

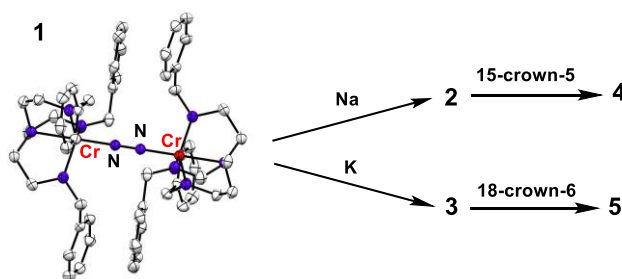
## The syntheses and Structures of Dinitrogen Chromium Complexes Supported with Triamidoamine Ligands

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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>3-</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, [ $\{\text{Cr}(\text{L}^{\text{R}})\}_2(\text{N}_2)$ ] (**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, [ $\{\text{CrNa}(\text{L}^{\text{Bn}})(\text{N}_2)(\text{Et}_2\text{O})\}_2$ ] (**2**) or [ $\{\text{CrK}(\text{L}^{\text{Bn}})(\text{N}_2)\}_4(\text{Et}_2\text{O})_2$ ] (**3**), respectively, and complexes **2** and **3** reacted with 15-crown-5 and 18-crown-6 to form their crown-ether adducts, [ $\text{CrNa}(\text{L}^{\text{Bn}}(\text{N}_2)(15\text{-crown-5}))$ ] (**4**) and [ $\text{CrK}(\text{L}^{\text{Bn}})(\text{N}_2)(18\text{-crown-6})$ ] (**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.