

Development of dehydrogenation of ammonia borane or hydrosilanes catalyzed by iron complexes

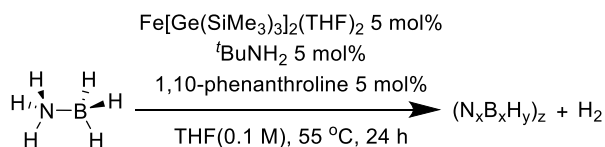
(¹*School of Engineering and* ²*Institute of Industrial Science, The University of Tokyo*) ○ Yoshinao Kobayashi¹, Yusuke Sunada^{1,2}

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Dehydrogenative reactions are the important reaction from the point of view of not only organic synthesis but also efficient hydrogen production. Precious metal compounds are often used as dehydrogenation catalysts due to their high catalytic performance. However, development of base metal catalysts that can replace the conventional precious metal catalysts is highly desired from the viewpoint of cost and availability. Because group 14 can contribute to stabilize the highly reactive coordinatively unsaturated metal species due to their high *trans* influence and strong electron donating property, we focused on the synthesis of base metal complexes bearing group 14 ligands to develop the novel catalysts¹. In this presentation, we wish to report the synthesis of 14 electron coordinatively unsaturated iron(II) complexes having germanium ligands, and application of the obtained complex as the catalyst toward dehydrogenation of ammonia borane. Catalytic dehydrogenation of hydrosilanes catalyzed by iron complexes will also be demonstrated.

First, iron digermyl complex $\text{Fe}[\text{Ge}(\text{SiMe}_3)_2(\text{THF})_2]_2$ (**1**) was obtained by the reaction of commercially available FeBr_2 and 2 eq. of $\text{KGe}(\text{SiMe}_3)_3$ in 74% isolated yield². The molecular structure of this complex was determined by X-ray diffraction analysis. The iron center adopts the distorted tetrahedral coordination geometry. Then we checked the catalytic performance of **1** in the dehydrogenation of ammonia borane (AB), because AB is identified as an appropriate solid hydrogen storage material due to its high hydrogen content. We found that combination of complex **1** (5 mol%) and *tert*-butylamine (5 mol%) in the presence of 1,10-phenanthroline (5 mol%) resulted in efficient dehydrogenation of AB in THF at 55°C (Scheme 1).

Catalytic dehydrogenation of hydrosilanes mediated by iron complexes to form organosilicon compounds such as disilanes will also be demonstrated in this presentation.



Scheme 1 Dehydrogenation of ammonia borane catalyzed by combination of **1**, *t*BuOH, and 1,10-phenanthroline.

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1) Arata, S.; Sunada, Y. *Dalton. Trans.* **2019**, 48, 2891. 2) Kobayashi, Y.; Sunada, Y. *Catalysts* **2020**, 10, 29.