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Vanadium nitride functionalization and denitrogenation by carbon disulfide and dioxide†

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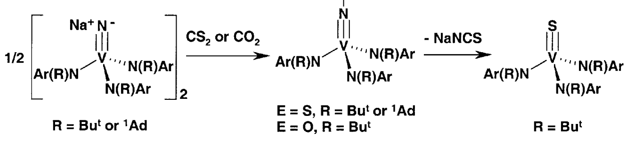
A dramatic difference in behavior is observed for the dithiocarbamate and carbamate complexes [Ar(Bu^t)N]$_3$V(NCE$_2$)Na(THF)$_2$ (E = S or O, respectively), prepared from the corresponding nitride species {[Ar(Bu^t)N]$_3$V≡NNa}$_2$ by way of a nucleophilic addition reaction involving carbon disulfide or dioxide, and is rationalized with the aid of DFT calculations.

The vanadium(III) trisanilide complex [Ar(Bu^t)N]$_3$V[1] (**1**, Ar = 3,5-Me$_2$C$_6$H$_3$) provides a robust platform for stabilizing interesting main-group functionalities.[2] For example, the nucleophilicity of the nitrido substituent in (**1**-NNa)$_2$, generated upon treatment of **1** with sodium azide, facilitated the preparation of **1**-NPCl$_2$ via a metathesis reaction with PCl$_3$. A series of transformations yielded ultimately the monomeric iminophosphinimide **1**-NPNBu^t.[2] Herein, we report that addition reactions involving nucleophilic (**1**-NNa)$_2$, or the new adamantyl derivative {[Ar(^{1}Ad)N]$_3$VNNa}$_n$ (**2**-NNa)$_n$, and the electrophiles CS$_2$ or CO$_2$ generate the vanadium trisanilide dithiocarbamate and carbamate complexes **1**-NCS$_2$Na(THF)$_2$, **2**-NCS$_2$Na(THF)$_2$ and **1**-NCO$_2$Na(THF)$_2$ (Scheme 1). The unanticipated spontaneous conversion of **1**-NCS$_2$Na(THF)$_2$ to the corresponding terminal sulfide **1**-S (with NaNCS extrusion) is rationalized with the aid of DFT calculations.

Dark red **1**-NCS$_2$Na(THF)$_2$ was isolated in 89% yield by treatment of a yellow-green THF solution of (**1**-NNa)$_2$ with 2 equiv. CS$_2$ and expeditious low-temperature (−35 °C) work-up. As a solution in THF-d$_8$, **1**-NCS$_2$Na(THF)$_2$ exhibits a partially resolved 1 : 1 : 1 triplet in its ^{51}V NMR spectrum at −54 ppm ($^1J_{^{14}N^{51}V}$ 100 Hz),[3] due to coupling with one of the adjacent ^{14}N nuclei.‡ This phenomenon is attributed to interaction of the vanadium center with the nitrido nitrogen, which evidently experiences a more symmetrical electric field gradient than those nitrogens contained in the three anilide ligands. Utilization of ^{13}C-labeled carbon disulfide, *i.e.* preparation of **1**-N^{13}CS$_2$Na(THF)$_2$, was required to observe the relevant broad singlet at 237 ppm ($\Delta\nu_{1/2}$ = 340 Hz) in the ^{13}C NMR spectrum. ^{51}V NMR spectroscopy revealed a broad resonance at −56 ppm ($\Delta\nu_{1/2}$ = 274 Hz) for **1**-N^{13}CS$_2$Na(THF)$_2$, likely a consequence of ^{13}C coupling masking the coupling to ^{14}N.

Surprisingly, storage of a THF solution of **1**-NCS$_2$Na(THF)$_2$ at 23 °C for 24 h resulted in complete conversion to **1**-S (^{1}H and ^{51}V NMR), an analogue of the known sulfide **2**-S.[4] Removal of solvent *in vacuo* and dissolution of the remaining red residue in diethyl ether followed by filtration through a fine sintered-glass frit gave, upon drying, dark red microcrystalline **1**-S in 94% yield. Collected on the frit was a white salt identified as sodium thiocyanate (96% yield) by comparing its ^{13}C NMR spectrum in D$_2$O with that obtained for a commercially available sample (133.7 ppm).[5] This finding balances the equation of decomposition of **1**-NCS$_2$Na(THF)$_2$ to generate **1**-S (Scheme 1). Characterization of **1**-S includes the observation of a singlet at 659 ppm in its ^{51}V NMR spectrum, cf. 676 ppm for 2-S,[4] as well as an X-ray structure.§ Furthermore, following the procedure outlined by Gambarotta and co-workers for the preparation of **2**-S,[4] a dark green solution of **1** in diethyl ether was treated with elemental sulfur in order to prepare **1**-S independently (93% isolated yield).



Scheme 1

Kinetic data obtained by single-pulse ^{1}H NMR spectroscopy indicate that the decay of **1**-NCS$_2$Na(THF)$_2$ to form **1**-S is first-order in vanadium (k_{obs} at 25 °C = $2.2 \pm 0.1 \times 10^{-4}$ s^{-1}),† thus we favor an intramolecular mechanism for this conversion. Hence, a four-membered V–N–C–S ring is implicated either as a short-lived (not observed) intermediate complex or in the transition state leading to thiocyanate extrusion. Species containing a related M–N(Ph)–C–E ring have been characterized by crystallography (M = Ta, E = S)[6] or proposed as intermediates (M = V, E = O).[7]

Given that the three anilide ligands provide a protected pocket, which has proven critical for preventing the dimerization of derivatives of (**1**-NNa)$_2$,[2] it is surprising that intramolecular nucleophilic attack on the V center by one of the S atoms is possible. It was surmised accordingly that **2**-NCS$_2$Na(THF)$_2$, incorporating a more highly constrained pocket, would exhibit a greater kinetic resistence to thiocynate extrusion. Forthwith, the dithiocarbamate complexes **2**-NCS$_2$Na(THF)$_2$ and **2**-N^{13}CS$_2$Na(THF)$_2$ were prepared by a protocol analogous for, and in yields consistent with, their Bu^t counterparts (*vide supra*). The new reagent (**2**-NNa)$_n$ employed in these syntheses was obtained in 64% yield from the reaction of [Ar(^{1}Ad)N]$_3$V[4] (**2**) with NaN$_3$. The NMR data obtained for **2**-NCS$_2$Na(THF)$_2$ [^{51}V: −17 ppm (t, $^1J_{^{14}N^{51}V}$ 88 Hz)] and **2**-N^{13}CS$_2$Na(THF)$_2$ [^{51}V: −20 ppm (br, $\Delta\nu_{1/2}$ 252 Hz); ^{13}C: 234 ppm (br, $\Delta\nu_{1/2}$ 230 Hz)] in THF-d$_8$ were similar to those determined for **1**-NCS$_2$Na(THF)$_2$ and **1**-N^{13}CS$_2$Na(THF)$_2$, respectively. Indeed, **2**-NCS$_2$Na(THF)$_2$ was found to be stable in solution for extended periods (days) at room temperature. Only upon refluxing a THF solution of **2**-NCS$_2$Na(THF)$_2$ for several hours was a trace amount of **2**-S observed (< 5% by ^{1}H and ^{51}V NMR), in addition to traces of the free aniline HN(^{1}Ad)Ar along with other unidentified products. Note that the sulfide **2**-S, as prepared independently,[4] is stable to this regimen.

In light of the fascinating reactivity of **1**-NCS$_2$Na(THF)$_2$, we were intrigued by the prospect of preparing and probing the behavior of the carbamate analogue **1**-NCO$_2$Na(THF)$_2$. Addition of excess anhydrous CO$_2$ gas to a cooled (0 °C) THF solution of (**1**-NNa)$_2$ and subsequent removal of volatile material *in vacuo* generated quantitatively (> 95%) orange microcrystalline **1**-NCO$_2$Na(THF)$_2$. However, in striking con-

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† Electronic supplementary information (ESI) available: synthetic, spectroscopic, analytical, and computational results for all new complexes. Fig. S1: frontier orbitals of model anions: See http://www.rsc.org/suppdata/cc/b1/b111550m/

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trast to the behavior of **1**-$NCS_2Na(THF)_2$, **1**-$NCO_2Na(THF)_2$ exhibits thermal stability at room temperature or upon refluxing in THF solution for several hours. The ^{51}V NMR spectrum obtained for **1**-$NCO_2Na(THF)_2$ features a very broad resonance centered at *ca.* −230 ppm ($\Delta\nu_{1/2}$ 1060 Hz). To verify independently the accessibility and properties of **1**-O, 1 equiv. pyridine *N*-oxide was added to a dark green solution of **1** to give free pyridine and **1**-O, which was isolated in 94% yield as a fine orange powder. A distinctive, relatively sharp singlet at −171 ppm ($\Delta\nu_{1/2}$ 290 Hz) was recorded in the ^{51}V NMR spectrum for **1**-O.

To gain an understanding of the difference in stability/reactivity of **1**-$NCS_2Na(THF)_2$ *vs.* **1**-$NCO_2Na(THF)_2$, DFT methods were employed.† Model compounds incorporating dimethylamide groups in lieu of anilide ligands were utilized to reduce calculation cost. The apparent dichotomy in reactivities was clarified vastly upon analysis of the frontier MOs for the complexes under scrutiny (Fig. S1, ESI†). Significantly, the HOMO–LUMO gap for the model anion $(Me_2N)_3V(NCS_2)^-$ is less than half of that calculated for $(Me_2N)_3V(NCO_2)^-$, reducing its relative stability considerably. This difference in energies is attributed to the combination of two phenomena: (i) the HOMO of $(Me_2N)_3V(NCO_2)^-$ is stabilized with respect to that of $(Me_2N)_3V(NCS_2)^-$ by means of a substantial V–N π-bonding contribution and (ii) the LUMO for $(Me_2N)_3V(NCS_2)^-$ is stabilized by the presence of an N–C bonding interaction, which is negligible in the LUMO for $(Me_2N)_3V(NCO_2)^-$. Another factor that may facilitate conversion of **1**-$NCS_2Na(THF)_2$ to **1**-S *via* intramolecular nucleophilic attack is the presence of longer C–E bonds (optimized at 1.71 and 1.25 Å for E = S and O, respectively).¶

Fig. 1 depicts calculated relative enthalpy values for the system comprised of $(Me_2N)_3VN^-$, CO_2 and CS_2 as a function of the important transformations.¶ This scenario permits comparison of the CO_2 and CS_2 reaction pathways, keeping constant the system's chemical formula along the hypothetical reaction coordinate (*i.e.* formally adding CO_2 and CS_2 as necessary). Consumption of CS_2 as opposed to CO_2 is favored by *ca.* 23.4 kcal mol^{-1}. Moreover, thiocyanate ejection from $(Me_2N)_3V(NCS_2)^-$ is substantially more exothermic than corresponding extrusion of cyanate from $(Me_2N)_3V(NCO_2)^-$. The observed lack of cyanate extrusion from **1**-$NCO_2Na(THF)_2$ may be kinetic in origin, as treatment of **1**-O with NaNCO under forcing conditions similarly resulted in no reaction.

Chemical shielding constants were determined by DFT for the ^{51}V nuclei in models of all vanadium(v) complexes with which we are here concerned. Remarkably good agreement with the experimental ^{51}V NMR chemical shifts was exhibited, lending strong support to our structural assignments.¶ Calculations were performed also on the model terminal chalcogenides $(Me_2N)_3VE$ (E = O, S, Se), a series of particular interest since the chemical shift values differ dramatically in the three real systems **1**-O, **1**-S, and **2**-Se [*ca.* −171 (*vide supra*), 659 (*vide supra*) and 1001 ppm,[4] respectively]. As anticipated,[8] variations in the diamagnetic component are minimal (< 10 ppm), rendering changes in the shielding of V due mostly to the paramagnetic contribution. As a consequence of reduced electronegativity of the terminal substituents, the HOMO–LUMO gap decreases for the heavier chalcogenide congeners, *i.e.* **1**-S or **2**-Se, facilitating a higher degree of field-induced mixing between the occupied and vacant frontier orbitals. The relative paramagnetic contribution to the chemical shielding of the V center is thus increased,[3c,8,9] ultimately accounting for the observed downfield shifts *vis-à-vis* **1**-O. Isolobal molybdenum nitride and phosphide derivatives exhibit analogous NMR phenomena.[10]

In summary, this work illuminates both experimentally and by way of DFT calculations the fascinating properties and behaviors of the new family of dithiocarbamate and carbamate functionalities constructed atop a vanadium trisanilide platform.

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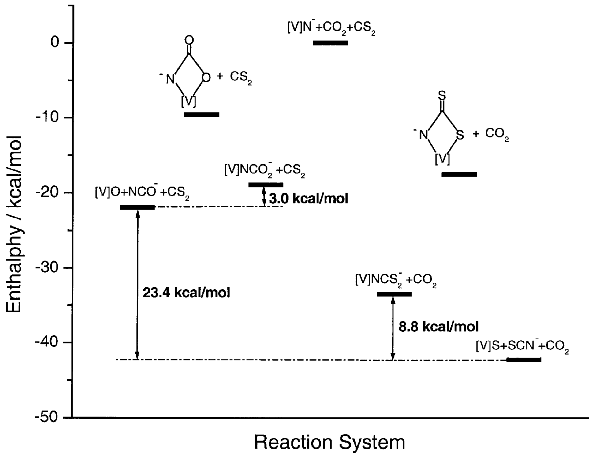

Fig. 1 Relative enthalpies for states of the system comprised of $(Me_2N)_3VN^-$, CO_2, and CS_2 as a function of relevant transformations. Values were computed using DFT methods ([V] = $V(NMe_2)_3$) consisting of geometry optimization for each of the depicted local minima. Possible transition states were not explored.

Notes and references

‡ See ESI for the ^{51}V NMR spectrum of **1**-$NCS_2Na(THF)_2$.

§ *Crystal data for* **1**-S: $C_{36}H_{54}N_3SV$, M = 611.82, monoclinic, space group $C2/c$, a = 30.398(5), b = 10.645(2), c = 22.194(4) Å, β = 93.515(3)°, V = 7168(2) $Å^3$, T = 183(2) K, Z = 8, μ(Mo-Kα) = 0.361 mm^{-1}, D_c = 1.134 g cm^{-3}, 10 185 reflections measured, 3352 unique (R_{int} = 0.0436), 3351 observed [$I > 2\sigma(I)$]. The final R_1 and $wR_2(F^2)$ were 0.0873 [$I > 2\sigma(I)$] and 0.1606 (all data), respectively. See ESI for an ORTEP drawing of complex **1**-S.† CCDC reference number 176564. See http://www.rsc.org/suppdata/cc/b1/b111550m/ for crystallographic data in CIF or other electronic format.

¶ See ESI for details and tables: isotropic shielding, paramagnetic and diamagnetic contributions, Mulliken and Hirshfeld charges, and relative enthalpies.

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