Zinc Hydride Complexes $NaZn_2(CH_3)_2H_3$ and $NaZnH_3$

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Abstract: The reaction of methylzinc iodide in tetrahydrofuran with sodium hydride yields a compound of the composition $NaZn_2(CH_3)_2H_3$. This compound is a slightly weaker reducing agent than $LiAlH_4$ as judged by its reactions with organic compounds. Moderate heating under high vacuum converts $NaZn_2(CH_3)_2H_3$ into $NaZnH_3$. The latter substance is shown by X-ray powder diffraction to be distinct from an equimolar mixture of NaH and ZnH_2.

While the hydrides of many elements have been studied in detail, zinc hydride[2] and zinc hydride complexes[3–6] have received relatively little attention. Several aspects of zinc hydride chemistry which are worthy of further investigation are the occurrence of hydride-bridged complexes,[6] the application of zinc hydrides as reducing agents,[4] and the possibility of forming simple hydride complexes such as $NaZnH_3$. The present work with CH_3ZnH derivatives has a bearing on all three of these areas.

Experimental Section

Organozinc hydrides, like the parent organozincs, are air-sensitive and therefore require vacuum-line or inert atmosphere techniques in their preparation and handling.[6,7] Some of the preparative and analytical methods have been outlined previously.[6]

Preparation of $NaZn_2(CH_3)_2H_3$. The reaction of $Zn(CH_3)_2$ with HCl or $ZnCl_2$ was used to generate CH_3ZnCl for subsequent reaction with NaH or LiH. However, the results were not reproducible, as shown by the variation of n from 0.33 to 1.0 in the formula $MH[(CH_3)_{2-n}ZnH_n]_2$. A better procedure involves the reaction of CH_3ZnI with NaH, for which $n = 0.86 \pm 0.08$ in four different preparations. In a good preparation, 22.8 g (0.16 mol) of CH_3I in 50 ml of freshly distilled tetrahydrofuran was refluxed 8 hr with 15 g (0.23 mol) of Zn–Cu couple (5% Cu), giving a solution of CH_3ZnI.[8] Excess Zn–Cu couple was filtered off, the solution was diluted with 150 ml of tetrahydrofuran and cooled to 0°, and 6.5 g (0.27 mol) of sodium hydride (Fluka) was rapidly added with stirring. After 2 hr the solution was allowed to warm to room temperature and stirring was continued for an additional 14 hr. The precipitate of NaI was filtered off and the colorless solution was stored at −20° to prevent the slow decomposition to metallic zinc which occurs at room temperature. *Anal.* Calcd for $NaZn_2(CH_3)_2H_3$: Na:Zn:CH_4(upon hydrolysis):H_2(upon hydrolysis), 1.0:2.0:2.0:3.0. Found: 1.02:2.00:2.06:2.82. (The foregoing Na value is corrected for the NaI content, which approaches 0.28 *M* in some solutions.) This crude solution was used directly for the reduction of organic compounds. However, a product free from NaI may be prepared by cooling the solution in a Dry Ice bath for several days, whereupon large colorless needle-like crystals form. These may be filtered off at −78°,[9] washed with several 10-ml portions of cold dry tetrahydrofuran, and then held under vacuum at −22° for several hours to remove excess tetrahydrofuran. Under these conditions the crystals lose solvent to form a white powder, which unlike the parent crystals does not melt on warming to room temperature. *Anal.* Found: Na:Zn:CH_3:H, 1.01:1.98:1.98:3.01. In addition, 2.3 mol of tetrahydrofuran was retained per mole of Na for this sample; however, the exact value varies from one preparation to the next. No iodide was detected in the product. The compound slowly turns gray when stored at room temperature but remains white when stored at −78°.

Preparation of $NaZnH_3$. When a sample of $NaZn_2(CH_3)_2H_3 \cdot x$THF at room temperature is exposed to high vacuum, both dimethylzinc and THF are slowly evolved. After several hours of pumping at room temperature, followed by slow warming to 100° while pumping, the evolution of volatiles ceased. The sample thus prepared had a light gray appearance. *Anal.* Calcd for $NaZnH_3$: H, 3.3; Zn, 71.5; Na, 25.2. Found: H, 3.3; Zn, 71.5; Na, 24.6. Various other procedures such as pumping on the parent compound at room temperature for 72 hr produce the same compound. The gray color appears most pronounced when starting with $NaZn_2(CH_3)_2H_3$ which has decomposed to a small extent. Nearly white $NaZnH_3$ may be prepared from fresh samples of the parent methylzinc hydride complex. Sodium trihydrozincate appears to be insoluble in tetrahydrofuran and in pyridine.

Preparation of ZnH_2. The reaction of $LiAlH_4$ with $Zn(CH_3)_2$ was employed.[2] *Anal.* Calcd for ZnH_2: H, 3.00; Zn, 97.0. Found: H, 3.16; Zn, 91.3. The sample gave a positive flame test for Li, which may partially account for the 6% impurity.

Physical Measurements. Spectroscopic measurements were carried out as described previously,[6] with the exception that in the Raman experiment 5145-Å Ar-ion laser excitation was used and samples were cooled to −50° or lower. X-Ray powder patterns were obtained with Cu Kα radiation and a 114-mm diameter camera. NaCl was used as calibrant for the film shrinkage correction.

Reduction of Organic Compounds. Unless otherwise stated, 1–2 mmol of the organic compound and 1–10 ml of dry tetrahydrofuran were placed in a dry, two-necked, 25-ml flask and stirred under a nitrogen atmosphere. Excess sodium methylzinc hydride solution was added. After several hours of stirring, the reaction mixture was hydrolyzed by dropwise addition of excess aqueous 10–15% sodium hydroxide and extracted with ether. The organic layer was dried over anhydrous sodium sulfate, filtered, and stripped of solvent under reduced pressure. The product was generally purified by vacuum distillation and identified by nmr and/or infrared spectra. In cases where the reaction was carried out at reflux temperature, a larger excess of the organozinc hydride was added to offset the slow decomposition of this compound. Details are available elsewhere.[10]

Results and Discussion

$NaZn_2(CH_3)_2H_3$. The reaction of alkali metal hydrides with CH_3ZnX (X = Cl or I) was chosen as a potentially convenient route to CH_3ZnH (eq 1); however, when X = I the reaction readily proceeds to yield an anionic hydride complex (eq 2). This product

$$CH_3ZnX + MH = MX + CH_3ZnH \qquad (1)$$

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(1) Alfred P. Sloan Fellow, 1967–1969.

(2) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, an H. I. Schlesinger, *J. Amer. Chem. Soc.*, 73, 4885 (1951); E. Wiberg, W. Henle, and R. Bauer, *Z. Naturforsch. B*, 6, 393 (1951); E. Wiberg and W. Henle, *ibid.*, *B*, 7, 249 (1952).

(3) G. Wittig and P. Hornberger, *Justus Liebigs Ann. Chem.*, 577, 11 (1952).

(4) (a) F. W. Frey, Jr., P. Kobetz, G. C. Robinson, and T. O. Sistrunk, *J. Org. Chem.*, 26, 2950 (1961); (b) P. Kobetz and W. E. Becker, *Inorg. Chem.*, 2, 859 (1963); (c) P. Kobetz, U. S. Patents, 3,171,848 and 3,171,849 (1965).

(5) N. A. Bell and G. E. Coates, *J. Chem. Soc. A*, 823 (1968).

(6) (a) G. J. Kubas and D. F. Shriver, *J. Amer. Chem. Soc.*, 92, 1949 (1970); (b) *Inorg. Chem.*, 9, 1951 (1970).

(7) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(8) K. H. Thiele, *Z. Anorg. Allg. Chem.*, 319, 183 (1962).

(9) Reference 7, p 154.

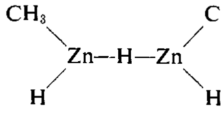
(10) G. J. Kubas, Ph.D. Thesis, Northwestern University, 1971.

Table I. Vibrational Data for $NaZn_2(CH_3)_2H_3$, $NaZnH_3$, and ZnH_2

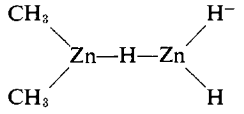
	$NaH(CH_3ZnH)_2\cdot 2.3THF$		$NaZnH_3$		ZnH_2
Origin	Raman	Ir	Raman	Ir	Ir
Zn-H			1650 w, br		
Zn-H		*ca.* 1500 s, br		*ca.* 1500 s, br	1540 s, br
THF	1491 w				
THF	1452 w				
THF	1245 w				
C-H	1139 s				
C-H	1124 m				
?			1029 w, br		1050 w
THF	1034 w				
THF	923 w				
Zn-H		500-800 br			700? vw
Zn-C	513 s				
Zn-C	508 sh				
Zn-C	490 m				

$$2CH_3ZnI + 3NaH = 2NaI + NaZn_2(CH_3)_2H_3 \qquad (2)$$

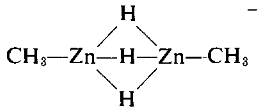
may be viewed as the CH_3ZnH analog of the complex formed between a dialkylzinc and alkali metal hydrides,[4,6a] *e.g.*, $NaH[Zn(CH_3)_2]_2$. However, the analogy may be purely formal because we have no structural information on $NaZn_2(CH_3)_2H_3$. Based on various fragmentary data, several structures or aggregates of these appear equally likely (I, II, III). Molecular weight measurements did not appear feasible becaues the compound dissociates to some extent. Structure I is favored by analogy with the dialkylzinc complexes,[6a] structure II would account for the ready loss of $Zn(CH_3)_2$ in the solid state, and structure III is favored by the lack of Zn-H stretch above 1700 cm^{-1} (Table I), which is the region characteristic of terminal ν(Zn-H). On the other hand, structures I and II appear to be favored by ^1H nmr, which in tetrahydrofuran displays a single resonance in the region of terminal Zn-H,[6] 2.91 ppm downfield from TMS.



I



II



III

$NaZn_2(CH_3)_2H_3$ as a Reducing Agent. In many of its reactions with organic compounds, $NaZn_2(CH_3)_2H_3$ appears similar to $LiAlH_4$ (Table II), but in a number of other reactions (Table III) the zinc reagent is found to be a somewhat weaker reducing agent. In no case was the reaction sufficiently unusual to generate great enthusiasm about the potential of $NaZn_2(CH_3)_2H_3$ in organic synthesis. However, the zinc reagent is easily prepared and may find some applications where a slightly milder reducing agent than $LiAlH_4$ is required. The facile reduction of benzonitrile to the corresponding imine (Table III) is a case in point.

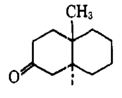
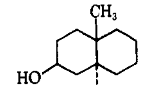
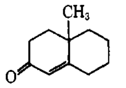
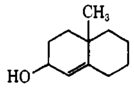
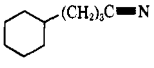
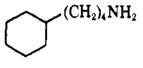
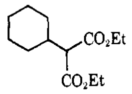
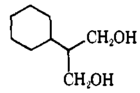
$NaZnH_3$. Perhaps the most interesting aspect of $NaZn_2(CH_3)_2H_3$ is its role as precursor to the first ternary hydride of zinc, $NaZnH_3$. As outlined in the Experimental Section, $NaZnH_3$ is generated at or above room temperature by exposing the sodium methylzinc hydride complex to high vacuum (eq 3). The $NaZnH_3$

$$NaZn_2(CH_3)_2H_3\cdot xTHF = NaZnH_3 + (CH_3)_2Zn + THF \quad (3)$$

product varies in appearance from white to gray. However, good analytical results and freedom from infrared or Raman CH_3 or tetrahydrofuran frequencies indicate a fairly pure product. In all cases it appears that traces of zinc metal in the alkylzinc hydride complex yield a gray product. When a sample of $NaZnH_3$ is heated for 2.5 hr at 100° about 10% of its hydrogen is lost. Thus $NaZnH_3$ has somewhat greater thermal stability than ZnH_2.[2] In contrast to ZnH_2, $NaZnH_3$ is rapidly hydrolyzed by water. As shown in Table I, the vibrational spectra of $NaZnH_3$ and ZnH_2 are similar. This situation is analogous to that found for $KMgH_3$ and MgH_2 by Ashby, Kovar, and Arnott.[11]

Comparison of powder patterns, Table IV, indicates that $NaZnH_3$ is not an equimolar mixture of NaH and ZnH_2. Weak to very weak lines are found in the

Table II. Reductions with $NaZn_2(CH_3)_2H_3$ Affording Results Similar to Reductions with $LiAlH_4$[a]

Compound	Time, hr	Product	Yield, %
	2		98
	2		
$CH_3(CH_2)_{10}CO_2Et$	1	$CH_3(CH_2)_{11}OH$	
	5		67
	24		84
$CH_3(CH_2)_5C{\equiv}CCH_2OH$	4	$CH_3(CH_2)_5CH{=}CHCH_2OH$	92

[a] Reductions were performed in THF at room temperature, except for that of the last entry, which involves refluxing THF.

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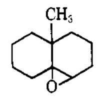
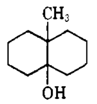
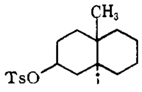
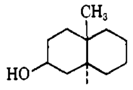
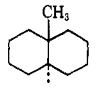
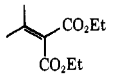
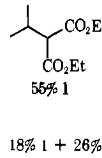
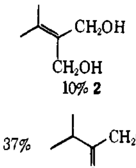
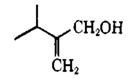
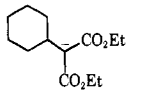
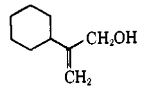
(11) E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

Table III. Comparison of Results of $NaZn_2(CH_3)_2H_3$ Reductions with Results of $LiAlH_4$ Reductions

Compound	Reagent	Temp	Time, hr	Solvent	Product
$C_6H_5C{\equiv}N$	$NaZn_2(CH_3)_2H_3$	Room	1	THF	$C_6H_5CH{=}NH$
$C_6H_5C{\equiv}N$	$NaZn_2(CH_3)_2H_3$	Room	24	THF	$C_6H_5CH_2NH_2$
$C_6H_5C{\equiv}N$	$LiAlH_4$	Room	1	THF	$C_6H_5CH_2NH_2$
	$NaZn_2(CH_3)_2H_3$	Room	6	THF	No reaction
	$NaZn_2(CH_3)_2H_3$	Reflux	7	THF	
	$LiAlH_4$[a]	Room	5	Et_2O	
	$NaZn_2(CH_3)_2H_3$	Reflux	6	THF	
	$LiAlH_4$[a]	Reflux	13	DME	
	$NaZn_2C(H_3)_2H_3$	Room	24	THF	 +  55% 1 10% 2
	$LiAlH_4$	Room	30[b]	Et_2O	18% 1 + 26% 2 + 37% 
	$NaZn_2(CH_3)_2H_3$	Reflux	4	THF	No reaction
	$LiAlH_4$	Reflux	4	DME	 (major product)[c]

[a] A. R. Hochstetler, unpublished data, Northwestern University, 1965. [b] Product distribution is time dependent: N. H. Anderson, unpublished data, Northwestern University, 1964. [c] J. A. Marshall, N. H. Anderson, and A. R. Hochstetler, *J. Org. Chem.*, **32**, 113 (1967).

Table IV. X-Ray Powder Patterns, d_{hkl} (Å), for $NaZnH_3$, NaH, Zn, and ZnH_2

$NaZnH_3$	NaH[a]	Zn[b]	ZnH_2[c]
5.87 vw	2.83 vs	2.47 m	6.27 w
4.90 s	2.44 s	2.31 m	4.50 m
3.26 m	1.73 s	2.09 vs	4.16 m
3.11 vs	1.47 s	1.69 w	3.79 m
2.84 w	1.41 m	1.34 w	3.27 s
2.51 m	1.22 w	1.33 w	3.12 m
2.45 w		1.24 vvw	2.94 w
2.38 vw			2.83 w
2.28 vw			2.61 vw
2.23 vw			2.50 w
2.16 vvw			2.40 w
2.09 vw			2.29 w
2.02 vvw			2.23 m
1.98 w			2.18 m
1.79 vw			2.14 vvw
1.70 vvw			2.08 m
1.67 vw			2.02 vw
1.62 w			1.98 vw
1.55 w			1.90 vw
1.47 vvw			1.77 w
1.35 vw			1.63 vvw
			1.61 vvw
			1.57 vvw
			1.51 w
			1.42 vw
			1.35 w

[a] "Powder Diffraction File," Joint Committee on Powder Diffraction Standards, Philadelphia, Pa., Inorganic Volume PD1S-5iRS, entry 2-809, 1960. [b] See reference of footnote *a*, entry 4-831. [c] Sample is *ca.* 96% pure so this pattern may contain some lines due to minor impurities.

$NaZnH_3$ sample which are near to the *d* values of the prominent NaH lines. Similarly, the very weak feature at 2.09 Å may correspond to the strongest diffraction line of zinc. Consideration of intensities and relative complexities of the powder patterns leads to the conclusion that at the worst very small percentages of NaH and Zn are present. Furthermore, the crystallinity is good for the $NaZnH_3$ sample since sharp diffraction patterns are obtained with relatively short exposures.

The $NaZnH_3$ powder diffraction pattern is fairly complex and does not correspond to the simple cubic lattice of the perovskite structure, which is common for ABX_3 compounds. In this connection, the compound $NaZnF_3$ is known to crystallize in tetragonal[12] and orthorhombic[13] forms, which represent distortions of the ideal perovskite structure. Even though structural similarities often exist between metal fluorides and metal hydrides, the $NaZnH_3$ powder pattern does not appear to be indexable on the basis of one of the distorted perovskite lattices. The related hydrides, $BaLiH_3$ and $SrLiH_3$, crystallize with the ideal perovskite structure,[14] and the more closely related $KMgH_3$ has this same structure.[11] A comparison of these various ABH_3 compounds reveals that the conventional tolerance factor,[15] $t = (r_A + r_H)/\sqrt{2}(r_B + r_H)$, has a value ranging between 0.90 and 0.95 for the cubic crystals, whereas the tolerance factor is 0.79 for $NaZnH_3$, which

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(12) W. L. W. Ludekens and A. J. E. Welch, *Acta. Crystallogr.*, **5**, 841 (1952).

(13) W. Rüdorff, J. Kändler, G. Lincke, and D. Babel, *Angew. Chem.*, 71, 672 (1959).

(14) C. E. Messer, J. C. Eastman, R. C. Mers, and A. J. Maeland, *Inorg. Chem.*, **3**, 776 (1964).

(15) Tolerance factors were calculated as recommended by H. D. Megaw, *Proc. Phys. Soc., London*, **58**, 133 (1946), using Gouldschmidt radii, which for the A ions are corrected for coordination number 12. A hydride radius of 1.40 Å was employed.

apparently does not have a perovskite-type structure. This result parallels the stability range found for oxide perovskites where $0.8 \lesssim t \leq 1$.

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Crystal and Molecular Structure of an Unusual Five-Coordinated Aminecarboxylic Acid Nickel(II) Chelate

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Abstract: The complex 1,5-diazacyclooctane-*N,N'*-diacetatoaquonickel(II) dihydrate ($NiO_7N_2C_{10}H_{22}$) crystallizes in the monoclinic space group $P2_1/c$ with a = 14.412 (5), b = 7.316 (5), c = 14.431 (5) Å, β = 112.90 (4)°, and Z = 4. The measured and calculated densities are, respectively, 1.59 and 1.616 g cm^{-3}. A single-crystal study was undertaken using a Picker diffractometer equipped with a GE single-crystal orienter. A full-matrix least-squares refinement on 1622 unique nonzero reflections resulted in a final value of R = 0.083 without the inclusion of hydrogen atoms. The tetradentate aminecarboxylate ligand is coordinated in a plane with a water molecule occupying an apical position to form an approximate square pyramid. The unique aspect of the structure is a sterically forced five-coordination sphere about the nickel atom with a methylene hydrogen blocking the sixth coordination position. Complexes of this ligand are of particular interest since they appear to maintain their five-coordinate geometry in aqueous solution, a property seldom encountered for five-coordinate complexes.

The ability to stabilize various geometries by steric hinderance offers an approach to the study of metal ions in less common coordination geometries and oxidation states.[1,2] Recent studies of the complexes of a novel tetradentate ligand, 1,5-diazacyclooctane-*N,N'*-diacetic acid (DACODA), synthesized in this laboratory, have indicated that one of the normal octahedral sites is not available for coordination.[3] The approach was to design a tetradentate ligand which would coordinate in a plane and force a portion of the chelate framework across one of the axial coordination positions. By adding two acetic acid arms to the nitrogen of 1,5-diazacyclooctane (DACO), such a ligand is obtained. On coordination the two glycinate rings must be nearly coplanar, thus fixing a planar coordination for the tetradentate ligand, as shown in Figure 1. The eight-membered diazacyclooctane ring's geometry is then brought into play, as illustrated in Figure 1. Carbon atoms 3 and 7 of the DACO ring may be positioned in one of three ways: (1) both carbons over the central metal ion, (2) one carbon over the metal and one away from the metal ion, or (3) both carbon atoms away from the central metal ion. From space-filling models, (3) is not expected because hydrogen atoms from different methylene groups are forced into the same location. Both of the remaining two configurations are possible; however, the one with only one carbon forward over the metal might be favored because it allows a solvent molecule to coordinate at one of the axial sites, presumably fixing a square-pyramidal geometry. Because of the unusual properties observed for various metal ion complexes of DACODA and because of the similarity of the solid- and solution-state geometries,[3] the structure of the nickel(II) complex was undertaken, and the results of this study are given in this report.

Experimental Section

Unit Cell and Data Collection. The compound was made by mixing $NiSO_4$ with the barium salt of 1,5-diazacyclooctane-*N,N'*-diacetic acid,[4] filtering off the $BaSO_4$, and evaporating the resulting solution to form the blue-green crystals of 1,5-diazacyclooctane-*N,N'*-diacetatoaquonickel(II) dihydrate ($NiO_7N_2C_{10}H_{22}$). From $h0l$, $h1l$, and $h2l$ Weissenberg photographs and a $0kl$ precision photograph, the systematic absences of $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $h0l$ fixed the space group as $P2_1/c$.[5] A crystal 0.20 × 0.17 × 0.14 mm in size was mounted along its b axis and aligned on a GE single-crystal orienter, using a Picker diffractometer. The lattice constants at room temperature were measured directly as a = 14.412 (5), b = 7.316 (5), c = 14.431 (5) Å, β = 112.92 (4)°. The observed density (from flotation ρ_{obsd} = 1.59 g cm^{-3}) is in good agreement with the calculated density (ρ_{calcd} = 1.616 g cm^{-3} for Z = 4, M = 341.01 g mol^{-1}).

The previously mentioned crystal was used to collect the data with Zr-filtered Mo Kα radiation. A θ–2θ scan rate of 2°/min was used. A 4-sec background was recorded on each side of the scan, and a 40-sec peak scan was employed. Data were collected in the form of hkl and $hk\bar{l}$ out to 2θ = 45°. Those reflections with a net count of less than 6% of background were considered unobserved. Of

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