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Preliminary communication

PREPARATION AND CHARACTERIZATION OF THE FIRST STABLE ORGANOZINC HYDRIDE, $PhZn_2H_3$

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Summary

The first stable organozinc hydride $PhZn_2H_3$ has been obtained by treatment of Ph_2Zn with $LiAlH_4$ in THF solution; the compound is characterized by the IR spectrum, X-ray powder diffraction pattern and DTA—TGA.

In 1951, Schlesinger and coworkers [1] 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 $LiZnMe_2AlH_4$ and $LiZn_2Me_4AlH_4$ [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]. Although, we have recently prepared a number of RMgH compounds and other workers have prepared several RBeH compounds [6—8], no such organozinc hydrides are known. We wish to report at this time the synthesis and characterization of the first stable organozinc hydride.

When $LiAlH_4$ (1.3 *M*) was allowed to react slowly with a THF solution of diphenylzinc (0.4 *M*) in 1/4 molar ratio, a clear solution resulted. Since ZnH_2 is very insoluble in THF, the reaction course observed in diethyl ether (eq. 1) is undoubtedly not involved here.

$$LiAlH_4 + 4Ph_2Zn \xrightarrow{Et_2O} 2ZnH_2 + 2Ph_2Zn + LiAlPh_4 \qquad (1)$$

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 of eq. 2 in THF.

$$4Ph_2Zn + LiAlH_4 \xrightarrow{THF} 4PhZnH + LiAlPh_4 \quad (2)$$

A PMR spectrum of the reactions 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 at 5.65 and 5.76 ppm downfield from the THF multiplet, is assigned to the *meta—para* protons of the phenyl group of Ph—Zn [9] and $LiAlPh_4$ [5] respectively. The 1/1 ratio of the multiplets at 5.65 and 5.76 ppm downfield to the THF multiplet suggest 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. 2). 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 $PhZn_2H_3 \cdot THF$ (Anal. Found; Zn/H/Ph/THF 1.00/1.48/0.49/0.46. Calcd. for $PhZn_2H_3 \cdot THF$ 1.00/1.50/0.50/0.50). The solvated THF was removed under vacuum (25°C/0 mmHg for 0.5 h) 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 infrared spectroscopy. These results favor a disproportionation reaction of PhZnH into $PhZn_2H_3$ and Ph_2Zn as expressed by eq. 3.

$$3PhZnH \rightarrow PhZn_2H_3 + Ph_2Zn \quad (3)$$

The infrared spectrum of the dissolvated $PhZn_2H_3$ (containing ~5% THF) was recorded as a nujol mull (1650—1560s(br), 1450vs, 1375vs, 1360—1300m(br), 1242m, 1175w(br), 1040s, 910(sh), 885ms, 722m, 705s, 675w, 618s(br), 530vs(br), 460s(br), and 260m cm^{-1}). The Zn—H stretching vibration for $PhZn_2H_3$ was determined by preparing $PhZn_2D_3$ by the method above (eq. 2 and 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 $PhZn_2H_3$ were shifted to 1180 and 990 cm^{-1} in the case of $PhZn_2D_3$ indicating the 1650—1560 and 1360—1300 cm^{-1} bands as the Zn—H terminal and bridging stretching vibrations respectively [9]*. The Zn—H deformation bands at 618 and 530 cm^{-1} due to the terminal and bridging Zn—H stretching vibrations 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 at 14.5vs, 12.5s(br), 8.45s, 7.01ms, 5.61m, 5.42w, 5.12w, 4.65m, 4.25w, 3.92m, 3.80w, 3.65w, 3.51w, 3.40w, 3.00m, 2.82w, 2.55w, 2.43w, 2.31w, 2.21vw.

Vacuum DTA—TGA studies showed that $PhZn_2H_3$ decomposed at 120°C. 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 3/8 molar ratio in THF, a clear solution forms. The IR spectrum of the solution gave a band at 445 cm^{-1} due to Zn—Ph and showed the absence of any Al—H stretching vibration above 1650 cm^{-1}. These results indicate that $PhZn_2H_3$ can be better prepared directly by the reaction of $LiAlH_4$ with Ph_2Zn in 3/8 ratio (eq. 4).

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*A 1825 cm^{-1} absorption has been observed in the infrared spectrum of $[HZn(CH_3)C_2H_4N(CH_3)_2]_2$ [10]. [10].

$$3LiAlH_4 + 8Ph_2Zn \xrightarrow{THF} 4PhZn_2H_3 + 3LiAlPh_4 \qquad (4)$$

When the above solution was kept at room temperature overnight, a crystalline solid separated whose analysis was consistent with the formula $PhZn_2H_3$. The infrared spectrum, X-ray powder diffraction pattern and DTA—TGA were found to be consistent with the product from eq. 2 and 3.

The same compound $PhZn_2H_3$ is also formed in the reaction of Ph_2Zn with $LiAlH_4$ in 2/1 molar ratio. The infrared spectrum of the reaction solution and X-ray and DTA—TGA studies of the product suggest the following reaction pathway (eq. 5).

$$2Ph_2Zn + LiAlH_4 \xrightarrow{THF} PhZn_2H_3 + LiAlHPh_3 \qquad (5)$$

An attempt to prepare the methyl analogue, $MeZn_2H_3$, was made. When $LiAlH_4$ (1.3 *M*) in THF was added to a THF solution of Me_2Zn (0.4 *M*) 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 $LiAlMe_4$ (692, 570 and 405 cm^{-1}) [4, 9] and the absence of any Al—H stretching in the region 1700 cm^{-1}. A PMR spectrum of the reaction solution gave a sharp singlet at 2.59 ppm upfield from THF due to the methyl protons attached to zinc. These observations favor the following reaction route (eq. 6).

$$4Me_2Zn + LiAlH_4 \xrightarrow{THF} 4MeZnH + LiAlMe_4 \qquad (6)$$

However, the possibility of a triple metal complex as observed earlier in the reaction of Me_2Zn with $LiAlH_4$ in 2/1 ratio [3], can not be ruled out completely at this stage. When the above reaction mixture was concentrated, a colorless crystalline solid separated within 15 minutes. The solid was unstable and decomposed rapidly at room temperature to give a gray solid which was found to be predominantly zinc metal. Analysis of the crystalline solid immediately after crystallization showed that the empirical formula corresponded roughly to $MeZn_2H_3$; however, the methane and hydrogen analysis was low.

This report contains evidence for the first stable organozinc hydride. We are continuing our studies in this area and preparations of other RM_2H_3 compounds are being attempted. An evaluation of these compounds as stereoselective reducing agents is in progress.

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