

The reactions in mechanisms 6-8 were essentially represented as concerted reactions. Preequilibria involving Cr^{2+} or protons are not depicted explicitly. This is of course arbitrary and cannot be justified on kinetic grounds alone. The only excuse we may have for omitting such preequilibria is that we obtained no evidence for them.

Acknowledgment. We wish to thank Mrs. E. Kissa-Meidani for technical assistance.

Registry No. 1, 76156-52-0; 1, intermediate complex, 76136-72-6; 2, 76136-73-7; 3, 76156-53-1; 4, 76136-74-8; maleic acid, 110-16-7; fumaric acid, 110-17-8; succinic acid, 110-15-6; acetic acid, 64-19-7; V^{2+} , 15121-26-3.

Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

Nature of Alkyl-Hydrogen Exchange Reactions Involving Aluminum and Zinc. 5. Reactions of Diphenylzinc with Lithium Aluminum Hydride in Diethyl Ether and Tetrahydrofuran. Preparation of PhZn_2H_3

E. C. ASHBY* and A. B. GOEL

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The reactions of diphenylzinc with lithium aluminum hydride in diethyl ether and THF have been studied in detail. Although ZnH_2 as an insoluble solid and $\text{LiAlPh}_n\text{H}_{4-n}$ in solution are formed when the $\text{Ph}_2\text{Zn}:\text{LiAlH}_4$ ratio is 2:1, 3:2, 1:1, and 1:2 in ether, no ZnH_2 is formed when Ph_2Zn is allowed to react with LiAlH_4 in THF in ratios varying from 4:1 to 1:2. Instead, PhZn_2H_3 is formed which is insoluble in THF. This compound is reported for the first time, and its existence is supported by IR, X-ray powder diffraction, and DTA-TGA studies. When ZnH_2 , prepared by the reaction of Ph_2Zn with LiAlH_4 in ether, was allowed to react with Ph_2Zn and cyclopentadiene independently in THF, the insoluble products PhZn_2H_3 and CpZn_2H_3 formed. Reaction of cyclohexanol with ZnH_2 is also discussed.

Introduction

In 1951, Schlesinger and co-workers¹ reported the formation of ZnH_2 in the reaction of LiAlH_4 with Me_2Zn in ether solution. Recently, we have reported the formation of triple metal complexes of the types $\text{LiZnMe}_2\text{AlH}_4$ and $\text{LiZn}_2\text{Me}_4\text{AlH}_4$ ^{2,3} by the reaction of LiAlH_4 with Me_2Zn in THF. The reaction of Ph_2Zn with LiAlH_4 in THF was considered of interest in order to determine if similar triple metal complexes containing a phenyl group could possibly be prepared or whether this reaction would lead to PhZnH in a manner similar to the reaction of LiAlH_4 with Ph_2Mg in THF which produced PhMgH .^{4,5} We have prepared a number of RMgH compounds,^{4,5} and other workers have prepared several RBeH compounds.^{6,8} More recently we reported the first stable organozinc hydride⁹ followed by a report of the preparation of $\text{RZnH}\cdot\text{py}$ complexes.¹⁰ Herein we wish to report the preparation of PhZn_2H_3 and the details of the reaction of LiAlH_4 and Ph_2Zn in ether and THF.

Experimental Section

Apparatus. Reactions were performed under dry nitrogen at the bench or in a glovebox equipped with a recirculating system using manganese oxide to remove oxygen.¹¹ Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer using KBr and CsI liquid or mull cells. NMR spectra were recorded on a Varian-A-60. The X-ray powder diffraction pattern data were obtained on a Phillips-

Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu $\text{K}\alpha$ radiation. " d " spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually. DTA-TGA data were obtained under vacuum with the use of a modified Mettler Thermoanalyzer II.

Analyses. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.¹¹ Lithium was determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc in the absence of other metals was determined by EDTA titration. Phenyl groups present in the complexes were determined as benzene by hydrolysis of the samples with water and analyzing the filtrate by GLC using a SE 30 column at 70 °C. Mesitylene was used as the solvent, and hexanol was used as the internal standard.

Materials. Solutions of LiAlH_4 (Ventron, Metal Hydrides Division) were prepared in ether and THF in the usual manner. Dimethylzinc was prepared by the procedure of Noller.¹² Methyl iodide was obtained from Fisher Scientific. The iodide was dried over anhydrous MgSO_4 and distilled prior to use. The zinc-copper couple was obtained from Alfa Inorganics. The reactions of the zinc-copper couple with methyl iodide were allowed to proceed overnight. Dimethylzinc was distilled from the reaction mixture under nitrogen. Diethyl ether and tetrahydrofuran (Fisher Certified reagent grade) were distilled under nitrogen over LiAlH_4 and NaAlH_4 , respectively. Diphenylzinc was prepared by the reaction Ph_2Hg with a 100% excess of zinc metal at 130-140 °C.

Lithium tetraphenylaluminate (LiAlPh_4) was prepared by the addition of PhLi solution in ether to Ph_3Al in ether with continuous stirring. A viscous insoluble layer separated from the ether and crystallized from solution overnight. The white solid is soluble in THF but insoluble in diethyl ether. Analysis of the white solid gave the following results. Anal. Calcd for $\text{LiAl}(\text{C}_6\text{H}_5)_4$: Li:Al:Ph = 1.0:1.0:4.0. Found: 1.00:1.06:4.10.

X-ray powder diffraction data for LiAlPh_4 showed the following lines (\AA): 8.5 s, 6.8 w, 6.0 w-m, 5.4 vw, 4.8 vw, 4.4 vs, 4.15 s, 3.8 w, 3.25 m-s, 2.95 m, 2.82 w, 2.76 w, 2.63 w, 2.55 w, 2.43 w, 2.30 vw, 2.25 vs, 2.13 vs, 2.05 vs, 2.00 vw, 1.90 w, 1.78 w, 1.58 w.

Infrared Study of the Reaction of LiAlH_4 with Ph_2Zn . (a) In Diethyl Ether. A 100-mL portion of a 0.10 M solution of Ph_2Zn in diethyl

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Table I. Elemental Analyses of the Reaction Products of Ph_2Zn and LiAlH_4 (in 1:2, 1:1, and 3:2 Molar Ratio) in Et_2O

reactants			anal. (ratio)			$\nu(\text{Al-H})$ of filtrate, cm^{-1}	chem shift separation (δ_{int})
mmol of Ph_2Zn	mmol of LiAlH_4	ratio	precipitate Zn:Al:H	filtrate Li:Zn:Al:H:Ph			
4.50	9.02	1:2	1.00:0.06:2.12	1.02:0.02:1.00:2.92:1.04	1730	0.61	
4.60	4.60	1:1	1.00:0.04:2.09	1.04:0.02:1.00:1.98:2.06	1712	0.61	
12.35	8.2	3:2	1.00:0.03:2.06	1.04:0.04:1.03:1.00:3.05	1679	0.60	

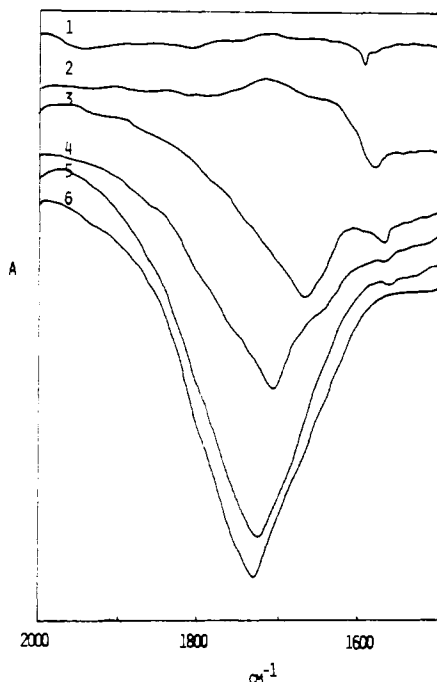


Figure 1. Infrared spectra of the supernatant solution obtained on addition of LiAlH_4 to Ph_2Zn in diethyl ether. $\text{Ph}_2\text{Zn}:\text{LiAlH}_4$ ratio: (1) pure Ph_2Zn ; (2) 2:1; (3) 3:2; (4) 1:1; (5) 1:2; (6) pure LiAlH_4 .

ether was placed in a three-neck round-bottom flask equipped with a condenser, a magnetic stirrer, and an addition funnel. To this was added dropwise a 0.7 M solution of LiAlH_4 in diethyl ether in regular increments with continuous stirring. After each addition, the mixture was stirred for 0.5 h and the precipitate formed allowed to settle. A small sample of the clear supernatant was withdrawn for infrared analysis. The addition of LiAlH_4 was continued until it was in large excess. The entire experiment was repeated by reversing the mode of addition with use of 0.65 M Ph_2Zn and 0.375 M LiAlH_4 solutions. Figure 1 shows the infrared spectra of starting materials and the solutions produced on reaction of Ph_2Zn and LiAlH_4 at several stoichiometric ratios.

(b) In THF. The above experiment was repeated in a similar manner by using Ph_2Zn and LiAlH_4 in THF. The infrared spectra of the supernatant solutions were recorded (Figure 2).

Reaction of Ph_2Zn with LiAlH_4 in 1:2, 1:1, 3:2, and 2:1 Stoichiometric Ratios in Diethyl Ether. Lithium aluminum hydride (0.375 M) solution in diethyl ether was added in various stoichiometric proportions to magnetically stirred Ph_2Zn solution in diethyl ether (0.70 M) at a very slow rate (due to the slightly exothermic nature of the reaction) so that the reaction temperature could be kept at 25 °C. Reaction mixtures were stirred for an additional 0.5 h, and the resulting precipitate was filtered, washed with ether, and dried under vacuum. Elemental analyses of the precipitates and filtrates are summarized in Table I.

Reaction of Ph_2Zn with LiAlH_4 in 4:1 Ratio in THF. To 20 mL of a 0.4 M Ph_2Zn solution in THF (8.0 mmol) was added 1.55 mL of 1.3 M LiAlH_4 in THF (2.01 mmol) dropwise with continued stirring at room temperature. No precipitate formed, and the infrared spectrum of the resulting clear solution (scanned after $\frac{1}{2}$ h) exhibited the absence of any Al-H stretching bands above 1650 cm^{-1} . The analysis of the solution revealed that it contained Li, Zn, Al, H, and Ph in ratios 1.04:4.04:1.00:3.95:8.15.

When the above solution was kept at room temperature overnight, some colorless crystals separated from solution. The crystals, after

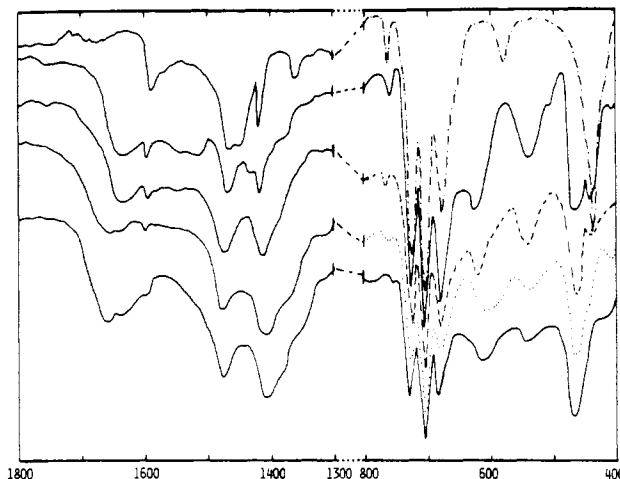


Figure 2. Infrared study of the reactions of Ph_2Zn with LiAlH_4 in tetrahydrofuran in ratios (1) pure Ph_2Zn , (2) 4:1, (3) 8:3, (4) 2:1, and (5) 1:1.

washing with THF and drying under a dry nitrogen stream, were analyzed. Anal. Calcd for $\text{PhZn}_2\text{H}_3 \cdot 0.5\text{THF}$: Zn:H:Ph:THF = 1.00:1.50:0.50:0.25. Found: 1.00:1.49:0.51:0.27. Anal. Calcd for PhZn_2H_3 after drying under reduced pressure for 21 h: Zn:H:Ph = 1.00:1.50:0.50. Found: 1.00:1.48:0.49. The solid contained about 64% of the starting zinc.

Reaction of Ph_2Zn with LiAlH_4 in 8:3 Ratio in THF. When Ph_2Zn (8.0 mmol) and LiAlH_4 (3.0 mmol) in THF (22.5 mL) were allowed to react in the above-described manner, a clear solution resulted. The IR spectrum of the solution gave no Al-H stretching band above 1650 cm^{-1} . When the above solution was kept at room temperature overnight, a crystalline solid separated out of solution which after drying under vacuum corresponded in analysis (Anal. Calcd for PhZn_2H_3 : Zn:H:Ph = 1.00:1.50:0.50. Found: 1.00:1.48:0.51.), IR spectrum, and X-ray powder pattern to the product of the above reaction. The insoluble solid after 24 h contained about 90% of the starting zinc.

Reaction of Ph_2Zn with LiAlH_4 in 2:1 Ratio in THF. A total of 4.0 mmol of LiAlH_4 in THF (3.1 mL) were added dropwise to a well-stirred solution of Ph_2Zn (8.0 mmol) in THF to give a clear solution. The reaction solution after 1 h of stirring was analyzed, which showed that it contained Li, Zn, Al, H, and Ph in the ratios 1.03:2.02:1.00:3.92:4.08. The infrared spectrum of the solution exhibited a band at $\sim 1660\text{ cm}^{-1}$ (characteristic of LiAlHPh_2). After the solution was kept overnight at room temperature, a crystalline solid appeared which corresponded in analysis to PhZn_2H_3 . Anal. Found: Zn:H:Ph = 1.00:1.47:0.51. The X-ray powder pattern and infrared spectrum in Nujol were identical with the products of the above reactions.

Reaction of Ph_2Zn with LiAlH_4 in 1:1 Ratio in THF. The reaction of Ph_2Zn (4.0 mmol) with LiAlH_4 (4.0 mmol), carried out similarly to the above reactions, produced a clear solution. The analysis of the solution showed that it contained Li, Zn, Al, H, and Ph in the ratio 1.02:1.03:1.00:3.97:2.05. The infrared spectrum of the solution exhibited a band at 1680 cm^{-1} (characteristic of LiAlH_2Ph). When this solution was kept at room temperature overnight, a crystalline solid appeared which was found to correspond to PhZn_2H_3 . Anal. Found: Zn:H:Ph = 1.00:1.53:0.50.

Reaction of Me_2Zn with LiAlH_4 in 4:1 Ratio in THF. A total of 2.5 mmol of a 1.3 M solution of LiAlH_4 in THF was added in 10 mmol of a 0.40 M solution of Me_2Zn in THF. The resulting clear solution was stirred for ~ 15 min, and then a small sample was subjected to infrared analysis, which showed the absence of any Al-H stretching bands above 1650 cm^{-1} and the presence of a Zn-Me group

(810, 675, and 560 cm^{-1}) and LiAlMe_4 (692, 570, and 405 cm^{-1}).^{4,11} The elemental analysis of the solution revealed that it contained Li, Zn, Al, H, and Me in the ratio 1.04:4.07:1.00:3.90:1.00. When the above solution was concentrated, a colorless crystalline solid precipitated within 15 min, which analyzed to be MeZn_2H_3 . Anal. Found: Zn:H:Me = 1.00:1.40:0.42. The solid was found to be very unstable and decomposed rapidly at room temperature to give a gray solid which was found to be predominantly zinc metal.

Reaction of Ph_2Zn with ZnH_2 in 1:1 Ratio in THF. To ZnH_2 (6.00 mmol) prepared by the reaction of Ph_2Zn (6.0 mmol) with LiAlH_4 (6.0 mmol) in ether were added 20 mL of THF and 15 mL of a 0.4 M solution of Ph_2Zn (6.0 mmol) in THF. The reaction mixture was stirred at room temperature for 24 h, and the insoluble solid was filtered, washed with THF, and analyzed. Anal. Calcd for insoluble solid, PhZn_2H_3 : Zn:H:Ph = 1.00:1.50:0.50. Found: 1.00:1.46:0.52. Calcd for filtrate, Ph_2Zn : Zn:Ph = 1.00:2.00. Found: 1.00:2.03. The filtrate contained about 64% of the starting Ph_2Zn as determined by IR analysis. The insoluble solid contained the remaining 36% of the zinc.

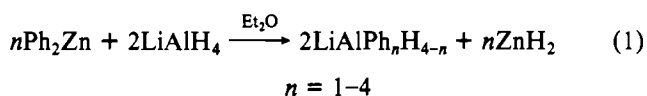
Reaction of Cyclopentadiene with ZnH_2 in 1:1 Ratio in THF. To a well-stirred slurry of ZnH_2 (7.5 mmol) in THF (30 mL) was added cyclopentadiene (7.5 mmol) dropwise. The reaction mixture was stirred at room temperature for ~24 h and the insoluble solid separated by filtration. The solid was then washed with THF and dried under vacuum. The solid was analyzed and the IR spectrum in Nujol obtained. Anal. Calcd for CpZn_2H_3 : Zn:H = 1.00:1.50. Found: 1.00:1.51. The solid contained about 95% of the starting zinc.

Reaction of ZnH_2 with Cyclohexanol in 1:1 Ratio in THF. A THF solution of cyclohexanol (5.0 mmol) was added to a well-stirred slurry of ZnH_2 (5.0 mmol) in THF (30 mL) and the reaction mixture stirred for ~24 h. The insoluble solid was filtered, washed with THF, dried under reduced pressure, and analyzed. Anal. Calcd for $\text{HZnOC}_6\text{H}_{11}$: Zn:H:C₆H₁₁OH = 1.00:1.00:1.00. Found: 1.00:0.97:1.02. The insoluble solid accounted for almost all of the starting zinc.

Results and Discussion

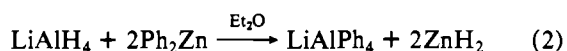
Addition of Ph_2Zn to LiAlH_4 in 2:1, 3:2, 1:1, and 1:2 ratios in ether, or the corresponding inverse addition, results in the precipitation of ZnH_2 . This result is not consistent with the earlier report² concerning the reaction of dimethylzinc with LiAlH_4 in ether which states that ZnH_2 precipitates immediately on addition of Me_2Zn to LiAlH_4 , but a solution of triple metal complexes forms when the mode of addition is reversed; i.e., when LiAlH_4 is added to Me_2Zn , a clear solution results.

An infrared study of the reaction of LiAlH_4 with Ph_2Zn shows that the reaction proceeds stepwise exchanging phenyl groups attached to zinc for the hydride attached to aluminum as shown in eq 1. The precipitate formed in the reactions (eq

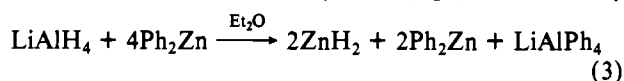


1) initially was shown to be ZnH_2 by infrared, elemental, and X-ray powder diffraction analyses, and the filtrate of the reaction (eq 1) was characterized as $\text{LiAlPh}_n\text{H}_{4-n}$ by infrared spectroscopy (when $n = 1-3$). The Al-H stretching bands were observed at 1670-1680, 1710, and 1730 cm^{-1} , respectively. The NMR spectrum of Ph_2Zn in ether shows two multiplets due to ortho (downfield) and meta-para (upfield) protons of the phenyl groups in a 2:3 ratio. The upfield multiplet is centered at 5.93 ppm relative to the triplet of ether, and the chemical shift separation between the two highest peaks of the multiplets is 0.40 ppm. The NMR spectra of the filtrates of the reaction (eq 1) also gave two multiplets with a chemical shift separation, δ_{int} , of about 0.60 ppm in every case.⁵

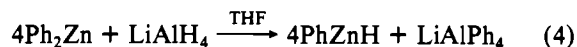
In the reaction of Ph_2Zn with LiAlH_4 in a 2:1 molar ratio in diethyl ether, the insoluble product contains a mixture of LiAlPh_4 and 2ZnH_2 (eq 2). The ZnH_2 was characterized by X-ray powder diffraction.



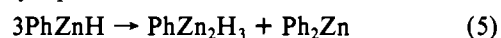
When LiAlH_4 (1.3 M) was allowed to react slowly with a THF solution of Ph_2Zn (0.4 M) in a 1:4 molar ratio, a clear solution resulted. Since ZnH_2 is very insoluble in THF, the reaction course observed in diethyl ether (eq 3) is undoubtedly



not involved here. An infrared spectrum of the reaction mixture in THF showed bands at 444 and 465 cm^{-1} , characteristic of Zn-Ph and LiAlPh_4 ,⁵ respectively, and also showed the absence of any Al-H stretching bands above 1650 cm^{-1} .⁵ However, a broad band at 1640 cm^{-1} was observed which may be due to terminal Zn-H stretching. The infrared data favor the pathway in eq 4 in THF.

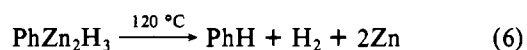


A ¹H NMR spectrum of the reaction solution showed three sets of multiplets downfield from the THF multiplet. The multiplet centered at 5.14 ppm downfield from THF is due to the ortho protons of the phenyl groups, and the multiplets of 5.65 and 5.76 ppm downfield from the THF multiplet are assigned to the meta-para protons of the phenyl group of Ph-Zn^{11} and LiAlPh_4 ,⁵ respectively. The 1:1 ratio of the multiplets at 5.65 and 5.76 ppm downfield to the THF multiplet suggests that the number of phenyl groups attached to zinc are the same as that attached to aluminum which again supports the proposed reaction course (eq 4). Interestingly, when the solution of the above reaction was kept at room temperature overnight, a crystalline solid separated from solution. The crystals, when washed with fresh THF and analyzed, corresponded to the empirical formula $\text{PhZn}_2\text{H}_3 \cdot 0.5\text{THF}$. The solvated THF was removed under vacuum, forming an amorphous solid. The supernatant solution of the reaction mixture contained 36% of the initial zinc as Ph_2Zn (calcd 33%) as determined by elemental analysis and IR and NMR spectroscopy. These results favor the following disproportionation reaction of PhZnH into PhZn_2H_3 and Ph_2Zn as expressed by eq 5.



The infrared spectrum of PhZn_2H_3 has been recorded as a Nujol mull (Table II). The Zn-H stretching vibration for PhZn_2H_3 was determined by preparing PhZn_2D_3 by the method above (eq 2-3) using LiAlD_4 and comparing the infrared spectra of PhZn_2H_3 with PhZn_2D_3 . The bands at 1650-1560 and 1366-1300 cm^{-1} observed for PhZn_2H_3 (Figure 3) were shifted to 1180 and 990 cm^{-1} in the case of PhZn_2D_3 , indicating that the 1650-1560- and 1360-1300- cm^{-1} bands are the Zn-H terminal and bridging stretching vibrations, respectively.^{13,14} The Zn-H deformation vibrations observed at 618 and 530 cm^{-1} were shifted to 420 and 365 cm^{-1} , respectively, in the deuterated compound. The X-ray powder diffraction pattern of PhZn_2H_3 gave lines (Table III) which were found to be different from that of ZnH_2 .

Vacuum DTA-TGA studies showed that PhZn_2H_3 decomposed at 120 °C (eq 6, Figure 4). The evolved gases were H_2 and benzene.

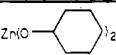
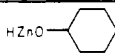
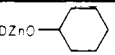


We have also observed that, when LiAlH_4 is added dropwise to a well-stirred solution of Ph_2Zn in a 3:8 molar ratio in THF, a clear solution forms. The IR spectrum of the solution exhibits a band at 445 cm^{-1} due to Zn-Ph and shows the absence

(13) G. J. Kubas and D. F. Shriver, *J. Am. Chem. Soc.*, **92**, 1949 (1970).

(14) An 1825- cm^{-1} absorption has been observed in the infrared spectrum of $[\text{HZnN}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$: N. A. Bell and G. E. Coates, *J. Chem. Soc. A*, 823 (1968).

Table II. Infrared Spectral Data (cm⁻¹) of PhZn₂H₃, CpZn₂H₃, and HZnOR Products in Nujol

PhZn ₂ H ₃ ^a	PhZn ₂ H ₃ ^b	CpZn ₂ H ₃	Zn(O) 	HZnO 	PhZn ₂ D ₃ ^c	DZnO 	CpZn ₂ D ₃
1650-1560 s, b	1650-1540 s, b	1640-1500 m, b	1455 vs 1372 vs	1780 w	1450 vs	1460 vs	1455 vs
1450 vs	1450 vs	1460 vs	1350 sh	1570-1500 mb	1375 vs	1380 s	1376 s
1375 vs	1375 vs	1378 s	1252 m	1460 vs	1330 m	1370 s	1175 s
1360-1300 m, b	1360-1300 m, b	1340 m, b	1185 sh	1380 s	1242 m	1270 s	
1242 m	1242 m	1070 sh	1105 vs	1370 s	1180 s	1150 s	1041 m
1175 w, b	1175 w, b	1041 m	1075 sh	1285 w	1040 s	1085 s	990 m
1040 s	1040 s	890 m	1028 s	1150 sh	990 m	1030 m	890 m
910 sh	910 sh	805 w	982 vs	1085 s	910 sh	980 s	725 m
885 ms	885 ms	725 m	950 sh	1030 m	885 ms	890 m	705 m
722 m	722 m	705 m	920 w	980 s	722 m	845 m	675 w
705 s	705 s	675 w	890 s	890 m	705 s	790 w	458 s, b
675 w	675 w	630 sh	845 m	840 m	675 w	722 m	419 s
618 s, b	618 s, b	572	790 m	792 w	462 s	705 m	360 s
530 vs, b	530 vs, b	495 s, b	722 w	722 m	420 s	678 w	
460 s, b	460 s, b	450 s, b	610 vs	705 m	365 s, b	585 m	
260 m	260 m		550 vs	678 w	260 m	508 m	
			490 m	592 s		460 s, b	
			442 s	510 s, b		422 m	
			362 m	465 s, b		360 s	
			318 w	422 m			

^a The product has been prepared by the reaction of Ph₂Zn with LiAlH₄ in THF in molar ratios (i) 4:1, (ii) 8:3, (iii) 2:1, and (iv) 1:1. ^b Prepared by the reaction of Ph₂Zn with ZnH₂ in THF in a 1:1 ratio. ^c Prepared by the reaction of Ph₂Zn with LiAlD₄ in a 8:3 ratio in THF.

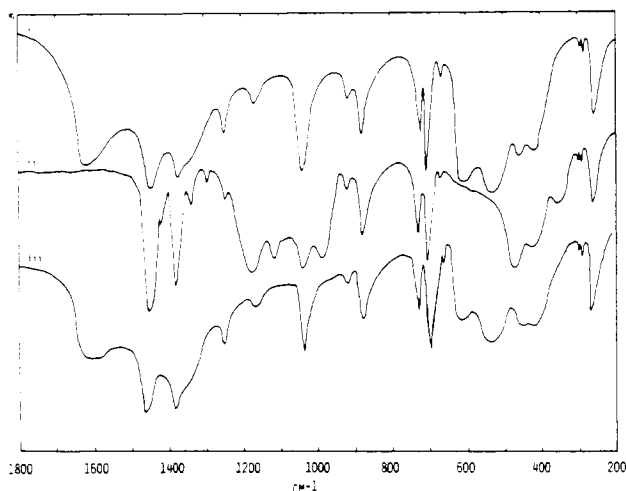
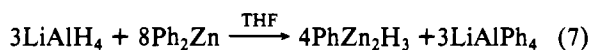


Figure 3. Infrared spectra (in Nujol) of (i) PhZn₂H₃ prepared by the reaction of 8Ph₂Zn + 3LiAlH₄, (ii) PhZn₂D₃ prepared by the reaction of 8Ph₂Zn + 3LiAlD₄, and (iii) PhZn₂H₃ prepared by the reaction of Ph₂Zn + ZnH₂.

of any Al-H stretching vibration above 1650 cm⁻¹. These results indicate that PhZn₂H₃ can be better prepared directly by the reaction of LiAlH₄ with Ph₂Zn in a 3:8 ratio (eq 7).



When this solution was kept at room temperature overnight, a crystalline solid separated whose analysis was consistent with the formula PhZn₂H₃. The infrared spectrum, X-ray powder diffraction pattern, and DTA-TGA were found to be consistent with the product from eq 4 and 5.

The same compound PhZn₂H₃ is also formed in the reaction of Ph₂Zn with LiAlH₄ in 2:1 and 1:1 molar ratios. The infrared spectrum of the reaction solution and X-ray and DTA-TGA studies of the product suggest the reaction pathway in eq 8 and 9.

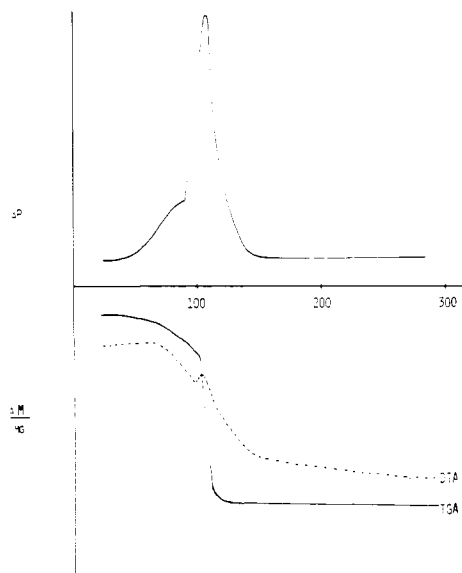
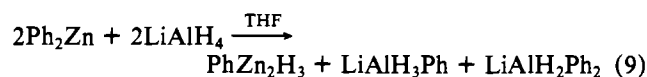
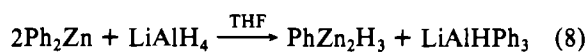
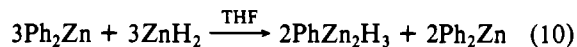


Figure 4. Vacuum DTA-TGA of PhZn₂H₃ (heating rate 4°/min).

In an attempt to prepare PhZnH from Ph₂Zn and ZnH₂ in equimolar ratio, an insoluble solid was formed. This insoluble solid was found to be PhZn₂H₃ by analysis, and the supernatant solution contained about 64% of the starting Ph₂Zn. The course of the reaction is demonstrated by eq 10. The IR spectrum of the solid (in Nujol) was found to be similar to that observed above (eq 4-8).



An attempt to prepare the methyl analogue, MeZn₂H₃, was made. When LiAlH₄ in THF was added to a THF solution of Me₂Zn in 1:4 ratio, a clear solution resulted. An infrared spectrum of the solution showed the presence of the Zn-Me group (810, 675, and 560 cm⁻¹) and LiAlMe₄ (692, 570, and 405 cm⁻¹)^{4,13} and the absence of any Al-H stretching in the region 1700 cm⁻¹. A ¹H NMR spectrum of the reaction solution exhibited a sharp singlet at 2.59 ppm upfield from THF due to the methyl protons attached to zinc (Figure 5). These observations favor the reaction route in eq 11. How-

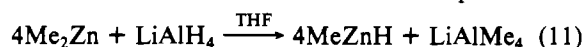


Table III. X-ray Powder Diffraction Pattern Data (*d* Spacings, Å) of PhZn_2H_3 and HZnO-c-Hx Products

ZnH_2^a	$\text{PhZn}_2\text{H}_3^b$	$\text{PhZn}_2\text{H}_3^c$	$\text{Zn(O-cyclohexyl)}_2$	HZnO-cyclohexyl	$2\text{ZnH}_2 + \text{LiAlH}_4^d$
4.52 vs	14.5 vs	14.5 vs	10.6 vs	10.5 vs	8.5 s
4.23 s	12.5 sb	12.5 m	8.00 m	7.90 m	6.8 w
3.81 vw	8.45 s	10.9 s	5.08 w	5.05 w	6.0 m
3.40 m	7.01 ms	8.45 s	4.75 s	4.70 sd	5.4 vw
2.97 vs	5.61 m	7.0 m	4.56 s	3.70 vw	4.8 vw
2.61 w	5.42 w	5.40 w	3.68 vw	3.42 vw	4.4 vs
2.47 vw	5.12 w	4.62 m			4.15 s
2.90 m	4.65 m	4.25 m			3.80 w
2.225 m	4.25 m	3.92 m			3.25 m
2.135 w	3.92 m	3.80 w			2.95 m
2.085 w	3.80 w	3.65 w			2.82 w
1.905 w	3.65 w	3.00 vw			2.76 w
1.764 w	3.51 w				2.63 w
1.688 w	3.40 w				2.55 w
	3.00 m				2.13 vw
	2.82 w				2.05 vs
	2.55 w				1.90 w
	2.43 w				1.78 w
	2.31 w				1.58 w
	2.21 vw				

^a Prepared from the reactions of Ph_2Zn with LiAlH_4 in diethyl ether in molar ratios (i) 3:2, (ii) 1:1, and (iii) 1:2. ^b Prepared by the reaction of Ph_2Zn with LiAlH_4 in THF in ratios (i) 4:1, (ii) 8:3, and (iii) 2:1. ^c Prepared by the reaction of Ph_2Zn with ZnH_2 in THF. ^d Obtained from the reaction of Ph_2Zn with LiAlH_4 in a 2:1 ratio in ether.

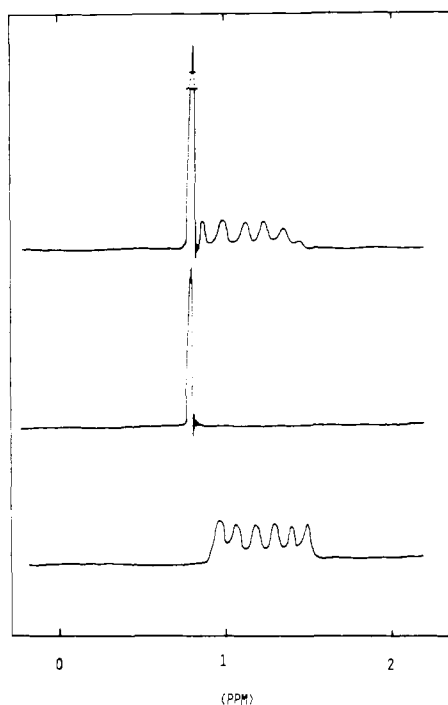


Figure 5. Proton NMR spectra (ppm) of (i) $4\text{Me}_2\text{Zn} + \text{LiAlH}_4$, (ii) pure Me_2Zn , and (iii) LiAlMe_4 in THF.

ever, the possibility of a triple metal complex as observed earlier in the reaction of Me_2Zn with LiAlH_4 in a 2:1 ratio³ cannot be ruled out. When the above reaction mixture was concentrated, a colorless crystalline solid separated within 15 min. The solid was unstable and decomposed rapidly at room temperature to give a gray solid which was found to be predominantly zinc metal. In an attempted analysis of the crystalline solid immediately after crystallization, the empirical formula corresponded roughly to MeZn_2H_3 ; however, the methane and hydrogen analyses were low.

Zinc hydride prepared by the reaction of Ph_2Zn with LiAlH_4 in diethyl ether was allowed to react with cyclopentadiene in a 1:1 ratio in THF (eq 12). The insoluble solid obtained was

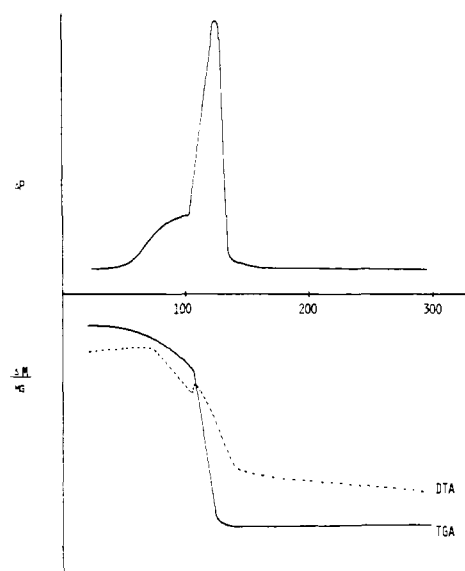
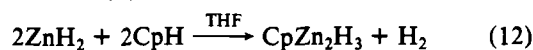


Figure 6. Vacuum DTA-TGA of CpZn_2H_3 (heating rate $4^\circ/\text{min}$).

found to correspond to CpZn_2H_3 by elemental analysis. The reaction was found not to proceed further even after further stirring at room temperature. The IR spectrum of the solid in Nujol exhibited bands at 725 and 705 cm^{-1} , suggesting the presence of a cyclopentadienyl group, and the Zn-H stretching bands were observed at 1640 – 1500 and 1340 cm^{-1} due to terminal Zn-H and bridging (ZnH_2Zn) Zn-H. These bands were shifted to 1175 and 990 cm^{-1} in the deuterio analogue prepared by the reaction of ZnD_2 with cyclopentadiene. The compound CpZn_2H_3 was found to be amorphous and did not produce a suitable X-ray pattern. Vacuum DTA-TGA studies showed that CpZn_2H_3 decomposed at 180°C with H_2 and cyclopentadiene evolution (Figure 6).

During this present investigation, efforts have been made to prepare alkoxyzinc hydrides, ROZnH , by the reaction of alcohol with zinc hydride, similar to the preparation of soluble alkoxy magnesium hydrides.¹⁵ In this connection, cyclohexanol was selected to react with ZnH_2 since its magnesium derivative,

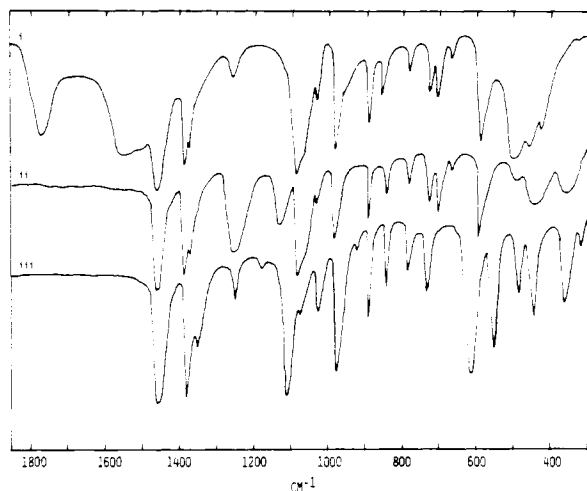


Figure 7. Infrared spectra (in Nujol) of (i) HZnO-c-Hx, (ii) DZnO-c-Hx, and (iii) Zn(O-c-Hx)₂.

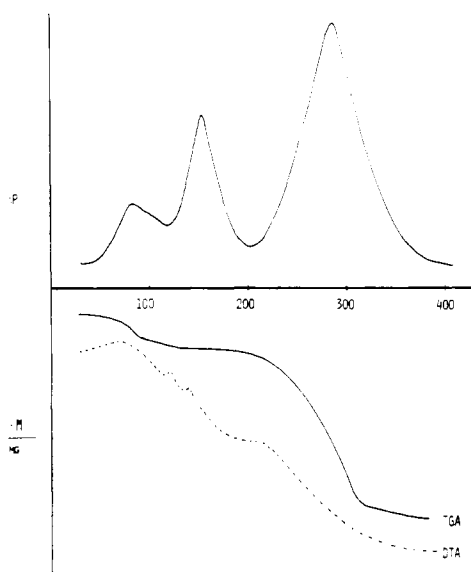
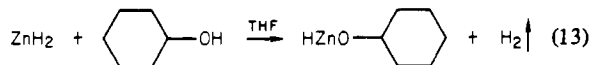


Figure 8. Vacuum DTA-TGA of HZn(O-c-Hx) (heating rate 4°/min).

HMgO-c-Hx, was found to be soluble in THF (both disproportionation products, i.e., MgH₂ and Mg(O-c-Hx)₂, are insoluble in THF). When cyclohexanol was allowed to react with ZnH₂ in a 1:1 ratio in THF and the resulting insoluble solid analyzed, the product corresponded to a compound of empirical formula HZnO-c-Hx (eq 13). The IR spectrum



(Table II, Figure 7) of this solid showed a band at 1780 cm⁻¹

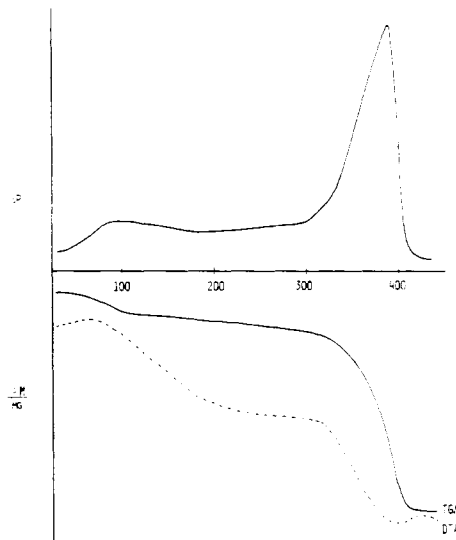


Figure 9. Vacuum DTA-TGA of Zn(O-c-Hx)₂ (heating rate 4°/min).

which was not present in either ZnH₂ or Zn(O-c-Hx)₂, which might be due to the Zn-H (terminal) stretching frequency. This band was shifted in the deuterio analogue at 1270 cm⁻¹. The broad band at 1570–1500 cm⁻¹ which shifted to 1150 cm⁻¹ in the deuterio analogue could be due to a bridging (ZnH₂Zn) system. The X-ray powder diffraction data of this product showed lines due to Zn(O-c-Hx)₂ (Table III). Vacuum DTA-TGA studies (Figure 7) showed that the product decomposed at 90, 155, and 290 °C evolving THF, H₂, and cyclohexene. The THF and cyclohexene were confirmed by GLC.

Since the IR of the product of the reaction (eq 13) suggests it to be a product different than that of a mixture of ZnH₂ and Zn(O-c-Hx)₂ and the X-ray powder pattern gave lines due to Zn(O-c-Hx)₂, the integrity of this compound is in doubt. We are continuing our efforts to prepare other alkoxy and aryloxy derivatives.

This report contains evidence for the first stable organozinc hydride. We are continuing our studies in this area, and the preparation of other RM₂H₃ compounds are being attempted. An evaluation of these compounds as stereoselective reducing agents is in progress.¹⁶

Registry No. PhZn₂H₃, 65123-79-7; MeZn₂H₃, 76137-14-9; CpZn₂H₃, 76137-15-0; HZnOC₆H₁₁, 68986-25-4; Zn(O-c-Hx)₂, 68986-27-6; PhZn₂D₃, 76137-16-1; DZn(O-c-Hx), 76124-27-1; CpZn₂D₃, 76137-17-2; LiAlPh₄, 62126-57-2; Ph₂Zn, 1078-58-6; LiAlH₄, 16853-85-3; Me₂Zn, 544-97-8; ZnH₂, 14018-82-7; CpH, 542-92-7; HO-c-Hx, 108-93-0; LiAlD₄, 14128-54-2; LiAlMe₄, 14281-94-8.

(16) This work was supported by the Office of Naval Research to whom we are indebted.