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

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Reactions between [(Tren^{TIPS})U^{VI}≡N] (1, Tren^{TIPS} = {N(CH₂CH₂-NSiPr₃)₃}³⁻) and [M^{II}(η⁵-C₅R₅)₂] (M/R = Cr/H, Mn/H, Fe/H, Ni/H) were intractable, but M/R = Co/H or Co/Me afforded [(Tren^{TIPS})U^V=N(η¹:η⁴-C₅H₅)Co(η⁵-C₅H₅)] (2) and [(Tren^{TIPS})U^{IV}-NH₂] (3), respectively. For M/R = V/H [(Tren^{TIPS})U^{IV}-N=V^{IV}(η⁵-C₅H₅)₂] (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.^{1–4} The search for isolable terminal uranium-nitrides was accomplished by some of us just over a decade ago, first with [Na(12C₄)₂][(Tren^{TIPS})U^V≡N] (Tren^{TIPS} = {N(CH₂CH₂NSiPr₃)₃}³⁻; 12C₄ = 12-crown-4 ether)⁵ in 2012 and then [(Tren^{TIPS})U^{VI}≡N] (1) in 2013.⁶ The Tren^{TIPS} ligand has proven to be a ‘privileged’ ancillary ligand for terminal uranium-nitrides,^{7–10} and indeed the only other ligand class to have supported an isolable terminal uranium-nitride linkage is the siloxide ligand (Bu^tO)₃SiO¹⁻ used by Mazzanti.¹¹ 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),^{6,8,12,13} U=N=An (An = U, Th),^{13–28} and U≡N-M complexes (M = Mo, Rh, Ir, Mo).^{29,30} 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,²⁹ and M = Rh and Ir compounds were made by photolysis of azido precursors.³⁰ We decided to examine the potential of 1 to construct heterobimetallic nitride-bridged complexes since it already has a terminal,^{5–10} 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^{II}(η⁵-C₅R₅)₂] (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^{TIPS})U^{VI}≡N] (1) with [M^{II}(η⁵-C₅H₅)₂] (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. ¹H 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^{II}(η⁵-C₅H₅)₂] afforded the uranium(v)-imido complex [(Tren^{TIPS})U^V=N(η¹:η⁴-C₅H₅)Co(η⁵-C₅H₅)] (2) as red crystals. However, 2 co-crystallises with variable quantities of 1 and [Co^{II}(η⁵-C₅H₅)₂] (Fig. S5 and S6, ESI†). Indeed, a variable-temperature ¹H NMR study (Fig. S7, ESI†) revealed the dominance of 2 at low temperature (−60 °C) and a greater proportion of 1/[Co^{II}(η⁵-C₅H₅)₂] at higher temperature (25 °C), and hence 2 is in equilibrium with 1 and [Co^{II}(η⁵-C₅H₅)₂]. Whilst the optimal practical ratio for the reaction was found to be two equiv. of [Co^{II}(η⁵-C₅H₅)₂] to 1 we could only ever isolate 2 as a mixture (A) co-crystallised with 1 and [Co^{II}(η⁵-C₅H₅)₂]. Although the [Co^{II}(η⁵-C₅H₅)₂] can be sublimed out of A, when redissolved

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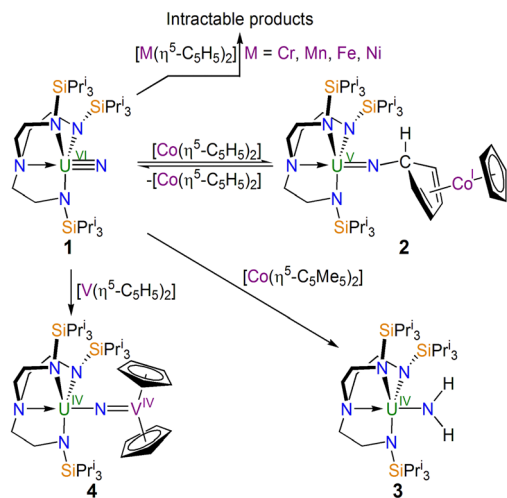
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Scheme 1 Synthesis of **2–4** from **1** and intractable reaction outcomes. The by-products are either not known or are not shown for clarity.

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,³¹ and whilst a radical reaction cannot be discounted the radical chemistry of **1** is quite slow in the absence of strong light,⁶ so we propose that $[Co^II(\eta^5-C_5H_5)_2]$ ($E^0 = \sim -1.32$ V vs. Fc)³² 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[†]). Of most salience, in addition to one cyclopentadienyl ring resonance of 5H (9.7 ppm) two pairs of 2H each for the η^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[†]). Of most interest is the near infrared region, where four absorptions ($\epsilon = \sim 10$ – 30 $M^{-1} cm^{-1}$) are found at ~ 6000 , ~ 7100 , ~ 9000 , and ~ 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.³³

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),^{5,6,8,12} slightly shorter than $(Tren^{TIPS})U^V = NR$ distances (~ 1.95 Å),⁶ 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).^{5,8} The N5–C34, C34–C35, and C34–C38 distances of 1.475(5), 1.516(5), and 1.525(15) Å

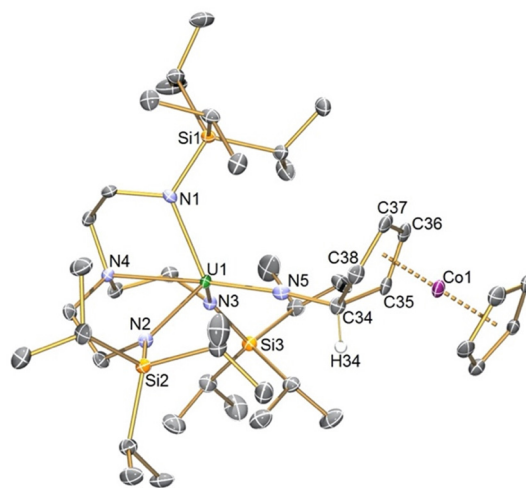


Fig. 1 Molecular structure of **2** with selective labelling at 120 K and displacement ellipsoids at 50%. Hydrogen atoms except for H34 are omitted for clarity.

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[†]) 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[†]). The computed charges and spin densities are consistent with U^V/Co^I . The U–N_{imido} 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 ρ value of 0.18 that is typical of a uranium(v)-imido complex.⁶

Noting the reaction between **1** and $[Co^II(\eta^5-C_5H_5)_2]$, 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 (~ -1.93 V vs. Fc)³² 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**).^{6,9,34}

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 $[(Tren^{TIPS})U^V = NH]$.³⁴ 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.³⁵ We note that $(C_5Me_5)^{1-}$ can provide protons *via* tuck-in/tuck-over complexes,³⁶ and that $[Co^{II}(\eta^5-C_5Me_5)_2]$ can act as a H-atom shuttle,³⁷ 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**⁶ and **2** but similar to the U–N amido distance in **3** (2.228(4) Å).^{6,34} 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_{amide} and –N_{amine} distances of 2.261(9)–2.285(8) and 2.674(10) Å are suggestive of U^{IV} over U^{III} .³⁸ The V1–N5 distance was found to be 1.680(9) Å, which compares to a V–N distance of 1.665 Å in $[Me_3SiN=V^{IV}(\eta^5-C_5H_5)_2]$.³⁹ Hence, **4** can be considered to result from partial N-atom transfer from U to V.

The ¹H 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 ²⁹Si{¹H} NMR spectrum of **4** (Fig. S9, ESI†) exhibits a resonance at –76.2 ppm which falls in the range of U^{IV} complexes.⁴⁰

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} ,³ 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 .³

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 ~ 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 $[(Me_3Si)_2N]_3-U^{IV}=E^-$ ($E = O, NSiMe_3$),⁴¹ suggesting antiferromagnetic coupling which is also implied by a maximum in the χ_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 $S = 1/2$,⁴¹ 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.^{6,8,41} 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.⁴²

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 α -spin HOMO (268a) and HOMO–1 (267a) are 5f character, and the β -spin 267b orbital is the $2a_{1g}$ orbital of a bent metallocene (sd-hybrid). HOMOs–12, –20, and –21 reveal principally V–N π , π , and σ -bond interactions with weaker U–N π - and σ -components, respectively, and these interactions are also found

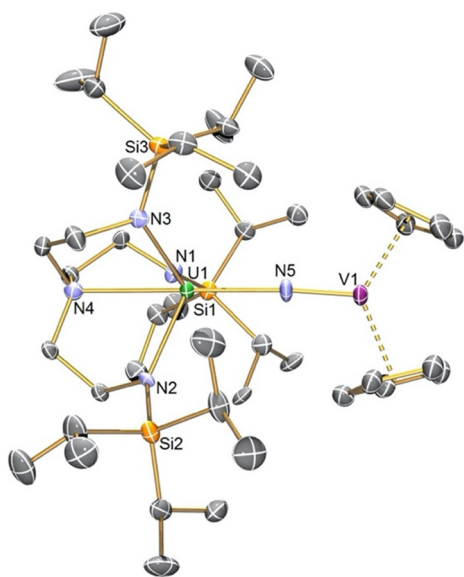


Fig. 2 Molecular structure of **4** with selective labelling at 120 K and displacement ellipsoids at 50%. Hydrogen atoms are omitted for clarity.



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**⁺ reveals a very similar bonding picture, except that after HOMO (269a) and HOMO–1 (268a) which are 5f-character the 2a_{1g} orbital is now found as HOMO–2 (267a) in the α - rather than β -spin manifold, and then the analogous V–N π , π , and σ -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[†]) are consistent with **4** being described as a U^{IV}/V^{IV} 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^{IV} and V^{IV} 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,[†] 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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