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PAPER

Ligand-controlled synthesis of vanadium(I) β -diketiminates and their catalysis in cyclotrimerization of alkynes[†]

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Three dimeric vanadium(1) β -diketiminates [V{ μ -(η^6 -ArN)C(Me)CHC(Me)C(N-Ar)}]₂ (Ar = 2,6-Me₂C₆H₃ (**2**), 2,6-Et₂C₆H₃ (**3**), 9-anthracenyl (**4**)) were prepared and isolated upon reduction of their corresponding dichloro precursors VCl₂(Nacnac). Compounds **2–4** all show a structure with each vanadium atom being η^2 bonded to the β -diketiminate framework and η^6 bonded to a flanking ring of a β -diketiminato ligand, attached to the other vanadium centre within the dimer. No metal-metal bonding interactions are observed in these dimers due to long vanadium–vanadium separations. Compounds **2–4** display an antiferromagnetic exchange between the two vanadium centres. An imido azabutadienyl complex (η^2 -PhCC(H)C(Ph)NC₆H₃-2,6-ⁱPr₂)VN(C₆H₃-2,6-ⁱPr₂)(OEt₂) (**5**) was isolated from the reduction of VCl₂(HC(C(Ph)NC₆H₃-2,6-ⁱPr₂)₂) by KC₈. Compounds **2–4** and the inverted-sandwich divanadium complex (μ - η^6 : η^6 -C₆H₅Me)[V(HC(C(Me)NC₆H₃-2,6-ⁱPr₂)₂)] (**1**) reduce Ph₂S₂ to give two vanadium dithiolates V(SPh)₂[(HC(C(Me)NC₆H₃-2,6-R₂)₂)] (R = Et (**6**), ⁱPr (**7**)) through an oxidative addition. Most notably, **1** and **3** catalyze the cyclotrimerization of alkynes, giving tri-substituted benzenes in good yields and a 1,3,5-triphenylbenzene coordinated intermediate **8** was isolated and characterized.

1. Introduction

Due to the ease of preparation and modification of their steric and electronic demands, β -diketiminates have been widely used as ancillary ligands in the assembly of metal complexes.¹ Of particular interest for the β -diketiminato ligands is their ability to support reactive metal fragments, which can be applied as active catalysts¹⁻¹⁰ and to model relevant active sites in biological systems.^{11,12} It is noteworthy that β -diketiminato ligands have also been employed to stabilize high-valent transition metals. For example, Mindiola, Warren and Power have recently demonstrated that β -diketiminates can support high-valent reactive early transition metal–ligand multiple bonding functionalities, such as alkylidenes,^{13,14} alkylidynes,¹⁵ imides,¹⁶⁻¹⁹ and phosphinidenes.²⁰ Furthermore, transition metal β -diketiminates also show their high reactivity toward the activation of thermodynamically robust molecules, such as alkanes^{21,22} and dinitrogen.^{23,24}

In addition to stabilizing the high-valent metal centres, β -diketiminates also support low-valent transition metal complexes,²⁵ which not only demonstrate interesting electronic structures, but also novel reactivity. For example, we and Theopold's group recently reported the synthesis of inverted sandwich type complexes $(\mu - \eta^6 \cdot \eta^6 - \text{Arene})[M(\text{Nacnac})]_2$ (Arene = C_6H_6 , C_6H_5Me for M = Cr and Arene = C_6H_5Me for M = V; Nacnac = $HC(C(Me)NC_6H_3-2,6^{-i}Pr_2)_2)$.^{25e-h} In contrast to the usual low-spin organometallic compounds, these β -diketiminatesupported inverted sandwich complexes exhibit high-spin states, a septet state for M = Cr and a quintet state for $M = V^{26}$ Not only do these dinuclear inverted sandwich complexes feature unusual electronic schemes, but they are very reactive species. Reactivity studies of these complexes establish that they behave as two equivalents of multi-electron reductants, M(Nacnac). For example, monomeric diimido and dioxo products were isolated from the reactions of $(\mu - \eta^6 : \eta^6 - C_6 H_5 Me)[M(Nacnac)]_2$ (M = Cr, V) and organic azides, azobenzene and dioxygen via reductive cleavage processes.^{25e-g} Warren also described that the β -diketiminate supported univalent cobalt^{25c} and nickel^{25d} complexes are good synthons for the preparation of mono-imido complexes.

However, it is worthy to mention that the sterically encumbering $HC(C(Me)NC_6H_3-2,6^{-i}Pr_2)_2$ is so far the most frequently used β -diketiminate to assemble metal complexes. There is no systematic study on the structures and reactivity of metal β -diketiminate compounds as a consequence of the steric variation of the ancillary ligands.

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[†] Electronic supplementary information (ESI) available: X-ray crystallographic data of **2–8** including CIF files. CCDC reference numbers 788574– 788579. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01061h

In this work, we report that besides the di-vanadium inverted sandwich type complex $(\mu-\eta^6:\eta^6-C_6H_5Me)[V(Nacnac)]_2$ with Nacnac = HC(C(Me)NC₆H₃-2,6^{-*i*}Pr₂)₂, vanadium β -diketiminate can exist in a different form. Upon reducing the steric hindrance of the supporting β -diketiminato ligand, a different type of di-vanadium β -diketiminato complex [V{ μ - $(\eta^{6}-ArN)C(Me)CHC(Me)C(NAr)]_{2}$ (Ar = 2,6-Me₂C₆H₃, 2,6-Et₂C₆H₃, 9-anthracenyl) is isolated, where two "V(Nacnac)" molecules are connected to each other via coordination of one of the phenyl rings of one V(Nacnac) to the other vanadium centre in an η^6 fashion. On the other hand, a two-electron reduction reaction of a V(III) precursor supported by sterically encumbering Nacnac (HC(C(Ph)NC₆H₃-2, 6^{-i} Pr₂) results in the cleavage of the backbone C-N bond and gives rise to the formation of terminal imide stabilized by the azabutadienyl scaffold. The synthesized univalent di-vanadium β -diketiminato complexes are reducing. They all react with diphenyldisulfide to give V(SPh)2(Nacnac) via a reductive S-S bond cleavage reaction. Moreover, they all catalyze the cyclotrimerization reaction of alkynes to give tri-substituted benzenes

2. Experimental

General information

Unless stated otherwise, all operations were performed using standard Schlenk techniques or in a Vacuum Atmospheres dry box under an atmosphere of nitrogen. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled under nitrogen from purple sodium benzophenone ketyl. n-Hexane was distilled under nitrogen from CaH₂. Distilled solvents were transferred under vacuum into vacuum-tight glass vessels before being transferred into a dry box. C_6D_6 was purchased from Aldrich and was degassed and dried over 4 Å sieves. The 4 Å sieves and Celite were dried in vacuo overnight at a temperature just above 200 °C. The inverted sandwich divanadium complex $(\mu-\eta^6:\eta^6-C_6H_5Me)[V(HC(C(Me)NC_6H_3-2,6 {}^{i}Pr_{2}_{2}_{2}_{2}_{2}$ (1)^{25f} and VCl₂[HC(C(Me)NC₆H₃-2,6-R₂)₂] (R = Me, Et)²⁷ were prepared following the literature method. All other compounds were used as received. ¹H and ¹³C NMR spectra were recorded on Varian Unity INOVA 500 MHz or Bruker DMX 600 MHz spectrometers at room temperature. ¹³C NMR spectra are proton decoupled. Chemical shifts of ¹H and ¹³C spectra are reported with respect to internal solvent: 7.16 ppm and 128.00(t) ppm (C_6D_6) and external solvent: 7.16 ppm for ²H spectra.

Synthesis of VCl₂[HC(C(C₆H₅)NC₆H₃-2,6-^{*i*}Pr₂)₂]

A sample of 630.0 mg (1.148 mmol) of (THF)Li-[HC(C(C₆H₅)NC₆H₃-2,6-'Pr₂)₂] was dissolved in 10 mL of tetrahydrofuran (THF) in a 20 mL vial. Meanwhile, a sample of 515.0 mg (1.378 mmol) of VCl₃(THF)₃ was suspended in 5 mL of THF, also in a 20 mL vial. Both resultant solutions were kept at -35 °C for 30 min, at which point the ligand solution was added to the stirred suspension of VCl₃(THF)₃. The mixture was allowed to warm to room temperature and then stirred for a further 12 h at room temperature. The solution became dark brown and was filtered through a pad of Celite and washed by 4 mL of THF twice. The filtrate was stripped to dryness under vacuum and the resultant solid was extracted into 15 mL of diethyl ether. The solution was concentrated and kept at –35 °C to produce dark brown singlecrystal X-ray quality crystals. The isolated yield was 65.1% (469.0 mg) in one crop. Anal. calcd for $C_{40}H_{48}N_2Cl_2V$: C 70.58, H 6.83, N 4.22; Found: C 71.04, H 6.63, N 3.89. $\mu_{eff} = 2.92 \ \mu_B$ (Evans' method, C_6D_6).

Synthesis of $[V{\mu-(\eta^6-2,6-Me_2C_6H_3-N)C(Me)-CHC(Me)C(N-2,6-Me_2C_6H_3)}]_2$ (2)

A sample of 200.0 mg (0.468 mmol) of [HC(C(Me)N-2,6- $Me_2C_6H_3)_2$ [VCl₂ was dissolved in 10 mL of tetrahydrofuran (THF) in a 20 mL vial. Meanwhile, a sample of 189.8 mg (1.4041 mmol) of KC₈ was suspended in 2 mL of THF also in a 20 mL vial. Both resultant solutions were kept at -35 °C for 30 min, at which point, to the stirred suspension of KC8 was added the vanadium complex solution. The solution was allowed to warm to room temperature and quickly turned into dark brown from red. It was then stirred for a further 10 h at room temperature. The solution was filtered through a pad of Celite and washed by 4 mL of THF twice. The filtrate was stripped to dryness under vacuum and the resultant solid was extracted into 10 mL of diethyl ether. The solution was concentrated and kept at -35 °C to produce single-crystal X-ray quality crystals. The isolated yield was 10.0% (16.7 mg) in one crop. Anal. calcd for C₄₂H₅₀N₄V₂ (2): C 70.77, H 7.07, N 7.86; Found: C 70.24, H 6.87, N 7.46. $\mu_{\text{eff}} = 2.92 \ \mu_{\text{B}}$ (Evans' method, $C_6 D_6$).

Synthesis of $[V{\mu-(\eta^6-2,6-Et_2C_6H_3-N)C(Me)-CHC(Me)C(N-2,6-Et_2C_6H_3)]_2$ (3)

A sample of 170.0 mg (0.352 mmol) of [HC(C(Me)N-2,6- $Et_2C_6H_3)_2$]VCl₂ was dissolved in 8 mL of tetrahydrofuran (THF) in a 20 mL vial. Meanwhile, a sample of 104.6 mg (0.774 mmol) of KC₈ was suspended in 4 mL of THF also in a 20 mL vial. Both resultant solutions were kept at -35 °C for 30 min, at which point, to the stirred suspension of KC8 was added the vanadium complex solution. The resultant mixture was allowed to warm to room temperature and quickly turned into dark brown from deep red. It was then stirred for a further 10 h at room temperature. The solution was filtered through a pad of Celite and washed by 4 mL of THF twice. The filtrate was stripped to dryness under vacuum and the resultant solid was extracted into 10 mL of n-hexane. The solution was concentrated and kept at -35 °C to produce singlecrystal X-ray quality crystals. The isolated yield was 29.5% (42.8 mg) in one crop. Anal. calcd for $C_{50}H_{66}N_4V_2$ (3): C 72.79, H 8.06, N 6.79; Found: C 72.38, H 8.20, N 6.35. $\mu_{eff} = 2.86 \ \mu_B$ (Evans' method, C_6D_6).

Synthesis of $[V{\mu-(\eta^6-9-anthracenyl-N)C(Me)-CHC(Me)C(N-9-anthracenyl)}]_2$ (4)

A sample of 530.0 mg (0.882 mmol) of (THF)Li[HC(C(Me)N(9anthracenyl))₂] was dissolved in 10 mL of tetrahydrofuran (THF) in a 20 mL vial. Meanwhile, a sample of 330.0 mg (0.882 mmol) of VCl₃(THF)₃ was suspended in 5 mL of THF also in a 20 mL vial. Both resultant solutions were kept at -35 °C for 30 min, at which point, the β -diketiminate solution was added to the stirred suspension of VCl₃(THF)₃. The mixture was allowed to warm to room temperature and was stirred for a further 24 h. The suspension became dark green. The dark suspension was cooled to -35 °C, 262.0 mg (1.941 mmol) of KC₈ was added and the resultant mixture was stirred for 12 h. The suspension turned into gray black and was filtered through a pad of Celite and washed by 4 mL of THF twice. The filtrate was stripped to dryness under vacuum and the black residue was extracted into 20 mL of diethyl ether. Subsequently, the black ethereal solution was stripped to dryness and the black residue was extracted into *n*-hexane. The *n*-hexane solution was concentrated and kept at -35 °C to produce black single-crystal X-ray quality crystals. The isolated yield was 23.1% (222.0 mg) in one crop. Anal. calcd for C₇₂H₆₄N₄V₂ (4): C 79.54, H 5.93, N 5.15; Found: C 79.16, H 5.51, N 5.11. $\mu_{eff} = 2.49$ μ_{B} (Evans' method, C₆D₆).

Synthesis of $[\eta^4-2,6^{-i}Pr_2C_6H_3N(C_6H_5)CCHC(C_6H_5)]V(NC_6H_3-2,6^{-i}Pr_2)(OEt_2)]$ (5)

A sample of 277.0 mg (0.417 mmol) of VCl₂[HC(C(C_6H_5)NC₆H₃-2,6-^{*i*}Pr₂)₂] was dissolved in 10 mL of THF in a 20 mL vial. Meanwhile, a sample of 124.0 mg (0.917 mmol) of KC₈ was suspended in 10 mL of diethyl ether also in a 20 mL vial. Both resultant solutions were kept at -35 °C for 30 min, at which point, to the KC₈ suspension was added the VCl₂[HC(C(C₆H₅)NC₆H₃- $2,6^{-i}Pr_2$ solution. The mixture was allowed to warm to room temperature. The solution was then stirred for a further 12h. The solution became yellow-green and was filtered through a pad of Celite. All volatiles of the filtrate were removed under vacuum. The resultant residue was extracted with 10 mL of diethyl ether and the solution was filtered through a pad of Celite. The filtrate was kept at -35 °C for 2 d to afford dark yellow-green singlecrystal X-ray quality crystals. The yield was 47.2% (131.0 mg) in one crop. ¹H NMR (C₆D₆, 400 MHz): δ 7.88-6.78 (m, 17 H), 3.96 (m, 2 H, CHMe₂), 3.57 (m, 1 H, CHMe₂), 3.26 (m, 4 H, (CH₃CH₂)₂O), 3.08 (br, 1 H, CHMe₂), 1.64 (d, 3 H, CHMe₂), 1.54 (d, 3 H, CHMe₂), 1.22 (d, 6 H, CHMe₂), 1.19 (d, 6 H, CHMe₂), 1.12 (m, 6 H, (CH₃CH₂)₂O), 1.03 (d, 3 H, CHMe₂), 0.79 (d, 3 H, CHMe₂). ¹³C{¹H} NMR (C₆D₆, 100.7 MHz): δ 158.58, 147.75, 144.70, 142.49, 141.09, 140.06, 139.61, 129.24, 128.29, 127.93, 127.87, 126.49, 126.33, 124.66, 124.49, 123.49, 123.37, 122.39, 122.03, 115.89, 92.17, 77.69, 31.90, 29.96, 28.34, 25.92, 25.09, 24.69, 24.45, 23.65, 23.55, 23.49. Anal. calcd for C₄₃H₅₅N₂OV (5): C 77.45, H 8.31, N 4.20; Found: C 77.10, H 8.76, N 3.89.

Synthesis of $(C_6H_5S)_2V[HC(C(Me)NC_6H_3-2,6-R_2)_2]$ (R = Et (6), 'Pr (7))

General procedure for the synthesis (C_6H_5S)₂V[HC(C(Me)-NC₆H₃-2,6-R₂)₂] is given for R = 'Pr. To a 15 mL diethyl ether solution of **1** (156.0 mg, 0.150 mmol) in a 20 mL vial was added 64 mg (0.300 mmol) of diphenyldisulfide (Ph₂S₂) at room temperature. The solution quickly became forest green from dark green. The solution was further stirred for 15 h. All volatiles were then removed under vacuum. The green residue was extracted with 5 mL of *n*-hexane and filtered through a pad of Celite. The green filtrate was concentrated to 2 mL and was kept at -35 °C for 2 d to afford forest green single-crystal X-ray quality crystals. The yield was 62.3% (63.0 mg) in one crop. Anal. calcd for C₄₁H₅₁N₂S₂V (7): C 71.69, H 7.48, N 4.08, Found: C 71.33, H 7.54, N 3.92. μ_{eff} = 2.89 μ_{B} (Evans' method, C₆D₆). Anal. calcd for C₃₇H₄₃N₂S₂V (6):

C 70.45, H 6.87, N 4.44, Found: C 70.87, H 7.14, N 4.62. $\mu_{eff} = 2.94 \,\mu_{B}$ (Evans' method, $C_{6}D_{6}$)

Synthesis of $(\eta^6-1,3,5-Ph_3C_6H_3)V[HC(C(Me)NC_6H_3-2,6-Pr_2)_2]$ (8)

To a 15 mL diethyl ether solution of 1 (502.4 mg, 0.490 mmol) in a 20 mL vial was added 404.3 mg (3.960 mmol) of phenylacetylene (PhCCH) at -35 °C. The solution quickly became orange from dark green. The solution was further stirred for 15 h at room temperature. At which point, all volatiles were removed under vacuum. The orange residue was extracted with *n*-hexane and filtered through a pad of Celite. The orange filtrate was stripped to dryness under vacuum and the orange solid was dissolved in 4 mL of diethyl ether. The ether solution was concentrated and kept at -35 °C for 2 d to afford orange single-crystal X-ray quality crystals. The yield was 22.1% (167.2 mg) in one crop. Anal. calcd for C₅₃H₅₉N₂V (7): C 82.14, H 7.67, N 3.61, Found: C 82.26, H 7.95, N 3.63. $\mu_{eff} = 2.78 \mu_{B}$ (Evans' method, C₆D₆).

Crystallographic structure determinations

The chosen crystals were mounted on a glass fibre. Data collections were carried out on a NONIUS Kappa CCD diffractometer²⁸ with Mo radiation ($\lambda = 0.71073$ Å) at 200(2) K. Cell parameters were retrieved and refined using *DENZO-SMN* software²⁹ on all observed reflections. Data reduction was performed with the *DENZO-SMN* software.²⁹ An empirical absorption was based on the symmetry-equivalent reflections and applied to the data using the *SORTAV* program.³⁰ The *SHELXTL* program³¹ was used on a PC computer for the structure analysis. The structure was solved using the *SHELXS-97* program³² and refined using the *SHELXL-97* program³³ by full-matrix least squares on F² values. All non-hydrogen atoms are refined anisotropically. Hydrogen atoms attached to the carbons were fixed at calculated positions and refined using a riding model.

3. Results and discussion

3.1. Synthesis and characterizations of $[V{\mu-(\eta^6-ArN)C(Me)CHC(Me)C(NAr)}]_2$ (Ar = 2,6-Me₂C₆H₃ (2), 2,6-Et₂C₆H₃ (3), 9-anthracenyl (4))

According to the synthesis of the inverted sandwich divanadium complex $(\mu-\eta^6:\eta^6-C_6H_5Me)[V(HC(C(Me)NC_6H_3-2,6-'Pr_2)_2)]_2$ (1),^{25f} a two-electron reduction reaction of [HC(C(Me)NAr)_2]VCl₂ (Ar = 2,6-Me_2C_6H_3, 2,6-Et_2C_6H_3, 9-anthracenyl) and KC₈ in tetrahydrofuran instead of toluene at -35 °C gives rise to the formation of dinuclear complexes [V{ $\mu-(\eta^6-ArN)C(Me)CHC(Me)C(NAr)$]₂ (Ar = 2,6-Me_2C_6H_3 (2), 2,6-Et_2C_6H_3 (3), 9-anthracenyl (4)) as dark brown crystals in 10 to 30% yields as shown in Scheme 1. All compounds 2, 3 and 4 are highly air- and moisture-sensitive.

Single crystals of these three dimeric compounds, suitable for X-ray analysis, are obtained by keeping the diethyl ether (**2** and **4**) or *n*-hexane (**3**) solution at -35 °C. The crystallographic data collection parameters are summarized in Table 1. The molecular structures of **2**, **3** and **4** unambiguously indicate their dinuclear nature (Fig. 1). Compounds **2** and **3** are essentially isostructural, with the vanadium atoms being η^2 bonded to the

Table 1	Crystal	and	data	collection	parameters
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compound	2	3	4	5	7	8
Empirical formula	$C_{42}H_{50}N_4V_2$	C ₅₀ H ₆₆ N ₄ V ₂	$C_{72}H_{64}N_4V_2$	C43H55N2OV	$C_{41}H_{51}N_2S_2V$	$C_{53}H_{59}N_2V$
$M_{\rm w}$	712.74	824.95	1087.15	666.83	686.9	774.96
Space group	$P2_1/n$	$P\overline{1}$	P2/a	$P2_1/c$	$P2_1/a$	$P\overline{1}$
a/Å	9,9620(2)	11.7457(3)	24.8878(12)	12.5137(3)	18.0540(3)	13.2728(11)
b/Å	11.0806(2)	13.2452(3)	9.5634(5)	15.6445(3)	12.1652(2)	13.3879(11)
c/Å	16.8565(4)	14.0750(4)	25.2169(12)	19.3631(4)	18.3858(3)	14.0552(12)
$\alpha/^{\circ}$	90	92.5130(10)	90	90	90	98.915(3)
$\beta/^{\circ}$	99.8910(10)	91.6470(10)	112.559(2)	97.6610(10)	108.0990(10)	117.457(4)
$\gamma/^{\circ}$	90	91.8330(10)	90	90	90	92.696(3)
$V/Å^3$	1833.05(7)	2185.48(10)	5542.7(5)	3756.89(14)	3838.28(11)	2169.3(3)
Z	2	2	4	4	4	2
T/K	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$d_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.291	1.254	1.303	1.179	1.189	1.186
μ/mm^{-1}	0.545	0.466	0.386	0.298	0.397	0.266
$R_1,^a W R_2{}^b (I > 2\sigma(I))$	0.0508, 0.1468	0.0534, 0.1322	0.0714, 0.1662	0.0590, 0.1472	0.0593, 0.1498	0.1177, 0.2258

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}| . {}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})]\}^{1/2}. w = 1 / [(\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP)], where P = [max(F_{o}^{2} \text{ or } 0) + 2(F_{c}^{2})] / 3.$



Scheme 1 Synthesis of 2-4.

 β -diketiminate framework and η^6 coordinated to a flanking ring of a β -diketiminato ligand, which is attached to the other vanadium centre within the dimer. Both **2** and **3** show similar variations in vanadium-ring-carbon distances, ranging from 2.185(4) to 2.336(3) Å in **2** and 2.181(3) to 2.332(3) Å in **3**. The longest vanadium-ring-carbon distances are both observed between the vanadium and the *ipso* carbon atoms. The average C-C distance for the metal-coordinated flanking rings was determined to be 1.411 (2) and 1.422 Å (3), indicating a slight increase (*ca.* 0.02–0.03 Å) upon complexation.³⁵ A nonplanar conformation for the coordinated flanking rings in **3** is consistent with the larger increase in the C–C bond lengths. Moreover, the metal–flanking–ring interactions in **2** and **3** are also significant as evidenced by the vanadium–centroid distance of 1.744(4) Å in **2** and 1.750(3) Å in **3**, slightly shorter than those in complexes [Ar'MMAr'] (Ar' = 2,6-(2,6-ⁱPr₂C₆H₃)₂C₆H₃; M = Fe, Co),³⁶ [HC(C(Me)NC₆H₃-2,6-ⁱPr₂)₂]Fe(η^6 -C₆H₆),³⁷ 3,5-^{*i*}Pr₂Ar*Fe(η^6 -C₆H₆) (Ar* = 2,6-(2,4,6-ⁱPr₃C₆H₂)-3,5-^{*i*}Pr₂C₆H)³⁸ and [HC(C(Me)NC₆H₃-2,6-Me₂)₂]Co(η^6 -C₆H₃Me).^{25c} It is worth mentioning that all the planar vanadium-β-diketiminate sixmembered rings, C₃N₂V, in **2** and **3** are coplanar. Both **2** and **3** display long V…V separations, 4.181(5) and 4.188(1) Å, respectively, indicating no metal–metal bonding interaction.

Despite being structurally similar to 2 and 3, compound 4 exhibits a slightly different structure from that of 2 and 3. The vanadium atoms in 4 are ligated by the external flanking rings of the anthracenyl substitutents of a β -diketiminato ligand, which is attached to the other vanadium centre within the dimer. Consequently, such coordination results in two planar six-membered C₃N₂V rings of the dimer in a nearly orthogonal arrangement, so as to release steric pressure, in sharp contrast to a



Fig. 1 Molecular structures of 2 (left), 3 (central), and 4 (right) with thermal ellipsoids at 35% probability level. Selected bond lengths (Å) and angles (°): 2: V(1)-N(1), 2.058(2); V(1)-N(2), 2.034(2); V(1)-C(flanking ring) 2.336(3); 2.232(3); 2.191(4); 2.278(4); 2.185(4); 2.226(4); V(1)-centroid, 1.744(4); N(1)-V(1)-N(2), 88.73(10); $V(1) \cdots V(1A)$, 4.181(5). 3: V(1)-N(1), 2.066(3); V(1)-N(2), 2.042(3); V(1)-C(flanking ring) 2.332(3); 2.181(3); 2.253(3); 2.284(3); 2.156(3); 2.298(3); V(1)-centroid, 1.750(3); $V(1) \cdots V(1A)$, 4.188(1); N(1)-V(1)-N(2), 88.69(10). 4: V(1)-N(1), 2.025(4); V(1)-N(2), 2.020(4); V(1)-C(flanking ring) 2.468(5); 2.147(5); 2.264(5); 2.230(5); 2.162(5); 2.491(5); V(1)-centroid, 1.794(1); $V(1) \cdots V(1A)$, 5.038(3); N(1)-V(1)-N(2), 88.82(17).

parallel orientation of two planar six-membered C_3N_2V rings in **2** and **3**. As a result, the conformation in **4** results in a longer $V \cdots V$ separation of 5.038(3) Å. The metal–carbon distances to one of the external rings of the anthracenyl groups vary significantly, ranging from 2.147(5) Å to 2.491(5) Å. The longest distance is to the fused carbon bond C(28)–C(33) and the shortest distances are to C(29) and C(32), leading to a puckering outer ring.

Each of these three dinuclear compounds has 2 unpaired electrons based on Evans's method.³⁴ Unlike the dinuclear vanadium inverted sandwich complex 1, showing paramagnetic behaviour and featuring 4 unpaired electrons between 10 and 300 K, an antiferromagnetic coupling between the two magnetic centres was indeed observed for 2-4. Complex 3 was chosen for the solid state magnetic measurements. The variation of molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) with respect to temperature are shown in Fig. 2. Below 5 K, the values of $\mu_{\rm eff}$ drastically decreased, presumably due to the zerofield-splitting. The susceptibility data were fitted to the van Vleck equation, a spin Hamiltonian of the form $H = -2JS_1S_2$, with $S_1 = S_2 = 1$, from which g = 1.98 and J = -0.83 cm⁻¹ were thus obtained. The small coupling constant is consistent with the observation of the long $V \cdots V$ distance. As a result, 3 contains two vanadium(I) ions which exhibit intramolecular antiferromagnetic exchange interactions.



Fig. 2 Solid state magnetic susceptibility of **3** between 2 and 300 K. The solid line represents the fitting results.

3.2. Reduction of [HC(C(Ph)N-2,6-^{*i*}Pr₂C₆H₃)₂]VCl₂ and formation of azabutyldienyl framework

When the steric hindrance of the supporting β -diketiminato ligand is increased, by substituting two phenyl groups for two methyl groups of the backbone, a dark brown mononuclear vanadium complex [HC(C(Ph)N-2,6-⁷Pr₂C₆H₃)₂]VCl₂ is prepared and this was characterized by elemental analysis and solution magnetic measurements. As shown in Scheme 2, the reduction of the vanadium dichloride precursor by 2 equiv. of KC₈ is carried out in a THF solution and then recrystallization of the generated product in diethyl ether leads to the isolation of a yellow-green dia-



Scheme 2 Synthesis of 5.

magnetic trivalent vanadium imido complex (NacPh)VN(C₆H₃- $2,6^{-i}Pr_2$ (OEt₂) (5) (NacPh⁻ = PhCC(H)C(Ph)NC_6H_3-2,6^{-i}Pr_2) instead of the anticipated mononuclear complex [HC(C(Ph)N-2,6- ${}^{i}Pr_{2}C_{6}H_{3}$) V or a dinuclear product reminiscent of 2-4. As assayed by ¹³C NMR spectroscopy, the chemical shift for the vinylic carbon attached to the vanadium atom resonates at 158.6 ppm. This value is much more upfield shifted than those of the group IV imido azabutadienyl complexes. The molecular structure of 5 was determined by single-crystal X-ray crystallography and is depicted in Fig. 3, with selected bond lengths and angles underneath. The crystallographic data is summarized in Table 1. Besides the imido and azabutadienyl ligands, an Et₂O molecule is found to ligate to the vanadium atom, which reveals the electron-deficient nature of the vanadium centre. Moreover, bonding interactions between the vanadium atom and all carbons of the backbone ligand are observed and evidenced by the slightly long V(1)-C(20)(2.344(3) Å) and V(1)–C(13) (2.428(3) Å) bond lengths, which consequently results in long C(21)–C(20) (1.429(4) Å) and C(13)– N(1) (1.387(4) Å) double bonds and leads to a puckered fivemembered VCCCN ring. The short V(1)-C(21) bond (1.871(3) Å) suggests a double bond character. It is worth mentioning that the reported conformation of the five-membered MCCCN rings, where M is the group IV metal Ti, Zr or Hf in corresponding imido azadutadienyl complexes, are planar without M-C(backbone) bonding interactions.³⁹ The existence of the vanadium imido functionality is supported by the linear V(1)-N(2)-C(28) linkage and a very short V-N (imido) distance of 1.685(2) Å, which is much shorter than V(1)-N(1) (1.906(2) Å) and very close to those of the reported V-N(imido) bond lengths.40



Fig. 3 Molecular structure of 5 with thermal ellipsoids at 35% probability level. Selected bond lengths (Å) and angles (°): V(1)–N(1), 1.906(2); V(1)–N(2), 1.685(2); V(1)–C(13), 2.428(3); V(1)–C(20), 2.344(3); V(1)–C(21), 1.871(3); V(1)–O(1), 2.063(2); C(21)–C(20), 1.429(4); C(20)–C(13), 1.397(4); C(13)–N(1), 1.387(4); V(1)–N(2)–C(28), 168.71(21); O(1)–V(1)–N(2), 110.08(10); O(1)–V(1)–C(21), 112.64(11); O(1)–V(1)–N(1), 115.71(10).

Reductive C–N bond cleavage of the β -diketiminato ligands to give rise to a metal imido functionality with an azabutadienyl framework has been reported by Mindiola,^{39a,39d} Tokitoh^{39b} and Stephan,^{39c} but such reactions are so far observed for the group IV metals.³⁹ Complex **5** represents the first example that the reductive C–N bond cleavage reaction of the NCCCN ligand backbone occurs to a group V metal. In view of the recognition of **2–4**, **5** is generated from the transient univalent vanadium intermediate "{HC(C(Ph)N-2,6-'Pr₂C₆H₃)₂}V" upon reduction of its dichloride precursor. One of the C–N bonds of the ligand coordinates to the electron deficient vanadium centre and then

can not be stabilized *via* to of the 2,6- $^{i}Pr_{2}C_{6}H_{3}$ subs form the dimeric complex synthesis of **1**, **5** can actu of [HC(C(Ph)N-2,6- $^{i}Pr_{2}C_{6}$ wich dinuclear complex (2,6- $^{i}Pr_{2})_{2}$)]₂ is not formed. **3.3.** Synthesis of (C₆H₅S (6), ^{i}Pr (7)) We recently reported that zene can be easily split (PhN)_2V[HC(C(Me)N-2,6)]

subsequently undergoes C–N bond cleavage to give **5**. Apparently, the mononuclear intermediate [{HC(C(Ph)N-2,6-'Pr₂C₆H₃)₂}V] can not be stabilized *via* the intermolecular coordination of one of the 2,6-'Pr₂C₆H₃ substituents to the vanadium centres, to form the dimeric complex similar to **2** and **3**. In contrast to the synthesis of **1**, **5** can actually also be prepared *via* the reduction of [HC(C(Ph)N-2,6-'Pr₂C₆H₃)₂]VCl₂ in toluene; an inverted sandwich dinuclear complex (μ - η ⁶: η ⁶-C₆H₅Me)[V(HC(C(Ph)NC₆H₃-2 6-'Pr₂)] is not formed

3.3. Synthesis of $(C_6H_5S)_2V[HC(C(Me)NC_6H_3-2,6-R_2)_2]$ (R = Et (6), ^{*i*}Pr (7))

We recently reported that the N-N double bond of azobenzene can be easily split by 1 to give a diimdo complex $(PhN)_2V[HC(C(Me)N-2,6^{-i}Pr_2C_6H_3)_2]^{.25f,41}$ In light of the facile synthesis of a d¹ vanadium dithiolato complex $(\eta^5-Cp)_2V(SPh)_2$ from the reaction of $(\eta^5-Cp)_2V$ and Ph_2S_2 ,⁴² we then turned our attention to the preparation a d² vanadium dithiolato complex by treating 1–4 with Ph_2S_2 via a two-electron oxidative addition. As shown in Scheme 3, treatment of 1 or 3 with 2 equiv. of Ph₂S₂ afforded a forest green product, formulated as $(C_6H_5S)_2V[HC(C(Me)NC_6H_3-2,6-R_2)_2]$ (R = Et (6), ^{*i*}Pr (7)). Both compounds 6 and 7 have 2 unpaired electrons based on solution magnetic measurements (Evans's method).³⁴ The molecular configuration together with selected bond distances and angles of 7 is given in Fig. 4, which unambiguously indicates that the two phenylmercapto sulfur atoms and two β-diketiminato nitrogen atoms constitute a pseudo-tetrahedral geometry at the vanadium centre. Although the two angles of bent V-S-C (99.73(9) and 108.75(10)°) are significantly different, the V-S bond lengths are essentially the same, 2.2930(8) and 2.3051(8) Å. These two V-S bond lengths are significantly shorter than those found in $(\eta^5 Cp_{2}V(SPh)_{2}$ (2.448 (3) and 2.470(2) Å)⁴² and (η^{5} - $Cp_{2}V(SMe)_{2}$ (2.422(1) Å).⁴³ These differences are attributable to the much more electron deficient vanadium centre and the lesser steric demand of the β-diketiminato ligand.



Scheme 3 Synthesis of 6 and 7.

3.4. Catalytic cyclotrimerization of terminal alkynes by univalent vanadium β -diketiminato complexes 1–4

Since Reppe *et al.* first discovered catalytic cyclotrimerization of acetylenic compounds giving benzene and substituted benzenes by NiBr₂ in 1948,⁴⁴ the [2+2+2] cycloaddition reaction has been an effective tool for the construction of substituted arenes.⁴⁵ In fact, a variety of transition metals (particularly the late transition metals)⁴⁶⁻⁵² have been found to efficiently catalyze such reactions in homogeneous solutions. In view of the univalent vanadium in compounds **1–4** showing a strong tendency to



Fig. 4 Molecular structure of 7 with thermal ellipsoids at 35% probability level. Selected bond lengths (Å) and angles (°): V(1)–N(1), 1.965(2); V(1)–N(2), 1.982(2); V(1)–S(1), 2.2930(8); V(1)–S(2), 2.3051(8); N(1)–V(1)–N(2), 93.22(9); N(1)–V(1)–S(1), 116.19(7); N(2)–V(1)–S(1), 104.48(7); N(1)–V(1)–S(2), 118.04(7); N(2)–V(1)–S(2), 117.86(7); S(1)–V(1)–S(2),106.30(3).

be coordinated by benzene derivatives, we wondered if the assynthesized arene-coordinated vanadium β-diketiminates could catalyze the formation of tri-substituted benzenes from acetylenic compounds. To our delight, this is indeed the case. As shown in Scheme 4, treatment of complex 3 with 20, 60 or 100 equiv. of terminal alkynes, phenylacetylene and 1-heptyne in THF at room temperature affords the corresponding tri-substituted benzenes in good yields (62% for phenylacetylene and 81% for 1-heptyne). However, the regioselectivity of the alkyne cyclotrimerization reactions with the presence of 3 as the catalyst is not satisfied. The ratio of 1,3,5-trisubstituted benzenes to 1,2,4-trisubstituted benzenes is about 65:35 analyzed by ¹H NMR spectroscopy. Presumably, the poor regioselectivity is due to the less hindered supporting ligand. When compound 1 was employed to catalyze cyclotrimerization of phenylacetylene and 1-heptyne, the ratio of 1,3,5-trisubstituted benzenes to 1,2,4-trisubstituted benzenes is improved to 80:20, but the yields slightly decrease (yields: 50%) for phenylacetylene and 74% for 1-heptyne).



Scheme 4 Cyclotrimerization of terminal alkynes.

To prove the formation of tri-substituted benzenes catalyzed by the as-synthesized di-vanadium complexes, 5 equiv. of phenylacetylene is added to a diethyl ether solution of **1** and a 1,3,5triphenylbenzene-bound vanadium complex formulated as (η^{6} -1,3,5-Ph₃C₆H₃)V(HC(C(Me)NC₆H₃-2,6-'Pr₂)₂) (**8**) can be isolated in 22% yield from recrystallization. Compound **8** has 2 unpaired electrons ($\mu_{eff} = 2.78$ B.M.) at room temperature determined by Evans's method.³⁴ The molecular structure of **8** was determined by single-crystal X-ray crystallography. Unfortunately, due to its quick decomposition nature, the value of the R factor of **8** is high (0.1177), so all metric parameters may not be reliable and only an anisotropic structure is shown in Fig. 5. The coordinated benzene shows a puckering conformation with C(32) and C(35) atoms closer to the vanadium centre than the other four carbons. The failure to obtain the 1,2,4-triphenylbenzene–coordinated isomer is presumably due to the steric repulsion between 1,2-diphenyl groups of the 1,2,4-triphenylbenzene and the 2,6- $^{I}Pr_{2}C_{6}H_{3}$ of the ligand and of course the lower yield of the 1,2,4-triphenylbenzene isomer.



Fig. 5 Molecular structure of **8** with thermal ellipsoids at 35% probability level.

Conclusions

In conclusion, we have demonstrated that [V(Nacnac)] (Nacnac = β-diketiminate) can exist in two very different forms, which strongly depends on the bulk of the Nacnac ligands. Three dimeric complexes, $[V{\mu-(\eta^6-Ar-N)C(Me)CHC(Me)C(N-Ar)}]_2$ $(Ar = 2,6-Me_2C_6H_3 (2), 2,6-Et_2C_6H_3 (3), 9-anthracenyl (4)), were$ isolated. Complexes 2–4 display both vanadium atoms being η^2 chelated by the β -diketiminate framework and η^6 bonded to a flanking ring of a β -diketiminato ligand, attached to the other vanadium centres within the dimers. These dimers are strikingly different from our previously reported toluene-bridged inverted sandwich divanadium complex 1, which is supported by a sterically more demanding β -diketiminate. Not only do they exhibit different structures, but they also display very different electronic structures. In sharp contrast with the paramagnetic inverted sandwich divanadium complex 1 with two high-spin vanadium atoms, all compounds 2-4 display an antiferromagnetic exchange between the two vanadium centres. On the other hand, when the bulk of the ancillary β -diketiminato ligand is increased by substituting two phenyl groups for two methyl substituents on the ligand backbone, an imido complex (η²-PhCC(H)C(Ph)NC₆H₃-2,6-^{*i*}Pr₂)VN(C₆H₃- $2,6^{-i}Pr_2$ (OEt₂) (5) was actually obtained upon reduction of $[HC(C(Ph)N-2,6-^{i}Pr_{2}C_{6}H_{3})_{2}]VCl_{2}$. According to the characterizations of 1 and 2-4, the formation of 4 is presumably from the reductive cleavage of the C=N bond of the ligand backbone of the transient intermediate $[{HC(C(Ph)N-2,6-Pr_2C_6H_3)_2}V].$ Complexes 1-4 display reducing ability as evidenced by a facile two-electron oxidative addition of the S-S bond of Ph₂S₂ to the vanadium centres to give vanadium dithiolates 6 and 7. Most notably, these univalent divanadium complexes 1-4 catalyze the cyclotrimerization of alkynes, phenylacetylene and 1-heptyne. It is interesting to note that the regioselectivity of the trisubstituted benzene products is dependent of the steric bulk of the β diketiminate. While poor regioselectivity but good yields of the trisubstituted benzenes are obtained if catalyst **3** is employed, good regioselectivity and moderate yields of trisubstituted benzenes are obtained when complex **1** is used as a catalyst. An important intermediate, the 1,3,5-triphenylbenzene coordinated complex (η^6 -1,3,5-Ph₃C₆H₃)V{HC(C(Me)N-2,6-^{*i*}Pr₂C₆H₃)₂} (**8**), was isolated over the course of the cyclotrimerization reaction of phenylacetylene catalyzed by complex **1** and was characterized by single-crystal X-ray crystallography.

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