The Structure of Organozinc Reagents

RAYMOND E. DESSY[1] AND GORDON R. COE[2]

Department of Chemistry, University of Cincinnati,
Cincinnati 21, Ohio

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In recent years the structure of the group II organometallic halides has been the subject of a great deal of investigation and controversy. The problem lies in the values of the equilibrium constants involved in the modified Schlenk equilibrium[3,4] (shown in eq. 1)

$$R_2M\cdot MX_2 \rightleftharpoons R_2M + MX_2 \rightleftharpoons 2RMX \qquad (1)$$

and centers around the question of the existence of RMX species involving C–M–X linkages. This question may be answered if three criteria are met: (a) a label for M is available, (b) it is known that the species produced by eq. 2 and 3 are identical, and (c) a method of separating R_2M and MX_2 in their mixtures

$$R_2M + MX_2 \longrightarrow \qquad (2)$$

$$RX + M \longrightarrow \qquad (3)$$

exists. If these are available, then mixing M^*X_2 and R_2M and observing if any exchange of M takes place may provide the necessary information. If no exchange occurs, then the species RMX does not exist under the experimental conditions. If statistical exchange occurs, RMX does exist or ionic and/or nonionic exchange is occurring. Intermediate values would also point to one of the latter situations.

Among the organometallic compounds of subgroup IIb, it is well known that monomeric species such as RHgX exist,[5] and the equilibrium lies far to the right.

$$R_2Hg + HgX_2 \longrightarrow 2\,RHgX \qquad (4)$$

A preliminary report indicates that in the system M = Cd, R = Et, X = Br, exchange of radioactive cadmium label does not take place between $CdBr_2$ and Et_2Cd in tetrahydrofuran,[6] suggesting that the organocadmium compounds are best written as $R_2Cd\cdot CdX_2$ complexes. This same report suggests, on the basis of equilibrium constant measurements, that a similar situation exist in organozinc reagents in heptane.

We wish to report on the following tracer investigations in the zinc system. Equal molar amounts of sublimed zinc chloride, labeled with Zn^{65} and vacuum distilled diethylzinc were mixed in anhydrous ethyl ether (0.24 *M* in each) and allowed to equilibrate for 120 hours. 2,2′ Bipyridine (bipy) was added to separate the $ZnCl_2$ from the reaction mixture. The $ZnCl_2$·bipy complex is insoluble in Et_2O while the Et_2Zn·bipy complex is soluble. Washing the $ZnCl_2$·bipy complex with excess solvent permitted the quantitative separation of the two complexes. A sample of the original zinc chloride solution was hydrolyzed, burned to ZnO, and counted (399 c./min.-mg. ZnO). In one experiment the $ZnCl_2$.bipy was burned to ZnO and counted (197 c./min.-mg. ZnO) while in a second experiment the Et_2Zn·bipy complex was hydrolyzed with absolute ethanol, burned to ZnO, and counted (211 c./min.-mg. ZnO). These results clearly indicate statistical exchange. The analytical method of separation may have initiated the exchange but this seems unlikely. These experiments were twice repeated using vacuum distillation with water bath temperatures up to 110° as the method of separation and once again statistical exchange was observed.

Jander and Fisher[7] have reported on the conductance of ethylzinc iodide prepared by the methods symbolized by eq. 2 and 3. The similarity in conductance data shown by the products indicates the same specie(s) is (are) present in both products. The statistical exchange, therefore, suggests that (1) RZnX species do exist under these circumstances, or (2) ionic and/or nonionic exchange is occurring. Ionic exchange seems unlikely since the magnesium compounds, which do not exchange in ether, under certain conditions,[8] appear to be more ionic than the corresponding zinc compounds.[9]

The structure of the organozinc reagents also was investigated in tetrahydrofuran solution. In the isotopic exchange experiments bipyridine was again used as the separating agent. The quantitative separation of zinc chloride from the diethylzinc was not possible under these experimental conditions due to the increased solubility of the zinc chloride in tetrahydrofuran. Therefore the zinc chloride–bipyridine complex was washed free of the diethylzinc–bipyridine complex with excess tetrahydrofuran in duplicate experiments, burned to zinc oxide, and counted (320 c./min.-mg. ZnO and 324 c./min.-mg. ZnO). The original stock solution of zinc chloride had a specific activity of 640 c./min.-mg. ZnO. Once again statistical exchange is indicated.

It is important that the results of Allred and McCoy[10] on the apparent rapid exchange of methyl groups between dimethylzinc and dimethylcadmium in ether solution (τ_A 0.081 at 1 *M* concentrations) be kept in mind, as well as the results[11] of the exchange reactions in dialkylmetal–dialkymetal systems (R_2M and $R_2'M'$) involving organometallic compounds derived from group II metals where it has been shown that exchange is rapid except when mercury is one of the metals and probably goes through a nonionic pathway.

It is also known that the following equilibrium

$$R_2Cd + Hg \rightleftharpoons R_2Hg + Cd$$

exists,[12] similar to the reported exchange[13] $R_2Hg + Hg^* \rightleftharpoons R_2Hg^* + Hg$. These cases all involve exchange in R_2M, R_2M'; R_2M, $R_2'M$; R_2M, M' mixtures. These results, therefore, have no direct bearing on the interpretations made here involving R_2M, MX_2 systems except that they do suggest the availability of low energy

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[1] A. P. Sloan Fellow.

[2] Gulf Research Predoctoral Fellow.

[3] W. Schlenk and W. Schlenk, *Ber.*, **62**, 920 (1929).

[4] For a recent review, see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Inc., New York, N. Y., 1954, p. 104–109.

[5] Frank C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, N. Y., 1921, p. 85–106.

[6] A. B. Garrett, A. Sweet, W. L. Marshell, D. Riley, and A. Touma, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **13**, 155 (1952).

[7] G. Jander and L. Fisher, *Z. Elektrochem.*, **62**, 971 (1958).

[8] R. E. Dessy, S. I. E. Green, and R. Salinger *J. Am. Chem. Soc.*, in press.

[9] W. Strohmeier and F. Seifert, *Z. Elektrochem*, **62**, 971 (1958); **63**, 683 (1959).

[10] A. L. Allred and C. R. McCoy, *Tetrahedron Letters*, No. **25**, 27 (1960).

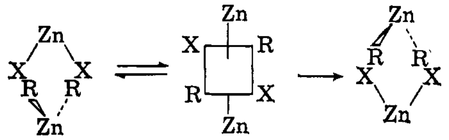
[11] R. E. Dessy, F. Kaplan, G. R. Coe, and R. M. Salinger, *J. Am. Chem. Soc.*, **85**, 1191 (1963).

[12] S. Hilpert and G. Gruttner, *Ber.*, **46**, 1675 (1913).

[13] O. A. Reutov, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **22**, 1 (1961).

nonionic exchange pathways in all these cases and their possible availability for metal exchange in R_2M, MX_2 systems.

The present work in ethyl ether would seem to indicate the existence of RZnX species or a nonionic exchange transition state of an octahedral form, as illustrated.



Solvent molecules have not been shown.

In a separate experiment, using a Mechrolab osmometer inside a glovebox filled with a nitrogen atmosphere, a solution of 0.05 M diethylzinc and 0.072 M zinc chloride in tetrahydrofuran showed a molarity of 0.125 M (0.100 + 0.025) which corresponds to a monomer of EtZnCl plus excess zinc chloride, or to a mixture of zinc chloride and diethylzinc in which there is no interaction between the species but certainly does not correspond to the dimer $Et_2Zn \cdot ZnCl_2$ which would indicate a molarity of 0.072 M (0.050 + 0.025). In view of the exchange data and the difficulty in the separation of diethylzinc from zinc chloride by vacuum distillation,[14] one may reasonably reject the possibility of the noninteraction of the diethylzinc and zinc chloride. (A solution of 0.005 M diethylzinc and 0.007 M zinc chloride also showed a molarity which corresponds to the monomer EtZnCl.)

With these results in mind and with the awareness of the many similarities exhibited by organozinc and organocadmium compounds, the lack of exchange in the dialkylcadmium, cadmium halide system[16] is rather disconcerting.

Experimental

Zinc Chloride.—Reagent grade fused sticks of zinc chloride were sublimed under vacuum before use.

Zinc^{65} Isotope.—The zinc^{65} isotope was purchased as a solution of zinc chloride in hydrochloric acid from the Oak Ridge National Laboratory, Oak Ridge, Tenn., operated for the U. S. Atomic Energy Commission by the Union Carbide Nuclear Company.

Labeled Zinc Chloride.—A stock solution of zinc^{65} chloride was prepared in the following manner: the reagent grade zinc chloride was first sublimed *in vacuo*, and 1.6685 g. collected. To this was added 60 λ of the radioactive isotope solution, the zinc chloride resublimed, and 0.7006 g. (5.141 mmoles) collected. The zinc chloride was dissolved in 20.56 ml. of anhydrous ethyl ether (0.24 M). A sample was taken, hydrolyzed, and burned to zinc oxide at 550°. The zinc oxide was counted using a Nuclear-Chicago Model 182 scaler and had a specific activity of 399 c./min.-mg. ZnO.

The technique was repeated using anhydrous tetrahydrofuran as the the solvent to prepare a 0.25 M solution, which had a specific activity of 640 c./min.-mg. ZnO.

Diethyl Zinc.—The diethyl zinc was purchased from Organic Specialties, 226–230 E. 12th St., New York 3, N. Y., and was vacuum distilled before use.

2,2′-Bipyridine.—Reagent grade 2,2′-bipyridine was purchased from Matheson Coleman and Bell and was used without further purification.

Solvents.—Anhydrous analytical reagent diethyl ether and reagent grade tetrahydrofuran were distilled from lithium aluminum hydride immediately before use.

Analytical Methods.—All molecular weights were determined with a Mechrolab osmometer Model 301 after standardization of the instrument with diphenyl mercury.

The insoluble $ZnCl_2 \cdot$bipy complex was isolated by adding 1.12 mmoles of bipy in ethyl ether to a mixture of 1.25 mmoles of zinc chloride and 1.25 of mmoles of diethylzinc dissolved in ethyl ether. The $ZnCl_2 \cdot$bipy was washed four times with excess solvent to separate it quantitatively from the diethylzinc. The diethyl zinc–bipyridine complex has an intense orange color and is soluble, so any complex coprecipitated was redissolved. A sample was taken, burned to zinc oxide in a furnace, cooled in a dessicator, weighed, and counted.

The $ZnCl_2 \cdot$bipy complex was isolated in a slightly different manner in tetrahydrofuran solution, since the complex is more soluble and can not be quantitatively separated. A 0.24 M solution of zinc chloride and diethylzinc was prepared by dissolving 1.25 mmoles of each in 5.00 ml. of solvent. A tetrahydrofuran solution of 3.75 mmoles of bipyridine was slowly added and the $ZnCl_2 \cdot$bipy precipitated. The precipitate was washed four times with excess solvent. A sample was taken, burned to ZnO, cooled, weighed, and counted.

The $Et_2Zn \cdot$bipy complex could be separated quantitatively in ethyl ether but could not be in tetrahydrofuran. In ether the $ZnCl_2 \cdot$bipy complex was quantitatively precipitated by adding a two fold excess of bipyridine and filtering through a medium porosity fritted glass crucible. A sample of the soluble $Et_2Zn \cdot$bipy was taken, hydrolyzed with absolute ethanol, burned to ZnO, cooled, weighed, and counted. The $Et_2Zn \cdot$bipy complex was shown to be free of $ZnCl_2 \cdot$bipy by hydrolyzing a sample with a small amount of absolute ethanol, dissolving it in dilute nitric acid, and adding silver nitrate. No silver chloride precipitate was present.

In all counting experiments, at least 5000 counts were collected. The bipyridine complexes were analyzed for chloride ion by the Volhard method.[15] The zinc analysis on the ethylzinc chloride samples for the molecular weight determinations was accomplished by hydrolyzing with a known excess of standard hydrochloric acid, and the excess hydrogen ion titrated with standard sodium hydroxide using methyl red as an indicator. The chloride ion analysis was again determined by the Volhard method.

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[14] Diethylzinc boils at 118° at 760 mm., but a temperature of 110° and 1 mm. was required to separate the diethylzinc from the reaction mixture.

[15] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The MacMillan Co., New York, N. Y., 1948, p. 475, 573.