Structure of Bis(iodozincio)methane in THF Solution

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Bis(iodozincio)methane, which has been shown to be an efficient reagent for organic synthesis, is obtained as THF solution. The structural information about the reagent as THF solution was corrected by small angle neutron scattering and by anomalous X-ray scattering. Those scattering experiments implied that the prepared bis(iodozincio)methane exists without forming any oligomer or aggregate.

Organometallic compounds have been useful reagents in organic synthesis; the structural information at the molecular level is indispensable for the design of their reactions. The main stream of the structural studies has used single crystal X-ray analyses. Some important organometallic compounds, however, can exist only in a solution and cannot be isolated as a single crystal. Moreover, the structure obtained by single crystal X-ray analyses does not agree with its structure in solvent. In our series of studies of the reaction using bis(iodozincio)methane (**1**), several characteristic molecular transformations have been developed.[1,2] The reagent **1** was prepared according to Eq 1, and obtained as THF solution.[3] The structure was analyzed by ^{1}H NMR analysis (Figure 1).[2b,4,5]

$$I{-}CH_2{-}I \;+\; Zn \xrightarrow[\text{THF, 0 °C}]{\text{0.1 mol\% PbCl}_2} \underset{\textbf{1}\text{ (50\% yield)}}{IZn{-}CH_2{-}ZnI} \qquad (1)$$

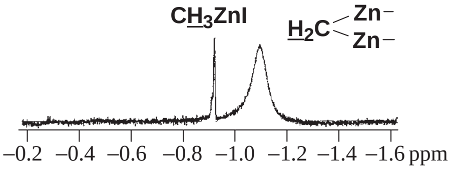
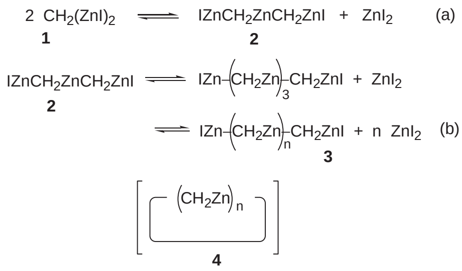


Figure 1. ^{1}H NMR of *gem*-dizinc in THF prepared as shown in Eq 1.

The broad signal at higher field (−1.1 ppm) was understood as a signal of a methylene which is substituted with two electropositive zinc atoms. However, it is impossible to tell from this ^{1}H NMR chart, what kind of atom is substituted on zinc besides a carbon atom. The structure of zinc reagent **1** in THF should be determined considering equilibrate transmetallation between the molecules of **1**, that is, Schlenk equilibrium.[6] The equilibrium would be discussed not only by equation (a) but also by equation (b) in Scheme 1. Schlenk equilibrium of **1** may induce a polymeric structure such as a linear compound **3** or a cyclic compound **4**.[7] We tried to determine the structure of **1** in solution by direct X-ray and neutron scattering techniques.



Scheme 1. Possible structural change of **1** in THF via Schlenk equilibrium.

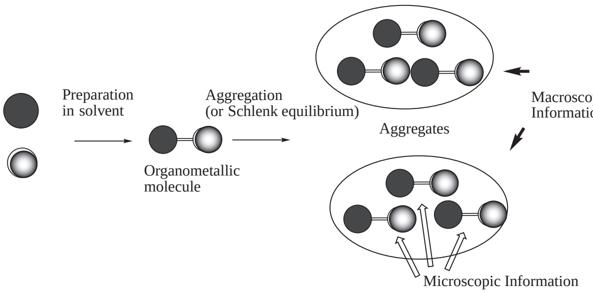


Figure 2. Structural study of an organometallic reagent in solution.

In general, structural studies of organometallics in solution have not progressed so well.[8,9] For this purpose, both macroscopic and microscopic structural information should be obtained. In other words, the size of a solute and the distance between atoms in the solute should be determined. The former reflects their aggregation including Schlenk equilibrium and the latter is a single molecular structure of the corresponding reagent (Figure 2). We tried to determine the sizes of **1** in THF solution by small angle neutron scattering (SANS),[10] and the distances between atoms by anomalous X-ray scatterings by synchrotron radiation.[11] The method will be available not only for **1** but also for many structural studies concerning organometallic reagents in solution.

First of all, we tried to determine the size of the solute in the prepared solution of **1**. Such information will also tell us about the homogeneity of the solution. Small-angle neutron scattering (SANS) will give information concerning the sizes of the aggregate of the solute.[10] The result is shown in Figure 3. Most of the SANS profile where $q > 0.07\,\text{Å}^{-1}$ was well identified with the simulated scattering curve of the sphere particles which have the radius of gyration (Rg) of 9.2 Å. At the smaller angle regions, those where q is less than 0.07, two components with $Rg = 15$ and 60 Å can be recognized, although the data are scattered due to weak scattering intensity. However, the contributions from

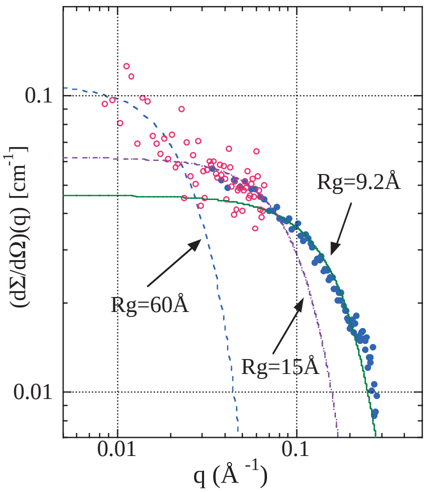


Figure 3. SANS profile for bis(iodozincio)methane (0.4 M) in THF-d_8. The two data sets plotted by dots were obtained at two different camera lengths (the sample-detector distance, ●:1 m, large angle region, ○:4 m, small angle region). These camera lengths cover different scattering vector, q, range ($q = 4\pi \sin q/l$, where 2q is the scattering angle and l is the wavelength of neutron). Three lines are simulated scattering curves. The data was collected by SANS-U of the Institute for Solid State Physics, University of Tokyo, Tokai, Ibaragi.

both of these components with larger *R*g can be said to be very small. The results show that only small particles (*R*g: about 9.2 Å) exist with high homogeneity in a THF solution of **1**. This means that the Schlenk equilibrium in Scheme 1 stays with bis(iodozincio)methane molecules which do not aggregate with each other so much. To investigate the inside of the small particles, we applied X-ray scattering.

To obtain a good scattering of the solute, one needs a strong X-ray beam. Although X-ray scattering by white X-rays of synchrotron radiation give the radial distribution function of the solute in large region, a difficulty arises to assign the each peaks of the radial distribution function to the corresponding atoms in the solution. To solve this problem, we applied anomalous X-ray scattering (AXS).[11] After we obtained the normal X-ray scattering in the area from small to large angle at 32.867 keV, anomalous X-ray scatterings around heavy atoms were measured to identify the peaks of the radial distribution function. The AXS was measured under irradiation of X-rays near the K-edge of zinc atom (9.961 keV) at 9.661 and 9.931 keV and near the K-edge of iodine atom (33.167 keV) at 33.117 and 32.867 keV. In Figure 4, the total pair distribution function (a) is shown in comparison with the Zn (zinc) environmental pair distribution function (b) and the I (iodine) environmental pair distribution function (c). Comparing these functions, one can easily assign the peaks in (a) to distances between each pair of atoms.

Thus, two scattering measurements of dizinc **1** in THF will tell us the detailed structure in solution. Before these scattering analyses, we cannot tell the structure of bis(iodozincio)methane which was prepared as shown in Scheme 1, as Schlenk equilibrium may change the structure of **1** into **2**, **3**, or **4**. The SANS experiment concluded that the solution of **1** consisted of small homogeneous particles. That is, it is not necessary to consider the possibility of polymeric structure via Schlenk equilibrium. The radius of gyration of these small homogeneous particles was 9.2 Å, as shown in Figure 3, and it is hard to decide if the structure of the particle is monomeric **1** or dimeric **2**. The AXS data in Figure 4 showed that the molecule in the solution has atoms within 6–7 Å. This means that the reduction of diiodomethane with zinc in THF (Scheme 1) gave monomeric bis(iodozincio)methane (**1**). In other words, under the reaction condition, it is not necessary to consider the contributions of Schlenk equilibrium which form polymethylene zinc.

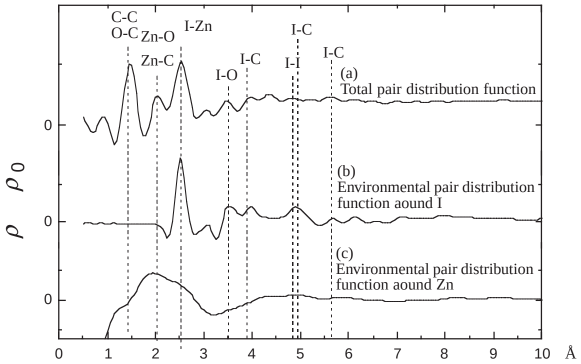


Figure 4. (a) Pair distribution function of bis(iodozincio)methane (**1**). (b) Pair distribution function based on AXS at Zn-atm K-edge. (c) Pair distribution function based on AXS at I-atm K-edge. The data collected by Photon Factory of the Institute of Material Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki.

The obtained information about the structure of **1** in solution will be useful for the design of the reaction. At the same time, the profiling of the reaction pathway using **1** by ab initio calculation requires such information.[12,13] The method is not only for the analysis of **1** but also for the general organometallics, although the measurements require neutron and synchrotron beam lines.

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