Report for MERIT long-term overseas dispatch

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Host: Sjoerd Harder group (Friedrich-Alexander University, Germany)Term: 2023/9/4-2023/11/23Topic: Synthesis of low valent magnesium/ calcium complexes bearing trianionic bulky ligand

Background and my work

Low valent main group element (MG) species is generally quite unstable. Thus, the synthesis has still been limited and the properties, such as molecular structure and reactivity have been left unexplored. Recently, this field is highly emphasized because it has been found that low valent MG compounds can mimic the reactivity of transition metal complexes, which are widely employed as catalysts in our lives. Harder group, the host of my visit, focuses on low valent group 2 metal, for example, magnesium (Mg) and calcium (Ca).

In the area of organic synthetic chemistry, Mg and Ca are employed usually in a +II oxidation state, except for

elemental metal. This is derived from the instability of low valent (0 or +1) state of these elements. Harder group reported synthesis of +1 and 0 valent Mg and Ca compounds, which are found to be reactive for activation of small molecules.



Figure 1. Reported low-valent Mg compounds.

During this staying, I worked on the synthesis of dinuclear low valent Mg or Ca complexes bearing a trianionic bulky ligand. There are mainly two reasons to change the ligand from monoanionic one to trianionic one; i) stabilization for the low valent species by strong electron-donating ability of the ligand, ii) control the reactivity and structure of the resultant compound by countercation, which would be introduced to neutralize the extra anion charge. In the first half of the dispatch period, I worked on the synthesis of ligands, and in the latter half, the complexation with Mg/Ca and the following reduction reaction. As a result of the investigation of reaction conditions, M(+II) complexes were synthesized for both M = Mg and Ca. The next step was the synthesis of low-valent complexes by reduction, but the target compounds could not be obtained.

Life in the laboratory

The number of members in the laboratory was about 20, which was slightly smaller than our group in Japan. While the experimental facilities for handling unstable compounds (e.g., glove box) and measurement equipment (e.g., NMR) were almost the same, the composition of the members was very different. While more than half of the members in my laboratory are master or undergraduate students, most of the members in Harder group were doctoral students. The fact that all members have a deep understanding of their own research themes and related issues, as well as a wealth of experimental experience, was a great strength of the group. I was also impressed by the very frank discussions. Some of the members took a 30-minute coffee break every day around 3:00 p.m. to relax and discuss each other's research and new papers. Sometimes the

results of experiments based on the ideas that came out of these discussions were actually presented at the meetings, and I could feel that this was helping to advance the research efficiently.

Life in Germany

In Erlangen, where I stayed, the entire city is like a school town of Friedrich-Alexander University, with campuses scattered all over the place. Therefore, there were many students, and the population seemed to be younger than in Germany as a whole. Therefore, English was often understood, and it was an easy environment to live in.

When I arrived in Germany in early September, the weather was surprisingly warm and sunny, even for the locals. However, in October, there was a lot of rain and many very cold days. Especially in November, it was completely winter-like, and there were even times when it snowed.

Since the monthly fee of 49 euros allows unlimited travel on almost all trains and buses in Germany, I visited

various places in southern Germany every weekend. There are many castles, churches, and other historic sites in southern Germany, and I was able to enjoy the beautiful scenery and local culture to the fullest. The town squares were also very lively with numerous stalls selling crafts, sausages, beer, etc.



Students were also very active in socializing with each other, and various events were held, including barbecues and beer tastings. The barbecue in particular was held jointly with other laboratories, so I was able to talk with students with whom I normally have few opportunities to interact, which was both enjoyable and very stimulating at the same time.

Acknowledgements

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