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# Reactivity of a triamidoamine terminal uranium(vi)-nitride with 3d-transition metal metallocenes†

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**Reactions between [(Tren<sup>TIPS</sup>)U<sup>VI</sup>≡N] (1, Tren<sup>TIPS</sup> = {N(CH<sub>2</sub>CH<sub>2</sub>-NSiPr<sub>3</sub>)<sub>3</sub>}<sup>3-</sup>) and [M<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>] (M/R = Cr/H, Mn/H, Fe/H, Ni/H) were intractable, but M/R = Co/H or Co/Me afforded [(Tren<sup>TIPS</sup>)U<sup>V</sup>=N(η<sup>1</sup>:η<sup>4</sup>-C<sub>5</sub>H<sub>5</sub>)Co(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] (2) and [(Tren<sup>TIPS</sup>)U<sup>IV</sup>-NH<sub>2</sub>] (3), respectively. For M/R = V/H [(Tren<sup>TIPS</sup>)U<sup>IV</sup>-N=V<sup>IV</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (4), was isolated. Complexes 2–4 evidence one-/two-electron uranium reductions, nucleophilic nitrides, and partial N-atom transfer.**

In recent years molecular uranium-nitrides have attracted burgeoning attention due to their importance as actinide electronic structure benchmarks and in small molecule activations.<sup>1–4</sup> The search for isolable terminal uranium-nitrides was accomplished by some of us just over a decade ago, first with [Na(12C<sub>4</sub>)<sub>2</sub>][(Tren<sup>TIPS</sup>)U<sup>V</sup>≡N] (Tren<sup>TIPS</sup> = {N(CH<sub>2</sub>CH<sub>2</sub>NSiPr<sub>3</sub>)<sub>3</sub>}<sup>3-</sup>; 12C<sub>4</sub> = 12-crown-4 ether)<sup>5</sup> in 2012 and then [(Tren<sup>TIPS</sup>)U<sup>VI</sup>≡N] (1) in 2013.<sup>6</sup> The Tren<sup>TIPS</sup> ligand has proven to be a ‘privileged’ ancillary ligand for terminal uranium-nitrides,<sup>7–10</sup> and indeed the only other ligand class to have supported an isolable terminal uranium-nitride linkage is the siloxide ligand (Bu<sup>t</sup>O)<sub>3</sub>SiO<sup>1-</sup> used by Mazzanti.<sup>11</sup> In addition to terminal uranium-nitrides, a variety of low- (two-) coordinate bridging uranium-nitrides are now known, including U≡NAM (AM = Li, Na, K, Rb, Cs),<sup>6,8,12,13</sup> U=N=An (An = U, Th),<sup>13–28</sup> and U≡N-M complexes (M = Mo, Rh, Ir, Mo).<sup>29,30</sup> The latter remain few in number, likely largely reflecting the limited synthetic methodologies available for constructing such

linkages: M = Mo was accessed by partial nitride transfer from Mo to U,<sup>29</sup> and M = Rh and Ir compounds were made by photolysis of azido precursors.<sup>30</sup> We decided to examine the potential of 1 to construct heterobimetallic nitride-bridged complexes since it already has a terminal,<sup>5–10</sup> nucleophilic nitride installed at uranium which could in principle simplify its use in synthesis.

Here we report on our findings, where we have examined the reactivity of 1 towards 3d transition metal metallocenes [M<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>] (M/R = V/H, Cr/H, Mn/H, Fe/H, Co/H, Co/Me, Ni/H). The reactions with M = Cr, Mn, Fe, and Ni appeared to proceed but proved intractable. However, reactions with M/R = Co/H, Co/Me, and V/H produced isolable derivatives that evidence one- and two-electron reductions of uranium, nucleophilic nitrides, and partial N-atom transfer.

In separate reactions, Scheme 1, mixing [(Tren<sup>TIPS</sup>)U<sup>VI</sup>≡N] (1) with [M<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (M = Cr, Mn, Fe, Ni) in cold (−78 °C) toluene afforded, after solvent was removed, crude brown solids. However, in all cases no products could be isolated cleanly. <sup>1</sup>H NMR spectroscopy revealed numerous paramagnetically shifted resonances (up to 66 ppm wide range of resonances, Fig. S1–S4, ESI†) and hence the product identities and/or extent of decomposition is unclear.

In contrast to the reactions between 1 and M = Cr, Mn, Fe, and Ni, with M = Co an identifiable product could be obtained, Scheme 1. Specifically, treating 1 with nineteen valence electron [Co<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] afforded the uranium(v)-imido complex [(Tren<sup>TIPS</sup>)U<sup>V</sup>=N(η<sup>1</sup>:η<sup>4</sup>-C<sub>5</sub>H<sub>5</sub>)Co(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] (2) as red crystals. However, 2 co-crystallises with variable quantities of 1 and [Co<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (Fig. S5 and S6, ESI†). Indeed, a variable-temperature <sup>1</sup>H NMR study (Fig. S7, ESI†) revealed the dominance of 2 at low temperature (−60 °C) and a greater proportion of 1/[Co<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] at higher temperature (25 °C), and hence 2 is in equilibrium with 1 and [Co<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]. Whilst the optimal practical ratio for the reaction was found to be two equiv. of [Co<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] to 1 we could only ever isolate 2 as a mixture (A) co-crystallised with 1 and [Co<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]. Although the [Co<sup>II</sup>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] can be sublimed out of A, when redissolved

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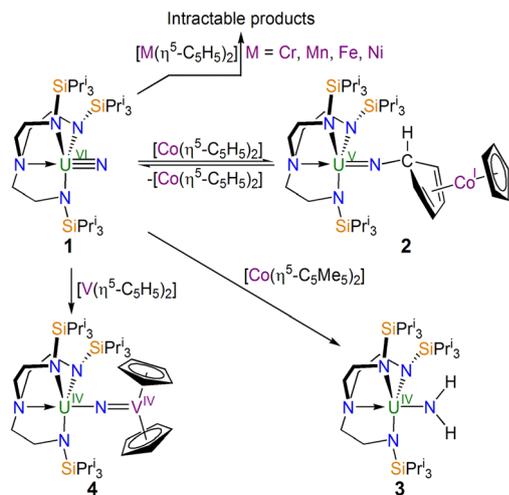
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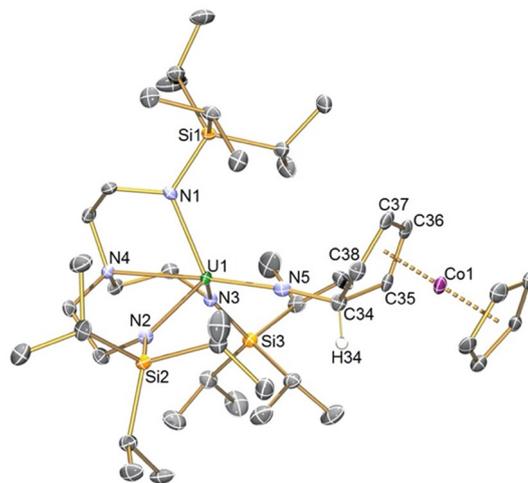
**Scheme 1** Synthesis of **2–4** from **1** and intractable reaction outcomes. The by-products are either not known or are not shown for clarity.

in addition to **2** resonances for **1** and  $[Co^II(\eta^5-C_5H_5)_2]$  are still observed in the resulting  $^1H$  NMR spectrum demonstrating an immutable equilibrium.

Nucleophilic attack of eighteen valence electron  $[Co^III(\eta^5-C_5H_5)_2]^+$  is known,<sup>31</sup> and whilst a radical reaction cannot be discounted the radical chemistry of **1** is quite slow in the absence of strong light,<sup>6</sup> so we propose that  $[Co^II(\eta^5-C_5H_5)_2]$  ( $E^0 = \sim -1.32$  V vs. Fc)<sup>32</sup> initially reduces **1** to give “[ $Co^III(\eta^5-C_5H_5)_2$ ] $^+[(Tren^{TIPS})U^V \equiv N]^-$ ”, and then nucleophilic attack of a cyclopentadienyl ring by the nitride occurs. The nucleophilic attack rehybridises one of the cyclopentadienyl carbon atoms from  $sp^2$  to  $sp^3$ , formally forming a Co-cyclopentadiene unit, hence retaining an eighteen valence electron cobalt moiety.

Given the issue in isolating **2**, its characterisation was probed using **A** as far as was reasonably practicable. The  $^1H$  NMR spectrum of **A** exhibits resonances for **2** over the range 23.5 to  $-4.2$  ppm (Fig. S5 and S6, ESI $^\dagger$ ). Of most salience, in addition to one cyclopentadienyl ring resonance of 5H (9.7 ppm) two pairs of 2H each for the  $\eta^4$ -diene portion of the cyclopentadiene ring are located at 17.9 and 10.6 ppm, and the H-atom residing on the ring  $sp^3$  C-atom resonates at  $-1.5$  ppm. We recorded the UV/Vis/NIR spectra of **1** and  $[Co^II(\eta^5-C_5H_5)_2]$  and then subtracted them from the corresponding spectrum of **A** to unambiguously identify absorptions that correspond to **2** (Fig. S12–S14, ESI $^\dagger$ ). Of most interest is the near infrared region, where four absorptions ( $\epsilon = \sim 10$ – $30$  M $^{-1}$  cm $^{-1}$ ) are found at  $\sim 6000$ ,  $\sim 7100$ ,  $\sim 9000$ , and  $\sim 10600$  cm $^{-1}$  which represent  $^2\Gamma_4$  to  $^2\Gamma_4$ ,  $^2\Gamma_4$ ,  $^2\Gamma_4$ , and  $^1\Gamma_5 + ^1\Gamma_6$  absorptions, respectively, that are characteristic of uranium(v) in  $C_{3v}$  symmetry.<sup>33</sup>

The solid-state structure of **2** was determined, Fig. 1, confirming its formulation and also *exo*-attack by the nitride. The U1–N5 distance of 1.925(3) Å is longer than the terminal  $U^VI \equiv N$  distance of 1.799(7) Å in **1** and group **1** capped and terminal  $(Tren^{TIPS})U^V \equiv N$  distances (1.801(7)–1.840(3) Å),<sup>5,6,8,12</sup> slightly shorter than  $(Tren^{TIPS})U^V = NR$  distances ( $\sim 1.95$  Å),<sup>6</sup> though similar to  $[(Tren^{TIPS})U^V \equiv NM]_2$  (AM = Li, Na, K, Rb, Cs)  $U^V \equiv N$  distances (1.833(4)–1.929(6) Å).<sup>5,8</sup> The N5–C34, C34–C35, and C34–C38 distances of 1.475(5), 1.516(5), and 1.525(15) Å



**Fig. 1** Molecular structure of **2** with selective labelling at 120 K and displacement ellipsoids at 50%. Hydrogen atoms except for H34 are omitted for clarity.

are consistent with N–C and C–C single bonds, and the presence of the Co-bound diene is reflected by C35–C36, C36–C37, and C37–C38 distances of 1.414(5), 1.422(5), and 1.414(6) Å. All other distances in **2** are as anticipated. Overall, the metrical data are consistent with **2** being a uranium(v)-imido complex consistent with the UV/Vis/NIR data.

Density functional theory (DFT) calculations on **2** (Fig. S26, S27 and Tables S1–S3, S6, ESI $^\dagger$ ) reveal a somewhat delocalised picture, however the principal UN- and Co-related bonding combinations could be identified and natural bond orbital (NBO) and natural localised molecular orbital (NLMO) analyses identify the  $\sigma^2\pi^4$  bonding motif of the imido (Fig. S27, ESI $^\dagger$ ). The computed charges and spin densities are consistent with  $U^V/Co^I$ . The U–N<sub>imido</sub> Nalewajski–Mrozek bond order is 2.73, and quantum theory of atoms-in-molecules (QTAIM) analysis reveals a UN 3,–1-bond critical point with a  $\rho$  value of 0.18 that is typical of a uranium(v)-imido complex.<sup>6</sup>

Noting the reaction between **1** and  $[Co^III(\eta^5-C_5H_5)_2]$ , we examined the analogous reaction with  $[Co^II(\eta^5-C_5Me_5)_2]$ , Scheme 1:  $[Co^II(\eta^5-C_5Me_5)_2]$  is a stronger reducing agent ( $\sim -1.93$  V vs. Fc)<sup>32</sup> compared to  $[Co^II(\eta^5-C_5H_5)_2]$ , meaning an excess of Co-reagent would be less likely to be needed possibly simplifying purification, and the former is sterically more congested which may impede *exo*-addition. Thus, we treated **1** with one equiv. of  $[Co^II(\eta^5-C_5Me_5)_2]$ , and after work-up and recrystallisation isolated the previously reported emerald green amido complex  $[(Tren^{TIPS})U^{IV} = NH_2]$  (**3**).<sup>6,9,34</sup>

The formation of **3** seems at first surprising, but can be rationalised. Assuming that the reaction proceeds by U-reduction to form “[ $Co^III(\eta^5-C_5Me_5)_2$ ] $^+[(Tren^{TIPS})U^V \equiv N]^-$ ”, protonation to give  $[(Tren^{TIPS})U^V = NH]$  could occur, and it is known that oxidation of  $[(Tren^{TIPS})U^{IV} = NH]^-$  results in the formation of **3** and **1** via disproportionation of  $[(Tren^{TIPS})U^V = NH]$ .<sup>34</sup> Alternatively, given the reducing nature of  $[Co^II(\eta^5-C_5Me_5)_2]$ , it could be that double reduction of **1** occurs to give “[ $(Tren^{TIPS})U^{IV} \equiv N$ ] $^{2-}$ ”, which would be very reactive. Indeed, the closely related complex  $[(Tren^{TIPS})U^{IV} \equiv NLi_2]_2$  contains bridging nitrides and of all the group 1



cations is only stable with Li because of the highly polarised nature of the  $U^{IV}\equiv N$  linkage with substantial destabilising charge accumulation at the nitride.<sup>35</sup> We note that  $(C_5Me_5)^{1-}$  can provide protons *via* tuck-in/tuck-over complexes,<sup>36</sup> and that  $[Co^{II}(\eta^5-C_5Me_5)_2]$  can act as a H-atom shuttle,<sup>37</sup> and either process could potentially expedite the formation of **3** from **1**.

Since the exact nature of divalent group 4 metallocenes can be ambiguous, we lastly examined the reaction of **1** with  $[V^{II}(\eta^5-C_5H_5)_2]$ , Scheme 1. Accordingly, a 1:1 mixture was stirred in toluene, and after work-up the red complex formulated as  $[(Tren^{TIPS})U^{IV}-N=V^{IV}(\eta^5-C_5H_5)_2]$  (**4**) was isolated in 82% yield.

The solid-state structure of **4** confirms its gross formulation, Fig. 2. The U1–N5 distance of 2.261(9) Å is much longer than the U–N distances in **1**<sup>6</sup> and **2** but similar to the U–N amido distance in **3** (2.228(4) Å).<sup>6,34</sup> Whilst the U1–N5 distance in **4** would be incompatible with U/V oxidation state combinations of VI/II and V/III, IV/IV and III/V were possible. However, the U–N<sub>amide</sub> and –N<sub>amine</sub> distances of 2.261(9)–2.285(8) and 2.674(10) Å are suggestive of  $U^{IV}$  over  $U^{III}$ .<sup>38</sup> The V1–N5 distance was found to be 1.680(9) Å, which compares to a V–N distance of 1.665 Å in  $[Me_3SiN=V^{IV}(\eta^5-C_5H_5)_2]$ .<sup>39</sup> Hence, **4** can be considered to result from partial N-atom transfer from U to V.

The <sup>1</sup>H NMR spectrum of **4** (Fig. S8, ESI†) covers the range 72.5 to –6.6 ppm; the resonance at 72.5 ppm corresponds to the vanadocene moiety, with the remaining resonances spanning 32.5 to –6.6 ppm which is qualitatively consistent with  $U^{IV}$ . The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **4** (Fig. S9, ESI†) exhibits a resonance at –76.2 ppm which falls in the range of  $U^{IV}$  complexes.<sup>40</sup>

The UV/Vis/NIR spectrum of **4** (Fig. S15–S17, ESI†) above 22 500  $cm^{-1}$  is dominated by charge-transfer bands and a prominent absorption is found at  $\sim 18\,000\,cm^{-1}$  ( $\epsilon = \sim 1500\,M^{-1}\,cm^{-1}$ ). Below 15 000  $cm^{-1}$  the spectrum evidences weak ( $\epsilon = \sim 30\text{--}70\,M^{-1}\,cm^{-1}$ ) f–f absorptions. The NIR region has the appearance of  $U^{IV}$ ,<sup>3</sup> but we could not completely rule

out the broad feature at 18 000  $cm^{-1}$  being f–d transitions of  $U^{III}$  rather than d–d transitions of  $V$ .<sup>3</sup>

Given the potential ambiguity of the U/V oxidation states in **4** we turned to quantum chemical calculations. However, DFT geometry optimisation always led to the U–N and V–N distances being too short and long, respectively (both  $\sim 1.95$  Å). Therefore, to first resolve the oxidation state question we turned to state-averaged complete active space self-consistent field (SA-CASSCF) calculations using the unoptimised crystal structure of **4** with an active space of 3 electrons in 12 orbitals (3d and 5f) examining low spin ( $S_{tot} = 1/2$ , **4'**) and high spin ( $S_{tot} = 3/2$ , **4''**) multiplicities (see ESI† for details). The ground state is found to be dominated by  $U^{IV}$  ( $5f^2$ ) and  $V^{IV}$  ( $3d^1$ ) configurations, consistent with the foregoing characterisation data overall. Interestingly, the ground Kramers doublet after spin–orbit coupling is dominated by  $S_{tot} = 1/2$  states, suggesting that there is an antiferromagnetic interaction between the  $V^{IV}$  and  $U^{IV}$  ions. Furthermore, the calculations show that there significant covalency and crystal field splitting of the 3d- and 5f-orbitals quenching the orbital angular momentum of **4** (see ESI†).

To confirm the SA-CASSCF findings, we collected variable-temperature SQUID magnetometry data on powdered **4** in an external 0.1 T field (Fig. S18, ESI†). The effective magnetic moment of **4** is  $2.71\mu_B$  at 300 K and this decreases steadily until at 8 K ( $1.21\mu_B$ ) when it drops more rapidly reaching  $0.42\mu_B$  at 1.8 K. The magnetic moment for **4** falls far more quickly with decreasing temperature than for isolated  $U^{IV}$  in  $[(Me_3Si)_2N]_3-U^{IV}=E^-$  ( $E = O, NSiMe_3$ ),<sup>41</sup> suggesting antiferromagnetic coupling which is also implied by a maximum in the  $\chi_M$  vs.  $T$  plot of **4** at 4.8 K. The magnetisation at 1.8 K and 7 T (Fig. S21, ESI†) of  $0.24\mu_B\,mol^{-1}$  is also far smaller than the sum of an isolated  $[(Me_3Si)_2N]_3-U^{IV}=E^-$  and a free  $S = 1/2$ ,<sup>41</sup> again reflecting the presence of U–V magnetic exchange.

The X-band EPR spectrum of powdered **4** (Fig. S22, ESI†) exhibits an eight line spectrum ( $^{51}V$ ,  $I = 7/2$ ) with  $g = 1.971$  ( $A_{x,y}(^{51}V) = 35\,MHz$  and  $A_z(^{51}V) = 220\,MHz$ ). However, this is incompatible with the low-temperature SQUID magnetometry data which indicates a  $S_{eff} = 1/2$  state with  $g \sim 0.7$ . Indeed, the SA-CASSCF results suggest a strongly axial ground doublet state (Table S5, ESI†), and previous work has continuously highlighted the effective high-symmetry behaviour of pseudo- $C_3$   $U^{IV}$  fragments.<sup>6,8,41</sup> Taking the data together, we suggest that **4** is actually EPR silent, and that due to the high sensitivity of EPR a trace impurity has been observed instead. We suggest that this is most likely  $[HN=V^{IV}(\eta^5-C_5H_5)_2]$  given the similarity of our EPR data to related vanadium(IV)-imido EPR data which are also isotropic.<sup>42</sup>

To probe the nature of the U–N–V linkage in **4** we performed DFT single point energy calculations on the **4'** and **4''** spin-state formulations (Fig. S28–S31, Tables S1–S5, S7, ESI†). DFT computes **4'** to be  $0.96\,kJ\,mol^{-1}$  more stable than **4''** which again suggests antiferromagnetic coupling. For **4'** the  $\alpha$ -spin HOMO (268a) and HOMO–1 (267a) are 5f character, and the  $\beta$ -spin 267b orbital is the  $2a_{1g}$  orbital of a bent metallocene (sd-hybrid). HOMOs–12, –20, and –21 reveal principally V–N  $\pi$ ,  $\pi$ , and  $\sigma$ -bond interactions with weaker U–N  $\pi$ - and  $\sigma$ -components, respectively, and these interactions are also found

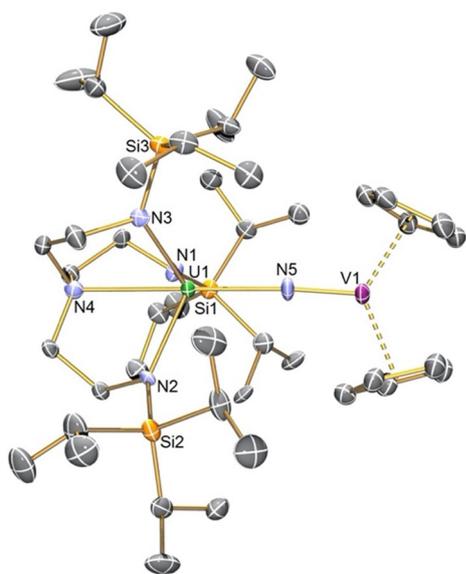


Fig. 2 Molecular structure of **4** with selective labelling at 120 K and displacement ellipsoids at 50%. Hydrogen atoms are omitted for clarity.



in the NBO and NLMO analysis confirming that the V–N and U–N bonds are largely of imido and amido character, respectively. Inspection of **4**<sup>+</sup> reveals a very similar bonding picture, except that after HOMO (269a) and HOMO–1 (268a) which are 5f-character the 2a<sub>1g</sub> orbital is now found as HOMO–2 (267a) in the  $\alpha$ - rather than  $\beta$ -spin manifold, and then the analogous V–N  $\pi$ ,  $\pi$ , and  $\sigma$ -bond combinations are now HOMOs–13, –21, and –22. The computed bond order, charge, spin density, NBO, NLMO, and QTAIM data (Tables S1–S3 and S7, ESI<sup>†</sup>) are consistent with **4** being described as a U<sup>IV</sup>/V<sup>IV</sup> complex where partial N-atom transfer from U to V has occurred.

To conclude, we have examined the reactivity of **1** towards a range of 3d-transition metal metallocenes. Although several metals (Cr, Mn, Fe, Ni) did not give tractable products, cobaltocene generated a uranium(v)-imido that results from one-electron reduction of uranium and nucleophilic attack of a cyclopentadienyl ligand by the nitride. In contrast, using decamethylcobaltocene resulted in two electron reduction of uranium and formation of a uranium(IV)-amido complex. The reaction of **1** with vanadocene resulted in a two electron redox couple resulting in U<sup>IV</sup> and V<sup>IV</sup> centres; since the nitride in **4** can be described as being formally of amido- and imido-type bonding character towards U and V, respectively, then **4** can be regarded as representing partial N-atom transfer from U to V. Nevertheless, there is clearly some electronic communication across the U–N–V linkage resulting in antiferromagnetic U–V exchange coupling. These complexes expand the still limited range of transition metal capped uranium-nitrides, and whilst demonstrating that constructing heterobimetallic actinide–nitride–metal linkages certainly benefits from starting with the nitride pre-installed at the actinide ion the resulting chemistry can still be complex and dictated by the nature of the transition metal fragment.

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## Data availability

Data are available in the ESI,<sup>†</sup> from the CCDC, or from the authors on request. CCDC codes 2373740 (2) and 2373741 (4).

## Conflicts of interest

There are no conflicts to declare.

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