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FULL PAPER

Formation of organozincate species from diorganozinc compounds and salts†

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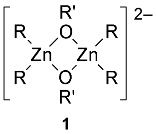
Stirring a benzene solution of a diorganozinc compound with an insoluble alkali metal alkoxide (MeOK or MeONa) or potassium amide (PhN(Me)K) formed a solution containing a species having a salt : R_2Zn composition of 1 : 2. A salt (*t*-BuOK) that is soluble in benzene also forms a 1 : 2 species and, when the salt to R_2Zn ratio is sufficiently high, forms a 1 : 1 species. Controlled heating at reduced pressure of solutions prepared from an alkali metal alkoxide and an excess of a diorganozinc compound leaves materials with alkoxide : R_2Zn ratios of 1 : 2 or 1 : 1. Reactions of benzene solutions of diorganozinc compounds with (p-MeC_6H_4)SK or Ph_2PK form solutions of composition R_3ZnK.

Solutions with organozincate compositions such as R_3ZnK and R_3ZnLi undergo reactions not significant with R_2Zn or RZnX.[1] Addition of appropriate salts to diorganozinc compounds also might form organozincates (*e.g.*, eqn. (1)), and indeed a few

$$R_2Zn + M^+A^- \longrightarrow R_2ZnA^-M^+ \qquad (1)$$

reports have indicated that some salts enhance reactivity.[1,2] When we began this work the principal studies of compositions and structures that resulted from combining R_2Zn and a salt involved hydride as the anion.[3] Solids that had salt : R_2Zn compositions of 1 : 1 and 1 : 2 were obtained with LiH or NaH. In an earlier report we described preliminary results of a study of R_2Zn compounds and potassium alkoxides.[4] A solid was obtained that X-ray diffraction analysis showed to contain the organozincate dianion **1** (R = Et, R′ = *t*-Bu). Less direct evidence suggested that solutions of R_2Zn compounds and potassium alkoxides contain species with alkoxide : R_2Zn ratios of 1 : 1 and 1 : 2. This paper presents additional information and adds studies of R_2Zn with other classes of salts.



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Results and discussion

R_2Zn with MeOK and MeONa

Although MeOK is virtually insoluble in benzene, it dissolved completely when stirred with a benzene solution containing ≥2 equivalents of Et_2Zn. Except where noted, benzene (or benzene-d_6) was the solvent in this work; an amount of R_2Zn was used that would form a 0.2–0.6 M solution. The ^{1}H NMR spectra of all solutions in which MeOK had dissolved showed only one MeO absorption and one set of Et absorptions. As the MeOK : Et_2Zn ratio in solution increased the CH_2Zn absorption moved upfield (≈0.1 ppm) and the CH_3CH_2Zn absorption moved downfield (≈0.4 ppm). When >0.5 equivalent of MeOK was used undissolved solid remained. ^{1}H NMR absorption areas indicated that the MeOK : Et_2Zn ratio in solution never exceeded 0.5 : 1, even when a large excess of MeOK was used. MeOK also dissolved in solutions of Bu_2Zn or *s*-Bu_2Zn to form solutions in which the MeOK : R_2Zn ratio reached but never exceeded 0.5 : 1.[5] The ratio of 0.5 : 1 persisted when mixtures prepared with an excess of MeOK were heated at 70 °C or subjected to ultrasonic radiation. MeONa, also insoluble in benzene, formed solutions having MeONa : Et_2Zn ratios ≤0.5 : 1 and NMR spectra almost identical to those of solutions prepared with MeOK.

Solutions prepared in benzene or diethyl ether from MeOK and an excess of Et_2Zn were heated at reduced pressure to remove volatile materials.[6] With temperatures in the range 60–90 °C and pressures in the range 1–5 Torr viscous liquids remained. These liquids dissolved in benzene-d_6, and ^{1}H NMR spectra of the solutions showed a MeOK : Et_2Zn ratio of 0.5 : 1. Similar experiments with Et_2Zn and MeONa (benzene), Bu_2Zn and MeOK (benzene), and Bu_2Zn and MeONa (diethyl ether) also resulted in oils that dissolved in benzene-d_6; ^{1}H NMR spectra of these solutions indicated MeOM : R_2Zn ratios of 0.5 : 1.[7]

Formation of species having the stoichiometry of one MeOK or MeONa to two R_2Zn is suggested by repeated observations of this composition in both solutions formed using an excess of an alkoxide salt and oils formed by removing excess of R_2Zn.

R_2Zn with *t*-BuOK

t-BuOK is significantly soluble[8] in benzene and forms solutions having higher R′OK : R_2Zn ratios than does MeOK. In ^{1}H NMR studies with Et_2Zn, Bu_2Zn, *s*-Bu_2Zn, or $(Me_3SiCH_2)_2Zn$ and varying amounts of *t*-BuOK only one *t*-BuO absorption and one set of R absorptions were seen. Some broadening but no additional absorption was evident in spectra (toluene-d_8 solutions) at −80 °C. Therefore R and *t*-BuO of all species present must equilibrate rapidly relative to the NMR timescale.

The ^{1}H NMR absorption of CH_2Zn moved upfield with increasing *t*-BuOK : Et_2Zn ratio but, particularly as the reactant ratio approached 1 : 1, formation within a few minutes of a precipitate (the solid shown[4] by X-ray diffraction to contain

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† This paper is dedicated to the memory of Ron Snaith.

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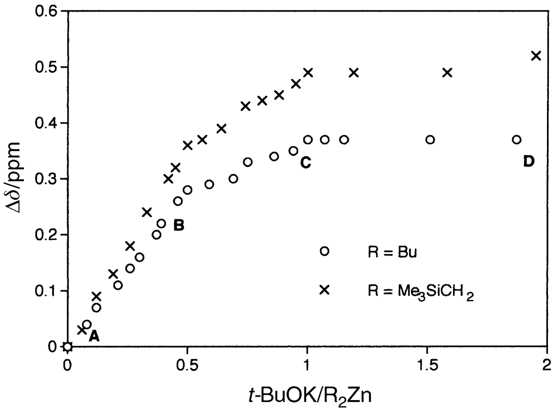


Fig. 1 Plots of the upfield shifts of the ^1H NMR absorption of CH_2Zn *versus* the *t*-BuOK : R_2Zn ratio for R = butyl or Me_3SiCH_2. The R_2Zn concentration in all solutions is ≈0.4 M.

organozincate dianion **1** (R = Et, R′ = *t*-Bu)) limited study. When R was Bu, *s*-Bu, or Me_3SiCH_2, solutions prepared using various *t*-BuOK : R_2Zn ratios did not form precipitates. Fig. 1 shows typical plots of upfield shifts (Δδ) of the ^1H NMR absorption of CH_2Zn *versus* the *t*-BuOK : R_2Zn ratio. As *t*-BuOK : R_2Zn increases from 0 to 0.5 : 1 (**A**–**B**) the absorption position changes linearly. From 0.5 to 1 : 1 (**B**–**C**) the change continues but to a lesser degree. Above 1 : 1 (**C**–**D**) the absorption remains constant (its position unchanged at a *t*-BuOK : R_2Zn ratio of 5 : 1). A species having a *t*-BuOK : R_2Zn ratio of 1 : 2 must form in region **A**–**B** and incorporate most of the *t*-BuOK in the solution. At **C** most solute must be in a species having a *t*-BuOK : R_2Zn ratio of 1 : 1. The constant absorption position in region **C**–**D** is most readily interpreted by assuming that essentially all R_2Zn is incorporated into the 1 : 1 species which, however, exchanges relatively rapidly with additional *t*-BuOK.[9] If that is the case, then in region **C**–**D** the position of the ^1H NMR absorption of *t*-BuO should move from that of the 1 : 1 species toward that of free *t*-BuOK. Unfortunately, the *t*-BuO absorption is virtually the same at all reactant ratios. If only species having *t*-BuOK : R_2Zn ratios of 1 : 2 and 1 : 1 are present, then the **B**–**C** region should be linear. Owing to the limited range of chemical shifts, the presence in that region of another component (*t*-BuOK : R_2Zn between 0.5 and 1 : 1) cannot be excluded.

The small range of CH_2Zn NMR absorptions (0.5 ppm for Me_3SiCH_2, 0.3 ppm for Bu) is an obvious limitation. ^{13}C NMR spectra of the Bu_2Zn system were investigated, but the CH_2Zn absorptions spanned a range of only 0.3 ppm. Nevertheless, several considerations suggest the validity of the indications that species form with *t*-BuOK : R_2Zn ratios of 1 : 1 and 1 : 2. (1) The observations are reproducible; various experiments gave data having the features seen in Fig. 1. (2) Plots[4] by the Job method[10] of data from the Me_3SiCH_2 system indicate one species having a *t*-BuOK : $(Me_3SiCH_2)_2Zn$ ratio of 1 : 1 and a second having a ratio of approximately 1 : 2. (3) Solutions having compositions in the **B**–**C** region show NMR absorptions for two species when treated in ways described below that might slow exchange.

Lowering the temperatures of solutions prepared in toluene-d_8 led to more absorptions. The ^1H NMR spectrum at −80 °C of a solution prepared with a *t*-BuOK : $(Me_3SiCH_2)_2Zn$ ratio of 0.74 : 1 (to fall in the **B**–**C** region) showed two *t*-BuO absorptions, *ca.* 1 : 2 in intensity, and two sets of Me_3SiCH_2 absorptions, *ca.* 1 : 1 in intensity (intensities are approximate because absorptions were broad and the *t*-BuO absorptions overlapped). The absorptions could be due to species having *t*-BuOK : $(Me_3SiCH_2)_2Zn$ ratios of 1 : 2 and 1 : 1. Absorptions of a similar solution prepared from Bu_2Zn broadened at lower temperatures and at −80 °C two absorptions (approximately 1 : 1) were resolved for CH_3CH_2.

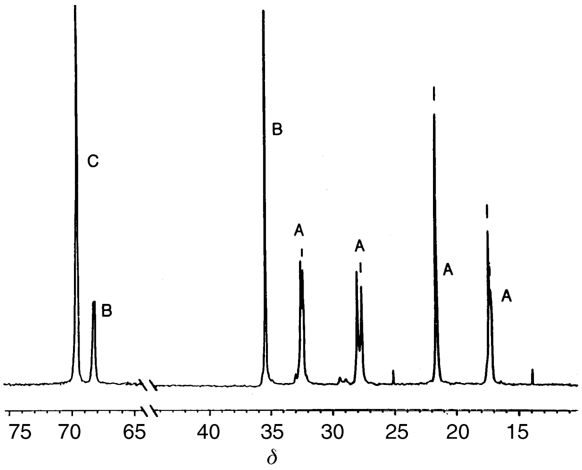


Fig. 2 ^{13}C NMR spectrum (75 MHz) of a benzene-d_6 solution prepared from *t*-BuOK, 18C6, and Bu_2Zn (0.75 : 0.75 : 1). Absorptions of butyl are labeled A, of *t*-butoxy B, and of 18C6 C.

Adding a coordinating agent for K^+, such as 18-crown-6 (18C6), is another possible way of slowing equilibration. The ^1H NMR spectrum of a solution in which *t*-BuOK : 18C6 : Bu_2Zn was 0.75 : 0.75 : 1 had two *t*-BuO and two CH_2CH_2Zn absorptions, and the position of the 18C6 absorption was typical of 18C6 coordinated to K^+; the ^{13}C spectrum (Fig. 2) had two absorptions for all C of butyl except CH_3.[11] These results are consistent with the presence of two species having *t*-BuOK : Bu_2Zn ratios of 1 : 2 and 1 : 1. When *t*-BuOK : 18C6 : Bu_2Zn was 0.4 : 0.4 : 1 or 1.5 : 1.5 : 1, only single sets of ^1H and ^{13}C NMR absorptions were noted for Bu and *t*-BuO (although in the latter case the ^1H NMR absorption of *t*-BuO and the ^{13}C NMR absorption of CO of *t*-BuO were broad). At ratios <0.5 : 1 the 1 : 2 species must equilibrate rapidly with excess of Bu_2Zn and at ratios >1 : 1 the 1 : 1 species must equilibrate relatively rapidly with excess of *t*-BuOK.

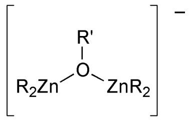
A second liquid phase formed when 18C6 was added to solutions prepared from *t*-BuOK and $(Me_3SiCH_2)_2Zn$, and essentially all solute was in the lower phase when equimolar amounts of the three components were used. This likely indicates that the solute is ionic, since organometallic ions in aromatic solvents often reside in such lower phases.[13] In fact, ^1H NMR spectra of the lower phases show an absorption characteristic for 18C6 coordinated with K^+ and, when the ratio of *t*-BuOK and 18C6 to $(Me_3SiCH_2)_2Zn$ is less than 1 : 1, generally show two *t*-BuO absorptions and two sets of Me_3SiCH_2 absorptions.[11]

A viscous liquid indicated by its ^1H NMR spectrum (benzene-d_6) to have a *t*-BuOK : Et_2Zn ratio of 1 : 2 remained when volatile material was removed at 60–65 °C and 5 Torr from a solution prepared from *t*-BuOK and excess of Et_2Zn in diethyl ether. Subjecting the viscous liquid to 120–130 °C at 0.1 Torr resulted in a white crystalline solid identical to the 1 : 1 precipitate from Et_2Zn and *t*-BuOK in benzene. A similar viscous oil and solid were obtained by subjecting a solution prepared in benzene first to 40 °C and 2 Torr and then to 90 °C and 0.1 Torr. Yet higher temperatures and lower pressures resulted in no observable changes until gray solid (Zn metal) formed when the temperature reached 250 °C. A viscous liquid (solidified at 0 °C) indicated by its ^1H NMR spectrum (benzene-d_6) to have a *t*-BuOK : Bu_2Zn ratio of 1 : 2 also remained when volatile material was removed at 30–40 °C and 0.5 Torr from a solution of *t*-BuOK and excess of Bu_2Zn in benzene. The ^1H NMR spectrum (benzene-d_6) of the solid (mp 84–89 °C) that remained after subjecting this oil to 75 °C and 0.01 Torr showed a *t*-BuOK : Bu_2Zn ratio of 1 : 1. A similar viscous liquid and solid were obtained by similar treatment of a solution prepared in diethyl ether.

Conclusions about R_2Zn–alkoxide preparations

Although all R_2Zn–alkoxide solutions exhibit only single sets of R and alkoxide NMR absorptions at ambient temperature, several pieces of evidence indicate that species form that have alkoxide : R_2Zn ratios of 1 : 1 and 1 : 2. (1) Plots of absorption position *versus* alkoxide : R_2Zn ratio indicate the presence of 1 : 1 and 1 : 2 species. (2) Solutions prepared using alkoxide : R_2Zn ratios between 0.5 and 1 : 1 have multiple NMR absorptions at low temperatures. (3) Solutions prepared using alkoxide–18C6 : R_2Zn ratios between 0.5 and 1 : 1 have multiple NMR absorptions. (4) MeOK and MeONa dissolve in R_2Zn solutions to form solutions having precisely 1 : 2 compositions. (5) Removing solvent and R_2Zn from solutions prepared with excess of R_2Zn tends to produce materials with alkoxide : R_2Zn ratios of 1 : 2 or 1 : 1.[14] (6) Greater stability of R_2Zn solutions when alkoxide salts are dissolved in them suggests the formation of new species. Pure *s*-Bu_2Zn or its solutions in hydrocarbon solvents, for example, decompose slowly at ambient temperature. When two solutions of *s*-Bu_2Zn, one also containing 0.5 equivalent of *t*-BuOK, were heated at 70 °C for 30 min decomposition in the solution without alkoxide was evident by deposition of gray solid (Zn) and appearance of significant new ^1H NMR absorptions (*e.g.* for $=CH_2$); the solution containing alkoxide did not deposit a solid and had an unchanged NMR spectrum.

The 1 : 1 species in solution presumably have structures like that (**1**) of the solid obtained from Et_2Zn and *t*-BuOK. The 1 : 2 species probably have structures such as **2**. In solutions in which alkoxide : R_2Zn <0.5 : 1 only **2** and free R_2Zn might be present. Conceivably, species that contain more R_2Zn per alkoxide also could be present. The observation that the ^1H NMR absorption of MeO and the ^{13}C NMR absorption of CO of *t*-BuO drift somewhat downfield as the R′O : R_2Zn ratio increases from 0 to 0.5 : 1 could be an indication that not all R′O is incorporated into **2** until the ratio reaches 0.5 : 1. The ranges of R′O absorption positions are small, however, and could be due to effects of the changing medium on the absorptions of **2** rather than to the presence of an additional species.



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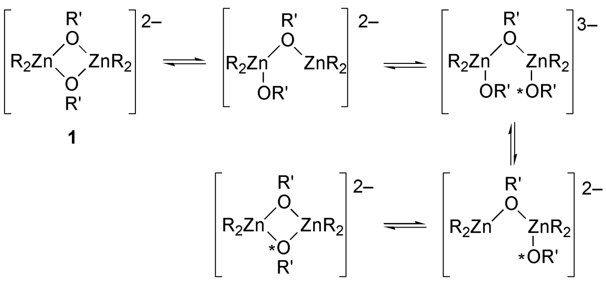
The multiple absorptions in the presence of 18C6 probably are due to decreased rates of exchange between species similar to those present in its absence. With *t*-BuOK : R_2Zn ratios <0.5 or >1 : 1, however, only single *t*-BuO and R absorptions are seen in the presence of 18C6. Averaged absorptions are expected for ratios <0.5 : 1 since exchange of a species such as **2** with free R_2Zn should be rapid. For ratios >1 : 1 in the presence of 18C6 the 1 : 1 species (presumably **1**) must exchange rapidly with excess of *t*-BuO groups. Yet the possibility that exchange occurs by initial cleavage of **1** to form R_2Zn or R_2ZnO-*t*-Bu^- probably is ruled out by the evidence that at lower *t*-BuOK : R_2Zn ratios the 1 : 1 and 1 : 2 species do not exchange rapidly. Perhaps exchange occurs (Scheme 1) by cleavage of *only one Zn–O bridge bond* followed by addition of *t*-BuO to the less substituted Zn, loss of one of the two equivalent *t*-BuO, and regeneration of the Zn–O bridge bond, a sequence in which the two R_2Zn of **1** never separate.

R_2Zn with other salts

$Bu_4N^+X^-$. Bu_4NCl is relatively soluble in benzene. Combining Et_2Zn and Bu_4NCl in that solvent resulted in formation of a second, dense, liquid phase which turned into a gum-like solid that did not dissolve on heating in benzene. ^1H NMR spectra of the materials remaining in the upper phases when varying amounts of reactants were used indicated that the lower phases had a Bu_4NCl : Et_2Zn ratio of 1 : 1. Experiments using chloroform-*d* as the solvent also produced solids that did not dissolve significantly when heated with the solvent. Bu_2Zn and Bu_4NCl in benzene formed a dense phase which remained *liquid*. ^1H NMR absorptions of this phase were very broad, but the areas of the CH_2N and CH_2Zn absorptions indicated a Bu_4NCl : Bu_2Zn ratio of 1 : 1.



Scheme 1

Bu_4NBr and Bu_2Zn in benzene produced homogeneous solutions. As the Bu_4NBr : Bu_2Zn ratio increased from 0 to 0.5 : 1 the ^1H NMR absorption of CH_2Zn moved (0.25 ppm) linearly downfield (rather than upfield as observed with alkoxides). As the ratio increased further the absorption moved further downfield (0.04 ppm between ratios of 0.5 and 1 : 1, and 0.03 ppm more between 1 and 4 : 1). A 1 : 2 species must form, but the subsequent changes in absorption position are too small to interpret. Bu_4NCl and $(Me_3SiCH_2)_2Zn$ resulted in homogeneous solutions and similar NMR observations: the CH_2Zn absorption moved ≈0.15 ppm downfield as the Bu_4NCl : $(Me_3SiCH_2)_2Zn$ ratio went from 0 to 0.5 : 1, and ≈0.05 ppm as it went from 0.5 to 1.0 : 1.

PhN(Me)K. This salt is quite insoluble in benzene, but some dissolved when stirred with benzene solutions of Et_2Zn, *i*-Bu_2Zn, $(CH_3CH_2CHEtCH_2)_2Zn$, or $(Me_3SiCH_2)_2Zn$. The ^1H NMR absorption of CH_2Zn moved upfield (maximum of 0.47 ppm) with increasing intensity of the PhNMe absorptions. The spectra of solutions obtained after stirring for 24 h indicated a PhN(Me)K : R_2Zn ratio of 1 : 2. Using more PhN(Me)K did not increase the ratio and heating mixtures in an effort to introduce more of the salt resulted in decomposition, evidenced by formation of gray solid and appearance of new absorptions in ^1H NMR spectra. Neither sonication nor addition of 18C6 significantly increased the PhN(Me)K : Et_2Zn ratio.

TolSK and Ph_2PK. White solid remained when a benzene solution of Et_2Zn was stirred at ambient temperature with TolSK (Tol = *p*-methylphenyl) or Ph_2PK. The Et absorptions in ^1H NMR spectra of the resulting solutions, however, were shifted in position from those of Et_2Zn. When, after continued stirring, the NMR spectra showed no further changes (for experiments with TolSK this also required heating at 70 °C for 20–30 min), *no Tol or Ph absorptions were present*. The ^1H NMR absorptions of all such solutions were essentially identical, δ −0.09 (CH_2) and 1.60 (CH_3) (absorptions of Et_2Zn are δ 0.12 and 1.11).

Several pieces of evidence indicate that solutions of Et_3ZnK (eqns. 2 and 3) are formed. (1) Analysis[15] shows that a basic group ("Et^-"), Zn, and K are in 3 : 1 : 1 ratio. (2) The NMR spectra of the solutions are identical to those observed

$$3\,Et_2Zn + 2\,TolSK \longrightarrow 2\,Et_3ZnK + (TolS)_2Zn\downarrow \quad (2)$$

$$3\,Et_2Zn + 2\,Ph_2PK \longrightarrow 2\,Et_3ZnK + (Ph_2P)_2Zn\downarrow \quad (3)$$

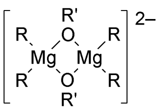
for an Et_3ZnK solution prepared[1] in an established way. (3) A dense phase formed when 18C6 was added to a solution prepared from TolSK or Ph_2PK or to a solution of authentic Et_3ZnK. The 18C6 absorption (δ 3.00) in ^1H NMR spectra of these phases is characteristic of 18C6 coordinated to K^+.

R_3ZnK solutions exhibiting only ^1H NMR absorptions of R of R_2Zn also were obtained using TolSK with i-Bu_2Zn, $(Me_3SiCH_2)_2Zn$, or $(Tol)_2Zn$ and Ph_2PK with i-Bu_2Zn, $(CH_3CH_2CHEtCH_2)_2Zn$, $(Me_3SiCH_2)_2Zn$, or $(Tol)_2Zn$. A dense phase formed when 18C6 was added to the solution of $(Me_3SiCH_2)_3ZnK$ or i-Bu_3ZnK. In ^1H NMR spectra of the dense phases the 18C6 absorption is characteristic of $K(18C6)^+$ and the absorption areas indicate that R and 18C6 are in 3 : 1 ratio.

Conclusion

An R_2Zn compound in benzene and an alkali metal alkoxide, tetraalkylammonium halide, or potassium amide form species having a 2 : 1 ratio of the reactants. A 1 : 1 species also forms when the salt to R_2Zn ratio is sufficiently high, but only the 2 : 1 species is observed when the salt itself is insoluble.

Zinc lacks a partially filled d shell and in many respects resembles magnesium, so comparison with results from reactions of R_2Mg and salts is pertinent. NMR studies with sodium or potassium alkoxides demonstrated that when $R'OM : R_2Mg$ is 1 : 1, the highest ratio found in mixed species, the dominant species in solution is **3**.[16] A second set of absorptions is seen when $R'OM : R_2Mg$ is less than 1 : 1,[17] but sharp absorptions of **3** continue to be evident until the reactant ratio drops below 0.5 : 1. $(s\text{-Bu})_2Mg$–alkoxide solutions even have separate absorptions for stereoisomers of structure **3** (containing different arrays of *R* and *S* *s*-Bu groups). The discrete absorptions seen for **3** indicate that, unlike its zinc counterpart **1**, it does not exchange rapidly relative to the NMR timescale with other solution components. The more rapid exchanges in R_2Zn solutions may reflect the lesser tendency[18] of R_2Zn than of R_2Mg to form bonds to donor oxygen atoms. Equilibrium constants for combining with an alkoxide are smaller for R_2Zn than for R_2Mg and exchange between species in solution is more rapid. Formation of a second phase with a tetraalkylammonium halide, found for R_2Zn in this work, also has been noted for R_2Mg.[19]



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R_2Zn compounds and TolSK or Ph_2PK form solutions of composition R_3ZnK. Low solubility[20] of $(TolS)_2Zn$ and $(Ph_2P)_2Zn$ must be crucial in leading to formation of R_3ZnK rather than of species incorporating TolSK or Ph_2PK.

Experimental

Procedures involving organometallic compounds were performed under a nitrogen atmosphere using Schlenk techniques, a glove box, and a vacuum line. ^1H NMR absorption positions are relative to internal C_6D_5H (δ 7.15) for benzene-d_6 solutions and internal CD_5CD_2H (δ 2.09) for toluene-d_8 solutions. Notations used are: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; br, broad. ^{13}C NMR absorption positions are relative to internal C_6D_6 (δ 128.0). Samples to be treated ultrasonically were sealed in glass tubes and placed in a 60 kHz E/MC Corp. Ultrasonic Cleaner, model 450.

Hydrocarbon solvents, including deuteriated solvents, were distilled from CaH_2 and stored over molecular sieves (4 Å) under a nitrogen atmosphere. Diethyl ether was distilled from sodium–benzophenone immediately prior to use. Diorganozinc compounds were synthesized from organic halides using standard procedures. Their ^1H NMR absorptions (needed for comparison with spectra obtained in this work) are available[12] except for those of $(CH_3CH_2CHEtCH_2)_2Zn$: (benzene-d_6) δ 0.37 (d, CH_2Zn), 0.92 (t, CH_3), 1.10 (m, CH_2CH) and 1.48 (m, CH). *N*-Methylaniline was distilled from NaOH. *t*-BuOK was sublimed (100 °C, <0.1 Torr). The other reactants (Aldrich) were used as received. To prepare potassium *N*-methylanilide, the mineral oil was removed from a mineral oil suspension of KH (35%, 5.89 g corresponding to 2.0 g of KH, 0.050 mol) by repeatedly washing the mixture with benzene and decanting the supernatant liquid. Benzene (45 mL) was added followed by dropwise addition to the stirred suspension of a solution of *N*-methylaniline (10.7 g, 0.10 mol) in benzene (45 mL). Gas (H_2) evolution was immediately evident. The suspension was stirred for 24 h and then transferred to centrifuge tubes and centrifuged. The supernatant liquid was withdrawn using a syringe and replaced with an equal volume of benzene. The mixture was agitated by sonication until the suspension was well mixed; the suspension was centrifuged and the benzene removed. Washing the solid with additional benzene was repeated. The remaining solid was heated (80 °C) at reduced pressure for 24 h to remove residual solvent (5.1 g, 0.035 mol, 70%). Potassium *p*-methylbenzenethiolate (96%) and potassium diphenylphosphide (84%) were prepared in the same manner except that only 0.06 mol of *p*-methylbenzenethiol or diphenylphosphine was used.

NMR studies

In the glove box the salt was weighed into a vial equipped with a magnetic stirring bar. Benzene-d_6 (ordinarily 0.5 mL) was added and the mixture stirred for a few minutes. The dialkylzinc compound then was weighed into the vial and the contents were stirred for 5–10 min. If solid was present then stirring was continued for 12–24 h. For the preparations with potassium *p*-methylbenzenethiolate a 20–30 min period of heating at 60–70 °C was added. The preparation then ordinarily was transferred with a pipette to an NMR tube which had been modified by adding an extension of routine glass tubing to facilitate sealing with a flame. The tube was closed with a septum, removed from the glove box, frozen in liquid nitrogen, and sealed at the extension. When solid remained, either the preparation was centrifuged before addition to the NMR tube or, after addition, the NMR tube was centrifuged to collect the solid at the unobserved (by the spectrometer) end. When a preparation resulted in two liquid phases, each was transferred to an NMR tube; those preparations had to be done on a somewhat larger scale.

Listed below for representative preparations are (1) any notable features, (2) (in parentheses) the salt : R_2Zn ratio (18C6 : salt : R_2Zn when 18C6 also is present), and (3) the NMR spectra. The listed ratio ordinarily is based on the amounts of reagents used. For preparations having undissolved solid, however, it is based on the relative intensities of ^1H NMR absorptions. For the solutions used to obtain plots (*e.g.* Fig. 1) of $\Delta\delta$ *versus* salt : R_2Zn ratio the listed ratios also are based on the relative intensities of ^1H NMR absorptions, but closely match the ratios expected from the amounts of compounds used to prepare the solutions. Except where noted, spectra were taken at ambient temperature, the solvent is benzene-d_6, and the amount of R_2Zn used in the preparation would provide a 0.2–0.6 M concentration of this compound. The field strength of the spectrometer is given only when the description is field dependent.

MeOK–Et_2Zn. (0.5) ^1H NMR: δ −0.02 (q, CH_2), 1.51 (t, CH_3CH_2) and 3.57 (s, CH_3O).

MeONa–Et$_2$Zn. (0.5) ^{1}H NMR: δ −0.05 (q, CH_2), 1.53 (t, $C\mathit{H}_3CH_2$) and 3.51 (s, CH_3O).

MeOK–Bu$_2$Zn. (0.5) ^{1}H NMR: δ 0.02 (t, CH_2Zn), 1.13 (t, $C\mathit{H}_3CH_2$), 1.25 (m, $C\mathit{H}_2CH_3$), 1.87 (m, $C\mathit{H}_2CH_2Zn$) and 3.49 (s, CH_3O).

MeOK–*s*-Bu$_2$Zn. (0.5) ^{1}H NMR: δ 0.12 (m, CHZn), 1.17 (t, $C\mathit{H}_3CH_2$), 1.36 (d, $C\mathit{H}_3CH$), 1.79 (m, CH_2) and 3.52 (s, CH_3O).

***t*-BuOK–Et$_2$Zn.** A solution resulted when *t*-BuOK (1.80 g, 16 mmol) and Et$_2$Zn (1.98 g, 16 mmol) were stirred in toluene (8.0 mL), but white crystals soon formed. The sample was heated to 80 °C to dissolve the solid. Crystals formed again on slow cooling to ambient temperature. The sample was then cooled at −5 °C for 24 h. The liquid was decanted and the crystals were washed twice with benzene and allowed to dry (mp 145–148 °C). A 6 mg sample of the crystals dissolved completely in 0.5 mL of benzene-*d*$_6$ (intensities of ^{1}H NMR absorptions indicated a 1 : 2 ratio of *t*-BuO and Et groups). ^{1}H NMR: δ −0.16 (q, CH_2), 1.18 (s, CH_3CO) and 1.62 (t, $C\mathit{H}_3CH_2$). ^{13}C NMR: δ 7.0 (CZn), 14.2 (CH_3), 33.8 ($\mathit{C}CO$) and 69.1 (CO).

***t*-BuOK–Bu$_2$Zn.** (0.5) ^{1}H NMR: δ −0.04 (t, CH_2Zn), 1.09 (s, CH_3CO), 1.25 (t, $C\mathit{H}_3CH_2$), 1.29 (m, $C\mathit{H}_2CH_3$) and 1.87 (m, $C\mathit{H}_2CH_2Zn$). ^{13}C NMR: δ 14.4 (CH_2Zn), 17.3 ($\mathit{C}H_3CH_2$), 30.5 ($\mathit{C}H_2CH_3$), 32.6 ($\mathit{C}H_2CH_2Zn$), 35.3 ($\mathit{C}H_3CO$) and 68.4 (CO). (1) ^{1}H NMR: δ −0.09 (t, CH_2Zn), 1.12 (s, CH_3CO), 1.20 (t, $C\mathit{H}_3CH_2$), 1.27 (m, $C\mathit{H}_2CH_3$) and 1.95 (m, $C\mathit{H}_2CH_2Zn$). ^{13}C NMR: δ 14.6 (CH_2Zn), 17.4 ($\mathit{C}H_3CH_2$), 30.7 ($\mathit{C}H_2CH_3$), 32.8 ($\mathit{C}H_2CH_2Zn$), 35.5 ($\mathit{C}H_3CO$) and 67.9 (CO). (0.75) (toluene-*d*$_8$) ^{1}H NMR: δ 0.00 (t, CH_2Zn), 1.10 (s, CH_3CO), 1.17 (t, $C\mathit{H}_3CH_2$), 1.25 (m, $C\mathit{H}_2CH_3$) and 1.87 (m, $C\mathit{H}_2CH_2Zn$). ^{1}H NMR (−80 °C): δ −0.27 (t, CH_2Zn), 1.09 (s, CH_3CO), 1.60 (t, $C\mathit{H}_3CH_2$), 1.40 and 1.52 (m and m, $C\mathit{H}_2CH_3$) and 2.24 (m, $C\mathit{H}_2CH_2Zn$).

***t*-BuOK–18C6–Bu$_2$Zn.** (0.4 : 0.4 : 1) ^{1}H NMR: δ 0.55 (t, CH_2Zn), 1.20 (t, $C\mathit{H}_3CH_2$), 1.60 (s, CH_3CO), 1.75 (m, $C\mathit{H}_2CH_3$), 2.15 (m, $C\mathit{H}_2CH_2Zn$) and 3.04 (s, 18C6). ^{13}C NMR: δ 17.1 (CH_2Zn), 21.5 ($\mathit{C}H_3CH_2$), 27.4 ($\mathit{C}H_2CH_3$), 32.4 ($\mathit{C}H_2CH_2Zn$), 35.4 ($\mathit{C}H_3CO$), 68.1 (CO) and 70.0 (18C6). (0.75 : 0.75 : 1) ^{1}H NMR: δ 0.42 (t, CH_2Zn), 1.19 (t, $C\mathit{H}_3CH_2$), 1.55 and 1.59 (s and s, CH_3CO), 1.73 (m, $C\mathit{H}_2CH_3$), 2.09 and 2.20 (m and m, $C\mathit{H}_2CH_2Zn$) and 3.06 (s, 18C6). ^{13}C NMR: δ 17.2 and 17.3 (CH_2Zn), 21.6 ($\mathit{C}H_3CH_2$), 27.7 and 28.2 ($\mathit{C}H_2CH_3$), 32.4 and 32.6 ($\mathit{C}H_2CH_2Zn$), 35.5 ($\mathit{C}H_3CO$), 68.3 (CO) and 69.9 (18C6). (1.5 : 1.5 : 1) ^{1}H NMR: δ 0.40 (t, CH_2Zn), 1.17 (t, $C\mathit{H}_3CH_2$), 1.49 (br, CH_3CO), 1.71 (m, $C\mathit{H}_2CH_3$), 2.09 (m, $C\mathit{H}_2CH_2Zn$) and 3.03 (s, 18C6). ^{13}C NMR: δ 17.3 (CH_2Zn), 21.6 ($\mathit{C}H_3CH_2$), 28.2 ($\mathit{C}H_2CH_3$), 32.7 ($\mathit{C}H_2CH_2Zn$), 35.1 ($\mathit{C}H_3CO$), 68.1 (CO) and 70.0 (18C6).

***t*-BuOK–*s*-Bu$_2$Zn.** (0.5) ^{1}H NMR: δ 0.18 (m, CHZn), 1.02 (t, $C\mathit{H}_3CH_2$), 1.08 (s, CH_3CO), 1.32 (d, $C\mathit{H}_3CH$) and 1.68 (m, CH_2). (1) ^{1}H NMR: δ 0.03 (m, CHZn), 1.07 (s, CH_3CO), 1.18 (t, $C\mathit{H}_3CH_2$), 1.40 (d, $C\mathit{H}_3CH$) and 1.86 (m, CH_2).

***t*-BuOK–(Me$_3$SiCH$_2$)$_2$Zn.** (1) ^{1}H NMR: δ −1.13 (s, CH_2), 0.32 (s, CH_3Si) and 1.09 (s, CH_3CO). (0.5) ^{1}H NMR: δ −1.01 (s, CH_2), 0.28 (s, CH_3Si) and 1.08 (s, CH_3CO). (0.74) (toluene-*d*$_8$) ^{1}H NMR: δ −1.01 (s, CH_2), 0.35 (s, CH_3Si) and 1.09 (s, CH_3CO). (−80 °C) δ −1.12 and −1.30 (s and s, CH_2), 0.38 and 0.42 (s and s, CH_3Si), 1.18 and 1.20 (s and s, CH_3CO).

***t*-BuOK–18C6–(Me$_3$SiCH$_2$)$_2$Zn.** (0.4 : 0.4 : 1) ^{1}H NMR (lower phase): δ −0.50 and −0.58 (s and s, CH_2), 0.44 and 0.47 (s and s, CH_3Si), 1.58 and 1.76 (s and s, CH_3CO) and 2.98 (s, 18C6). (0.8 : 0.8 : 1) δ −0.41 and −0.46 (s and s, CH_2), 0.46 and 0.49 (s and s, CH_3Si), 1.58 and 1.78 (s and s, CH_3CO) and 3.01 (s, 18C6). (1.5 : 1.5 : 1) δ −0.49 (s, CH_2), 0.48 (s, CH_3Si), 1.55 (s, CH_3CO) and 2.98 (s, 18C6).

Bu$_4$NCl–Bu$_2$Zn. (1) ^{1}H NMR (lower phase): δ 0.6 (br, CH_2Zn), 3.2 (br, CH_2N) and 1.0–2.2 (c, all other H).

Bu$_4$NCl–(Me$_3$SiCH$_2$)$_2$Zn. (0.5) ^{1}H NMR (300 MHz): δ −0.50 (s, CH_2Zn), 0.47 (s, CH_3Si), 0.95 (t, $C\mathit{H}_3CH_2$), 1.38–1.42 (c, $C\mathit{H}_2C\mathit{H}_2CH_2N$) and 2.88 (br m, CH_2N). (1) δ −0.44 (s, CH_2Zn), 0.48 (s, CH_3Si), 0.93 (t, $C\mathit{H}_3CH_2$), 1.37–1.41 (c, $C\mathit{H}_2C\mathit{H}_2CH_2N$) and 2.85 (br m, CH_2N).

Bu$_4$NBr–Bu$_2$Zn. (0.5) ^{1}H NMR (300 MHz): δ 0.51 (t, CH_2Zn), 0.8–1.9 (c, overlapping absorptions of $C\mathit{H}_3C\mathit{H}_2C\mathit{H}_2CH_2Zn$ and $C\mathit{H}_3C\mathit{H}_2C\mathit{H}_2CH_2N$) and 3.02 (br m, CH_2N). (1) δ 0.56 (t, CH_2Zn), 0.9–1.9 (c, overlapping absorptions of $C\mathit{H}_3C\mathit{H}_2C\mathit{H}_2CH_2Zn$ and $C\mathit{H}_3C\mathit{H}_2C\mathit{H}_2CH_2N$) and 2.99 (br m, CH_2N).

PhN(Me)K–Et$_2$Zn. (0.5) ^{1}H NMR (300 MHz): δ −0.02 (q, CH_2), 1.51 (t, $C\mathit{H}_3CH_2$), 2.66 (s, CH_3N), 6.04–6.20 (c, *o*-H and *p*-H) and 6.70 (t, *m*-H).

PhN(Me)K–*i*-Bu$_2$Zn. (0.5) ^{1}H NMR (300 MHz): δ 0.12 (d, CH_2Zn), 1.16 (d, $C\mathit{H}_3CH$), 2.15 (m, CH), 2.63 (s, CH_3N), 6.16–6.21 (c, *o*-H and *p*-H) and 6.95 (t, *m*-H).

PhN(Me)K–(CH$_3$CH$_2$CHEtCH$_2$)$_2$Zn. (0.5) ^{1}H NMR (300 MHz): δ −0.10 (d, CH_2Zn), 1.15 (t, $C\mathit{H}_3CH_2$), 1.20–1.85 (c, $C\mathit{H}(C\mathit{H}_2CH_3)_2$), 2.60 (s, CH_3N), 6.15–6.23 (c, *o*-H and *p*-H) and 6.94 (t, *m*-H).

PhN(Me)K–(Me$_3$SiCH$_2$)$_2$Zn. (0.5) ^{1}H NMR (300 MHz): δ −1.01 (s, CH_2), 0.32 (s, CH_3Si), 2.68 (s, CH_3N), 6.06–6.17 (c, *o*-H and *p*-H) and 6.89 (t, *m*-H).

TolSK–Et$_2$Zn. ^{1}H NMR: δ −0.08 (q, CH_2) and 1.62 (t, CH_3).

TolSK–18C6–Et$_2$Zn. ^{1}H NMR (lower phase): δ 0.28 (q, CH_2), 1.49 (t, CH_3) and 3.00 (s, 18C6).

TolSK–*i*-Bu$_2$Zn. ^{1}H NMR: δ −0.06 (d, CH_2), 1.18 (d, CH_3) and 2.20 (m, CH).

TolSK–18C6–*i*-Bu$_2$Zn. ^{1}H NMR (lower phase): δ 0.46 (d, CH_2), 1.34 (d, CH_3), 2.22 (m, CH) and 2.99 (s, 18C6).

TolSK–(Me$_3$SiCH$_2$)$_2$Zn. ^{1}H NMR: δ −1.13 (s, CH_2) and 0.24 (s, CH_3).

TolSK–18C6–(Me$_3$SiCH$_2$)$_2$Zn. ^{1}H NMR (lower phase): δ −0.50 (s, CH_2), 0.43 (s, CH_3) and 2.98 (s, 18C6).

TolSK–(Tol)$_2$Zn. ^{1}H NMR: δ 2.15 (s, CH_3), 7.05 (d, *m*-H) and 7.99 (d, *o*-H).

Ph$_2$PK–Et$_2$Zn. ^{1}H NMR: δ −0.09 (q, CH_2) and 1.59 (t, CH_3).

Ph$_2$PK–18C6–Et$_2$Zn. ^{1}H NMR (lower phase): δ 0.30 (d, CH_2), 1.51 (t, CH_3) and 2.99 (s, 18C6).

Ph$_2$PK–*i*-Bu$_2$Zn. ^{1}H NMR: δ −0.04 (d, CH_2), 1.18 (d, CH_3) and 2.20 (m, CH).

$Ph_2PK{-}(Me_3SiCH_2)_2Zn$. ^{1}H NMR: δ -1.12 (s, CH_2) and 0.24 (CH_3).

$Ph_2PK{-}(CH_3CH_2CHEtCH_2)_2Zn$. ^{1}H NMR: δ -0.16 (d, CH_2Zn), 1.18 (t, CH_3), 1.26 (m, $C\mathit{H}_2CH$) and 1.55 (m, CH).

$Ph_2PK{-}(Tol)_2Zn$. ^{1}H NMR: δ 2.17 (s, CH_3), 7.03 (d, *m*-H) and 7.96 (d, *o*-H).

Acknowledgements

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Notes and references

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3 G. J. Kubas and D. F. Shriver, *J. Am. Chem. Soc.*, 1970, **92**, 1949; G. J. Kubas and D. F. Shriver, *Inorg. Chem.*, 1970, **9**, 1951; E. C. Ashby and R. G. Beach, *Inorg. Chem.*, 1971, **10**, 2486; E. C. Ashby and J. J. Watkins, *Inorg. Chem.*, 1973, **12**, 2493. Also see D. F. Shriver, G. J. Kubas and J. A. Marshall, *J. Am. Chem. Soc.*, 1971, **93**, 5076.

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5 Separate ^{1}H NMR absorptions are seen for the diastereotopic methylene hydrogens of *s*-Bu_2Zn. As the ROK : *s*-Bu_2Zn ratio increases the absorptions move closer together, although without obvious broadening. At ratios of ≈0.4 : 1 and higher only one absorption is seen.

6 An excess of a solution (0.8–1.2 M) of R_2Zn was added to the alkoxide. The resulting suspension was stirred and then centrifuged. A flask containing the supernatant liquid was immersed in a bath; the temperature and pressure were gradually adjusted to the desired values and the flask was left under those conditions for 12–24 h.

7 Use of higher temperatures (100–170 °C) and lower pressures (<0.5 Torr) to remove more R_2Zn from materials having MeOM : R_2Zn ratios of 0.5 : 1 led to insoluble, white solids. The Et_2Zn–MeOK oil, for example, gave such a solid when heated at 100–110 °C at 0. 1 Torr for 24 h. Even higher temperatures (≥200 °C) led to obvious decomposition and gray solid (Zn).

8 Its solubility, for example, is 2.27 g/100 g at 25–26 °C in toluene: L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, 1967, p. 911.

9 NMR absorptions of R in the **C**–**D** region were not much broader than in the other regions. Particularly when *t*-BuOK : R_2Zn >1.2 : 1, however, *t*-BuO absorptions were broader, suggesting that not all *t*-BuO groups exchanged very rapidly relative to the NMR timescale.

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11 None of the absorptions is due to an R_2Zn(18C6) rotaxane since 18C6 does not form significant amounts of a rotaxane with Bu_2Zn or $(Me_3SiCH_2)_2Zn$.[12]

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13 J. L. Atwood, in *Inclusion Compounds*, eds. J. L. Atwood, J. E. Davies and J. E. D. MacNicol, Academic Press, London, 1984, vol. 1, ch. 9.

14 For the 1 : 2 materials that are liquids this composition cannot be due to chance interactions within a crystalline solid.

15 An aliquot of a reaction (carried out on a larger scale than the NMR preparations) was hydrolysed and titrated for base. Another aliquot was hydrolysed and then heated to remove most of the benzene. Following appropriate dilutions of this solution and of commercial standard solutions, K and Zn were determined by AA analysis.

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17 As the ratio decreases below 1 : 1 species such as $(R_2Mg)_2(OR')^-$ probably are increasingly significant and these exchange rapidly with excess of R_2Mg.

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20 $(PhS)_2Zn$, for example, is insoluble in a wide range of solvents and is thought to have a polymeric structure: F. F. Said and D. G. Tuck, *Inorg. Chim. Acta*, 1982, **59**, 1.