared from R_2Zn and RLi or RK, in which only organic groups are attached to zinc.[9]

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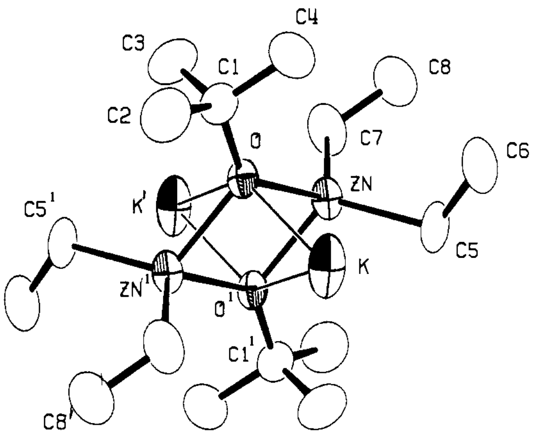

Figure 1. ORTEP drawing of $[Et_2Zn(t\text{-}BuO)_2ZnEt_2]^{2-}2K^+$. Atoms are shown with 50% probability ellipsoids. Primed atoms are related to unprimed atoms by the symmetry $-x + 1, -y, -z + 1$.

Solutions prepared by adding RLi to R_2Zn or adding RLi, RMgX, or R_2Mg to zinc halides (and in one recent study[12] both RMgX and t-BuOK to $ZnCl_2$) show a strong tendency to undergo 1,4-addition to α,β-unsaturated ketones[13] and also have been studied as polymerization catalysts.[14]

Mixing toluene solutions of t-BuOK and Et_2Zn produced a solid; warming the suspension dissolved the solid, and slow cooling of the solution led to formation of crystals suitable for single-crystal X-ray analysis. The ^1H NMR spectrum of a benzene-d_6 solution of the crystals (mp 145–148 °C) showed them to have an Et to t-Bu ratio of 2.0. As shown in the ORTEP diagram in Figure 1, the crystal is composed of units which formally are dimers of $Et_2ZnO\text{-}t\text{-}Bu^-K^+$ lying on inversion centers.[15] The Zn atoms share two bridging t-BuO groups, and each Zn also is bonded to two terminal ethyl groups. This structure is the Zn equivalent of **1**, the structure thought probable for compounds formed from equimolar amounts of R_2Mg and R'OK.[4] The ring bond angle at Zn (O–Zn–O') is 79.56 (2)° and at O (Zn–O–Zn') is 100.4 (3)°. The external bond angle at Zn (C(5)–Zn–C(7)) is 116.2 (4)°. Bond lengths involving Zn are Zn–O = 2.091 (4) Å, Zn–O' = 2.097 (4) Å, Zn–C(5) = 2.058 (7) Å, and Zn–C(7) = 2.054 (9) Å. The t-Bu groups are significantly out of the plane formed by the Zn and O atoms (C(1)) is 0.603 Å out of the plane) and have a trans relationship. The K atoms are located above and below the plane formed by the Zn and O atoms. One K–O distance (3.734 (5) Å) is much longer than ordinary K–O bonding distances;[16] the other (2.626 (5) Å) is unusually short.

The only prior studies of zincate species apparently are powder diffraction studies of lithium tetramethylzincate[10] and potassium tetraethynylzincate.[11] The Zn–C bond length, 2.07 (15) Å, in tetramethylzincate is similar to those observed in this work. By contrast, the Zn–C bonds in organozinc compounds with "neutral" zinc atoms generally are shorter. The Zn–C bonds in tetrameric MeZnOMe average 1.95 (3) Å, for example, though the Zn–O bonds (average 2.078 (15) Å) are similar to those found in this study.[17] We are aware of two structures that have one four-membered ring with alternating Zn and O atoms. In one, a dimer of EtZnOAr where Ar is 2,6-di-*tert*-butylphenyl, Zn–O (1.970 (1) and 1.990 (1) Å) and Zn–C (1.949 (2) Å) are much shorter than observed in this work, but the ring bond angles (O–Zn–O' = 81.56 (5)° and Zn–O–Zn' = 98.44 (5)°) are similar.[18] In the other, a dimer of EtZnO(Me)C=CHN(t-Bu)Et (each Zn also is bonded to one N), Zn–C (1.99 (2) Å) also is somewhat shorter than observed in this work; the unequal Zn–O distances are 2.02 (1) and 2.12 (1) Å, O–Zn–O' is 84.2 (5)°, and Zn–O–Zn' is 95.8 (5)°.[19]

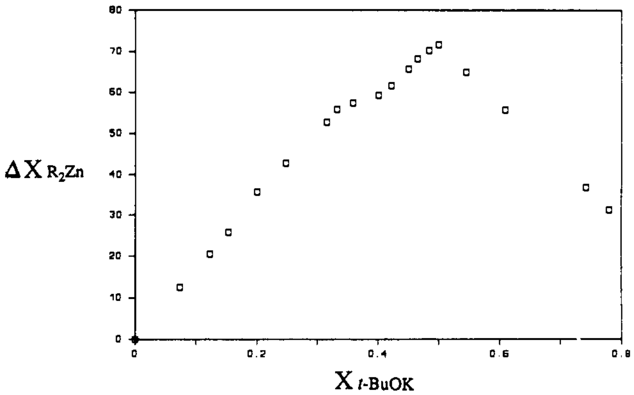

Figure 2. Job plot obtained from solutions of $(Me_3CSiCH_2)_2Zn$ and t-BuOK (combined concentrations 0.2 M) in benzene-d_6. Δ (Hz) is the ^1H NMR (300 MHz) chemical shift observed for CH_2Zn minus that observed in the absence of t-BuOK; X_{R_2Zn} and $X_{t\text{-}BuOK}$ are the mole fractions of $(Me_3CSiCH_2)_2Zn$ and t-BuOK, respectively, in total $(Me_3CSiCH_2)_2Zn$ plus t-BuOK.

Are zincate species formed in significant amounts in solution? Addition of R'OK to benzene or toluene solutions of R_2Zn often leads to suspensions; one prepared from Et_2Zn and t-BuOK (2:1) in diethyl ether produces addition product from benzaldehyde at least 10^3 times more rapidly than does a solution lacking t-BuOK.[20] Some R_2Zn–R'OK solutions can be obtained, however. ^1H and ^{13}C NMR spectra of these solutions have only single sets of absorptions for R and R', which at lower temperatures (down to −80 °C) are broader but not resolved into additional absorptions. Nevertheless, several observations suggest the formation of species that have the elements of R'OK and R_2Zn in ratios of 0.5 or 1.

(1) As t-BuOK is added, the ^1H NMR absorption of CH_2Zn moves upfield until the t-BuOK to R_2Zn (R = Bu or Me_3SiCH_2) ratio reaches 1.0, following which it remains constant, suggesting the presence of a species with that ratio. Plots between 0 and 1.0 show a minor inflection at a ratio of about 0.5.[21] The existence of a 1:1 species and of another with a ratio of about 0.5 also is suggested by data obtained by Job's[22] method. Figure 2 is a plot of such data for R = Me_3CSiCH_2.

(2) When benzene solutions (0.5–0.8 M) of Et_2Zn, Bu_2Zn, or

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(15) Crystal data for $[Et_2Zn(t\text{-}BuO)_2ZnEt_2]^{2-}2K^+$, $C_{16}H_{38}O_2K_2Zn_2$: triclinic, space group $P\bar{1}$; a = 8.365 (2) Å, b = 8.383 (2) Å, c = 9.316 (2) Å, α = 73.56 (2)°, β = 105.18 (2)°, γ = 114.51 (2)°; V = 562.2 Å^3, Z = 1, D_{calcd} = 1.392 g cm^{-3}. A total of 1961 unique reflections were measured on an Enraf-Nonius CAD-4 diffractometer in the range 2° < θ < 25° using graphite-monochromatized Mo Kα radiation, the $\omega/2\theta$ scan technique, and variable scan speed. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations (a fixed isotropic temperature factor, B = 5.0 Å^2, was used for H atoms) to R = 0.070 and R_w = 0.069 for 1680 reflections with $I > 3\sigma(I)$.

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(21) The plots do not seem to be linear in the range of ratios between 0.5 and 1.0. Nonlinearity could be due, at least in part, to the presence of additional species having t-BuOK to R_2Zn ratios between 0.5 and 1.0. Defining what is occurring in this 0–1.0 region is difficult, however, because the chemical shift range is small (~0.3 ppm for Bu and ~0.5 ppm for Me_3CSiCH_2), the chemical shifts (at least of the 1:1 species and of R_2Zn) are somewhat dependent on concentration, and the error in determining relative concentrations (by integration of appropriate absorptions) is significant.

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s-Bu$_2$Zn are stirred with solid MeOK, solutions are produced within a few minutes that have a MeOK to R$_2$Zn ratio of 0.5, which does not change on longer stirring, with sonication, or with heating.

(3) In some systems, liquids or solids with R′OK to R$_2$Zn ratios of 0.5 or 1.0 remain from removing R$_2$Zn at reduced pressure from preparations made from R′OK and R$_2$Zn. For example, subjecting a benzene solution containing *t*-BuOK and excess Bu$_2$Zn to 0.5 Torr at 30–40 °C for 12 h left a viscous liquid (solidified at 0 °C) that had a *t*-BuOK to Bu$_2$Zn ratio of 0.5. Subjecting that oil to 0.01 Torr and 75 °C for 12 h left a solid that had a ratio of 1.0.

(4) More ^{1}H and ^{13}C NMR absorptions for R (Bu and Me$_3$SiCH$_2$) and R′ (*t*-Bu) are seen at R to R′OK ratios in the 0.5–1.0 range when 18-crown-6 is added.[23] A possible explanation of these observations is that coordination of the crown ether with K$^+$ slows exchange between the 1:1 species and other species in solution.

We conclude that solutions prepared from R$_2$Zn and R′OK form zincate species, probably similar to the magnesiate species formed from R$_2$Mg and R′OK. Equilibration of R and OR′ groups between all species in the solutions is more rapid for Zn than for Mg, however, most likely reflecting a lesser tendency of R$_2$Zn than of R$_2$Mg to form bonds to oxygens.

Acknowledgment. We are indebted to the National Science Foundation for support of this work and for aiding in the purchase of the NMR spectrometers. We thank referees for particularly helpful comments.

Registry No. [Et$_2$Zn(*t*-BuO)$_2$ZnEt$_2$]$^{2-}$2K$^+$, 131130-36-4; *t*-BuOK, 865-47-4; Et$_2$Zn, 557-20-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic temperature parameters for [Et$_2$Zn(*t*-BuO)$_2$ZnEt$_2$]$^{2-}$2K$^+$ (7 pages); table of observed and calculated structure factor amplitudes for [Et$_2$Zn(*t*-BuO)$_2$ZnEt$_2$]$^{2-}$2K$^+$ (7 pages). Ordering information is given on any current masthead page.

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[23] Bu$_2$Zn and 18-crown-6 in benzene do not form significant amounts of a "threaded" [Pajerski, A. D.; BergStresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4844] Bu$_2$Zn(crown) species.

Lithium–Metalloid Exchange.[1] Dynamics and Equilibrium in the Li/I and Li/Te Exchange in Tetrahydrofuran: Iodine, Tellurium, and Mercury Ate Complexes

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The metal halogen exchange[2] and related transmetalations involving selenium,[1c,3] tellurium,[4] tin,[1d,5] and mercury[6] are powerful methods for the preparation of functionalized and unstable organolithium reagents. The mechanisms of these transformations have been variously described in terms of single electron transfer or four-center processes or ate complex intermediates.[1a,b,d,5,7] We have previously reported kinetic[1a] and spectroscopic[1b] studies which demonstrated that phenyllithium and iodobenzene combine to form the ate complex Ph$_2$I$^-$Li$^+$ at low temperatures in THF/HMPA. Described herein are results from spectroscopic studies which implicate ate complex intermediates in the Li/Hg, Li/Te, and Li/I exchanges in THF as well and extend and complement our earlier work. The exchange in pure THF is complicated by the interplay between the monomer–dimer equilibrium of phenyllithium (eq 1), the ate complex equilibrium (eq 2), and the unexpected degenerate process of eq 3. For M = I (n = 1), all three processes occur on the DNMR time scale between −78 and −115 °C.

$$2(\mathrm{PhLi})_1 \overset{K_1}{\rightleftharpoons} (\mathrm{PhLi})_2 \tag{1}$$

$$(\mathrm{PhLi})_1 + (\mathrm{Ph})_n\mathrm{M} \overset{K_2}{\rightleftharpoons} (\mathrm{Ph})_{n+1}\mathrm{M}^-\mathrm{Li}^+ \tag{2}$$

$$(\mathrm{Ph})_n\mathrm{M} + (\mathrm{Ph})_{n+1}\mathrm{M}^-\mathrm{Li}^+ \overset{K_3}{\rightleftharpoons} (\mathrm{Ph})_{n+1}\mathrm{M}^-\mathrm{Li}^+ + (\mathrm{Ph})_n\mathrm{M} \tag{3}$$

^{7}Li and ^{13}C NMR spectra of phenyllithium solutions that contain increasing amounts of metalloid species are presented in Figures 1 and 2. These define the exchange processes in qualitative terms. The addition of diphenylmercury to phenyllithium (Figure 1A) produced a new sharp signal in the ^{7}Li NMR at δ −0.9,[8] which has been assigned to tetrahedrally coordinated Li$^+$(THF)$_4$[9] of Ph$_3$Hg$^-$Li$^+$.[10] Since only this signal was present when exactly 1 equiv of diphenylmercury had been added, the formation constant of Ph$_3$Hg$^-$Li$^+$ (K_2 of eq 2) is large. With less than 1 equiv, the remaining (PhLi)$_n$ signals were identical with those of phenyllithium itself at the appropriate concentration. Hence the exchange processes depicted in eqs 2 and 3, where M = Hg and n = 2, are both slow on the NMR time scale at −105 °C.

The addition of 1 equiv of diphenyl telluride (Figure 1B) or iodobenzene (Figure 1C) produced a similar signal at δ −0.8, which we have assigned to the lithium of Ph$_3$Te$^-$Li$^+$ and Ph$_2$I$^-$Li$^+$. As with Ph$_3$Hg$^-$Li$^+$, the formation constant (K_2) for each is large, since no phenyllithium signals were visible. At intermediate points in the titrations, the spectra contained broad signals indicative of rapid exchange. While the (PhLi)$_2$ signal at δ 1.5 was unaffected, as it was in the mercury case, (PhLi)$_1$ and ate complex signals had become part of the broad signal between δ −1 and 1. We assign this averaged signal to (PhLi)$_1$ and Ph$_3$Te$^-$Li$^+$ (Figure

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[8] Lithium shifts are referenced to 0.1 M LiCl in methanol.

[9] Lithium-7 is quadrupolar ($I = {}^3/_2$) and gives sharp lines only in highly symmetrical (tetrahedral or octahedral) environments.

[10] The rate of reaction of phenyllithium in THF with butyl iodide to form butylbenzene is reduced when diphenylmercury is added due to the formation of Ph$_3$Hg$^-$Li$^+$.[1a] Diphenylmercury does not form significant amounts of Ph$_3$Hg$^-$Li$^+$ in *ether* at room temperature: Wittig, G.; Meyer, F. J.; Lange, G. *Justus Liebigs Ann. Chem.* **1951**, *571*, 167. No simple triorganomercury ate complexes have been observed, but they have been suggested as intermediates: Seitz, L. M.; Hall, S. D. *J. Organomet. Chem.* **1968**, *15*, C7. Trisilyl complexes are well-known: Sadurski, E. A.; Ilsley, W. H.; Thomas, R. D.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7761. See also: Schmidbauer, H.; Gasser, O.; Fraser, T. E.; Ebsworth, E. A. V. *J. Chem. Soc., Chem. Commun.* 1977, 334.

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