

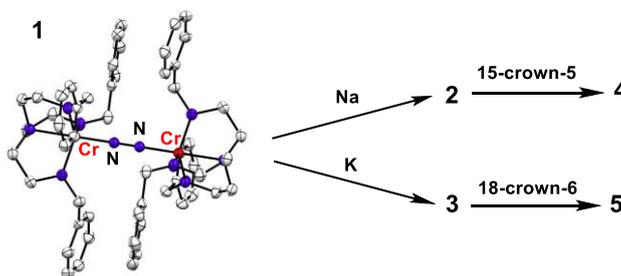
## The syntheses and Structures of Dinitrogen Chromium Complexes Supported with Triamidoamine Ligands

(Graduate School of Engineering, Aichi Institute of Technology) ○Yoshiaki Kokubo, Yuji Kajita, and Hideki Masuda

**Keywords:** Chromium Complex; Dinitrogen Complex; Dinitrogen Activation; Dinuclear Complex; Triamidoamine Ligand

Transition metal dinitrogen complexes are intensively studied for N<sub>2</sub> reduction. Catalytic reduction of N<sub>2</sub> to NH<sub>3</sub> was achieved by Schrock with a molybdenum dinitrogen complex supported with a triamidoamine ligand.<sup>1</sup> Nishibayashi group also reported a catalytic reduction of N<sub>2</sub> by using Mo complex and water as a proton source recently.<sup>2</sup> In contrast to the many variations of Mo and W complexes with dinitrogen, examples of chromium complex are rare.

In this study, we synthesized triamidoamine ligand with benzyl (L<sup>Bn</sup> = tris(2-amidoethyl)amine, R = Bn) and prepared a novel chromium complex by reacting CrCl<sub>3</sub> with L<sup>R</sup> under N<sub>2</sub>. The structure of chromium complex revealed a dichromium complex with a bridging N<sub>2</sub> ligand, [Cr(L<sup>R</sup>)<sub>2</sub>(N<sub>2</sub>)] (**1**) (Scheme 1), which is composed of two species, **1a** and **1b**, in a unit cell. The N—N bonds in **1a** and **1b** are 1.188(4) and 1.185(7) Å, respectively. The N—N stretching vibration ( $\nu(^{14}\text{N}-^{14}\text{N})$ ) of **1** was observed at 1772 cm<sup>-1</sup>. Complex **1** reacted with Na or K to give a dinitrogen-chromium(II) complex with an alkaline ion, [CrNa(L<sup>Bn</sup>)(N<sub>2</sub>)(Et<sub>2</sub>O)]<sub>2</sub> (**2**) or [CrK(L<sup>Bn</sup>)(N<sub>2</sub>)]<sub>4</sub>(Et<sub>2</sub>O)<sub>2</sub> (**3**), respectively, and complexes **2** and **3** reacted with 15-crown-5 and 18-crown-6 to form their crown-ether adducts, [CrNa(L<sup>Bn</sup>(N<sub>2</sub>)(15-crown-5)] (**4**) and [CrK(L<sup>Bn</sup>)(N<sub>2</sub>(18-crown-6)] (**5**), respectively (Scheme 1). Their structures were confirmed by X-ray analysis. The IR spectra gave the  $\nu(^{14}\text{N}-^{14}\text{N})$  at 1813 cm<sup>-1</sup> for **2**, at 1804 and 1774 cm<sup>-1</sup> for **3**, at 1813 cm<sup>-1</sup> for **4**, and at 1807 cm<sup>-1</sup> for **5**, respectively. Additionally, all of complexes, **1**, **2**, **3**, **4**, and **5**, reacted with a reductant and a proton source to give NH<sub>3</sub> and/or N<sub>2</sub>H<sub>4</sub>, and **1** gave only N<sub>2</sub>H<sub>4</sub> when using HCl. In this presentation, we will report crystal structures, characterization, and reactivities of these dichromium-dinitrogen complexes.



Scheme 1

1) R. R. Schrock et al., *Science* **2003**, *301*, 76. 2) Y. Nishibayashi et al., *Nature*, **2019**, *568*, 536.