

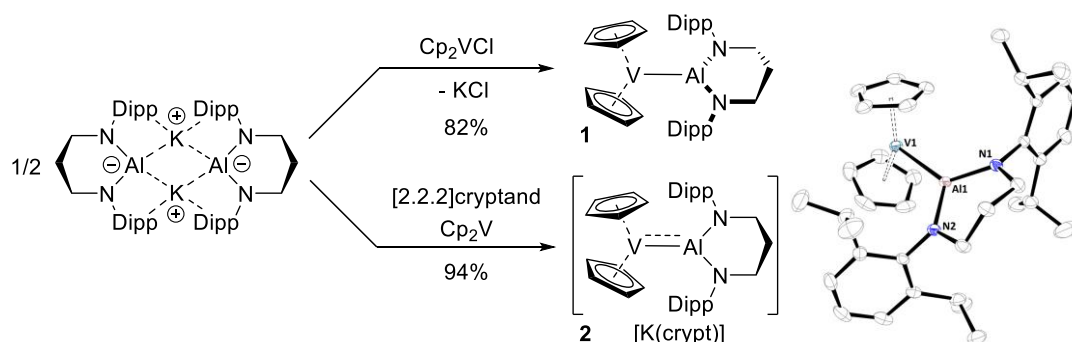
Synthesis and Characterization of Alumanyl Complexes of Vanadium

(Graduate School of Engineering, Nagoya University) ○Pavel Zatsepin, Makoto Yamashita

Keywords: Aluminium, Vanadium, Alumanyl ligand, oxidation state, unpaired electron

Anionic aluminium(I) nucleophiles, alumanyl anions, have recently captivated the inorganic chemistry community.¹ Alumanyl anions are isolobal with carbenes and hence feature a strongly donating, Lewis basic electron pair while simultaneously bearing an empty *p*-orbital imparting electrophilicity at the same Al centre. Unlike carbenes however, investigations of transition metal(TM)-alumanyl coordination chemistry are scarce. The existing literature on TM-alumanyls is focused mainly on late metals.² Late TMs are relatively electronegative compared to Al so late TM–Al bonds tend to be polarised such that the TM centre bears a partial negative (δ^-) charge and Al bears a partial positive (δ^+) charge. Our group has recently reported rare earth-alumanyl complexes of Sc(III) and Y(III) in which this situation is reversed.³ However, these *d*⁰ metal complexes give little opportunity to explore the electronic effects of a σ -donating/ π -accepting Al(I) ligand on a more electropositive metal. In this work we report the first example of a group-5 element bound to such an aluminium moiety.

With yields exceeding 80%, on scales of hundreds of milligrams the V(III) complex [Cp₂VAI(NN)] (**1**) (NN = *N,N'*-(2,6-diisopropylphenyl)propylenediamide) and 1-electron-reduced counterpart [Cp₂VAI(NN)][K(crypt)] (**2**) (crypt = [2.2.2]cryptand) could be prepared. These are first examples of group-5 complexes possessing a TM–Al bond. Reaction of [Cp₂VAI(NN)] with hydrogen yields the 18-electron complex [Cp₂V(μ₂-H)₂Al(NN)] which possesses a shorter V–Al distance than that of its precursor in the solid state. The features of these compounds will be discussed in the presentation.



(Left) Scheme of synthesis of **1** and **2**. (Right) X-ray structure of **1** with H atoms omitted.

Refs: 1. Most recent review: Coles, M. P.; Evans, M. J. *Chem. Commun.* **2023**, doi: 10.1039/D2CC05963K 2. Representative examples: (a) McManus, C. *et al. Chem. Sci.* **2021**, *12*, 13458. (b) Morisako, S. *et al. Angew. Chem. Int. Ed.* **2019**, *58*, 15031 3. (a) Sugita, K.; Yamashita, M. *Chem. Eur. J.* **2020**, *26*, 4520. (b) Feng, G. *et al. J. Am. Chem. Soc.* **2022**, *144*, 22662.