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Back-bonding between an electron-poor, high-oxidation-state metal and poor π -acceptor ligand in a uranium(V)–dinitrogen complex

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Abstract

A fundamental bonding model in coordination and organometallic chemistry is the synergic, donor–acceptor interaction between a metal and a neutral π -acceptor ligand where the ligand σ -donates to the metal, which π -back-bonds to the ligand. This interaction typically involves a metal with an electron-rich, mid-, low-, or even negative, oxidation state and a ligand with a π^ orbital. Here, we report that treatment of a uranium–carbene complex with an organo-azide produces a uranium(V)–bis(imido)–dinitrogen complex, stabilised by a lithium counter-ion. This complex, which has been isolated in crystalline form, involves an electron-poor, high-oxidation-state uranium(V) $5f^1$ ion that is π -back-bonded to the poor π -acceptor ligand dinitrogen. We propose that this is made possible by a combination of cooperative heterobimetallic uranium–lithium effects and the presence of suitable ancillary ligands rendering the uranium ion unusually electron-rich. This electron-poor back-bonding could have implications for the field of dinitrogen activation.*

Introduction

In coordination and organometallic chemistry, a well-established fundamental bonding model is that neutral π -acceptor ligands, such as isoelectronic dinitrogen (N_2) and carbon monoxide (CO), can ligate end-on to metals in a synergic donor-acceptor interaction.¹ In this classical bonding model σ -donation from the ligand lone pair to the metal is complemented by metal π -back-bonding to a formally vacant π^* acceptor molecular orbital of the ligand resulting in weak ligand activation, Fig. 1. It naturally follows that a key requirement of metal-to-ligand back-bonding is that the metal must be in a medium to low, or even negative, formal oxidation state so that it is sufficiently electron-rich to possess the requisite valence electrons for back-bonding. An inherent consequence of this scenario is that a low oxidation state metal centre will exhibit more radially extended valence orbitals compared to higher oxidation states, thus enabling effective spatial overlap with the ligand π^* orbitals. Thus, a high oxidation state and electron-poor metal is usually inherently ill-suited, if not incapable, of engaging in π -back-bonding to π -acceptor ligands.

For N_2 complexes, although $[U(N)_2(N_2)_n]$ ($n = 1-5$) species formally containing uranium in oxidation state +VI have been spectroscopically detected when trapped under cryogenic matrix isolation conditions,^{2,3} no classical molecular N_2 -complex isolable on macroscopic scale is known above a metal oxidation state of +III, otherwise strong activation to give reduced N_2^{n-} ($n = 2, 4$) with high oxidation state metals occurs.^{3,4} CO is a better π -acceptor ligand than N_2 , so metal oxidation state +IV but electron-rich carbonyl anions such as $[PtCl_5(CO)]^{1-}$, $[OsF_5(CO)]^{1-}$, $[OsCl_5(CO)]^{1-}$ are known,⁵⁻⁷ yet despite the fact these M(IV) ions are electron-rich they are exceedingly rare and only the latter is structurally authenticated.⁷ Transient or matrix isolation-trapped M(IV) $[M(O)_2(CO)_n]$ ($M = Rh, n = 1$; $M = Mo, W, n = 4$) species have been detected spectroscopically,^{8,9} and the formally +VI osmium dication $[OsO_2(CO)_4]^{2+}$ has been reported, but was too unstable to be isolated and fully characterised.¹⁰ Very recently the Fe(IV) dication $[Fe(\eta^5-C_5Me_5)_2(CO)]^{2+}$ was structurally authenticated,¹¹ but is stabilised via C_5Me_5 -to-CO ligand-to-ligand

π -back-bonding. This bonding type is a departure from the classical model, and appears to be unique to metallocene complexes, being similarly proposed for d^0 M(IV) $[M(\eta^5-C_5Me_5)_2(H)_2(CO)]$ (M = Zr, Hf) species detected spectroscopically at low temperature.^{12,13} In summary, all the species discussed in this paragraph are, despite their high oxidation states, either d-electron rich, kinetically trapped at low temperatures, or utilise ligand-to-ligand not metal-to-ligand back-bonding, and they represent quite different bonding situations to non-classical, cationic carbonyl complexes where the M-CO σ -bonding component dominates the bonding picture with little or no π -back-bonding contributions.^{14,15}

For early actinides, outside of cryogenic matrix isolation conditions^{2,3} N_2 derivatives tend to be strongly activated and reduced to side-on-bound $(N_2)^{n-}$ by polymetallic-mediated reductions,¹⁶⁻¹⁹ or complete cleavage to nitrides occurs.^{20,21} Very few isolable, structurally characterised end-on CO, N_2 , or NO actinide complexes are known,²²⁻²⁹ and all terminal end-on complexes are supported by *tris*(cyclopentadienyl) ligand sets.^{22-25,27-29} The back-bonding in these systems stems not from metal orbitals but cyclopentadienyl ligand orbitals,³⁰ reminiscent of transition metal analogues,¹¹ or in the case of NO formal full reduction to $(NO)^{1-}$ occurs,²⁹ so these are quite different from the classical metal-to-ligand back-bonding model.¹ Notably, all uranium complexes with end-on CO or N_2 involve electron-rich $5f^3$ uranium(III).^{22-25,28} Although 5f orbitals are radially more expanded than ‘core-like’ 4f orbitals, they only just penetrate the valence region, so such metal-to-ligand interactions and π -acceptor ligand activation is weak, as evidenced by their reversible coordination and dominance of ligand-to-ligand back-bonding. However, it should be noted that even though actinide-metallocenes represent a non-classical case of donor-acceptor bonding,³⁰ they fundamentally comply with the classical requirements of electron rich metal ions in a medium to low metal oxidation state.

We recently reported the synthesis of the silyl-phosphino-carbene uranium(IV) complex $[\text{U}(\text{BIPM}^{\text{TMS}})\{\text{C}(\text{SiMe}_3)(\text{PPh}_2)\}(\text{Cl})][\text{Li-2,2,2-cryptand}]$ (**1**, $\text{BIPM}^{\text{TMS}} = \text{C}(\text{PPh}_2\text{NSiMe}_3)_2$) that contains two types of covalent $\text{U}=\text{C}$ carbene double bond.³¹ In order to establish the fundamental properties of **1** we have examined its reactivity towards a wide range of substrates. Here, we report that treatment of **1** with an organo-azide produces a 5f¹ high oxidation state uranium(V)-*bis*(imido) $\{\text{U}(\text{NR})_2\}^{1+}$ derivative. This carbene to *bis*(imido) motif transformation is unknown in carbene chemistry, and the uranium(V)-*bis*(imido) complex that is formed contains an end-on bound molecule of N_2 which bridges end-on to a lithium counter-ion. This isolable, crystalline complex features a +V high oxidation state metal classically back-bonded to a neutral π -acceptor ligand despite formally involving an electron-poor metal with only one valence electron. This unusual situation occurs with an electron in a 5f-orbital, ostensibly one of least radially expanded orbitals of the Periodic Table.

Results and Discussion

Synthesis. Treatment of **1** with one equivalent of 1-adamantyl-azide (AdN_3) in benzene results in immediate effervescence of N_2 and the red solution turning black. After work-up blackish-red crystals of $[\text{U}(\text{BIPM}^{\text{TMS}})(\text{NAd})_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)(\text{Li-2,2,2-cryptand})]$ (**2**) are obtained from toluene in 28% crystalline yield (by uranium content), Fig. 2. Complex **2** is formed irrespective of whether the reaction is conducted under N_2 or Ar, suggesting that the coordinated N_2 derives from the azide. Analysis of the reaction mother liquor by Nuclear Magnetic Resonance (NMR) spectroscopy reveals that more than one uranium-containing product is formed. The by-products have resisted all attempts to isolate and characterise them, but hydrolysis of the mother liquor and analysis by NMR spectroscopy and chromatographic methods reveals the presence of $\text{BIPM}^{\text{TMS}}\text{H}_2$, $\text{Me}_3\text{SiCH}_2\text{PPh}_2$, and $\text{LiCl-2,2,2-cryptand}$ in an approximate 1:2:1 ratio. This gives mass balance for the reaction and accounts for the superficially low yield of **2**, since the theoretical maximum in a scenario where sacrificial uranium-containing by-products form is substantially lower than 100%. The reaction that

produces **2** is clearly complex and most likely involves ligand scrambling, but **2** is consistently the sole isolable uranium complex from multiple reactions.

Structural characterisation. The solid-state molecular structure of **2** was determined by X-ray crystallographic studies, Fig. 3. The salient feature of **2** is the presence of a molecule of N₂ bridging between uranium and lithium ions, the latter of which is encapsulated within a 2,2,2-cryptand ligand in an irregular six-coordinate geometry. The coordination sphere of uranium is completed by a tridentate BIPM^{TMS} carbene ligand *trans* to the N₂ ligand, and two mutually *trans*-imido units resulting in a distorted octahedral geometry.

The U1-N1 distance of 2.605(8) Å is longer than the sum of single bond covalent radii of uranium and nitrogen (2.41 Å),³² and the strongly activated U-N₂ bond length of 2.220(9) Å in [$\{(\text{Ph})(\text{Bu}^t)\text{N}\}_3\text{Mo}(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)\text{U}\{\text{N}(\text{Bu}^t)(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)\}_3$],³³ but, by the 3σ-criterion, compares reasonably well to the U-N distance of 2.492(10) Å reported for weakly activated [$(\eta^5\text{-C}_5\text{Me}_5)_3\text{U}(\text{N}_2)$].²⁸ Interestingly, there is little variation of the U-N_α-N_β angles in those three molecules, being 175.1(7), 173.8(7), and 180°, respectively, presumably reflecting that they are all back-bonded linkages no matter whether they result from metal- or ligand-to-ligand back-bonded electron density. We suggest that the U1-N1 distance can be considered long as a result of weak back-bonding, the fact that it resides *trans* (175.9(2)°) to the strong carbene donor of the BIPM^{TMS} ligand, and that the uranium ion is bonded to several stronger donor ligands overall. The N1-N2 distance of 1.139(9) Å is elongated slightly compared to the N-N distance in free-N₂ (1.0975 Å),¹ again indicating weak back-bonding, and is shorter than the 1.23(1) Å distance in [$\{(\text{Ph})(\text{Bu}^t)\text{N}\}_3\text{Mo}(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)\text{U}\{\text{N}(\text{Bu}^t)(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)\}_3$],³³ but is indistinguishable from the 1.120(14) Å N-N distance in [$(\eta^5\text{-C}_5\text{Me}_5)_3\text{U}(\text{N}_2)$].²⁸

The U1-N5 and U1-N6 distances of 1.906(6) and 1.897(6) Å, respectively, are typical of uranium-bis(imido) units,³⁴ though we note the N5-U1-N6 angle (159.1(2)°) departs substantially from linearity, presumably to avoid steric clashing between the bulky Ad and BIPM^{TMS} ligand substituents. The U1-C1 distance of 2.461(7) Å in **2** compares well to the analogous distance of 2.400(3) Å in the uranium(VI)-carbene-imido-oxo complex [U(BIPM^{TMS})(NC₆H₂-2,4,6-Me₃)(O)(DMAP)] (DMAP = 4-dimethylaminopyridine),³⁵ but considering the formal uranium(V/VI) oxidation states of these two complexes the U=C bonds are long reflecting the presence of several multiple bond donor ligands. For example, in the uranium(V)-carbene complex [U(BIPM^{TMS})(Cl)₂(I)] the U=C distance is 2.268(10) Å,³⁶ and we suggest the long U=C bond in **2** arises from the uranium ion being electron rich from the two imido ligands and that the *bis*(imido) combination is the primary bonding motif with binding of the BIPM^{TMS} being secondary.

The N2-Li1 distance of 2.008(15) Å compares well to the sum of the single bond covalent radii of nitrogen and lithium (2.04 Å),³² and is indeed reminiscent of Li-NR₂ distances generally, suggesting that the N₂ carries partial anionic character resulting from back-bonding from the 5f¹ uranium(V) ion. During crystallographic refinement of **2** the possibility that the N₂ could be other diatomic small molecules (C₂, CN, CO, NO, O₂) or a disordered chloride was considered in detail, but is ruled out by a combination of incompatibility with the crystallographic metrical data, chemical unfeasibility of their occurrence, and the oxidation state formulation confirmed by the characterisation data below.

Spectroscopic and magnetic characterisation. The NMR spectra that could be obtained for **2**, noting its poor solubility once isolated, are well resolved and essentially within diamagnetic ranges (Supplementary Information Fig. 1-4), however this is common for uranium(V) complexes which are weakly paramagnetic and the data for **2** are consistent with those of related uranium(V)-BIPM complexes.³⁶⁻³⁸ The Raman spectrum of **2** (Supplementary Information Fig. 5) exhibits a broad

$\nu(\text{N}_2)$ absorption centred at $\sim 1940\text{ cm}^{-1}$, which compares reasonably well to a computed $\nu(\text{N}_2)$ value of 2038 cm^{-1} from a Density Functional Theory (DFT) analytical frequencies calculation of **2** using atomic coordinates from the experimentally determined crystal structure (see below). Additionally, it has been shown^{39,40} that $\nu(\text{N}_2)$ is proportional to $d(\text{N}_2)$ to the 3/2-power as:

$$\nu(\text{N}_2) = -1840[d(\text{N}_2)]^{3/2} + 4130 \text{ (Eqn 1.)}$$

Using Eqn 1 and the N1-N2 distance of $1.139(9)\text{ \AA}$ in **2**, a $\nu(\text{N}_2)$ frequency centred at 1890 cm^{-1} is predicted, and noting that by the 3σ -criterion the N1-N2 distance spans the range 1.112 - $1.166\text{ \AA}$ the $\nu(\text{N}_2)$ frequency is predicted to, and does, fall in the range 1813 - 1972 cm^{-1} . Considering that the N1-N2 solid-state distance is determined in close proximity to the heavy uranium and that N_2 -containing molecules, including N_2 itself, frequently deviate by up to 300 cm^{-1} from predictions^{39,40} based on Eqn 1, the fit for **2** is remarkably good. The $\nu(\text{N}_2)$ frequency of **2** is $\sim 390\text{ cm}^{-1}$ lower (Δ) than that of free N_2 (2331 cm^{-1}) (*1*), indicating weak, but not insignificant, back-bonding and activation. For comparison, the $\nu(\text{N}_2)$ frequency of $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{U}(\text{N}_2)]$ is 2207 cm^{-1} ($\Delta = 124\text{ cm}^{-1}$, $\nu(\text{N}_2)$ predicted to be 1949 cm^{-1} by Eqn 1),²⁸ suggesting very weak back-bonding in that case, whereas the $\nu(\text{N}_2)$ frequency of $[\{(3,5\text{-Me}_2\text{-C}_6\text{H}_3)(\text{Ad})\text{N}\}_3\text{Mo}(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)\text{U}\{\text{N}(\text{Bu}^t)(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)\}_3]$ is 1568 cm^{-1} ($\Delta = 763\text{ cm}^{-1}$) suggesting strong back-bonding in that case.³³ These spectroscopic data correlate with the observed stabilities of **2** and $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{U}(\text{N}_2)]$,²⁸ where the latter requires a pressure of 80 psi to form, with N_2 release observed when the pressure is returned to 14.7 psi (1 atm), whereas the former forms at 1 atm pressure and does not release N_2 even when placed under dynamic vacuum (0.01 mm Hg), nor exchange with $^{15}\text{N}_2$ when refluxed in toluene under $^{15}\text{N}_2$, which instead results in decomposition to unidentifiable products and any remaining **2** shows no sign of $^{15}\text{N}_2$ -incorporation. Further confirming this trend, the related carbonyl complex $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{U}(\text{CO})]$ exhibits a $\nu(\text{CO})$ frequency that is 221 cm^{-1} lower than free CO ,²⁵ and this compound liberates CO only after several hours under vacuum. The attenuated total reflectance infrared (ATR-IR) spectrum of **2** (Supplementary Information Fig. 6) exhibits several weak

absorptions in the range 1900-2100 cm^{-1} , but none of these could be definitively assigned as a $\nu(\text{N}_2)$ absorption, and attempts to perform ^{15}N -labelling studies proved intractable.

The ultraviolet/visible/near-infrared (UV/Vis/NIR) electronic absorption spectrum of **2** (Supplementary Information Fig. 7) is dominated by strong charge transfer bands that tail from the UV region to $\sim 12,000 \text{ cm}^{-1}$. The NIR region exhibits weak ($\epsilon = 10\text{-}20 \text{ L mol}^{-1} \text{ cm}^{-1}$) Laporte forbidden f-f absorptions in the range 5555-11,000 cm^{-1} that are characteristic of intra-configurational transitions from the ground $^2\text{F}_{5/2}$ to excited $^2\text{F}_{7/2}$ term multiplets of uranium(V).⁴¹ These absorptions are modelled well by Time-Dependent DFT, revealing that they all involve electronic promotions within the U-N₂ unit (Supporting Information Fig. 8).

The uranium(V) formulation of **2** is supported by Electron Paramagnetic Resonance (EPR) spectroscopy. The solid-state X-band EPR spectrum of **2** at 5 K (Supplementary Information Fig. 9) exhibits a resonance peak at $g_z = 3.80$, which is similar to the axial g_z feature of terminal uranium(V)-nitrides supported by tripodal ligands ($g \sim 3.7$);⁴² as for those nitrides, no $g_{x,y}$ features are observed for **2** within the available magnetic field range, 0-18,000 Gauss, suggesting that $g_{x,y} < 0.4$. This resonance peak is observable only below 50 K, consistent with 5f-electron character since rapid relaxation can occur due to the high orbital angular momenta of 5f-orbitals.

Unequivocal confirmation of the +V oxidation state assignment of **2** comes from variable-temperature superconducting quantum interference device (SQUID) magnetometry, Fig. 4 and Supplementary Information Fig. 10. A powdered sample of **2** exhibits a magnetic moment of 2.33 Bohr magneton units (μ_B) at 298 K (2.28 μ_B in solution), in close agreement with a theoretical magnetic moment of 2.54 μ_B for a single uranium(V) ion. Characteristic of uranium(V), the magnetic moment decreases slowly, until at 50 K ($\mu_{\text{eff}} = 2.04 \mu_B$) the magnetic moment decreases

rapidly, reaching $0.94 \mu_B$ at 2 K since this ion is an open shell magnetic doublet at all temperatures.⁴¹⁻⁴⁴

Computational characterisation. In order to probe the nature of the bonding in **2** we performed DFT calculations (see Supplementary Information Tables 1-32). In general, the computed bond lengths and angles of the geometry optimised structure are within $0.05 \text{ \AA}$ and 2° of the experimental crystal structure. However, the U1-N1 distance of $2.439 \text{ \AA}$ in the geometry optimised gas-phase structure is $\sim 0.16 \text{ \AA}$ shorter than the distance in the experimental solid-state crystal structure. Furthermore, inspection of a space filling representation of **2** (Supplementary Information Fig. 11) clearly shows that the $\text{N}_2\text{-Li-2,2,2-cryptand}$ fragment could approach closer to the $\text{U(BIPM}^{\text{TMS}}\text{)(NAd)}_2$ unit of **2** without any obvious steric clashing. Moreover, an analytical frequencies calculation on the geometry optimised coordinates computes a N_2 stretch of 1712 cm^{-1} , which does not compare well with the experimentally determined value.

In order to probe this further, we performed potential energy surface scans along the U1-N1 vector, both on the full molecule and on a simplified model (**2 core**) in which phenyl and adamantyl groups are replaced with methyl groups, SiMe_3 is substituted for SiH_3 and only the coordinating atoms of the cryptand are retained (Supplementary Information Fig. 12). Several levels of theory have been employed, and the results are summarised in Fig. 5. DFT Perdew-Burke-Ernzerhof (PBE) scans give minimum energies between $2.35\text{-}2.41 \text{ \AA}$, whereas Hartree-Fock (HF) scans show minima at around $2.50 \text{ \AA}$. Second-order Møller-Plesset perturbation theory (MP2) calculations yield similar conclusions to HF. Restricted Active Space-Self Consistent Field (RASSCF) calculations have also been performed; the choice of active space is discussed in detail in the Supplementary Information, and the natural orbitals are shown in Supplementary Information Fig. 13 and their occupancies, at each point in the scan, in Supplementary Information Table 1. These calculations give an energy minimum at $2.56 \text{ \AA}$, with a significantly shallower potential compared to the already rather shallow

HF and DFT scans; the point at 2.61 Å is only 0.80 kJ mol⁻¹ higher in energy. It may be that including further correlation shifts the minimum even closer to the crystal structure geometry, as may the additional sterics of the full molecule. We note that the very shallow potentials shown in Fig. 4 are well within the range of crystal packing forces,⁴⁵ and hence conclude that the discrepancy of the experimental vs computed U1-N1 distance is either the result of solid-state crystal packing effects that are not accounted for in gas phase calculations and/or correlation energy effects not well described by DFT.

Noting the experimental vs computed U1-N1 discrepancy, to obtain an experimentally relevant description of the electronic structure of **2** DFT studies were performed using the crystallographic coordinates and not geometry optimised ones. The good agreement of TD-DFT and analytical frequencies calculations using those coordinates to experimental observations provides validation of this approach. The computed Multipole Derived Charges (MDC-q) on the U1, C1, Li1, and N₂ units are +3.36, -2.14, +0.66, and -0.51. In a purely ionic bonding situation these values would be +5, -2, +1, and 0, so the computed data reflect charge donation to the U1 and Li1 ions from the ligands and back-bonding from uranium to the N₂ ligand. Consistent with this, the computed spin densities on U1 and N₂ unit are -0.6 and -0.51, confirming transfer of ~0.5 of an electron from the formal 5f¹ U1 to N₂. In further support of this back-bonding picture, the U1-N1 and N₂ computed Nalewajski-Mrozek bond orders are 0.66 and 2.75, respectively, showing a weak U-N₂ back-bond and modest reduction of the N₂ bond order (3 in free N₂). As suggested by the U1-C1 distance, the U1-C1 bond is poorly developed with a bond order of 0.92, reflecting the presence of the two imido groups with U1-N5 and U1-N6 bond orders of 2.57 and 2.59 that are consistent with strong triple bonds. For comparison the U1-N3 and U1-N4 bond orders are 0.77 and 0.79, respectively, and a highly polar N2-Li1 interaction is confirmed by a computed bond order of 0.13.

The highest occupied Kohn-Sham molecular orbital (HOMO) of **2** is the U-N₂ back-bond, Fig. 6. This is consistent with the formal 5f¹ +V oxidation state of the uranium ion in **2** and back-bonding to N₂. The U-C_{carbene} double bond is principally represented by HOMO-1 (π) and HOMO-2 (σ) (Supplementary Information Fig. 14). The U-N_{imido} bonding interactions are represented by HOMO-3 to HOMO-11, but these MOs are extensively mixed. Therefore, in order to obtain a clearer and chemically more intuitive description of the bonding in **2** we turned to Natural Bond Orbital (NBO) theory.

NBO calculations on **2** (Supplementary Information Fig. 15) reveal one U-N₂ back-bonding interaction that is composed of 31% U1 and 69% N1 character. As expected, the N component is essentially pure 2p-orbital character from the π^* -orbital manifold of N₂ and the uranium contribution is 95% 5f and 5% 6d character. The N₂ lone pair donation to U is described in an NBO of exclusively N-character (62% 2s and 38% 2p character), in-line with its dative, and weak, nature. Confirming analysis of the Kohn-Sham electronic structure, NBO returns a $\sigma^2\pi^2$ U-C double bond interaction and also two $\sigma^2\pi^2\pi^2$ U-N_{imido} triple bond interactions. The U=C bonds are quite polar, being composed of 10% uranium and 90% carbon character with the uranium component dominated by 5f character (80:20 5f:6d), whereas the U-N_{imido} bonds have 20% uranium and 80% nitrogen character with a 5f:6d ratio of 70:30.

DFT and NBO methods are orbital-based, and in order to probe the chemical bonding in **2** in an alternative way we examined the topology of the electron density using Quantum Theory of Atoms in Molecules (QTAIM). A U1-N1 3,-1 bond critical point (BCP) was found, with an electron density $\rho(r)$ of 0.04 e bohr⁻³. In QTAIM analysis covalent bond tends to have $\rho(r) > 0.1$ so the value for **2** is consistent with a polar bonding interaction, which is also reflected by the total energy density $H(r)$ (-0.01) at the BCP. The presence of the back-bond is unequivocally confirmed by examination of the bond ellipticity, $\epsilon(r)$. Single (σ^2 , e.g. H₃CCH₃) and triple ($\sigma^2\pi^2\pi^2$, e.g. HC $\equiv$ CH)

bonds exhibit spherical distributions of electron density around the bond path at the BCP and so $\epsilon(r) \sim 0$, however double bonds ($\sigma^2\pi^2$, e.g. $\text{H}_2\text{C}=\text{CH}_2$) are asymmetric and so $\epsilon(r) > 0$, being 0.45 for $\text{H}_2\text{C}=\text{CH}_2$.⁴⁶ Here, the $\epsilon(r)$ value for the U1-N1 bond in **2** is 0.39, confirming a single π -back-bond. For comparison, the U1-C1, av. U-N_{imido}, and N1-N2 $\rho(r)/H(r)/\epsilon(r)$ data are 0.08/−0.03/0.24, 0.20/−0.14/0.01, and 0.6/−0.91/0.01, respectively. Taken together with all the other data, the consistent picture that emerges is a U-N₂ donor-acceptor interaction with a π -back-bond that only weakly activates the N $\equiv$ N triple bond, and polarised covalent U-C_{carbene} double and U-N_{imido} triple bonds.

Discussion. Complex **2** represents a departure from the traditional requirements of synergic, donor-acceptor metal-to-ligand interactions. This situation arises in an electron-poor, high oxidation state complex, involving the poor π -acceptor N₂, utilising a single electron in a 5f-orbital, which is one of the least radially expanded orbitals, and therefore one of the least likely candidates for this scenario to occur. So how can this situation arise? We propose two factors that may be responsible. The heterobimetallic uranium-lithium combination may cooperatively assist in trapping the N₂, and certainly heteropolymetallic cooperative effects are increasingly being recognised as crucial to binding and activating N₂ in heterogeneous Haber Bosch chemistry and in homogeneous molecular analogues.^{1,47} Recognising that electron-poor, high oxidation state metals can also back-bond to N₂ by tuning the ligand environment could have implications for N₂-activation chemistry given the vast scale that industrial Haber Bosch and biomimetic nitrogenase processes operate on.⁴⁸ The uranium ion in **2** is bonded to two imido ligands and the tridentate BIPM^{TMS} carbene ligand. We suggest that with at least three strong multiply bonded π -donor ligands, the formally electron-poor 5f¹ uranium ion in **2** is evidently uncommonly capable of engaging in π -back-bonding even to a poor π -acceptor ligand. Uranium(V) is usually considered to be quite oxidising,⁴¹ but here the uranium is in such an electron rich ligand environment that it is now essentially reducing in nature. The isolation of crystalline **2**, and the prior report of meta-stable $[\text{OsO}_2(\text{CO})_4]^{2+}$ (reference 10) that contains one less

metal-ligand multiple bond linkage than stable **2**, suggests that such unusual bonding might be realised more widely by electron-poor metals when coordinated by very electron-rich ancillary ligands.

Conclusions and Summary

To conclude, we have found that reaction of a uranium-carbene complex with an organo-azide results in isolation of a crystalline uranium(V)-*bis*(imido)-dinitrogen complex. This complex features a +V high oxidation state metal classically back-bonded to a neutral π -acceptor ligand, and this is despite formally involving an electron-poor metal with only one valence electron that is ostensibly one of the least radially extended in the Periodic Table combined with a very poor π -acceptor ligand. We propose that this scenario arises due to a combination of cooperative heterobimetallic effects and that the uranium ion in this complex is unusually electron-rich to the point that a usually oxidising metal centre is now reducing in nature. This suggests that with suitable ancillary ligands isolable complexes with the unusual bonding situation reported here might be realised more widely when electron-poor metals are coordinated by very electron-rich ancillary ligands. Lastly, N₂-activation chemistry usually relies on the use of low-valent reducing metal ions, but this work suggests that in the suitable situations high oxidation state metals might also play a role in the binding and activation of dinitrogen.

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Data Availability

The X-ray crystallographic data for **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1869009. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif). All other data supporting the findings of this study are available within the Article and its Supplementary Information, or from the corresponding author upon reasonable request.

Author Contributions

E.L. and J.B. prepared and characterised the compound and its precursors. B.E.A. and N.K. performed the energy-scan calculations and analysed the results. E.L., A.J.W., I.J.V.-Y., and G.F.S.W. collected, solved, refined, and analysed the crystallographic data. E.L., L.R.D., J.D.C., and P.C. recorded and interpreted the Raman data. F.T. recorded and interpreted the EPR data. S.T.L. originated the central idea, supervised the work, analysed the data, performed the DFT, NBO, and QTAIM calculations and analysed the results, and wrote the manuscript with contributions from all authors.

Additional Information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available at www.nature.com/reprints. Correspondence and requests for materials should be addressed to S.T.L.

Competing Interests

The authors declare no competing interests.

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Figures and Schemes:

Figure 1 | The classical donor-acceptor bonding model for a transition metal (M) and a neutral diatomic $E\equiv E$ ($N\equiv N$ or $C\equiv O$) π -acceptor ligand. This model describes the requirement for a metal in a mid, low, or even negative oxidation state, to possess one or more metal valence electrons, to have a spatial reach of d-orbitals to overlap with ligand orbitals, and a ligand with a lone pair to donate to the metal and one or more accessible π^* orbitals to receive electron density from back-bonding. This work reports an example where the metal is high oxidation state and electron poor back-bonding with a spatially-limited f-electron to the poor π -acceptor ligand N_2 .

Figure 2 | Synthesis of compound 2 from precursor 1. The uranium(IV)-bis(carbene) compound **1** reacts with 1-adamantyl-azide in a 1:1 ratio to give the uranium(V)-carbene-bis(imido)-dinitrogen-lithium-cryptand complex **2**. This reaction is accompanied by the elimination of N_2 and formation of at least one other uranium by-product. Analysis of the hydrolysed mother liquor containing the uranium by-product reveals the presence of $\text{BIPM}^{\text{TMS}}\text{H}_2$, $\text{Me}_3\text{SiCH}_2\text{PPh}_2$, and LiCl -2,2,2-cryptand in an approximate 1:2:1 ratio.

Figure 3. Molecular structure of 2 at 150 K with 40% probability ellipsoids. Selected distances (Å) and angles (°) are U1-N1, 2.605(8); U1-C1, 2.461(7); U1-N3, 2.452(6); U1-N4, 2.451(6); U1-N5, 1.906(6); U1-N6, 1.897(6); N1-N2, 1.139(9); N2-Li1, 2.008(15); C1-U1-N1, 175.9(2); U1-N1-N2, 175.1(7); N1-N2-Li1, 175.4(8); P1-C1-P2, 169.9(5); N5-U1-N6, 159.1(2); N3-U1-N4, 127.26(19); C1-U1-N5 99.9(3); C1-U1-N6, 101.0(2); N1-U1-N5 78.2(2); N1-U1-N6 81.0(2).

Figure 4 | Variable-temperature effective magnetic moment data for 2. Data are plotted as μ_{eff} (μ_B) as a function of temperature (K) for powdered **2**, measured on a superconducting quantum interference device (SQUID) magnetometer in an applied magnetic field of 0.1 T. The line connecting the data points is a guide to the eye only.

Figure 5 | Computed potential energy surface scans of the relative energy (kJ mol^{-1}) vs the U1-N1 distance ($\text{\AA}$) of **2. ‘XRD’ and ‘Relaxed’ calculations are on the full molecule **2**. ‘Core’ is the model shown in Fig. 12 of the Supporting Information (**2 core**). All scans are rigid, *i.e.* in which all the geometric parameters of the non-hydrogen atoms are frozen, other than the U1-N1 distance, except the Relaxed / UPBE scan, in which all other geometric parameters are optimised at each point. For the rigid scans on **2 core**, the hydrogen atom positions are optimised at each point of the scan.**

Figure 6 | The singularly-occupied, α -spin highest occupied Kohn-Sham molecular orbital (338a, -1.715 eV) of **2. This molecular orbital represents the U-N₂ back-bonding interaction. Hydrogen atoms are omitted for clarity.**