Synthesis and reactions of β-diketiminato divanadium(I) inverted-sandwich complexes†

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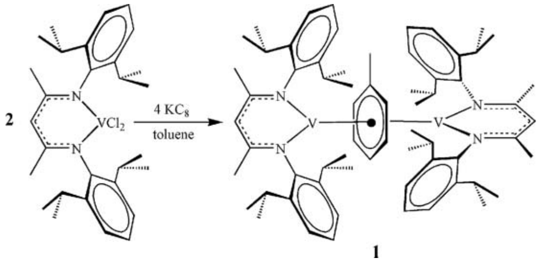
Reduction of VCl_2(Nacnac) (Nacnac = $HC(C(Me)NC_6H_3$-*i*$Pr_2)_2$) with KC_8 in toluene leads to the formation of a toluene-bridged inverted-sandwich divanadium(I) complex, (μ-η^6:η^6-C_7H_8)[V(Nacnac)]$_2$, which behaves as a source of V(Nacnac) and a multi-electron reductant in the two reactions studied in this report.

Low-valent and low-coordinate transition metal complexes are rare. This is partly due to the difficulty encountered by such metal ions in acquiring the stable 16 or 18 valence electrons in its orbitals. The employment of sterically demanding ligands can kinetically stabilize transition metal centers in low coordination numbers. Recently, β-diketiminates have received considerable attention as ancillary ligands for metal complexes.[1] Of particular interest is their ability to stabilize low-coordinate univalent main group[2] and d-block elements.[3–7] Low-valent vanadium complexes have been shown to catalyze remarkable organic transformations; for example, the epoxidation of olefins, the dehalogenation of organic halides catalyzed by $CpV(CO)_4$[8] and the activation of dinitrogen.[9] Accordingly, we are interested in pursuing low-valent vanadium complexes supported by β-diketiminates and exploring their reactivity. In this Communication, we describe the synthesis, characterization and reactivity studies of divanadium inverted sandwich complexes (μ-η^6:η^6-arene)[V(Nacnac)]$_2$ (Nacnac = $HC(C(Me)NC_6H_3$-*i*$Pr_2)_2$). The preliminary results indicate that these remarkable complexes can efficiently generate V(I)(Nacnac), from which a vanadium oxide and the first vanadium bis(imido) compound can be prepared.

Probably due to geometrical and electronic effects, the reduction of $[V(N_2N)Cl]_2$ (where $(N_2N)^{2-}$ = $(Me_3SiN(CH_2CH_2NSiMe_3)_2)^{2-}$) in toluene with one equivalent of KC_8 under N_2 afforded deep red nitrido complex $[V(N_2N)_2)(\mu\text{-}N)]_2$.[9] However, the addition of 2.5 equiv. of KC_8 to a deep brown-red solution of VCl_2(Nacnac)[10] in toluene under N_2 gave rise to a dark blue-green solution, from which an inverted-sandwich divanadium compound, (μ-η^6:η^6-C_7H_8)[V(Nacnac)]$_2$ (**1**), was isolated as a deep blue crystalline substance in 66 and 28% yield by recrystallizing from toluene and *n*-hexane, respectively (Scheme 1). The variation of χT with respect to temperature for **1** is shown in Fig. 1, and the magnetic susceptibility features an effective magnetic moment between 4.6 and 4.8 μ_B in the temperature range 9–300 K. The room temperature effective moment of 4.8 μ_B is in agreement with an $S = 2$ spin-only system. **1** is therefore best thought of as a V(I)–V(I) complex, in which each V(I) center possesses two unpaired electrons.



Scheme 1

X-Ray absorption measurements were performed to clarify the detailed electronic structure. To confirm the vanadium valency, we measured the V K-edge X-ray absorption spectrum of compound **1** and of reference compounds (V foil, V_2O_3 and VO_2) with various vanadium valencies, as shown in Figure S1 (ESI†). A plot of the X-ray absorption edge energy, E_0, of V for **1** and the reference compounds *vs.* its oxidation state displays a nearly linear relationship (Fig. 2), accordingly clearly indicating an oxidation state of +1 for V in **1**.

The dinuclear nature of **1** was deciphered by X-ray crystallography, as depicted in Fig. 3.‡ The two six-membered rings of V(Nacnac) adopt a planar conformation. Noteworthy are the slightly different distances between the vanadium atoms and the bridging toluene ligand. The V(2)–C distances to the toluene ring

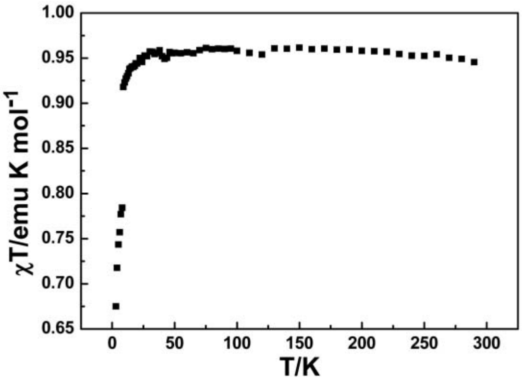


Fig. 1 Magnetic susceptibility of **1** between 2 and 300 K.

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† Electronic supplementary information (ESI) available: Experimental details of the syntheses, X-ray crystallographic data of **1**, **2** and **3**, and the V K-edge absorption spectra of V foil, **1**, V_2O_3 and VO_2. See DOI: 10.1039/b711816c

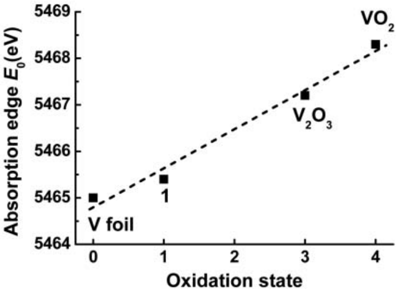

Fig. 2 The V K-edge X-ray absorption near edge structure (XANES) of **1** and reference samples: a plot of the X-ray absorption edge energy, E_0, of V *vs.* its oxidation state.

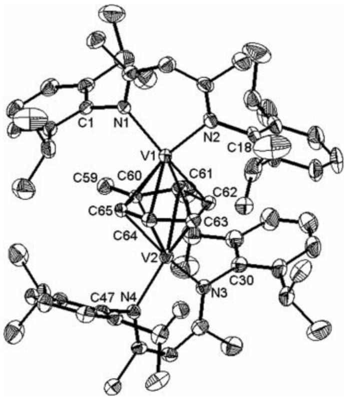

Fig. 3 Molecular structure of **1** with thermal ellipsoids at the 30% probability level.

are approximately equal and average 2.242 Å, while the corresponding V(1)–C distances range from 2.183(5) to 2.491(5) Å, the longest distance being to one of the methyl group-substituted carbon atoms of the ring. As a consequence, the whole molecule is distorted, in-as-much as both vanadium atoms tend towards the same edge of the bridging toluene, C(62)–C(63).

Transition metal systems in which benzene or toluene bridges two metal centers in a symmetrical η^6,η^6 fashion are rare,[11] an example being $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)(VCp)_2$,[11a] which undergoes arene exchange reactions when it is heated to 110 °C. However, dissolution of $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6D_6)[V(Nacnac)]_2$ (prepared by reducing $VCl_2(Nacnac)$ with KC_8 in C_6D_6) in toluene at room temperature lead to the liberation of C_6D_6, as observed by ^2H NMR (see ESI†). This clearly indicates that complex **1** readily undergoes an arene exchange reaction at room temperature, presumably due to steric pressure imposed by the Nacnac ligand. The chemical reactivity of **1** also supports the conclusions, because **1** behaves as a source of V(Nacnac) and a multi-electron reductant upon reaction with appropriate substrates, such as N_2O and azobenzene.

Nitrous oxide, N_2O, is generally regarded as kinetically inert towards reduction[12] and is a poor ligand;[13] nevertheless, N_2O can either be split by low-valent and low-coordinate metal complexes through the N–O bond to form N_2 and metal oxides,[14] or *via* the N–N bond to form metal nitride and nitrosyl complexes.[15] Exposure of an ethereal solution of **1** to N_2O led to a quick color change to orange. A new crystalline dinuclear complex $(\mu\text{-}O)[V(O)(Nacnac)]_2$ (**2**) was isolated in moderate yield. The solution magnetic moment of compound **2**, of 2.71 μ_B at room temperature, is consistent with an $S = 1$ spin-only system. The structure of **2**, as depicted in Fig. 4, was determined by X-ray crystallography.‡ It reveals that neither V atom is coplanar with the NCCCN planes of the Nacnac ligands. Of particular interest is the non-linear V(1)–O(3)–V(2) array and the O(1)–V(1)–V(2)–O(2) dihedral angle of 66.4°, most likely to be a consequence of the minimization of steric repulsion between the two Nacnac ligands, in which two pairs of sterically encumbered $2,6\text{-}C_6H_3\text{-}i\text{Pr}_2$ groups exist in a staggered orientation.

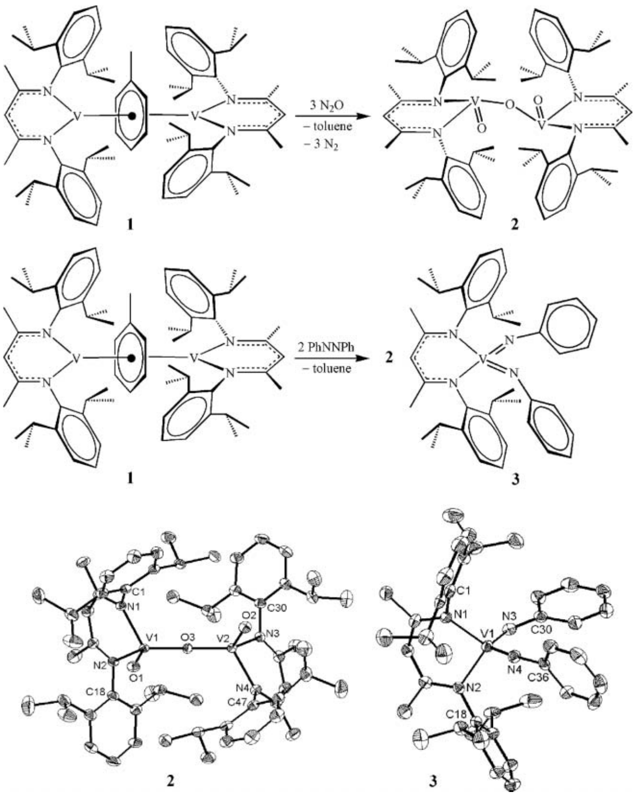

Fig. 4 Reactivity of **1** and X-ray molecular structures of **2** and **3** with thermal ellipsoids at the 30% probability level.

In contrast to the rich chemistry of bis(imido) compounds of group 6,[16] bis(imido) complexes of group 5,[17] particularly vanadium, have been less well explored due to the lack of synthetic approaches. Azobenzene reductive cleavage to form mononuclear bis(phenylimido) derivatives represents an intriguing N–N bond cleavage process.[16] The treatment of **1** with 2 equiv. of azobenzene in ether led to a quick color change to yellow. A yellow crystalline compound was thereby obtained in 68% isolated yield and formulated as the vanadium(V) bis(imido) complex $V(NPh)_2(Nacnac)$ (**3**) by virtue of a single crystal X-ray diffraction study.‡ It thus represents the first reported vanadium bis(imido) complex (Fig. 4). In the structure, the V atom has moved out of the NCCCN plane of the Nacnac ligand, enabling the aryl groups at the nitrogen atoms to tilt, thus relieving steric repulsion between the phenylimides and the *i*Pr substituents. Complex **3** in the solid state features two different imido substituents, one bent and one linear, and the sum of the imido bond angles of 316.9° is significantly smaller than the average sum of the imido bond angles of 328° for tetrahedral group 6 bis(imido) complexes.[18] However, the two imido groups of **3** quickly exchange in solution on the NMR time scale at room temperature.[19]

In conclusion, an attempt to prepare the putative two-coordinate vanadium(I) β-diketiminate complex V(Nacnac) led instead to the isolation and characterization of a reactive divanadium inverted sandwich complex, **1**. In the two reactions studied thus far, **1** behaves as a source of V(Nacnac), serving to transfer the dicoordinate V fragment. Compound **1** is shown to be electrochemically versatile, in that it servers as an 8e reductant in its azobenzene splitting reactions and as a 6e reductant in its N_2O activation. Further exploration of **1** by reacting it with other organic functionalities is ongoing and will be reported in due course.

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Notes and references

‡ *Crystallographic data* for **1**: $C_{68}H_{97}N_4V_2$, M_w = 1072.38, T = 200(2) K, monoclinic, space group $P21/n$, a = 17.6990(5), b = 15.3858(5), c = 24.9682(7) Å, β = 107.898(2)°, V = 6470.1(3) Å^3, Z = 4, D_c = 1.101 Mg m^{-3}, μ = 0.329 mm^{-1}, reflections collected: 33240, independent reflections: 11655 (R_{int} = 0.1042), Final R indices [$I > 2\sigma I$]: $R1$ = 0.0974, w$R2$ = 0.2198, R indices (all data): $R1$ = 0.1746, w$R2$ = 0.2533; **2**: $C_{132}H_{202}N_8O_7V_4$, M_w = 2216.78, T = 200(2) K, monoclinic, space group $P21/c$, a = 13.7676(2), b = 21.2023(4), c = 23.5956(5) Å, β = 106.4620(10)°, V = 6605.3(2) Å^3, Z = 2, D_c = 1.115 Mg m^{-3}, μ = 0.328 mm^{-1}, reflections collected: 32107, independent reflections: 11904 (R_{int} = 0.0909). Final R indices [$I > 2\sigma I$]: $R1$ = 0.0721, w$R2$ = 0.1908, R indices (all data): $R1$ = 0.0940, w$R2$ = 0.2072; **3**: $C_{47}H_{56}N_5V$, M_w = 741.91, T = 200(2) K, monoclinic, space group $P21/n$, a = 12.7056(4), b = 17.7171(6), c = 18.9744(9) Å, β = 98.778(2)°, V = 4221.2(3) Å^3, Z = 4, D_c = 1.167 Mg m^{-3}, μ = 0.272 mm^{-1}, reflections collected: 22694, independent reflections: 7898 (R_{int} = 0.1007). Final R indices [$I > 2\sigma I$]: $R1$ = 0.0848, w$R2$ = 0.1919, R indices (all data): $R1$ = 0.1688, w$R2$ = 0.2243. CCDC-645658 (**1**), CCDC-645659 (**2**), and CCDC-645660 (**3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711816c.

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