A Vanadium Alumanyl Complex: Synthesis, Characterization, Reactivity, and Application as a Catalyst for C–H Alumanylation of Alkenes

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ABSTRACT: A complex containing a V-Al bond is described. This species can be prepared by either transmetallation of a previously disclosed alumanylpotassium with Cp_2VCl or photolytic oxidative alumination of Cp_2V using the corresponding dialumane(4). Reaction of the resulting V-Al complex with H_2 gave a Cp_2V-dihydridoaluminate complex. These complexes were studied with X-ray crystallography, spectroscopy including vanadium K-edge XANES spectroscopy, and DFT calculations. Finally, the reactivity of these molecules was studied opening the way to a catalytic C–H alumanylation of alkenes.

Complexes featuring an X-type alumanyl ligand coordinated to a transition metal (TM) centre are quite rare. Although the first example was published over 25 years ago (Figure 1, **A**),[1] this subject had remained relatively dormant until the recent advent of alkali metal salts of alumanyl anions[2] as precursors in transmetallation reactions with TM halides (Figure 1, **B**, **C**).[3] Since aluminum has a low electronegativity (1.61, Pauling scale),[4] leading to a strong σ-donating character as a ligand, these complexes exhibited nucleophilic reactivity at the metal center.[3] However, despite recent advances, reports of TM–alumanyls have still generally been limited to late TMs with only three group 3 TM–Al complexes (Figure 1, **D**, **E**) standing as exceptions.[5] Given that the electronegativities of group 4 and 5 TMs are similar to that of Al, group 4 and 5 TM–Al bonds would represent a polarity-covalency regime that has yet to be surveyed. Herein, we report a V–Al complex with its synthesis, characterisation, reactivity, and application as a catalyst for C–H alumanylation of alkenes.

A salt elimination reaction between our previously reported diamino-Al anion **1** with one equivalent of Cp_2VCl afforded a V–Al complex **2** in 82% yield (Scheme 1). This complex **2** can also be generated by irradiation of the mixture consisting of Cp_2V and dialumane **3** with UV-B light at a sluggish pace. It should be noted that the synthesis of gallyl-vanadocene species (Figure 1, **F**)[6] using digallane in the presence of Cp_2V was reported without irradiation of UV-B light. Although **2** exhibited only broad resonances in ^1H NMR spectroscopy due to its paramagnetic character, single-crystal X-ray diffractometry (sc-XRD) revealed the structure of **2**. The V–Al distance of 2.5999(6) Å was shorter than the sum of the covalent radii (2.74 Å). Angles about the Al centre sum to 359.55°, indicating a

trigonal-planar geometry about the Al atom. A magnetic moment of 2.70 μ_B was observed by SQUID between 55K and 400K, somewhat under the spin-only value for an $S = 1$ spin system, 2.83 μ_B. Due to high spin V(III) being a non-Kramers ion, **2** is EPR-silent in X- and Q-band experiments; the zero field splitting is likely too great for a transition to be observed in the field-frequency window available to the instruments used. The UV-Vis spectrum of **2** (Figure S4) shows two peaks at 705 nm (127 M^{-1} cm^{-1}) and 590 nm (236 M^{-1} cm^{-1}), assignable to the $d–d$ transitions from the V-centred highest- and second highest-energy SOMOs to vacant orbitals of metal-ligand antibonding character, that are expected in this bent metallocene complex.[7]
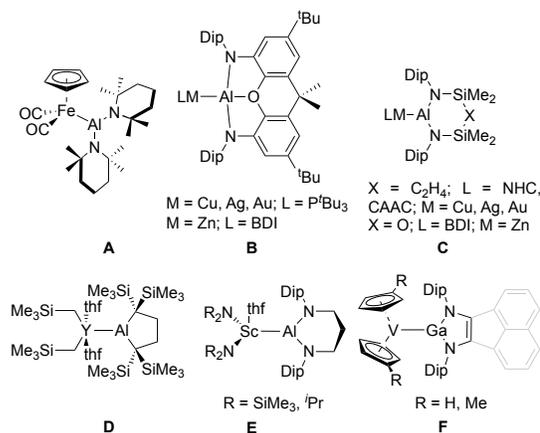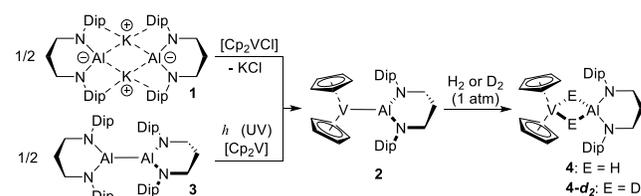
Figure 1. Previous examples of transition metal alumanyl complexes. Dip = 2,6-diisopropylphenyl.

Scheme 1. Synthesis of V–Al complex 2 and its reaction with H_2 or D_2.

Under an atmosphere of hydrogen gas, **2** was converted to **4** possessing two bridging hydride ligands with a color change from blue-green to pale red. The resulting **4** is diamagnetic and provides a sharp set of signals in its ^1H NMR spectrum. A singlet at 3.92 ppm

corresponds to the Cp ligands while another singlet at –13.72ppm is consistent with the presence of two hydride ligands, and the remaining resonances can be assigned to the diamino ligand. Although no ^{27}Al NMR signal of **4** was observed, a broad signal was found at –1105ppm ($\nu_{1/2}$ = 1300 Hz) in the [51]V NMR spectrum. The IR spectrum of **4** exhibited a strong absorption at 1535 cm^{-1}, that can be assigned as M–H vibration. Disappearance of this absorption in the IR spectrum of **4-d_2** (Fig. S14), similarly prepared from **2** with D$_2$, confirms the assignment, that is also supported by the vibrational analysis using DFT calculations (1612 and 1640 cm^{-1}, unscaled, see Fig. S63). The sc-XRD using crystals of **4** revealed a V–Al distance of 2.530(1) Å, notably shorter than that found in **2**. The bridging hydrides could be located from the differential Fourier map, and the angle between the H–Al–H and N–Al–N planes is 31.08° off from the idealized, 90° orientation. This distortion is likely a consequence of steric restrictions imposed by clashing of the diamino ligand and Cp ligands.
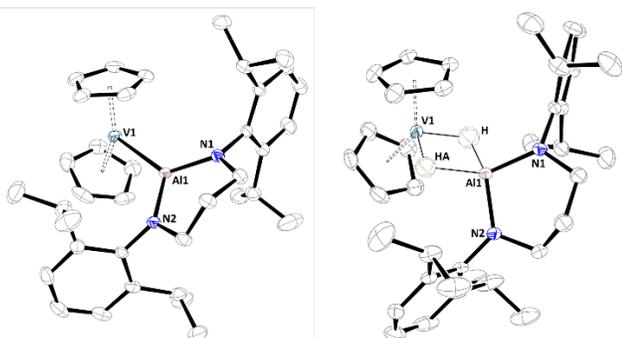

Figure 2. Crystal structures of **2** (left) and **4** (right) with thermal ellipsoids at the 50% probability level. H-atoms except hydride ligands (**4**) and co-crystalized solvent (**4**) omitted for clarity.

Although the above data clarifies the connectivity of **2** and **4**, the electronic structure is somewhat ambiguous because both Al and V atoms have similar electronegativity (Al: 1.61, V: 1.63, Pauling)[4] and flexibility in their oxidation states.[8] Polarization of the V–Al bond in **2** would have two possibilities as described in Figure 3(a). In case it is polarized as V$^+$---Al$^-$, **2** can be considered as alumanyl $[\text{Al(I)}]$–V(III) complex **2-I** with retention of Al-anion character – similar to that of the previously reported Al–Sc complex.[5b] If it would be polarized as V$^-$---Al$^+$, **2** should be considered as vanadocenyl(I) anion-substituted diaminoalumane **2-II**, formed *via* two-electron reduction of the V(III) center by Al(I) reagent. Considering the similar polarization between V and Al atoms and the related group 5 metallocene hydridoborate species,[9] one can speculate that **4** has three possible bonding situations $[\text{Figure 3(b)}]$. If V and Al atoms still have a polarized bond as V$^+$---Al$^-$, **4** should be described as alumanyl $[\text{Al(I)}]$–V(V)H$_2$ complex **4-I**, that would be consistent with the shorter V–Al distance in **4** than in **2**. The opposite polarization having V$^-$---Al$^+$ character would provide dihydrovanadate(III) anion-coordinated diaminoalumane **4-II**. In case two hydrogen atoms attached to the Al atom, it should be considered as (N$_2$AlH$_2$)$^-$ anion-coordinated cationic vanadocene **4-III** through μ^2-H$_2$Al coordination mode or two V–H–Al 3c-2e bonds with the bridging hydrides. To gain experimental insight into the oxidation state, vanadium K-edge X-ray absorption near edge structure (XANES) spectroscopy was employed (Figure 4; See Fig S56. for more details). The edge energy of **2** was slightly lower than other V(III) compounds such as $[\text{Cp}_2\text{VCl}]$ but notably higher than V(II) species such as $[\text{Cp}_2\text{V}]$. This may speak to the polar-*covalent* character of the V–Al bond with

significant sharing of electrons leading to a slightly reduced V(III) center. In contrast, the edge energy of **4** was found to be consistent with a V(III) oxidation state and clearly lower than those of V(IV) and V(V) species – strong evidence that assignment as **4-I** in the oxidation state of V(V) is not appropriate.
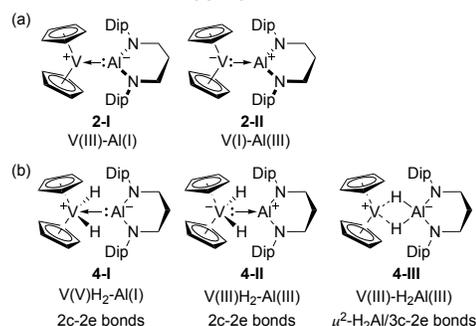

Figure 3. Several conceivable ways to describe bonding situation and oxidation state in **2** and **4**.
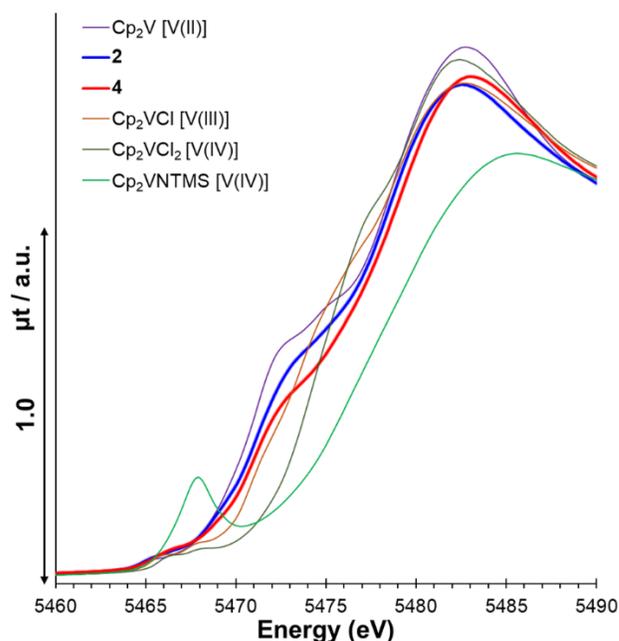

Figure 4. Vanadium K-edge XANES spectra of various reference compounds of vanadium in oxidation states (II) through (IV) and complexes **2** and **4**.

Further insight into the electronic structure and bonding of **2** and **4** was obtained with DFT calculations (see SI for further details). Computed geometries excellently reproduced those obtained by sc-XRD with the calculated V–Al distances of 2.6037 Å (for **2**) and 2.512 Å (for **4**). Quantum Theory of Atoms in Molecules (QTAIM) analysis was also performed (Figure 5). A bond critical point (BCP) was located along a path between V and Al atoms in **2** $[\text{Figure 5(a)}]$ indicating the existence of a bonding interaction. The value of the Laplacian of electron density $[\nabla^2\rho]$ at this BCP is –0.0612 and suggests that the V–Al bond in **2** is covalent, unlike species **E** in which the Sc–Al interaction was found to be ionic.[5] The AIM basin charges (q) of V and Al were 0.888 and 1.786 respectively, hence $\Delta q_{\text{Al-V}}$ = 0.898, a smaller charge difference than those calculated for covalently bonded Cu–, Ag–, Au–, or Zn–Al complexes is indicative of the less polarized V–Al bond in **2** relative to the late-TM–Al bonds.[3] In the case of **4**, no BCP was found between the V and Al atoms; rather, there are curved bond paths and BCPs between each metal and the bridging hydrides with a ring critical point (RCP) in the

centre of the plane containing these four atoms [Figure 5(b)]. This result clearly indicates the existence of two 3c–2e bonds in V–H–Al moieties. Hence, forms **2-I** and **4-III** are consistent with the results obtained from XANES spectra and DFT calculations.
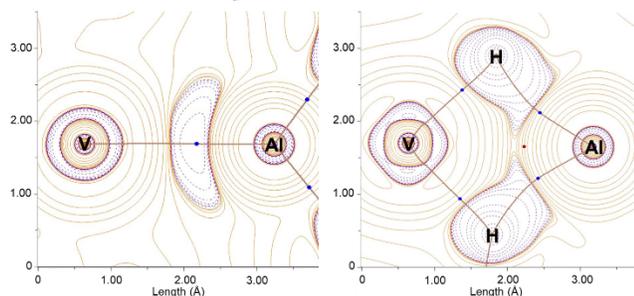

Figure 5. Topological QTAIM-derived plots of $\nabla^2\rho$ for **2** (left) and **4** (right). Solid, orange contours where $\nabla^2\rho > 0$; dashed, violet contours where $\nabla^2\rho < 0$. Blue dots are BCPs, crimson dots are RCPs, brown lines are bond paths.

Reactivity of the V–Al bonded species **2** and its H_2 adduct **4** was also evaluated (Scheme 2). A C_6D_6 solution of **2** was exposed to 1 atm of ethylene at ambient temperature leading to a color change from blue-green to purple. The ^1H NMR spectrum of the final product mixture displayed a complete consumption of **2** and formation of **4** and vinylalumane **5** in a 1:2 ratio. The existence of **5** was strongly supported by vinylic NMR signals at 5.92 and 5.64 ppm (by comparison with those of independently prepared **5**, Fig. S15). Recrystallization of the residue of this sample from hexane with the addition of several drops of THF provided colourless single crystals of **5-thf** as identified by sc-XRD (Fig. S57). Similarly, a stoichiometric reaction between 1-octene and **2** gave 1-octenylalumanes *(E)*-**6**/*(Z)*-**6** as a mixture in a 4/1 ratio with **4**. The identity of *(E)*-**6**/*(Z)*-**6** was further confirmed by comparison to an independently prepared sample as well by subsequent iodination to liberate 1-octenyl iodide (Figs. S21, S55) The regiochemistry of *(E)*- and *(Z)*-isomer was assigned with a characteristic $^3J_{HH}$ coupling constant. We propose that this alumination reaction proceeds through a 1,2-insertion of alkenes to V–Al bond to afford 1,2-dimetallated alkane **7**, a step that was recently demonstrated by Crimmin for Fe–Al bonds,[10] followed by a β-hydride elimination with putative formation of [Cp₂VH], which could decompose to Cp₂V with spontaneous generation of H_2.[11] In fact, we observed a purple color confirmed as Cp₂V by UV-Vis (Figure S39) after the reaction finished. Although **4** did not react with atmospheric ethylene at ambient temperature, heating at 80 °C led to the formation of an ethylalumane **8** with consumption of **4**. Since this represents a hydroalumination of ethylene, we assumed the dissociation of hydroalumane intermediate **9** from **4**. In fact, dissolution of **4** in THF-d_8 leads to noticeable colour change from red to purple with visible effervescence of H_2 and **9-thf-d8** was identified in the ^1H NMR spectrum.

Scheme 2. Reactions of 2 and 4 with alkenes and THF.
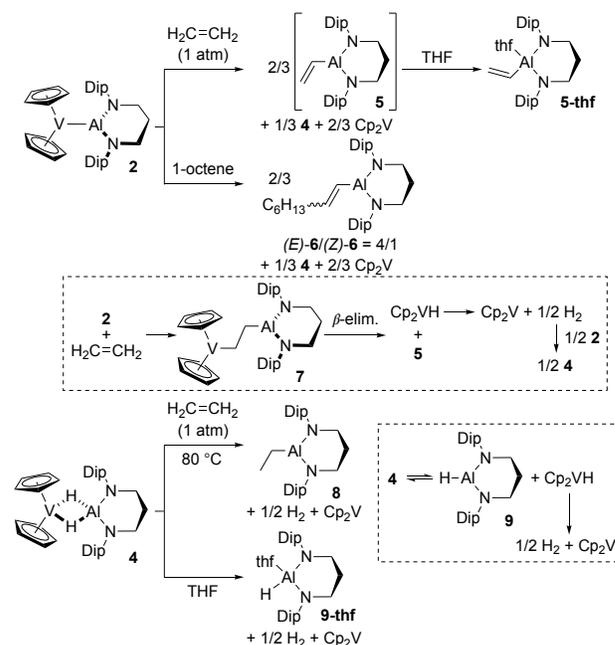
To confirm the dissociation of **8** from **4**, an isotopic labeling experiment was performed with deuterium-enriched **4-d_2** (Scheme 3). Heating **4-d_2** under 1 atm of H_2 in C_6D_6 at 85 °C led to a gradual increase of the characteristic hydride signal of **4** at −13.72ppm with an appearance of a triplet signal of HD in the ^1H NMR spectrum. We hypothesise that the formation of HD may be mediated by [Cp₂VD] which should be generated from **4-d_2** as this kind of reaction is known for [Cp₂MH] (M = Nd, Ta) and [Cp*₂VH] complexes.[12] Following the 1:1 mixture of **4-d_2** and **4** and heating at 80 °C, ^1H NMR spectroscopy at -50 °C displayed two sets of hydride signals indicative of the presence of **4-d_1** alongside **4**. Finally, addition of independently synthesized **(9)₂** to **4-d_2** resulted in the appearance of a hydride signal of **4-d_1** at −13.69 ppm further supporting the lability of **9** and the putative [Cp₂VH] from **4**.

Scheme 3. Isotope labelling experiments probing the equilibrium between 4 and 9+Cp₂VH.
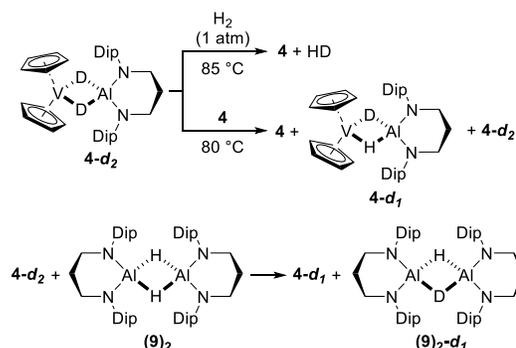
Considering all the reactions described here, we noticed the potential for Cp₂V to act as a catalyst in the C–H alumanylation of alkenes in the presence of dialumane **3** under irradiation of UV-B light. Mixing **3** with a large excess of 1-octene and a catalytic amount of Cp₂V (10 mol% V to Al) in hexane under 310 nm irradiation at room temperature for 5 hours gave the corresponding 1-octenylalumanes *(E)*-**6**/*(Z)*-**6** in 71%/16% yield as judged by the ^1H NMR spectrum of the crude mixture [Scheme 4(a)]. This is an unusual C–H functionalization in the context of vanadium chemistry; oxovanadium

compounds are well-known in C–H hydroxylation through a hydrogen abstraction mechanism.[13] The catalytic cycle [Scheme 4(b)] would involve a photochemical generation of **2** from Cp₂V and **3**, insertion of 1-octene to form dimetallated alkane **10**, β-hydride elimination to afford **11**, dissociation of (E)-**6**/(Z)-**6** to liberate Cp₂VH, and spontaneous H₂ evolution to regenerate Cp₂V, as the most of the elementary steps were experimentally confirmed. Considering the analogous vinylic C–H borylation reactions catalyzed by *late* TMs[14] are widely used for organic transformation, the unprecedented C–H alumanylation in this work would also have an impact to the organic synthesis field.

Scheme 4. Photocatalytic dehydrogenative alumination of 1-octene by vanadocene catalyst.
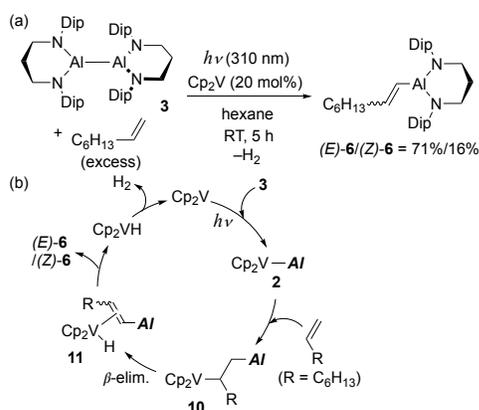
In summary, the first instance of a complex containing a V–Al bond has been prepared by either salt metathesis or by a photochemical route. This V–Al complex **2** reacts with H₂ to yield a vanadium dihydridoaluminate **4**. Combination of XANES analysis and DFT calculations provided insights into the oxidation states of each metal atom and bonding situations in **2** with 2c-2e V–Al bond and **4** with 3c-2e V–H–Al bonds. The bridging hydride species **4** was also shown to be labile towards release of hydidoalumane **9** and Cp₂VH as confirmed by control experiments. The vanadium alumanyl is also involved as an intermediate in a photocatalytic C–H alumanylation of alkenes using Cp₂V as a catalyst.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.
Experimental and computational details (PDF)
Crystallographic data for **1**, **2**, **5-thf**, **8**, and (**9**)₂ (CIF)
DFT coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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Dip

R–CH

HC–Al

Dip

+ 1/2 H₂

R–CH

CH₂

Dip

V

Al

Dip

Unsupported V–Al bond!

☑ *Synthesis* ☑ *Spectroscopy*
☑ *Theory* ☑ *Reactivity*

1/2

Dip

N

Al — Al

N

Dip

Dip

N

Dip

hv

V

Al

V