The Nature of Dialkyl- and Diarylzinc Hydride Complexes

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Abstract: Anionic organozinc hydride complexes of the type $MH(ZnR_2)_n$, where M = Li or Na, $n = 1$ or 2, have been studied in detail. General procedures have been devised to efficiently synthesize and characterize both the previously known compounds ($R = C_6H_5$, $n = 1$; $R = C_2H_5$, $n = 2$) and new compounds ($R = CH_3$, $n = 1$ or 2) in diethyl ether, dimethoxyethane, or tetrahydrofuran. For a given organozinc, stoichiometry of the product is dependent on the activity of the metal hydride and nature of the ether solvent. Molecular weight and ^{1}H nmr data demonstrate a mobile equilibrium: $MHZnR_2 + ZnR_2 = MH[ZnR_2]_2$ for the alkylzinc systems. At room temperature, a single, average hydride resonance is observed. For solutions containing excess dialkylzinc, this signal is found at the remarkable value of *ca.* 7 ppm to the low-field side of TMS. Resonances due to individual species in equilibrium appear at low temperatures (*ca.* −60°). The 1:2 species $MH[ZnR_2]_2$ presumably contains a Zn–H–Zn bridge. Broad infrared absorptions were observed in mull spectra of $LiHZn(C_2H_5)_2 \cdot X(C_6H_5)_2O$, which can be attributed to zinc–hydrogen vibrations.

Lewis acid–base complexes between metal alkyls, or aryls, and alkali metal hydrides have been previously synthesized for aluminum,[2,3] beryllium,[4,5] and zinc.[5–7] Generally, 1:1 adducts can be isolated, but 1:2 stoichiometries, $MH(M'R_n)_2$ (M′ = Al, Zn), also have been observed.[2,6,7] In the case of zinc, only two compounds of these types have been reported. Wittig and Hornberger[5] isolated $LiHZn(C_6H_5)_2$ as a monoetherate by heating a mixture of LiH and $Zn(C_6H_5)_2$ to 90° and extracting the resulting solid with diethyl ether. Frey and coworkers[6] briefly mentioned preparing a solution of sodium hydride and diethylzinc in dimethoxyethane, and Kobetz and Becker[7] later established the limiting stoichiometry to be $NaH[Zn(C_2H_5)_2]_2$ in the presence of excess sodium hydride. However, a solid could not be isolated owing to decomposition upon solvent removal *in vacuo*. According to their work, glycol ethers would dissolve sodium hydride in the presence of diethylzinc, while diethyl ether and tetrahydrofuran would not.

The 2:1 stoichiometries in solution suggest the existence of hydride-bridged species, $(C_2H_5)_2Zn{-}H{-}Zn(C_2H_5)_2^-$. In this connection, a related compound, $[NaHBe(C_2H_5)_2]_2 \cdot 2(C_2H_5)_2O$, contains double hydride bridges between beryllium atoms, with diethyl ether coordinating to sodium ions rather than beryllium.[8]

In this study, several new organozinc hydride complexes have been prepared and characterized in various oxygen-donor solvents. Particular emphasis was placed on systems which may contain hydride bridges.

Experimental Section

Materials. Dimethylzinc and diethylzinc were prepared as neat liquids by modifications of Noller's procedure.[9] Grease-free equipment which employed O-ring joints and Teflon-in-glass needle valves were used exclusively for reaction and storage vessels. Dry alkyl iodide and excess vacuum-dried zinc–copper couple shavings (8% Cu), were allowed to react under nitrogen. In the case of methyl iodide, refluxing for 50 hr using a 60° bath was necessary to bring about conplete reaction. The resulting crystalline mass of alkylzinc iodide was then slowly heated to 180° on a preparative high vacuum line where the dialkylzinc was collected at −196°. This material was refluxed over fresh Zn–Cu shavings to remove unreacted alkyl iodide. Purity was checked by proton nmr and gas-phase infrared spectra. Diphenylzinc was prepared by refluxing zinc metal and diphenylmercury in xylene under nitrogen for 20 hr[10] and collected in a double-ended filter after crystallization,[11] mp 104–105°, lit. 107°. *Anal.* Calcd for $C_{12}H_{10}Zn$: Zn, 29.77. Found: Zn 29.82.

Lithium hydride (Matheson Coleman and Bell) claimed to be 90% pure and lithium deuteride (Metal Hydrides, Inc.) claimed to be 97% pure were used. Two types of sodium hydride were employed, both of excellent quality. The Research Inorganics Corporation's material, a 50% oil dispersion, was white and therefore presumed to be free of metal. Before use it was washed with hexane under an inert atmosphere. The second sample of NaH was obtained from Fluka AG Chemische Fabrik (Buchs, Switzerland) as nearly colorless oil-free pellets, which were found to be 99% pure by Na and H analysis.

All solvents were distilled under nitrogen and stored in glass containers equipped with Teflon-in-glass needle valves and O-ring joints. 1,2-Dimethoxyethane (MCB) was distilled from benzophenone ketyl and stored over sodium wire. Tetrahydrofuran, 2-methyltetrahydrofuran (MCB), and diethyl ether were distilled from $LiAlH_4$ and stored over calcium hydride or lithium hydride.

Synthetic Procedures. The high sensitivity of the reagents to air and moisture required manipulation on a preparative high-vacuum line[12] and transfer of all solids and solutions inside a nitrogen-filled filled drybox (Vacuum/Atmospheres Corp., Model Dri-lab HE-43-2). Reactions were carried out in a grease-free O-ring system. Ethylene–propylene rubber O rings were used wherever contact with ethers occurred. A grease-free vacuum-line filtration apparatus was used.[13] Typically, metal hydride, organozinc, and solvent were placed or distilled into an O-ring joint tube. The liquid alkylzincs were measured by vacuum-line distillation from a calibrated tube (0.01 ml graduations). The reaction mixture was agitated by a solenoid actuated stirrer[12] and maintained at 0–20° to prevent solvent distillation. Excess alkali metal hydride (which is completely insoluble in ethers) was then filtered off, using nitrogen pressure if necessary. The receiver containing the solution was removed under

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(1) Alfred P. Sloan Research Fellow, addressee for correspondence.

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nitrogen flush, capped with a needle-valve stopcock to O-ring joint adapater, and immediately analyzed or taken into the drybox for sampling.

Analyses. Solutions were hydrolyzed with water and noncondensible gases (at −196°) were collected for measurement by a Toepler pump. Ethane was quantitatively separated from hydrogen by a series of −196° U traps, but methane and hydrogen mixtures were not separated. The gases were identified by mass spectral analysis. Zinc[14] was determined by EDTA titration, and sodium[15] by precipitation as $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 6.5H_2O$. Ether content of solid complexes was determined by removal of volatiles under high vacuum, and PVT measurement of the ether fraction.

Preparation of $LiHZn(C_6H_5)_2$ and $NaHZn(C_6H_5)_2$ Complexes. In a typical preparation, diphenylzinc (1 mmol), metal hydride (3–5 mmol), and solvent (1–3 ml) were stirred for about 60 hr in the case of LiH, and 20 hr for the NaH reaction. When diethyl ether was used as solvent, slightly soluble, colorless crystals were formed, which were extracted from the excess metal hydride. The compound is a dietherate which readily loses all solvent *in vacuo*. *Anal.* Found for $NaHZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$: Zn/H_2 (upon hydrolysis), 1.03; $(C_2H_5)_2O/Zn$, 1.97. When tetrahydrofuran was used as the solvent 1:1 adducts of much higher solubility were formed, but the reaction is much slower. Preparation of the sodium salt required 60–70 hr.

Preparation of $LiHZn(CH_3)_2$ and $NaHZn(CH_3)_2$ Complexes. These compounds were synthesized in an analogous manner. With diethyl ether as solvent, $NaHZn(CH_3)_2 \cdot 2(C_2H_5)_2O$ precipitated as fine, white crystals. The very low solubility of the complex required many extractions to obtain a reasonable yield. Much more soluble complexes were obtained with tetrahydrofuran as solvent, but longer reaction periods were necessary (40 hr for the sodium salt). Unlike the diphenylzinc compound, which crystallized upon removal of THF, the dimethylzinc complex precipitated as an off-white powder, from which the last traces of THF were difficult to remove. *Anal.* Found for $NaHZn(CH_3)_2 \cdot 2(C_2H_5)_2O$: (noncondensable gases upon hydrolysis)/Zn, 2.90 (calcd, 3.00); $(C_2H_5)_2O/Zn$, 1.99. Found for $NaHZn(CH_3)_2$ in THF solution: (noncondensable gases upon hydrolysis)/Zn, 2.97 (calcd, 3.00); Na/Zn, 1.03.

Preparation of 1:2 Complexes, $MH(ZnR_2)_2$, in Dimethoxyethane. Dialkylzinc (1–3 mmol) and dimethoxyethane (1–2 ml) were stirred with at least 5 mmol of LiH or NaH for 50–60 hr or 15–20 hr, respectively. Despite the presence of excess metal hydride, only complexes of 1:2 stoichiometry were obtained, for both the dimethylzinc and diethylzinc reactions. Longer reaction periods did not decrease the alkylzinc/hydride ratio. Very concentrated, colorless solutions could be obtained, but solvent removal *in vacuo* resulted in loss of dialkylzinc and precipitation of alkali metal hydride, in agreement with Kobetz and Becker.[7] *Anal.* Found for $LiH[Zn(C_2H_5)_2]_2$ in DME solution: H_2 (upon hydrolysis)/C_2H_6(upon hydrolysis)/Zn, 1.00/3.89/2.01 (calcd, 1/4/2); integrated ratio of alkyl to hydridic protons in the nmr, 22:1 (calcd, 20:1). Found for $LiH[Zn(CH_3)_2]_2$ in DME solution: (noncondensable gases upon hydrolysis)/Zn = 2.54 (calcd, 2.50); integrated ratio of alkyl to hydridic protons in the nmr, 12:1 (calcd, 12:1).

Physical Measurements. ^1H nuclear magnetic resonance spectra were recorded on a Varian A60, equipped with a V-6040 variable temperature controller. Unless stated otherwise, the probe temperature was 35 ± 2° for all samples, which were either sealed on the vacuum line or syringed and capped with rubber septa inside the drybox. Samples sealed in nmr tubes appeared to be stable for a month or two but slow deposition of zinc was eventually observed.

Infrared spectra were obtained from Nujol or Fluorolube mulls between KBr plates using a Beckman IR 10. For solution studies, demountable Irtran-windowed cells with a 0.1-mm path length were employed.

Raman spectra were obtained using an instrument consisting of a SPEX 1400-II double monochromator and 6328 Å He–Ne laser excitation.[16] Solutions were observed in sealed A60 nmr tubes, and solid samples in Pyrex tubes. After each run, the position of the 6328.17-Å laser line was observed to calibrate the wavelength pipping signal.

Molecular weight determinations were performed using vapor pressure depression techniques, at 23 ± 0.01°. Depressions of 3–8 ± 0.05 mm were observed. Solute concentrations were varied by solvent addition or removal. Since thorough degassing of the liquid phase is essential, the latter procedure was employed for hydride containing samples. A previously described grease-free tensimeter was employed for molecular weight and pressure–composition studies.[17]

Results and Discussion

Stoichiometries of Formation. As shown in Table I each of the three organozincs exhibits unique coordination stoichiometries. Dimethylzinc appears to be intermediate in character between diphenylzinc and diethylzinc. The cation apparently has little bearing on the final outcome, since there are no gross differences in stoichiometry between lithium and sodium salts. The diphenylzinc–dimethoxyethane system leads to nonstoichiometric ratios, and the diethylzinc-diethyl ether system appears to react incompletely with metal hydride, even after 5 days of stirring. (For the former system the limiting stoichiometry was independently established by distillation of DME onto solid, unsolvated $NaHZn(C_6H_5)_2$. This resulted in precipitation of NaH and formation of a solution with a 1.6 zinc/hydride ratio, which is similar to that obtained by direct synthesis.) In tetrahydrofuran solution $Zn(C_2H_5)_2$/hydride ratios as low as 1.64 have been obtained with lithium hydride, or sodium hydride obtained from Research Inorganics Corp. However, Fluka sodium hydride with diethylzinc in either THF or DME gave ratios greater than 5, indicating incomplete reaction. Apparently the activity is quite different for the sodium hydride from these two sources. Our success in obtaining alkylzinc hydride complexes in THF or diethyl ether solution may be due to the greater reactivity of our sodium hydride samples than those used by Kobetz and Becker.[7]

Table I. Limiting Zinc/Hydride Ratios Obtained for Reactions of Organozincs with Excess LiH or NaH in Various Solvents

Organozinc	1,2-Dimethoxyethane	Tetrahydrofuran	Diethyl ether
$Zn(C_6H_5)_2$	1.6–1.8[a,b]	1.0[c]	1.0[c]
$Zn(CH_3)_2$	2.0	1.0[c]	1.0[c]
$Zn(C_2H_5)_2$	2.0	1.6[a]	3.8–3.1[a,b]

[a] Solutions with nonstoichiometric, but essentially reproducible ratios result in these instances. [b] The first value corresponds to LiH and the second to NaH reactions. [c] A solid complex of this stoichiometry may be isolated.

Nuclear Magnetic Resonance Experiments. A single peak, with a remarkable low-field chemical shift (Table II), due to hydridic protons was found for $LiH[Zn(C_2H_5)_2]_2$ in dimethoxyethane. The identity of the hydride signal was confirmed by the nmr spectrum of $LiD[Zn(C_2H_5)_2]_2$ which had no low-field signal but was identical in other respects with the protium form. Single resonances attributable to hydridic protons were observed for all soluble complexes. For sodium salts they occur at significantly higher fields (about 1 ppm) than for lithium salts, which may be due to strong ion-pair interaction between cation and hydridic anion. Solvent and organozinc splitting patterns remain un-

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[14] A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Longmans, Green, and Co. Ltd., London, 1661, p 433.

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[17] Reference 12, p 59.

Table II. Observed Chemical Shifts

Organozinc	Metal hydride	Solvent	Solvent/hydride	Zinc/hydride	δ_{int}[a]	$\delta_{hydride}$[b]
$Zn(C_2H_5)_2$					0.87	
$Zn(C_2H_5)_2$		$(C_2H_5)_2O$			0.95	
$Zn(C_2H_5)_2$		THF			1.07	
$Zn(C_2H_5)_2$		DME			1.11	
$Zn(C_2H_5)_2$	LiH	DME	4.8	2.00	1.25	5.98
$Zn(C_2H_5)_2$	NaH	DME	5.8	2.00	1.36	4.90
$Zn(C_2H_5)_2$	NaH	DME	11.4	2.71	1.34	5.69
$Zn(C_2H_5)_2$	NaH	DME	11.4	8.92	1.12	7.00
$Zn(CH_3)_2$	LiH	DME	4.0	2.00		5.44
$Zn(CH_3)_2$	NaH	DME	4.0	2.00		4.15
$Zn(CH_3)_2$	NaH	THF	13.3	1.00		3.40
$Zn(CH_3)_2$	NaH	THF	15.0	6.00		6.93
$Zn(C_6H_5)_2$		$(C_2H_5)_2O$			0.4	
$Zn(C_6H_5)_2$		THF			0.5	
$Zn(C_6H_5)_2$	NaH	THF	15.0	1.00	0.9	4.33

[a] $\delta_{int} = \delta(CH_2) - \delta(CH_3)$ ppm for $Zn(C_2H_5)_2$; $\delta_{int} = \delta($*meta, para*$) - \delta($*ortho*$)$ ppm where mean values of the multiplets were employed for $\delta($*meta, para*$)$ and $\delta($*ortho*$)$ of $Zn(C_6H_5)_2$. [b] Downfield from tetramethylsilane, ppm.

changed upon hydride complex formation. However, internal chemical shifts δ_{int} between the *ortho* and *meta-para* protons of diphenylzinc, and the methyl and methylene protons of diethylzinc, do exhibit significant variation.

Ladd[18] has shown that protons *ortho* to the metal–carbon bond in phenylmetallic compounds experience a large deshielding effect. Further he has shown that metals of lower electronegativity give greater deshielding of *ortho* protons and increased δ_{int}. Relative values of δ_{int} for diphenylzinc in various ethers conform to Ladd's observation since the most basic ethers, which should decrease the effective electronegativity of zinc, lead to the largest values of δ_{int} (Table II). Similarly, the very large increase in δ_{int} upon forming the 1:1 hydride adduct (Table II) confirms the assumption that the hydride ion is coordinated directly to zinc.

Narasimhan and Rogers[19] associated δ_{int} for the diethylzinc case with inductive shielding on the methylene protons. The methylene quartet shifts to higher field upon coordination of bases to zinc owing to increased electron density about zinc. The absolute value of δ_{int} increases since, in diethylzinc, the quartet is upfield from the triplet, which is a reversal of the normal order for ethyl compounds. Once again, complexation of hydride to diethylzinc leads to a large increase in δ_{int}. Shift of the methyl resonance to higher field in the dimethylzinc system is analogous.

Of greater consequence is the monotonic downfield shift of the hydride resonance exhibited upon increasing the dialkylzinc/hydride ratio by adding dialkylzinc to a solution of dialkylzinc hydride (Figure 1). These shifts are several parts per million in magnitude and can be accounted for by a rapid chemical exchange process between two or more species. A reasonable equilibrium would involve a 1:1 adduct and a hydride-bridged, 1:2 adduct.

$$M^+HZnR_2^- + ZnR_2 = M^+R_2ZnHZnR_2^- \qquad (1)$$

Assuming eq 1, the chemical shift of hydride in the 1:1 species, $HZnR_2^-$, has been experimentally determined to be 3.40 ppm, for a THF solution of $NaHZn(CH_3)_2$ (Table II). Addition of dialkylzinc to the solution would favor the right side of the equilibrium, increasing the concentration of 1:2 species. A limiting value of 7 ppm downfield from TMS is attained when the zinc/hydride ratio approaches 10 for both diethylzinc and dimethylzinc systems. This value, which is believed to be the lowest field resonance ever observed for a hydridic hydrogen, represents the chemical shift of hydride in the 1:2 species.

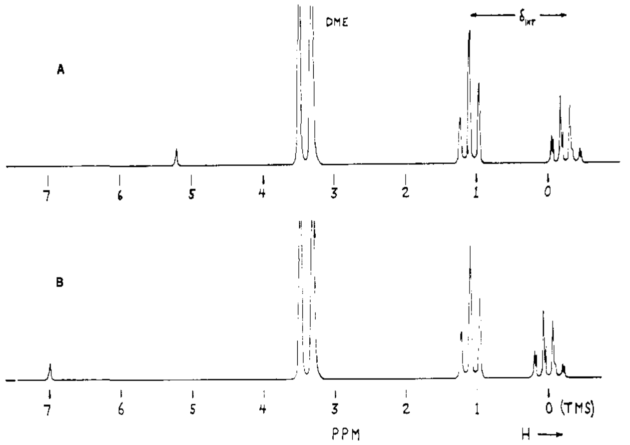

Figure 1. ^1H nmr spectra of sodium hydride and diethylzinc in dimethoxyethane with (A) zinc/hydride = 2 and (B) zinc/hydride = 9 (excess diethylzinc). The intensity of the hydride resonance at 7 ppm is exaggerated for clarity.

An equilibrium study was carried out for the NaH/$Zn(C_2H_5)_2$/THF system by adding known quantities of diethylzinc to an nmr tube containing a solution with initial zinc/hydride ratio of 1.75 and THF/$Zn(C_2H_5)_2$ = 5.8. Apparent equilibrium constants were calculated using the exchange-averaged chemical shift of the hydride as a measure of the composition[20] and results are summarized in Table III. The high concentrations are probably responsible for most deviations, but the consistency of K values appears adequate to demonstrate the existence of the proposed equilibrium. The

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(19) P. T. Narasimhan and M. T. Rogers, *J. Amer. Chem. Soc.*, **82**, 5983 (1960).

(20) The general calculational procedure is described by C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962). This was adapted to the present case by allowing their δ_{free} to represent the limiting low-field chemical shift (7 ppm) which is attributed to the hydride in species C (their notation). It may be shown that the present system requires a least-squares fit of $\delta_{free} - \delta_{obsd}$ *vs.* $(1 - C/A)$ with the fitting repeated as K is varied until a "best value" is obtained.

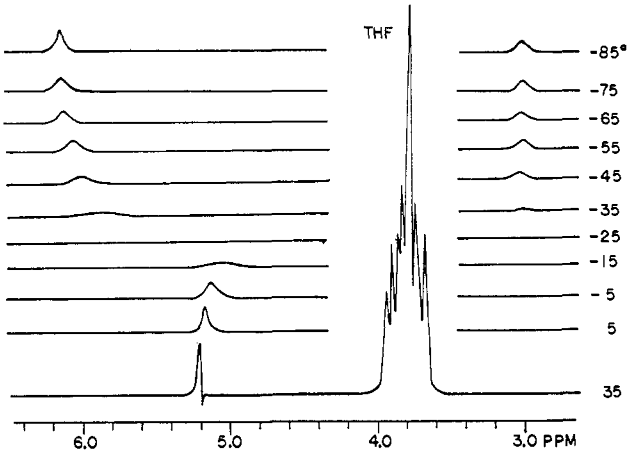

Figure 2. Low-temperature ^1H nmr spectra of lithium hydride and dimethylzinc in a mixture of THF and 2-methyl-THF, with zinc/hydride = 1.55, 2-methyl-THF/Zn = 3.2, and THF/Zn = 4.1.

loss of dialkylzinc upon removal of solvent from the 1:2 complexes (see previous section) is consistent with this mobile equilibrium.

The hydride signal also shifts upon sample dilution, but to a much lesser degree. For a dimethylzinc/sodium hydride ratio of 1.9 and THF/Zn ratios of 8.0 and 16.0, the respective hydride signals occurred at 6.05 and 5.95 ppm. Thus, dilution gives rise to shielding of the hydride nucleus, which can be interpreted in terms of equilibrium 1 as a decrease in concentration of 1:2 species. Molecular weight measurements exhibit a similar trend, which will be discussed later. Surprisingly the addition of diphenylzinc to $NaHZn(C_6H_5)_2$ in THF does not lead to a downfield shift of the hydride peak. Apparently equilibrium 1 is not significant for this system.

Table III. Apparent Equilibrium Constant for the System[a] $NaHZn(C_2H_5)_2 + Zn(C_2H_5)_2 = NaH[Zn(C_2H_5)_2]_2$

Zinc/hydride	δ_{obsd}[b]	% dimer	K[c] (mole fraction)$^{-1}$
1.75	4.64	60.7	120
1.79	4.78	63.3	117
1.97	5.23	72.2	104
2.48	6.10	86.5	107
3.00	6.55	91.5	157

[a] Tetrahydrofuran, 35°, THF/NaH = 9.1. [b] Downfield from TMS, ppm. [c] Back-calculated values; the "best" value of K = 111 ± 14 (mole fraction)$^{-1}$, see footnote 20.

In order to slow chemical exchange and observe resonances due to individual species in equilibrium, several low temperature experiments were performed. Dimethoxyethane and THF were found to be unsuitable solvents since exchange still occurred even down to their freezing points (*ca.* $-60°$), but 2-methyltetrahydrofuran (mp $< -90°$) or mixtures of 2-methyl-THF and THF were found to be suitable for the dimethylzinc hydride system. Figure 2 shows the broadening of the single hydride resonance, its eventual disappearance, and at lower temperatures the appearance of two new signals, which presumably arise from 1:1 and 1:2 species. Interestingly, the rate of chemical exchange is much higher for sodium salts than lithium salts, which may reflect differences in ion pairing energy. In the former case, the two signals are barely discernible even at $-90°$, but for the latter, two peaks are clearly visible at $-45°$. The low-field signal at -6.1 ppm is 0.8 ppm upfield from that observed at 35° for a solution with a dimethylzinc/hydride ratio of 6. Both signals are thought to represent the hydride-bridged species since the discrepancy is not considered significant in view of the variety of effects which may influence the chemical shifts at these two temperatures.

Table IV. Molecular Weight Determinations in Tetrahydrofuran at 23°

Compounds	Mole fraction of solvent	Obsd mol wt	Cor mol wt[a]
Sodium tetraphenylborate (calcd mol wt, 342)	0.9543	301	362
	0.9675	316	361
	0.9761	319	352
	0.9811	315	339
Lithium bromide (calcd mol wt, 87)	0.9662	115	139
	0.9786	111	125
	0.9842	106	115
	0.9871	102	109
$NaHZn(CH_3)_2$ (calcd mol wt, 119)	0.9565	102	126
	0.9631	99	120
	0.9679	99	115
	0.9716	96	109
	0.9757	99	109
$NaH[Zn(CH_3)_2]_2$ (calcd mol wt, 215)	0.9458	121	154[b]
	0.9588	127	152[b]
	0.9637	127	149[b]
	0.9711	129	145[b]
	0.9747	130	144[b]

[a] Corrected for solvent coordination, assuming four molecules of THF coordinating to each cation and one molecule of THF coordinating to each zinc atom. [b] These values represent an average molecular weight for all solute species. Assuming the equilibrium $NaHZn(CH_3)_2 + Zn(CH_3)_2 = NaH[Zn(CH_3)_2]_2$ a value of K = 113 ± 10 (mole fraction)$^{-1}$ may be calculated from these data.

Molecular Weight Studies. These studies were performed to gain further insight into the molecularity of the complexes. However, the determination of molecular weights of these ionic substances in a solvent such as THF may be complicated by partial dissociation of ion pairs and coordination of solvent to zinc or alkali metal cations. The former may not be a serious problem, since a model compound, sodium tetraphenylborate, has been shown to exist mainly as solvent-separated ion pairs in THF, with $K_{diss} = 10^{-4}$ at 25°.[21] However, coordination of solvent to solute, which decreases the amount of "free" solvent, leads to a larger vapor pressure depression than expected in the absence of coordination. If the number of coordinating solvent molecules is known, a correction can be applied. For $NaAl(n\text{-}C_4H_9)_4$ in cyclohexane, significant 4:1 coordination of THF to sodium ion occurs.[22] Anion solvation is negligible for this compound, but in the zinc systems, there is one open coordination site. Thus, up to five molecules of solvent might be expected to coordinate to a compound of the type $NaHZnR_2$, but the nature of ion pairing could reduce this number. Table IV shows the results for two model compounds and two zinc compounds. The sodium tetraphenylborate values corrected for solvation show very good agree-

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(22) E. Schaschel and M. C. Day, *ibid.*, **90**, 503 (1968).

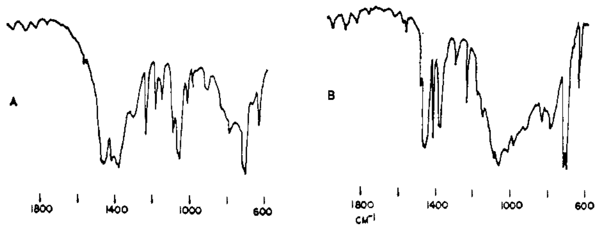

Figure 3. Infrared spectra for Nujol mulls of (A) $LiHZn(C_6H_5)_2$ and (B) $LiHZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$. The broad features at 1250–1650 cm^{-1} (A) and 900–1200 cm^{-1} (B) are due to Zn–H modes.

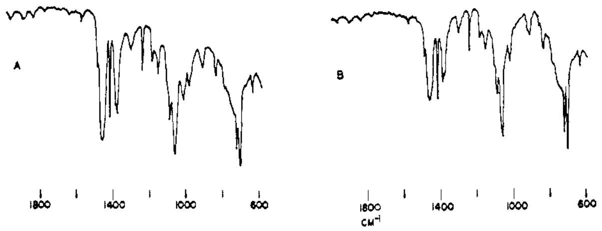

Figure 4. Infrared spectra for Nujol mulls of (A) $LiDZn(C_6H_5)_2$ and (B) $LiDZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$. A broad underlying feature at 900–1200 cm^{-1} (A) due to Zn–D modes is discernible.

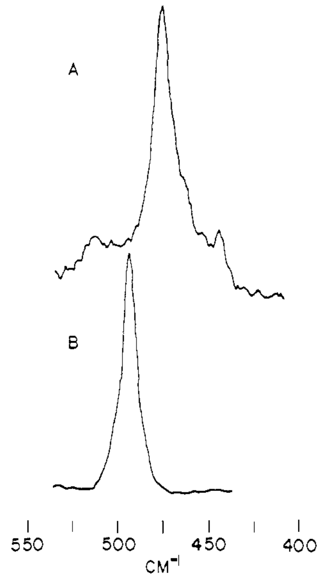

Figure 5. Raman spectra in dimethoxyethane of (A) $LiH[Zn(CH_3)_2]_2$ and (B) $Zn(CH_3)_2$, showing symmetric zinc–carbon stretching modes.

ment with the calculated value for an ion pair. Lithium salts tend to form solutions with abnormal colligative properties,[23] such as very low vapor pressures, which would result in observed molecular weights higher than calculated. Thus the high values for lithium bromide, shown in Table IV, are expected; however, extrapolation to infinite dilution gives good agreement with an ion-pair molecular weight. The data for $NaHZn(CH_3)_2$ indicate that it does possess this molecularity in solution. Thus, unlike the analogous beryllium compound in the solid state,[8] the anion is monomeric and not hydride-bridged in solution.

The molecular weight data given in Table IV for the solute of the composition $NaH[Zn(CH_3)_2]_2$ require special consideration since the proposed equilibrium (eq 1) appears to reduce the observed molecular weight through dissociation of the hydride-bridged species. Therefore the data were used along with the expected molecular weights for the species in equilibrium 1 and an equilibrium constant was calculated. A K of 113 ± 10 (mole fraction)$^{-1}$ was obtained. This compares favorably with the value of 111 which was obtained for the diethylzinc system by nmr measurements.

Infrared and Raman Studies. This aspect of the study was less fruitful than expected, but some interesting information has been obtained. A terminal zinc–hydride stretch should occur somewhere in the range 1600–2100 cm^{-1}.[24] However, such a band has not been located in the infrared or Raman for solid or solution spectra of 1:1 or 1:2 alkylzinc complexes, even though this region is virtually free from interfering organozinc or solvent bands. The only evidence for Zn–H vibrational frequencies comes from infrared spectra of the diphenylzinc hydrides in Nujol mulls. For $LiHZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$ a broad absorption is observed in the 900–1200-cm^{-1} region (Figure 3). As may be seen in Figure 3, this shifts to the 1250–1650-cm^{-1} region upon ether removal. The assignment of these broad features to hydride vibrations is verified by the spectra of $LiDZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$ and its desolvated partner, Figure 4, where the features mentioned above are absent. It appears that the ether-free deuterium complex has an infrared absorption around 900–1200 cm^{-1}, which agrees with the expected isotopic shift. It is possible that the very low frequency observed for the dietherate represents a metal–hydride stretch frequency of a double-hydride bridged species analogous to $[NaHBe(C_2H_5)_2]_2 \cdot 2(C_2H_5)_2O$.

It is well known that the symmetric zinc–carbon stretching frequency is significantly reduced upon complexation of an alkylzinc.[25] In the Raman spectra of dimethylzinc moieties, the symmetric zinc–carbon stretch shifted significantly upon complex formation. For example, it occurs at 504 cm^{-1} (lit.[26] 504 cm^{-1}) for neat dimethylzinc and shifts to 494 cm^{-1} for a solution in DME. The effect is even more pronounced (Figure 5) upon hydride complexation. The major peak, presumably due to the 1:2 species, now appears at 475 cm^{-1} for a DME solution of $LiH[Zn(CH_3)_2]_2$ while minor peaks and shoulders are attributed to other equilibrium species, notably $HZn(CH_3)_2^-$, to which the 445-cm^{-1} band possibly may be assigned. A study of the diphenylzinc system, using solid samples, yielded no useful information. However, since the Raman spectrum of diphenylzinc apparently has not been reported in the literature, the observed lines are given in Table V, along with those for its hydride complexes.

Etherate Formation. The pressure–composition diagram (Figure 6) was determined for a sample of the sodium hydride–diphenylzinc complex freshly crystallized from ether solution. A total of 2 ether molecules are retained per zinc, however a break at 0.5 ether/zinc shows that 1.5 of these are weakly held. Similarly, the lithium hydride–diphenylzinc complex forms a dietherate but a break occurs at 1 ether/zinc,

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(23) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 242.

(24) An 1825-cm^{-1} Zn–H absorption has been observed in the infrared spectrum of $[HZnN(CH_3)C_2H_4N(CH_3)_2]_2$: N. A. Bell and G. E. Coates, *J. Chem. Soc., A*, 823 (1968).

(25) D. F. Evans and I. Wharf, *ibid., A*, 783 (1968).

(26) H. S. Gutowsky, *J. Chem. Phys.*, 17, 128 (1949).

Table V. Observed Raman Frequencies (cm^{-1}) for Solid Phase Samples

$Zn(C_6H_5)_2$	$NaHZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$	$NaHZn(C_6H_5)_2$	$LiHZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$	$LiDZn(C_6H_5)_2 \cdot 2(C_2H_5)_2O$
209 (s)				
397 (w)			387 (w)	
455 (w)			444 (w)	
619 (m)	624 (m)	623 (m)	623 (m)	623 (m)
647 (m)	645 (m)	642 (m)	644 (m)	642 (m)
666 (m)				
732 (w)				
870 (w)	845 (w)		846 (w)	846 (w)
919 (w)				
999 (vs)	998 (vs)	998 (vs)	998 (vs)	997 (vs)
1022 (w)	1023 (w)	1023 (w)	1023 (w)	1023 (w)
1029 (w)				
1157 (w)		1156 (w)	1153 (w)	1154 (w)
1164 (w)				
1189 (w)				
1200 (w)	1195 (w)	1194 (w)	1195 (w)	1196 (w)
	1457 (w)		1457 (w)	1455 (w)
1560 (w)	1559 (w)	1561 (w)	1559 (w)	1558 (w)
1575 (s)	1571 (s)	1572 (s)	1573 (s)	1571 (s)
3448 (s)	3449 (s)	3448 (s)	3448 (s)	3448 (s)

indicating the second, more stable phase is a monoetherate. At 0° dissociation pressures for the dietherates are 51 and 7 mm for the sodium and lithium compounds, respectively, while the lower etherates have vapor pressures of 2 and *ca.* 0.5 mm, respectively. These results indicate that the ether is associated with the alkali metal in the solid state.

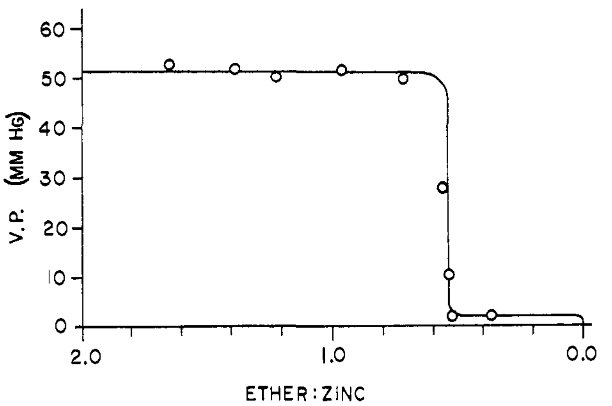
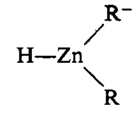


Figure 6. Phase diagram for the $NaHZn(C_6H_5)_2$–$(C_2H_5)_2O$ system, showing equilibrium vapor pressure of ether over the solid phase as a function of ether/$NaHZn(C_6H_5)_2$ in the solid phase.

Summary

Synthetic studies as well as nmr and solvent vapor-pressure depression indicate that two types of dialkylzinc hydride complexes exist in ether solvents. The 1:1 H/Zn containing species must contain a terminal zinc–hydrogen bond.



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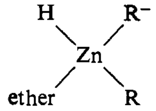
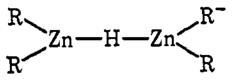


The hydride nmr signal for the 1:1 complex $HZnR_2^-$ is *ca.* 3 ppm higher field than in the 1:2 complex $H(ZnR_2)_2^-$. This difference is much larger than that between the corresponding alkyl groups. Therefore it is probable that a hydride rather than an alkyl bridge is involved in the 1:2 complex.



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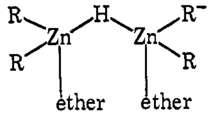

For solutions of intermediate stoichiometry the two complexes are in mobile equilibrium, yielding a single average nmr signal for the hydride at room temperature. Molecular weight measurements, as well as differences in nmr coalescence temperatures for the above-mentioned exchange averaging, show that the alkali metal is associated with these anions. By contrast to the dialkylzincs, diphenylzinc appears to form only 1:1 complexes with LiH or NaH.

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