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Terminal Uranium(V/VI) Nitride Activation of Carbon Dioxide and Carbon Disulfide: Factors Governing Diverse and Well-Defined Cleavage and Redox Reactions

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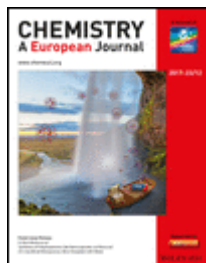
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Terminal Uranium(V/VI) Nitride Activation of Carbon Dioxide and Carbon Disulfide: Factors Governing Diverse and Well-Defined Cleavage and Redox Reactions

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Abstract

The reactivity of terminal uranium(V/VI) nitrides with CE_2 ($E=O, S$) is presented. Well-defined $C=E$ cleavage followed by zero-, one-, and two-electron redox events is observed. The uranium(V) nitride $[U(\text{Tren}^{\text{TIPS}})(\text{N})][\text{K}(\text{B15C5})_2]$ (**1**, $\text{Tren}^{\text{TIPS}}=\text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}_3)_3$; B15C5=benzo-15-crown-5) reacts with CO_2 to give $[U(\text{Tren}^{\text{TIPS}})(\text{O})(\text{NCO})][\text{K}(\text{B15C5})_2]$ (**3**), whereas the uranium(VI) nitride $[U(\text{Tren}^{\text{TIPS}})(\text{N})]$ (**2**) reacts with CO_2 to give isolable $[U(\text{Tren}^{\text{TIPS}})(\text{O})(\text{NCO})]$ (**4**); complex **4** rapidly decomposes to known $[U(\text{Tren}^{\text{TIPS}})(\text{O})]$ (**5**) with concomitant formation of N_2 and CO proposed, with the latter trapped as a vanadocene adduct. In contrast, **1** reacts with CS_2 to give $[U(\text{Tren}^{\text{TIPS}})(\kappa^2\text{-CS}_3)][\text{K}(\text{B15C5})_2]$ (**6**), **2**, and $[\text{K}(\text{B15C5})_2][\text{NCS}]$ (**7**), whereas **2** reacts with CS_2 to give $[U(\text{Tren}^{\text{TIPS}})(\text{NCS})]$ (**8**) and “S”, with the latter trapped as Ph_3PS . Calculated reaction profiles reveal outer-sphere reactivity for uranium(V) but inner-sphere mechanisms for uranium(VI); despite the wide divergence of products the initial activation of CE_2 follows mechanistically related pathways, providing insight into the factors of uranium oxidation state, chalcogen, and NCE groups that govern the subsequent divergent redox reactions that include common one-electron reactions and a less-common two-electron redox event. Caution, we suggest, is warranted when utilising CS_2 as a reactivity surrogate for CO_2 .

Introduction

The activation and cleavage of carbon dioxide and carbon disulfide, CE_2 ($E=O, S$), are burgeoning areas given current environmental and sustainability agendas.^[1] The former is an abundant, low-cost, and renewable C_1 source for fine chemicals and fuels production,^[2] and the latter is a versatile building block in organic synthesis that is often used to model CO_2 reactivity.^[3] In recent years f-elements,^[4] and especially uranium,^[5, 6] have emerged as effective, appealing candidates for the reductive activation of CE_2 ,^[7] but studies of such activations remain in the shadow of those involving transition metals.^[1-3, 8] Metal nitride chemistry is now well-developed for transition metals with a wide range of reactivity types.^[9] However, although electron-rich terminal $M\equiv N$ triple

bonds are primed for bond metathesis chemistry, and are therefore excellent candidates for nitrogen-atom transfer reactions with heteroallenes,[\[10\]](#) there are few examples of transition-metal nitride reactivity with CE_2 molecules.[\[8, 9\]](#) Germane to this work, $[V\{N(R)(Ar)\}_3(N)Na]_2$ ($R=tBu$ or Ad ; $Ar=3,5-Me_2C_6H_3$) reacts with CE_2 to give $[V\{N(R)(Ar)\}_3(NCE_2)][Na(THF)_2]$, which for $E=O$ reacts no further but for $E=S$ and $R=tBu$ extrudes $NaNCS$ following bond metathesis to give $[V\{N(tBu)(Ar)\}_3(S)]$.[\[10d\]](#) In contrast, $[Nb\{N(R)(Ar)\}_3(N)Na]_2$ reacts with CO_2 to give $[Nb\{N(R)(Ar)\}_3(NCO_2)][Na(THF)_n]$, but C–O splitting only occurs with addition of external electrophiles (such as Ac_2O , $O\{C(O)CF_3\}_2$, or $tBuCOCl$); this opens the door to elimination of the CO_2 -derived oxide as RCO_2^- and decarbonylation of the resulting niobium cyanate to niobium nitride to close a synthetic cycle.[\[10b\]](#) Regarding uranium, a promising candidate in this arena given its redox chemistry,[\[5, 6\]](#) it was not until recently that terminal uranium nitride complexes became available under ambient conditions,[\[11\]](#) and so their inherent reactivity patterns are yet to be established. Indeed, there are no other classes of terminal f-block nitrides available for reactivity studies,[\[12\]](#) and although a number of bridged diuranium nitrides are emerging,[\[6a\]](#),[\[6b, 13\]](#) their reactivity is also almost unknown so determining and comparing the reactivity of terminal to bridging uranium nitrides would present opportunities to better understand their intrinsic reactivities. Furthermore, uranium sometimes exhibits reactivity that parallels transition-metal chemistry, but also often exhibits divergent reactivity, and

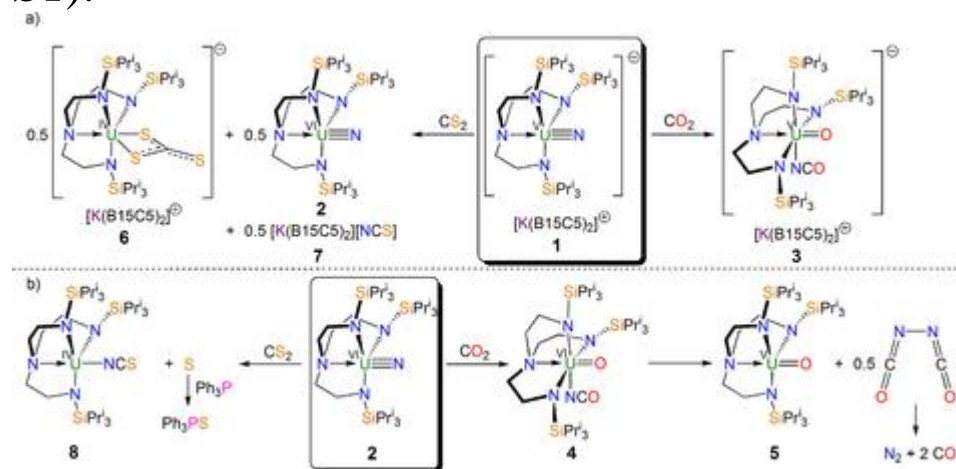
so it is of interest to compare terminal uranium and transition-metal nitride reactivity. Recently, we showed that the terminal uranium nitrides $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{N})][\text{K}(\text{B15C5})_2]$ [1, $\text{Tren}^{\text{TIPS}}=\text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}_3)_3$; B15C5=benzo-15-crown-5][14] and $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{N})]$ (2)[11a] react with CO by reductive carbonylation,[14, 15] to give cyanate derivatives followed by complete denitrification and N-atom transfer.[16] Whilst terminal $\text{M}\equiv\text{N}$ triple bond reactivity with CE_2 has potential for C–N bond formation chemistry, since so little reactivity has been reported the factors that govern their reactivity are yet to be elucidated. With the reactivity of 1 and 2 towards CO suggesting a rich seam of N-atom transfer reactivity we turned our attention to the reactivity of 1 and 2 towards CO_2 and CS_2 . Herein, we report the first benchmarking study of the reactivity of terminal f-block nitrides towards CO_2 and CS_2 with uranium(V) and (VI). In all cases we find facile CE_2 cleavage chemistry and that the split E and NCE products react further in zero-, one-, and two-electron redox processes. In contrast to the d-block, one-electron redox chemistry generally dominates in the f-block, and although becoming more common two-electron redox process are unusual so understanding the factors that promote such reactivity is important given the fundamental role electron transfer plays in chemical reactivity.[11, 13a]–[13c],[13e],[13g, 17] Calculated reaction profiles reveal outer-sphere reactivity for uranium(V) but inner-sphere mechanisms for uranium(VI) and provide insight into the factors that govern the observed reactivity. Thus this work furthers our understanding of the nature and

reactivity of terminal metal nitride reactivity, permitting mechanistic similarities and differences between terminal d- and f-block and bridging and terminal f-block metal nitride reactivity to be determined. Lastly, the divergent reactivities observed show that care should be taken extrapolating surrogate reactivity between CO₂ and CS₂.

Results and Discussion

Experimental terminal uranium(V) nitride reactivity with CO₂

Exposure of a degassed toluene solution of **1** to an atmosphere of CO₂ at -78 °C resulted in a colour change from yellow–brown to red–brown. After work-up and recrystallisation from benzene the orange complex formulated as the oxo–cyanate derivative [U(Tren^{TIPS})(O)(NCO)][K(B15C5)₂] (**3**) was isolated in 36 % crystalline yield (Scheme [1](#) a), which reflects the high solubility of this complex; analysis of the mother liquor by NMR spectroscopy suggests the formation of **3** is essentially quantitative (Supporting Information, Figure S1).



Scheme 1.

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a) Reactions of the terminal uranium(V) nitride complex **1** with CO₂ and CS₂ to give the uranium(V) oxo–cyanate **3** and the uranium(IV) trithiocarbonate **6**, uranium(VI) nitride **2**, and potassium bis(crown) thiocyanate **7**. b) Reactions of the terminal uranium(VI) nitride complex **2** with CO₂ and CS₂ to give the uranium(VI) oxo–cyanate **4**, which decomposes to the uranium(V) oxo **5**, N₂, and CO₂, and the uranium(IV) thiocyanate **8** with expulsion of elemental “S” that can be trapped by Ph₃P as Ph₃PS. A control reaction between **8** and Ph₃P confirms that the S does not originate from the NCS group of **8**.

The ¹H NMR spectrum of **3** spans 16 to –3 ppm, which suggests the presence of uranium(V) and the resonances are broad so inferences about the symmetry of the Tren^{TIPS} ligand (C_s or C₃ coordination) could not be discerned; however, the ²⁹Si NMR spectrum exhibits two resonances (–27.1 and –27.8 ppm), suggesting that the anion component of **3** possesses approximate C_s rather than C_{3v} symmetry.

The formation of cyanate and oxo functional groups is supported by inspection of the FTIR spectrum of **3**, which exhibits absorptions at 2194, 800, and 742 cm^{–1}, with the first attributed to cyanate and the latter two to oxo stretches, and these compare very well to calculated frequencies of 2195 and 799 and 747 cm^{–1}, respectively. The two stretches for the oxo result from coupling to the uranium–amine stretch to give asymmetric and symmetric combinations. The cyanate stretch compares well to a value of 2187 cm^{–1} for [U(Tren^{TIPS})(NCO)] (**d**),[\[14\]](#) prepared by reductive carbonylation of **2**, and those found in related examples of uranium cyanate complexes (ca. 2122–2201 cm^{–1}).[\[5a, 17i\]](#)

The UV/Vis/NIR spectrum of **3** (Supporting Information, Figure S8) exhibits a characteristic absorption at 6693 cm^{-1} ($\epsilon=43\text{ L mol}^{-1}\text{ cm}^{-1}$), consistent with uranium(V), as well as three other absorptions in that region resulting from splitting of the $7/2$ excited state of ${}^2\text{F}$ by the o_h crystal field into four levels (Γ_7' , two Γ_8' , and Γ_6 in double-group notation).[18] The uranium(V) assignment is confirmed by variable temperature SQUID magnetometry of **3** (Figure 1), which reveals a magnetic moment of $1.86\ \mu_B$ at 298 K, that compares well to a solution magnetic moment of $1.69\ \mu_B$ at 298 K; this changes little until 50 K where it falls more rapidly to $1.20\ \mu_B$ at 2 K consistent with the presence of uranium(V) that is a magnetic doublet.[19] Final confirmation of the presence of uranium(V) in **3** is provided by EPR spectroscopy (Supporting Information; Figure S15) which reveals a strong absorption at $g=2.85$ at 5 K, which is consistent with a Kramers uranium(V) ion; uranium(IV) would be expected to be EPR-silent under these measurement conditions.[20]

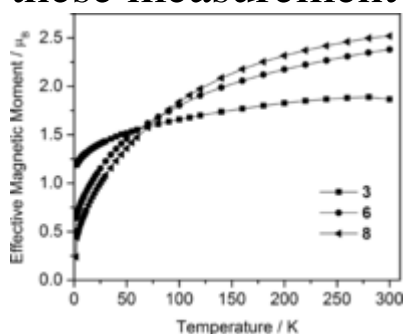


Figure 1.

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Variable temperature SQUID magnetometry of the effective magnetic moment (μ_B) of **3**, **6**, and **8** in the temperature range 2–298 K. Lines are to guide the eye only and have no further significance.

To confirm the structure of **3** we determined the molecular structure by single-crystal X-ray diffraction (Figure [2](#)). Complex **3** retains the separated ion-pair motif from **1**, and the structure reveals a pseudo octahedral uranium centre where the oxo is *trans* to the Tren-amine and the cyanate group is *trans* to a Tren-amide and mutually *cis* to the oxo. Competitive refinement of the diffraction data suggest that the cyanate is N- not O-bound, and this is supported by DFT calculations that show the former isomer to be more stable than the latter by 9 kcal mol⁻¹. The U–O, U–N_{cyanate}, and U–N_{amine} bond lengths of 1.848(7), 2.404(8), and 2.517(7) Å, respectively, are typical of such linkages, [[14](#), [17d](#), [21](#)] though the latter is towards the lower end of the range of Tren–N_{amine}–U distances, which suggests there might be a weak inverse *trans*-influence in the N→U=O unit. [[22](#)] The U–N_{amide} bond lengths span the range 2.302(7)–2.342(7) Å and can be considered long for uranium(V) when compared to Tren uranium complexes, which most likely reflects the electron-rich nature of this anionic fragment of the compound. The O–U–N_{amine} and N_{amide}–U–N_{cyanate} angles deviate from the octahedral ideal at 168.0(3) and 168.3(3)°, respectively, reflecting the steric demands of the Tren^{TIPS} ligand.

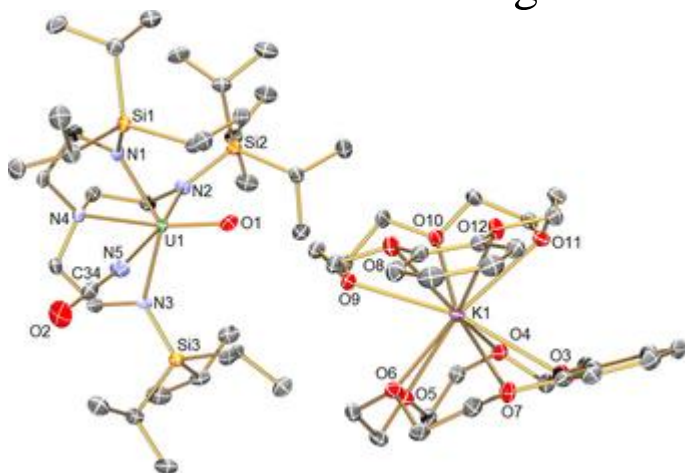


Figure 2.

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Molecular structure of **3** at 120 K with ellipsoids set at 50 % probability and hydrogen atoms omitted for clarity.[[36](#)] Only one of the two independent ate pairs in the crystallographic asymmetric unit is shown; the other pair is essentially identical with statistically indistinguishable bond lengths and angles. Selected bond lengths [Å] for the ate pair shown: U1–N1 2.316(7), U1–N2 2.302(7), U1–N3 2.342(7), U1–N4 2.517(7), U1–N5 2.404(8), U1–O1 1.848(7), N5–C34 1.199(13), C34–O2 1.163(13).

Experimental terminal uranium(VI) nitride reactivity with CO₂

When a degassed toluene solution of [U(Tren^{TIPS})(N)] (**2**) is exposed to an atmosphere of CO₂ at –78 °C the brown solution turns wine-red (Scheme [1](#) b). After quick work-up a red solid is obtained, and on the basis of the data presented below we formulate this red solid as [U(Tren^{TIPS})(O)(NCO)] (**4**), obtained in essentially quantitative yield. The ¹H NMR spectrum of the red solid retains the appearance of a diamagnetic complex, spanning 0–10 ppm, suggesting the retention of uranium(VI), but it is not particularly informative. We were unable to obtain the potentially more informative ²⁹Si NMR spectrum due to rapid decomposition of **4** in solution.

The FTIR spectrum of **4** exhibits strong absorptions at 2176 and 827 cm⁻¹, which are assigned as cyanate and oxo stretches, respectively. The former absorption compares well to the cyanate stretch for **3** and is supported by a calculated stretching frequency of 2198 cm⁻¹. Interestingly, the oxo stretch for **4**, unlike **3**, is now decoupled from the U–N_{amine} vibration resulting in only one absorption being

observed; this is also reproduced by the frequency calculation, which yields a calculated oxo stretching frequency of 812 cm^{-1} . Although the formation of **4** seems certain on the basis of **3** and computationally supported spectroscopy, despite exhaustive attempts we have been unable to obtain a crystal structure of **4** due to decomposition during recrystallisation attempts; however, this is consistent with the computed reaction profile (see below). Attempts to recrystallise **4** resulted in isolation of the known mono-oxo uranium(V) complex $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{O})]$ (**5**),[\[17d\]](#) as evidenced by single crystal X-ray diffraction and FTIR data which are devoid of any absorptions in the cyanate region and that show the characteristic oxo stretch of **5** at 910 cm^{-1} . Monitoring the conversion of **4** to **5** by ^1H NMR spectroscopy (for a representative spectrum, see the Supporting Information, Figure S2) reveals clean, quantitative conversion over 24 hours, with **4**:**5** ratios of 1:0 (<30 minutes), 2:1 (2 hours), 1:9 (5 hours), 0:1 (20 hours). The isolation of **5** suggests that a cyanate radical has been ejected from the coordination sphere of uranium; this could react with solvent to abstract a proton to give HNCO, or dimerise to the putative molecule diisooxocyan followed by facile decomposition to N_2 and CO .[\[23\]](#) Although the bond dissociation enthalpy of HNCO is high (ca. 110 kcal mol^{-1}),[\[24\]](#) suggesting that it could be formed (with toluene implicated as the H-source) we have not observed at any stage of the reaction any IR absorbances consistent with its formation;[\[25\]](#) further, production of HNCO ($\text{p}K_{\text{a}}=3.7$)[\[26\]](#) would be anticipated to result in extensive decomposition of **5**, which is not the case experimentally. To probe the possibility that diisooxocyan

is formed, we reacted 50 % $^{15}\text{N}_{\text{nitride}}$ -labelled **2** with CO_2 , but could not detect a ^{15}N NMR resonance for dissolved N_2 . Due to diamond absorbance from the probe tip in the region 2000–2250 cm^{-1} , we could not observe CO formation in solution by ReactIR, and sampling of the gas headspace resulted in IR spectra dominated by solvent vapour. Unfortunately, sampling and MS analysis of the headspace from the decomposition of **4** was inconclusive, which is likely due to concentration effects and the presence of N_2 even in high purity Ar gas. However, vacuum transfer of the headspace atmosphere from reactions that generate **4** onto a thawing toluene solution of vanadocene gave a weak absorption at 1895 cm^{-1} in the resulting IR spectrum, which is consistent with the formation of a vanadocene carbonyl.[\[5k\]](#) Attempts to trap the putative cyanate radical were inconclusive (see the Supporting Information). Attempts to oxidise **3** to **4** with numerous oxidants gave intractable product mixtures, but oxidation of **D[14]** with trimethylamine-*N*-oxide or 4-methylmorpholine-*N*-oxide gave mixtures of **D:4:5** in 6:1:1 and 3:2:2 ratios, respectively, which is not inconsistent with oxidation of **D** to **4** followed by decomposition to **5** (Supporting Information, Figures S6 and S7).

Experimental terminal uranium(V) nitride reactivity with CS_2

The reactions of CS_2 with **1** and **2** proceed very differently, in terms of the final products, to the CO_2 reactivity (Scheme [1](#) a). Addition of one equivalent of CS_2 to a solution of pentavalent **1** in toluene at $-78\text{ }^\circ\text{C}$ results in a colour change from yellow–brown to brown. After removal of solvent, a brown oil is formed, which after washing with

hexanes is isolated as a brown solid. Work-up of the hexane washings results in isolation of hexavalent **2**, suggesting that overall disproportionation has occurred. Extraction of the brown solid with aromatic solvent and recrystallisation resulted in the isolation of an orange complex formulated as the uranium(IV) trithiocarbonate complex $[\text{U}(\text{Tren}^{\text{TIPS}})(\kappa^2\text{-CS}_3)][\text{K}(\text{B15C5})_2]$ (**6**) in crystalline yields of about 4 %; this yield reflects the oily nature of this complex, and although it is low it is reproducible. The formulation of **6** suggests the presence of a uranium(IV) ion, which would account for the remainder of the disproportionation balance together with **2**. Inspection of crude reaction mixtures by ^1H NMR spectroscopy (Supporting Information, Figure S4) suggests that **2** and **6** are formed in a 1:1 ratio, as would be expected, and together they constitute about 90 % of the reaction mixture (ignoring the thiocyanate component, see below) and thus **2** and **6** constitute the major reaction products.

The ^1H NMR spectrum of **6** (Supporting Information, Figure S3) spans the range 9 to -26 ppm, which is in line with the uranium(IV) assignment. Further confirmation that **6** is a uranium(IV) complex comes from solid-state SQUID magnetometry (Figure [1](#)), which reveals a magnetic moment of $2.4 \mu_{\text{B}}$ at 298 K, whose value decreases with decreasing the temperature to $0.6 \mu_{\text{B}}$ at 2 K and tending to zero.[\[19\]](#)

The solid that remains after the toluene or benzene extraction was examined by FTIR spectroscopy revealing strong absorbances at 2060 and 2052 cm^{-1} , which are assigned as thiocyanate stretches.[\[6c\]](#),[\[6e\]](#),[\[6h\]](#) For mass balance this is proposed to be $[\text{K}(\text{B15C5})_2][\text{NCS}]$ (**7**),

confirmed by comparison to an authentic sample prepared independently from KNCS and B15C5 that also exhibits two thiocyanate stretches in its FTIR spectrum.

The molecular structure of **6** was determined by single-crystal X-ray diffraction to confirm its identity (Figure 3). The U–N_{amine} (2.670(3) Å) and U–N_{amide} (range: 2.277(3)–2.296(3) Å) distances are typical of U–N distances in Tren–uranium(IV) complexes.[21] Complex **6** the first example where the (CS₃)²⁻ dianion is terminally bound to one f-element centre, and is only the third example of a f-block trithiocarbonate complex.[6c],[6e],[6h] Befitting the unique coordination mode of the (CS₃)²⁻ dianion in f-block chemistry, the U–S bond lengths of 2.8415(8) and 2.8520(10) Å are shorter than in complexes where the (CS₃)²⁻ dianion bridges (range: 2.9488(19)–3.130(2) Å). The κ²-coordination mode of the (CS₃)²⁻ dianion appears to localise negative charge on the two coordinated sulfur atoms, resulting in some localisation of a C=S double bond on the remaining uncoordinated sulfur–carbon linkage; this is evidenced by a terminal C=S bond distance of 1.665(4) Å compared to the other two C–S bond lengths of 1.731(4) and 1.729(4) Å.

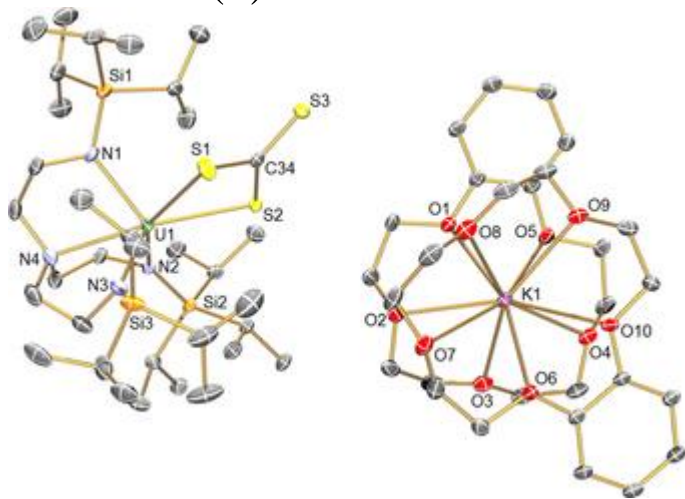


Figure 3.

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Molecular structure of **6** at 120 K with ellipsoids set at 50 % probability and hydrogen atoms omitted for clarity.[[36](#)] Selected bond lengths [Å]: U1–N1 2.277(3), U1–N2 2.290(3), U1–N3 2.296(3), U1–N4 2.670(3), U1–S1 2.8520(10), U1–S2 2.8415(8), S1–C34 1.729(4), S2–C34 1.731(4), S3–C34 1.665(4).

Experimental terminal uranium(VI) nitride reactivity with CS₂

Since the uranium(V) nitride **1** undergoes, overall, disproportion reactivity with CS₂ we were interested to determine how the analogous uranium(VI) nitride **2** would react since it lacks the requisite valence electron to engage in disproportionation chemistry. When a toluene solution of **2** is treated with CS₂ over six days, a new uranium-containing product is formed (Scheme [1](#) b). Work-up and recrystallisation from pentane affords the green uranium(IV)–thiocyanate complex [U(Tren^{TIPS})(NCS)] (**8**) in 51 % crystalline yield.

The ¹H NMR spectrum of **8** (Supporting Information, Figure S5) spans the range 9 to –37 ppm, consistent with the uranium(IV) formulation, and the ²⁹Si NMR spectrum exhibits only one resonance at 2.4 ppm that is consistent with a C_{3v} symmetric complex. The FTIR spectrum exhibits a strong absorbance at 2013 cm⁻¹ and this is typical of uranium(IV)–thiocyanate stretches.[[27](#)] In support of the uranium(IV) assignment, variable temperature SQUID magnetometry data of **8** reveal a magnetic moment of 2.52 μ_B at 298 K (2.91 μ_B by Evans method in solution) that decreases monotonously down to 0.24 μ_B at 2 K and tending to zero in-line with the magnetic singlet ground state of uranium(IV) at low temperature (Figure [1](#)).[[19](#)]

To confirm the identity of **8** we prepared it independently from [U(Tren^{TIPS})(Cl)] and KSCN (isolated in 53 % yield) and the characterisation data are in agreement. The formation of **8** suggests that elemental sulfur is the by-product of this reaction, presumably extruded from the putative complex [U(Tren^{TIPS})(S)(NCS)] analogously to **4**. Therefore, either post-reaction or all in one-pot, we treated the reactions with Ph₃P and observed the formation of Ph₃PS by ³¹P NMR spectroscopy (³¹P NMR: Ph₃P=−5.2; Ph₃PS=42.8 ppm). In a control experiment to rule out the abstraction of sulfur from **8** to give the plausible cyanide product [U(Tren^{TIPS})(CN)], we treated **8** with Ph₃P and found that no reaction occurs, even on extended reflux in toluene.

Final confirmation of the identity of **8** was obtained by examination of its single-crystal X-ray diffraction structure (Figure 4), which unambiguously reveals a complex of approximate *C*_{3v} symmetry with an *N*-bound thiocyanate ligand at uranium. The metrical data for **8** are unexceptional. [27]

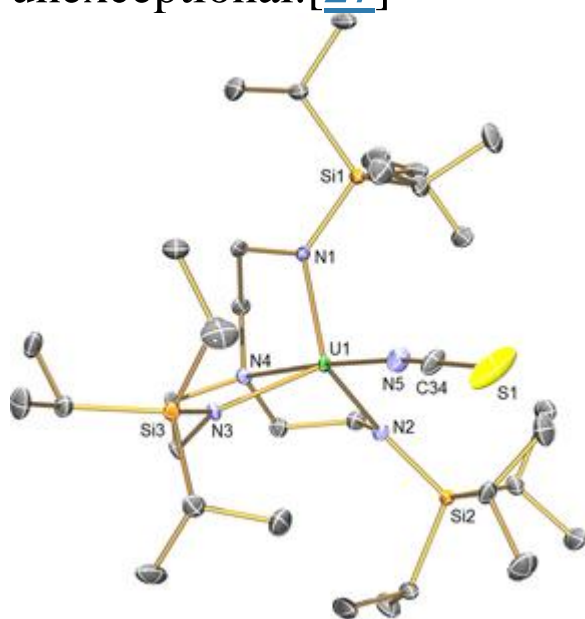


Figure 4.

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Molecular structure of **8** at 120 K with ellipsoids set at 50 % probability and hydrogen atoms omitted for clarity.[[36](#)] Only one of the two parts of the disordered NCS unit are shown. Selected bond lengths [Å]: U1–N1 2.238(3), U1–N2 2.240(3), U1–N3 2.237(3), U1–N4 2.626(4), U1–N5 2.377(4), N5–C34 1.181(11), C34–S1 1.589(9).

Given this diverse range of reaction outcomes, we modelled the reaction profiles by using DFT calculations (at B3PW91 level of theory) to provide useful insights for the mechanisms and in order to understand why such a diverse range of reactivity occurs and what the controlling factors are. In all cases the computed energy pathways were found to be kinetically accessible and thermodynamically favourable and completely consistent with experimental outcomes.

Computed reaction profiles of terminal uranium nitride reactivity with CO₂

The computed energy pathway for the reaction of complex **1** with CO₂ (Figure [5](#)) is reminiscent of the outer-sphere CO₂ addition reported by Cummins.[[10a](#)],[[10d](#)] In other words, the highly nucleophilic nitride attacks the incoming CO₂ molecule without any coordination to the poorly electrophilic U^vcentre. Indeed, a very low-lying outer-sphere addition transition state (TS), ts_{A-B} , was located (enthalpy barrier of 1.4 kcal mol⁻¹), where the CO₂ molecule bends to allow the π^* of CO₂, that is mainly located at the 2p orbital at the carbon atom, to overlap with the σ -lone pair of the nitride. This outer-sphere TS is lower in energy than the classical [2+2] cycloaddition route ($\Delta H^\ddagger=5.1$ kcal mol⁻¹; Figure S20). ts_{A-B} leads to the formation

of a η^1 -carbamate intermediate, that readily isomerises ($\Delta H^\ddagger=0.2$ kcal mol⁻¹) to a stable metal-based-four-membered ring (-23.1 kcal mol⁻¹). Finally, following a low-lying transition state, TS_{I-3'}, involving bond metathesis (-20.8 kcal mol⁻¹), the cleavage of the C–O bond occurs to give the oxo–cyanate that is 57.1 kcal mol⁻¹ more stable than the initial complex 1.

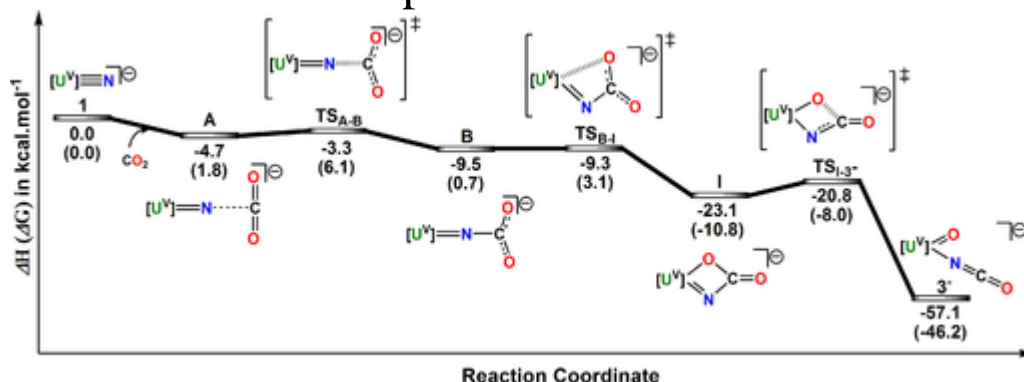


Figure 5.

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Energy profile (at 298 K) for the gas-phase reaction of CO₂ with the uranium(V) nitride 1 computed at the B3PW91 level of theory. [U]=[U(Tren^{TIPS})].

In the same way as for complex 1, the energy profile was computed for the reaction of complex 2 with CO₂ (Figure 6) at the same level of theory. Unlike 1, the outer-sphere mechanism is not found to be operative. Indeed, the U^{VI} centre is more electrophilic and at the same time the nitride is less nucleophilic compared to the U^V case, so that the CO₂ molecule needs to be activated through coordination to the Lewis acid centre to react. Hence, the reaction profile evolves firstly by a [2+2] cycloaddition step, surmounting an activation barrier of 12.1 kcal mol⁻¹ and leading to the formation of the intermediate II. The geometry of the latter is close to the intermediate I in uranium(V) nitride reactivity (Figure 5),

but energetically more unstable by almost 22 kcal mol⁻¹. The following step corresponds to the C–O bond-breaking, which proceeds via a bond metathesis transition state TS_{I-3} ($\Delta H^\ddagger=3.5$ kcal mol⁻¹) reminiscent of activated alkene metathesis[28] to give the oxo–cyanate (–38.1 kcal mol⁻¹). Although 4 is an enthalpic minimum with respect to the oxo 5 (–25.1 kcal mol⁻¹), when the Gibbs free energy term is considered the formation of 5 from 4 becomes more favourable by 5.7 kcal mol⁻¹ at –43.8 kcal mol⁻¹ owing to the entropic gain from N₂ and CO elimination. This is in-line with the strong electrophilic character of U^{VI} that prevents it from tightly binding to the cyanate radical (U–N distance of 2.36 Å in 4 vs. 2.27 Å for 3⁻) as it prefers a strongly anionic ligand. This finding is in-line with the initial experimental isolation of 4 but conversion into 5 on attempted recrystallisation of the former.

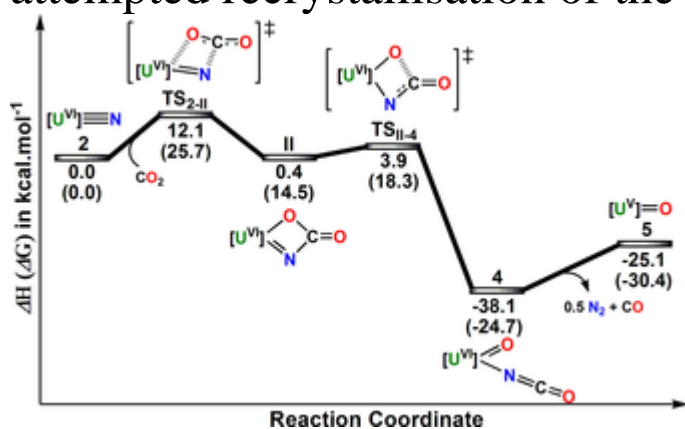


Figure 6.

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Energy profile (at 298 K) for the gas-phase reaction of CO₂ with the uranium(VI) nitride 2 computed at the B3PW91 level of theory. [U]=[U(Tren^{TIPS})].

The initial reactivity of 2 with CO₂ to give 4 clearly follows the same pattern as 1 reacting to give 3. However, although 3 is stable in the absence of O₂ or H₂O in solution

or the solid state, **4** is stable for only ca 30 minutes in solution and the cyanate group is rapidly lost. The formation of **5** suggests that the cyanate group is ejected as a radical in a homolytic U–N_{cyanate} bond cleavage step, which would provide the requisite electron for the one-electron reduction of the uranium(VI) centre. Comparing the computed barriers for the first step is informative regarding the nucleophilic nature of the nitride in **1** and **2**. The computed barrier for **2** (12.1 kcal mol⁻¹), although relatively low, is >30 kcal mol⁻¹ higher relative to the equivalent point computed for **1**. This indicates that the nitride is of lower nucleophilic character in **2** than in **1**,[\[29, 30\]](#) which can be attributed to the shorter U–N distance in the former than in the latter, inducing a stronger U–N interaction. On the other hand, the barrier for the C–O bond-breaking in the carbamate intermediates are similar for both complexes, indicating that the oxophilicity of uranium is affected very little by the oxidation state in these steps. However, the final oxo–cyanate **4** further evolves by ejecting the coordinated cyanate group yielding **5**.

The question then arises as to the fate of the cyanate radical; H-abstraction to give HNCO can seemingly be ruled out, but the coupling of cyanate radicals to give the putative molecule diisooxocyan followed by facile decomposition to N₂ and CO has been computationally described,[\[23\]](#) and seems a credible, if not conclusively proven, fate for the cyanate radical given the indirect supporting evidence by FTIR of the formation of vanadocene carbonyl as a CO trap. This step is computed to be endothermic in terms of enthalpy, but is favoured by

entropic effects (Figure 6) and indeed becomes exergonic overall when entropy is factored in (although it is known that the computation of entropy is not very accurate).[31] The difference between the reactivity of 3 and 4 is attributed to steric hindrance around the metal centre[32] as well as electronic effects in the latter. Indeed, the shorter distances in the U^{VI} complexes makes the geometry more compact around the metal centre and also induces stronger interactions with the oxo ligand with respect to the Tren^{TIPS} ligand. Therefore, in 4 the uranium centre is less available for interacting with the radical cyanate that undergoes the entropically driven radical coupling reaction to yield N₂+2CO.[4h, 33] This is reflected in the calculations where 4 is more stable from its start point by 38.1 kcal mol⁻¹, the corresponding uranium(V) component of 3 is more stable than its start point by a much larger 57.1 kcal mol⁻¹, which must to a significant extent reflect the size differences between uranium(V) and uranium(VI), where the former is larger so an additional ligand in the coordination sphere of uranium brings greater stability through the formation of another U–N bond with only a minimal thermodynamic penalty to pay from steric aspects. We further suggest that this reactivity can be rationalised on the basis that uranium(VI) is more oxidising than uranium(V) and so although the uranium(V) component in 3 is stable to such homolytic extrusion of cyanate this is not the case for uranium(VI) in 4. A parallel can be drawn here to the chemistry of terminal uranium nitrides under photolytic conditions,[11a, 13c] where the uranium(VI) nitride activates ancillary ligand C–H bonds but uranium(V) analogues do not; this can be rationalised

on the basis of the oxidising power of uranium(VI) compared to uranium(V). The fact that the cyanate linkage is lost in preference to the oxo group is testament to the highly favourable nature of the U=O bond, but also that one-electron redox events are far more common in f-element chemistry than two-electron redox events; if the uranium were to be reduced by two units to generate [U(Tren^{TIPS})(NCO)] instead this would require the elimination of oxidised O, which would be expected to be thermodynamically far uphill given the hard nature of electronegative oxide and its ability to stabilise high oxidation states at metals, that is, resist oxidation. We note there is precedent for elimination of the cyanate radical from uranium,[\[34\]](#) where in that report the reaction takes a different course because the cyanate radical can be intercepted by low valent and electron rich uranium(III), which is not an available pathway in the reaction with hexavalent 2.

Computed reaction profiles of terminal uranium nitride reactivity with CS₂

As for the reaction of 1 with CO₂, the reaction of 1 with CS₂ (Figure [7](#)) begins by a low-energy outer-sphere addition of CS₂ that after isomerisation yields the η²-N,S carbamate intermediate (−33.8 kcal mol^{−1}). From this intermediate, rather than the C–S bond breaking, which was found to be higher in energy (Supporting Information, Figure S21), a kinetically facile outer-sphere electrophilic attack of a CS₂ molecule to the pendant sulfur atom of the carbamate intermediates occurs (enthalpy barrier of only 2.0 kcal mol^{−1}). Such process does not work for the reaction with CO₂ as every attempt to locate this kind of

TS leads to the departure of the incoming CO₂ molecule. This yields, after an isomerisation process ($\Delta H^\ddagger=11.6$ kcal mol⁻¹), to a metal-based-six-membered ring intermediate (-36.5 kcal mol⁻¹). In this intermediate, a C-S bond is strongly activated and thus easily broken ($\Delta H^\ddagger=1.4$ kcal mol⁻¹) to form an isothiocyanate adduct to the thiocarbonate complex. In the last step, the driving force for the extrusion of NCS· and the subsequent oxidation of 1 by NCS· to give 2 and 7 is mainly due to the resulted high exothermicity of such sequence of events (-97.6 kcal mol⁻¹) as would be expected for two open shell radicals comproportionating to two closed shell species.

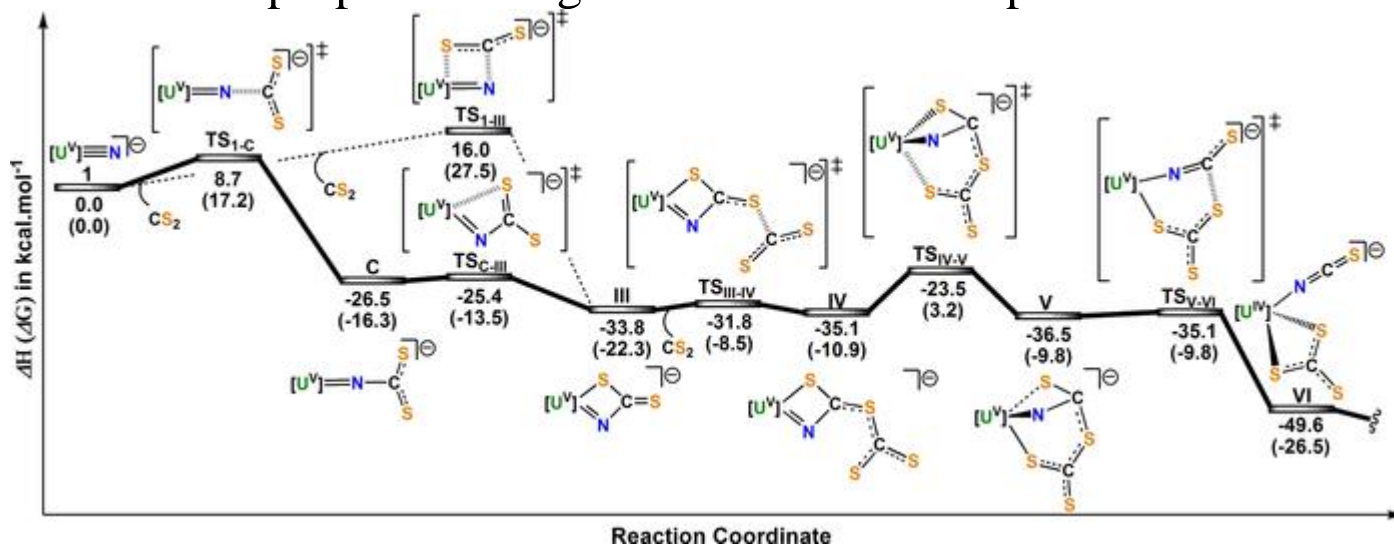


Figure 7.

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Energy profile (at 298 K) for the gas-phase reaction of CS₂ with the uranium(V) nitride 1 computed at the B3PW91 level of theory. [U]=[U(Tren^{TIPS})]. Extrusion of NCS· from VI and subsequently the oxidation of 1 by NCS· to give 2 and 7 is highly favoured (-97.6 kcal mol⁻¹; see the Supporting Information, Figures S17 and S19). Finally, the reactivity of complex 2 with CS₂ was investigated (Figure 8). Once again, like the analogous CO₂ reaction the outer-sphere mechanism does not operate

since the formed product of this step is endothermic (Supporting Information, Figure S22). Therefore, the two first steps of the reaction are similar to that found for the CO₂ reactivity previously described, that is a [2+2]-cycloaddition via TS_{2-VI} ($\Delta H^\ddagger=23.4$ kcal mol⁻¹) yielding a thiocarbamate complex (-3.7 kcal mol⁻¹) followed by a low-lying bond metathesis transition state TS_{VI-VII} ($\Delta H^\ddagger=5.1$ kcal mol⁻¹) with C-S bond disruption to form a terminal sulfidothiocyanate complex VII (-19.6 kcal mol⁻¹). Extrusion of sulfur by the PPh₃, computed as Ph₃P=S, as indeed can be done experimentally, is enthalpically highly favoured (-38.3 kcal mol⁻¹) yielding eventually complex 8 (overall exothermicity of reaction -57.9 kcal mol⁻¹).

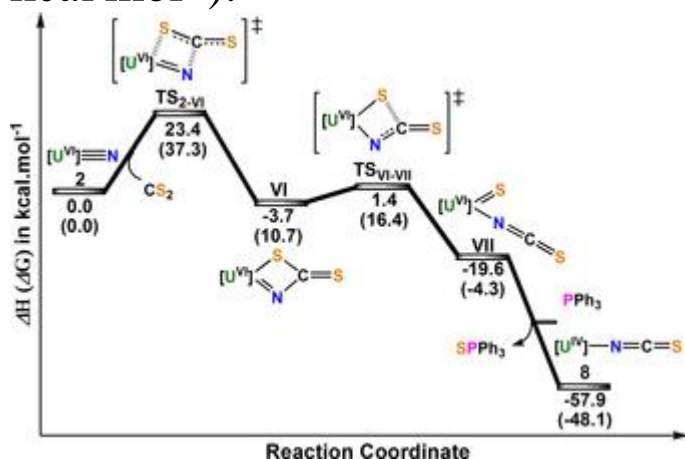


Figure 8.

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Energy profile (at 298 K) for the gas-phase reaction of CS₂ with the uranium(VI) nitride 2 computed at the B3PW91 level of theory. [U]=[U(Tren^{TIPS})].

Interestingly, for the reaction of 1 with CS₂, the thiocarbamate intermediate can easily be electrophilically attacked by another CS₂ molecule, accounting for the formation of the isothiocyanate adduct of terminal uranium(IV) trithiocarbonate. However, the NCS ligand

cannot react as the cyanate ligand in a radical way. Indeed, a radical coupling of two $\text{NCS}\cdot$ would ultimately lead to the formation of two CS molecules that are kinetically highly unstable.^[35] Instead, the $\text{NCS}\cdot$ extrusion occurs in a different way, by employing a redox process. The $\text{NCS}\cdot$ radical can react with complex 1, which acts as a single electron donor, yielding complex 2 by an esoteric but new way to prepare a uranium(VI) nitride, to give NCS^- that coordinates the countercation of 1 to form 7. This reaction is thermodynamically highly favourable (by $97.6 \text{ kcal mol}^{-1}$) and represents an alternative to the unfavourable radical coupling reaction for $\text{NCS}\cdot$. Including a solvation model, this reaction is of the same order of magnitude, being $-87.2 \text{ kcal mol}^{-1}$ (Supporting Information, Figure S18).

The uranium(VI) nitride 2 reacts with CS_2 to ultimately give the uranium(IV) thiocyanate 8 and elemental sulfur. However, the calculated reaction profile supports the idea that the nitride undergoes a nucleophilic attack of the CS_2 and by a subsequent bond metathesis generates a $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{S})(\text{NCS})]$ analogue of the CO_2 reaction with 2 to give 4. However, whereas for the analogous CO_2 reaction 4 extrudes cyanate, for the sulfur analogue the uranium(VI) sulfide–thiocyanate intermediate instead extrudes sulfur. Here, the former reaction is a more common one-electron redox event, whereas the latter is a less frequently observed example of a two-electron reduction. We suggest that the different reaction outcomes can be attributed directly to the hard nature of oxide compared to softer sulfide; even highly oxidising uranium(VI) cannot oxidise oxide, so the cyanate is

sacrificed and ejected for **4** but the softer sulfide can be oxidised to elemental sulfur by uranium(VI) and thus **8** is formed. The barrier for the [2+2] cycloaddition is the highest found (23.4 kcal mol⁻¹); that is, 14.7 kcal mol⁻¹ higher than for the outer-sphere reaction of CS₂ with **1**, which is possibly due to three effects: 1) the smaller size of uranium(VI) compared to uranium(V); 2) the difference of nucleophilicity of the nitride; and 3) the bond polarisation in CS₂. Also, this relatively high computed energy barrier nicely explains the fact that the corresponding reaction takes considerable time to occur experimentally with respect to the others. The barrier for the C–S bond disruption from the thiocarbamate complex is again low (5.1 kcal mol⁻¹) and similar to that found for **1**. In the terminal sulfide–thiocyanate complex, the thiocyanate ligand is strongly bonded (calculated BDE=25.6 kcal mol⁻¹). This is due to the relatively long U–S bond, which renders the uranium centre more available for coordination with an extra ligand. Indeed, we note that the uranium(VI) sulfide–thiocyanate is the least stable (–19.6 kcal mol⁻¹); this compares to –57.1 kcal mol⁻¹ for the uranium(V) oxo–cyanate, which is more stable than the uranium(VI) oxo–cyanate (–38.1 kcal mol⁻¹).

Finally, the most striking feature of the CS₂ reactivity is the completely different final outcomes of the reactions compared to the CO₂ reactions, but as suggested by the calculated reaction profiles, the reactions actually proceed initially through structurally related intermediates. The barriers for either the outer-sphere addition (16 kcal mol⁻¹) or the [2+2]-cycloaddition (23.4 kcal mol⁻¹) are

systematically higher than for the analogous reactions with CO₂ (11–13 kcal mol⁻¹). Therefore, this cannot be attributed to a difference in nucleophilicity of the nitride, but to the difference of bond polarisation in CS₂ versus CO₂. Indeed, in the latter, the carbon atom carries a formal δ^+ charge whereas it is δ^- in the former, making the formation of an empty 2p orbital at the carbon atom more complicated and thus increasing the barrier.

Conclusions

In summary, we report the first terminal f-block nitride reactivity study with CE₂ (E=O, S), where we observe cleavage at terminal uranium nitrides followed by zero-, one-, and two-electron redox events to give four different, yet related reactions that are well-defined; this highlights that care should be taken when using either as a reactivity surrogate of the other. For CO₂ the uranium(V) nitride reacts to give a uranium(V) oxo–cyanate by bond metathesis and cleavage of a C=O bond and the uranium(VI) nitride reacts to give an analogous uranium(VI) oxo–cyanate complex that subsequently decomposes to a uranium(V) oxo with elimination of a cyanate radical; the latter is proposed to dimerise to diisooxocyan that is unstable with respect to decomposition to N₂ and CO formation. In contrast, for CS₂ the uranium(V) nitride reacts to give a uranium(IV) trithiocarbonate along with uranium(VI) nitride and potassium thiocyanate, with formal overall disproportionation, but the uranium(VI) nitride reacts to give a uranium(IV) thiocyanate complex and extrusion of elemental sulfur that can be trapped as Ph₃PS by a Ph₃P scavenger.

Calculated reaction profiles consistently reproduce the experimental outcomes, and together the experimental and theoretical data suggest that the initial activation of CE_2 follows outer sphere attack of CE_2 by the nitrides for uranium(V) or direct [2+2] cycloaddition for uranium(VI). Irrespective of this, carbamate-type species are ultimately formed which then engage in multiple bond-metathesis steps, which may or may not involve redox chemistry. By dissecting each individual calculated step with reference to the experimental reaction outcome it has proven possible to delineate the effects that uranium oxidation state and nature of the coordinated E and NCE groups have on the resulting divergent reaction pathways. In one instance there is no subsequent redox chemistry, but the more common outcome is a subsequent one-electron redox step, which is a common feature of f-block chemistry. However, in one instance an unusual two-electron reduction event is found.

In a wider context, the outer-sphere reactivity of **1** parallels that of related transition metal(V) complexes, but the inner-sphere reactivity of **2** stands in contrast, and can be related to the stronger, less reactive $\text{U}\equiv\text{N}$ triple bond in **2** compared to **1**. Cleavage of CE_2 by **1** and **2** here is similar to that reported for diuranium nitride complexes, [\[6a\]](#), [\[6b\]](#) but **1** and **2** react further than the bimetallics, most likely because the bimetallics generally trap the products whereas monometallic **1** and **2** do not. A fuller comparison of terminal and bridging uranium nitrides will require mechanistic studies of the latter to complement the former reported herein.

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Ancillary

Supporting Information

- 1
 - 1aW. B. Tolman, *Activation of Small Molecules*, Wiley-VCH, Weinheim, 2006;
 - [CrossRef](#) |
 - [Go here for SFX](#)
 - 1bH. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. King, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stultls, W. Tumas, *Chem. Rev.* 2001, **101**, 953.
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 785](#) |
 - [Go here for SFX](#)
- 2
 - 2aC. Costentin, M. Robert, J.-M. Savéant, *Chem. Soc. Rev.* 2013, **42**, 2423;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 299](#) |
 - [Go here for SFX](#)
 - 2bE. E. Benson, C. P. Kubiak, A. J. Sathrum, M. Smieja, *Chem. Soc. Rev.* 2009, **38**, 89;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 607](#) |
 - [Go here for SFX](#)
 - 2cD. J. Darensbourg, *Chem. Rev.* 2007, **107**, 2388;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 754](#) |
 - [Go here for SFX](#)

- 2dT. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* 2007, **107**, 2365.
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 1555](#) |
 - [Go here for SFX](#)
- 3
- 3aB. Ochiai, T. Endo, *Prog. Polym. Sci.* 2005, **30**, 183;
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 119](#) |
 - [Go here for SFX](#)
- 3bK. K. Pandey, *Coord. Chem. Rev.* 1995, **140**, 37.
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 152](#) |
 - [Go here for SFX](#)
- 4Representative examples:
- 4aG.-C. Wang, Y.-M. So, K.-L. Wong, K.-C. Au-Yeung, H. H.-Y. Sung, I. D. Williams, W.-H. Leung, *Chem. Eur. J.* 2015, **21**, 16126;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 5](#) |
 - [Go here for SFX](#)
- 4bJ. Andrez, J. Pécaut, P.-A. Bayle, M. Mazzanti, *Angew. Chem. Int. Ed.* 2014, **53**, 10448;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 12](#) |
 - [Go here for SFX](#)

Angew. Chem. 2014, **126**, 10616;

 - [Wiley Online Library](#) |
 - [Go here for SFX](#)
- 4cY.-M. So, G.-C. Wang, Y. Li, H. H.-Y. Sung, I. D. Williams, Z. Lin, W.-H. Leung, *Angew. Chem. Int. Ed.* 2014, **53**, 1626;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 14](#) |
 - [Go here for SFX](#)

Angew. Chem. 2014, **126**, 1652;

 - [Wiley Online Library](#) |
 - [Go here for SFX](#)
- 4dK. Wang, G. Luo, J. Hong, X. Zhou, L. Weng, Y. Luo, L. Zhang, *Angew. Chem. Int. Ed.* 2014, **53**, 1053;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 16](#) |
 - [Go here for SFX](#)

Angew. Chem. 2014, **126**, 1071;

 - [Wiley Online Library](#) |
 - [Go here for SFX](#)
- 4eW. S. Ren, H. B. Song, G. F. Zi, M. D. Walter, *Dalton Trans.* 2012, **41**, 5965;
 - [CrossRef](#) |

- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 30](#) |
- [Go here for SFX](#)
- 4fW. S. Ren, G. F. Zi, D. C. Fang, M. D. Walter, *J. Am. Chem. Soc.* 2011, **133**, 13183;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 63](#) |
- [Go here for SFX](#)
- 4gD. Heitmann, C. Jones, D. P. Mills, A. Stasch, *Dalton Trans.* 2010, **39**, 1877;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 37](#) |
- [Go here for SFX](#)
- 4hW. J. Evans, T. J. Mueller, J. W. Ziller, *J. Am. Chem. Soc.* 2009, **131**, 2678;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 29](#) |
- [Go here for SFX](#)
- 4iW. J. Evans, D. B. Rego, J. W. Ziller, A. G. DiPasquale, A. L. Rheingold, *Organometallics* 2007, **26**, 4737;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 24](#) |
- [Go here for SFX](#)
- 4jN. W. Davies, A. S. P. Frey, M. G. Gardiner, J. Wang, *Chem. Commun.* 2006, 4853;
- [CrossRef](#) |
- [PubMed](#) |
- [Web of Science® Times Cited: 50](#) |
- [Go here for SFX](#)
- 4kW. J. Evans, J. M. Perotti, J. W. Ziller, *J. Am. Chem. Soc.* 2005, **127**, 3894;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 79](#) |
- [Go here for SFX](#)
- 4lW. J. Evans, J. M. Perotti, J. C. Brady, J. W. Ziller, *J. Am. Chem. Soc.* 2003, **125**, 5204;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 50](#) |
- [Go here for SFX](#)
- 4mW. J. Evans, C. A. Seibel, J. W. Ziller, *Inorg. Chem.* 1998, **37**, 770.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 110](#) |
- [Go here for SFX](#)
- 5Uranium-mediated CO₂ reactivity:
- 5aC. Camp, L. Chatelain, C. E. Kefalidis, J. Pécault, L. Maron, M. Mazzanti, *Chem. Commun.* 2015, **51**, 15454;
- [CrossRef](#) |

- [CAS](#) |
- [Web of Science® Times Cited: 5](#) |
- [Go here for SFX](#)
- 5bJ. A. Higgins Frey, A. S. P. Frey, F. G. N. Cloke, S. M. Roe, *Organometallics* 2015, **34**, 2102;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 4](#) |
- [Go here for SFX](#)
- 5cO. Cooper, C. Camp, J. Pécault, C. E. Kefalidis, L. Maron, S. Gambarelli, M. Mazzanti, *J. Am. Chem. Soc.* 2014, **136**, 6716;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 26](#) |
- [Go here for SFX](#)
- 5dA.-C. Schmidt, F. W. Heinemann, L. Maron, K. Meyer, *Inorg. Chem.* 2014, **53**, 13142;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 9](#) |
- [Go here for SFX](#)
- 5eC. L. Webster, J. W. Ziller, W. J. Evans, *Organometallics* 2014, **33**, 433;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 9](#) |
- [Go here for SFX](#)
- 5fA.-C. Schmidt, F. W. Heinemann, C. E. Kefalidis, L. Maron, P. W. Roesky, K. Meyer, *Chem. Eur. J.* 2014, **20**, 13501;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 9](#) |
- [Go here for SFX](#)
- 5gP. L. Arnold, Z. R. Turner, A. I. Germeroth, I. J. Casely, G. N. Nichol, R. Bellabarba, R. P. Tooze, *Dalton Trans.* 2013, **42**, 1333;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 13](#) |
- [Go here for SFX](#)
- 5hC. L. Webster, J. W. Ziller, W. J. Evans, *Organometallics* 2013, **32**, 4820;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 3](#) |
- [Go here for SFX](#)
- 5iJ. A. Higgins, F. G. N. Cloke, S. M. Roe, *Organometallics* 2013, **32**, 5244;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 10](#) |
- [Go here for SFX](#)
- 5jO. P. Lam, S. M. Franke, F. W. Heinemann, K. Meyer, *J. Am. Chem. Soc.* 2012, **134**, 16877;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 25](#) |

- [Go here for SFX](#)
- 5kV. Mougel, C. Camp, J. Pécault, C. Copéret, L. Maron, C. E. Kefalidis, M. Mazzanti, *Angew. Chem. Int. Ed.* 2012, **51**, 12280;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 58](#) |
- [Go here for SFX](#)
- *Angew. Chem.* 2012, **124**, 12446;

- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 5lC. L. Webster, J. W. Ziller, W. J. Evans, *Organometallics* 2012, **31**, 7191;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 19](#) |
- [Go here for SFX](#)
- 5mA.-C. Schmidt, A. V. Nizovtsev, A. Scheuer, F. W. Heinemann, K. Meyer, *Chem. Commun.* 2012, **48**, 8634;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 39](#) |
- [Go here for SFX](#)
- 5nE. M. Matson, W. P. Forrest, P. E. Fanwick, S. C. Bart, *J. Am. Chem. Soc.* 2011, **133**, 4948;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 57](#) |
- [Go here for SFX](#)
- 5oS. M. Mansell, N. Kaltsoyannis, P. L. Arnold, *J. Am. Chem. Soc.* 2011, **133**, 9036;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 90](#) |
- [Go here for SFX](#)
- 5pE. M. Matson, P. E. Fenwick, S. C. Bart, *Organometallics* 2011, **30**, 5753;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 33](#) |
- [Go here for SFX](#)
- 5qO. Bénaud, J.-C. Berthet, P. Thuéry, M. Ephritikhine, *Inorg. Chem.* 2010, **49**, 8117;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 24](#) |
- [Go here for SFX](#)
- 5rW. J. Evans, J. R. Walensky, J. W. Ziller, *Organometallics* 2010, **29**, 945;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 29](#) |
- [Go here for SFX](#)
- 5sO. P. Lam, S. C. Bart, H. Kameo, F. W. Heinemann, K. Meyer, *Chem. Commun.* 2010, **46**, 3137;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 68](#) |

- [Go here for SFX](#)
- 5tO. T. Summerscales, A. S. P. Frey, F. G. N. Cloke, P. B. Hitchcock, *Chem. Commun.* 2009, 198;
- [PubMed](#) |
- [Web of Science® Times Cited: 47](#) |
- [Go here for SFX](#)
- 5uS. C. Bart, C. F. Anthon, W. Heinemann, E. Bill, N. M. Edelstein, K. Meyer, *J. Am. Chem. Soc.* 2008, **130**, 12536;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 129](#) |
- [Go here for SFX](#)
- 5vl. Castro-Rodriguez, K. Meyer, *J. Am. Chem. Soc.* 2005, **127**, 11242;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 129](#) |
- [Go here for SFX](#)
- 5wl. Castro-Rodriguez, H. Nakai, L. N. Zhakharov, A. L. Rheingold, K. Meyer, *Science* 2004, **305**, 1757;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 194](#) |
- [ADS](#) |
- [Go here for SFX](#)
- 5xK. G. Moley, T. J. Marks, *Inorg. Chim. Acta* 1985, **110**, 127;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 39](#) |
- [Go here for SFX](#)
- 5yA. L. Arduini, J. D. Jamerson, J. Takats, *Inorg. Chem.* 1981, **20**, 2474.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 37](#) |
- [Go here for SFX](#)
- 6Uranium-mediated CS₂ reactivity:
- 6aL. Chatelain, R. Scopelliti, M. Mazzanti, *J. Am. Chem. Soc.* 2016, **138**, 1784;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 5](#) |
- [Go here for SFX](#)
- 6bM. Falcone, L. Chatelain, M. Mazzanti, *Angew. Chem. Int. Ed.* 2016, **55**, 4074;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 4](#) |
- [Go here for SFX](#)
- *Angew. Chem.* 2016, **128**, 4142;
- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 6cC. Camp, O. Cooper, J. Andrez, J. Pécault, M. Mazzanti, *Dalton Trans.* 2015, **44**, 2650;
- [CrossRef](#) |

- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 6](#) |
- [Go here for SFX](#)
- 6dE. M. Matson, A. T. Breshears, J. J. Kiernicki, B. S. Newell, P. E. Fanwick, M. P. Shores, J. R. Walensky, S. C. Bart, *Inorg. Chem.* 2014, **53**, 12977;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 6](#) |
- [Go here for SFX](#)
- 6eO. P. Lam, L. Castro, B. Kosog, F. W. Heinemann, L. Maron, K. Meyer, *Inorg. Chem.* 2012, **51**, 781;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 28](#) |
- [Go here for SFX](#)
- 6fN. A. Siladke, J. LeDuc, J. W. Ziller, W. J. Evans, *Chem. Eur. J.* 2012, **18**, 14820;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 10](#) |
- [Go here for SFX](#)
- 6gO. P. Lam, F. W. Heinemann, K. Meyer, *Angew. Chem. Int. Ed.* 2011, **50**, 5965;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 25](#) |
- [Go here for SFX](#)
- Angew. Chem.* 2011, **123**, 6088;
- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 6hC. Lescop, T. Arliguie, M. Lance, M. Nierlich, M. Ephritikhine, *J. Organomet. Chem.* 1999, **580**, 137;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 49](#) |
- [Go here for SFX](#)
- 6iJ. G. Brennan, R. A. Andersen, A. Zalkin, *Inorg. Chem.* 1986, **25**, 1756.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 78](#) |
- [Go here for SFX](#)
- 7
- 7aS. T. Liddle, *Angew. Chem. Int. Ed.* 2015, **54**, 8604;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 43](#) |
- [Go here for SFX](#)
- Angew. Chem.* 2015, **127**, 8726;
- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 7bH. S. La Pierre, K. Meyer, *Prog. Inorg. Chem.* 2014, **58**, 303;
- [CrossRef](#) |

- [Web of Science® Times Cited: 40](#) |
- [Go here for SFX](#)
- 7cB. M. Gardner, S. T. Liddle, *Eur. J. Inorg. Chem.* 2013, 3753;
- [Wiley Online Library](#) |
- [Web of Science® Times Cited: 24](#) |
- [Go here for SFX](#)
- 7dA. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* 2008, **455**, 341.
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 170](#) |
- [ADS](#) |
- [Go here for SFX](#)
- 8
- 8aJ. P. Krogman, B. M. Foxman, C. M. Thomas, *J. Am. Chem. Soc.* 2011, **133**, 14582;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 71](#) |
- [Go here for SFX](#)
- 8bA. R. Sadique, W. W. Brennessel, P. L. Holland, *Inorg. Chem.* 2008, **47**, 784;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 58](#) |
- [Go here for SFX](#)
- 8cC. H. Lee, D. S. Laitar, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* 2007, **129**, 13802;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 68](#) |
- [Go here for SFX](#)
- 8dC. C. Lu, C. T. Saouma, M. W. Day, J. C. Peters, *J. Am. Chem. Soc.* 2007, **129**, 4;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 84](#) |
- [Go here for SFX](#)
- 8eD. S. Laitar, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* 2005, **127**, 17196;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 289](#) |
- [Go here for SFX](#)
- 8fG. Fachinetti, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Am. Chem. Soc.* 1979, **101**, 1767.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 233](#) |
- [Go here for SFX](#)
- 9
- 9aJ. M. Smith, *Prog. Inorg. Chem.* 2014, **58**, 417;
- [CrossRef](#) |
- [Web of Science® Times Cited: 19](#) |
- [Go here for SFX](#)

- 9bC. T. Saouma, J. C. Peters, *Coord. Chem. Rev.* 2011, **255**, 920;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 74](#) |
 - [Go here for SFX](#)
- 9cR. A. Eikey, M. M. Abu-Omar, *Coord. Chem. Rev.* 2003, **243**, 83;
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 195](#) |
 - [Go here for SFX](#)
- 9dK. Dehnicke, J. Strähle, *Angew. Chem. Int. Ed. Engl.* 1992, **31**, 955;
 - [Wiley Online Library](#) |
 - [Web of Science® Times Cited: 218](#) |
 - [Go here for SFX](#)

Angew. Chem. 1992, **104**, 978;

 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Go here for SFX](#)
- 9eK. Dehnicke, J. Strähle, *Angew. Chem. Int. Ed. Engl.* 1981, **20**, 413;
 - [Wiley Online Library](#) |
 - [Web of Science® Times Cited: 351](#) |
 - [Go here for SFX](#)

Angew. Chem. 1981, **93**, 451.

 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Go here for SFX](#)
- 10
- 10aS. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* 2013, **135**, 11373;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 27](#) |
 - [Go here for SFX](#)
- 10bJ. S. Silvia, C. C. Cummins, *J. Am. Chem. Soc.* 2010, **132**, 2169;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 49](#) |
 - [Go here for SFX](#)
- 10cU. J. Kilgore, F. Basuli, J. C. Huffman, D. J. Mindiola, *Inorg. Chem.* 2006, **45**, 487;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 33](#) |
 - [Go here for SFX](#)
- 10dJ. K. Brask, V. Durà-Vilà, P. L. Diaconescu, C. C. Cummins, *Chem. Commun.* 2002, 902.
 - [CrossRef](#) |
 - [PubMed](#) |
 - [Web of Science® Times Cited: 30](#) |
 - [Go here for SFX](#)
- 11

- 11aD. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* 2013, **5**, 482;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 82](#) |
 - [ADS](#) |
 - [Go here for SFX](#)
- 11bD. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* 2012, **337**, 717.
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 108](#) |
 - [ADS](#) |
 - [Go here for SFX](#)
- 12D. M. King, S. T. Liddle, *Coord. Chem. Rev.* 2014, **266–267**, 2.
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 24](#) |
 - [Go here for SFX](#)
- 13
- 13aN. Tsoureas, A. F. R. Kilpatrick, C. J. Inman, F. G. N. Cloke, *Chem. Sci.* 2016, **7**, 4624;
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 2](#) |
 - [Go here for SFX](#)
- 13bC. Camp, J. Pécaut, M. Mazzanti, *J. Am. Chem. Soc.* 2013, **135**, 12101;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 52](#) |
 - [Go here for SFX](#)
- 13cR. K. Thomson, T. Cantat, B. L. Scott, D. E. Morris, E. R. Batista, J. L. Kiplinger, *Nat. Chem.* 2010, **2**, 723;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 94](#) |
 - [ADS](#) |
 - [Go here for SFX](#)
- 13dT. K. Todorova, L. Gagliardi, J. R. Walensky, K. A. Miller, W. J. Evans, *J. Am. Chem. Soc.* 2010, **132**, 12397;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 19](#) |
 - [Go here for SFX](#)
- 13eS. Fortier, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* 2010, **132**, 6888;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 66](#) |
 - [Go here for SFX](#)

- 13fA. R. Fox, P. L. Arnold, C. C. Cummins, *J. Am. Chem. Soc.* 2010, **132**, 3250;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 51](#) |
 - [Go here for SFX](#)
- 13gA. R. Fox, C. C. Cummins, *J. Am. Chem. Soc.* 2009, **131**, 5716;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 55](#) |
 - [Go here for SFX](#)
- 13hG. Nocton, J. Pécaut, M. Mazzanti, *Angew. Chem. Int. Ed.* 2008, **47**, 3040;
 - [Wiley Online Library](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 68](#) |
 - [Go here for SFX](#)

Angew. Chem. 2008, **120**, 3082;

 - [Wiley Online Library](#) |
 - [Go here for SFX](#)
- 13iW. J. Evans, K. A. Miller, J. W. Ziller, J. Greaves, *Inorg. Chem.* 2007, **46**, 8008;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 51](#) |
 - [Go here for SFX](#)
- 13jW. J. Evans, S. A. Kozimor, J. W. Ziller, *Science* 2005, **309**, 1835;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 138](#) |
 - [ADS](#) |
 - [Go here for SFX](#)
- 13kl. Korobkov, S. Gambarotta, G. P. A. Yap, *Angew. Chem. Int. Ed.* 2002, **41**, 3433;
 - [Wiley Online Library](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 99](#) |
 - [Go here for SFX](#)

Angew. Chem. 2002, **114**, 3583.

 - [Wiley Online Library](#) |
 - [Go here for SFX](#)
- 14P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* 2014, **53**, 10412;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 21](#) |
 - [Go here for SFX](#)

C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* 2014, **53**, 10412;

 - [Wiley Online Library](#) |

- [CAS](#) |
- [Web of Science® Times Cited: 21](#) |
- [Go here for SFX](#)
Angew. Chem. 2014, **126**, 10580.

- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 15
- 15aA. F. Cozzolino, J. S. Silvia, N. Lopez, C. C. Cummins, *Dalton Trans.* 2014, **43**, 4639;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 6](#) |
- [Go here for SFX](#)
- 15bB. L. Tran, M. Pink, X. Gao, H. Park, D. J. Mindiola, *J. Am. Chem. Soc.* 2010, **132**, 1458;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 53](#) |
- [Go here for SFX](#)
- 15cJ. S. Silvia, C. C. Cummins, *J. Am. Chem. Soc.* 2009, **131**, 446.
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 28](#) |
- [Go here for SFX](#)
- 16
- 16aF. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* 2012, **337**, 1526;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 39](#) |
- [ADS](#) |
- [Go here for SFX](#)
- 16bJ. J. Scepaniak, R. P. Bontchev, D. L. Johnson, J. M. Smith, *Angew. Chem. Int. Ed.* 2011, **50**, 6630;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 46](#) |
- [Go here for SFX](#)
Angew. Chem. 2011, **123**, 6760.

- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 17
- 17aD. P. Halter, F. W. Heinemann, J. Bachmann, K. Meyer, *Nature* 2016, **530**, 317;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 9](#) |
- [ADS](#) |
- [Go here for SFX](#)

- 17bC. Camp, M. A. Antunes, G. Garcia, I. Ciofini, I. C. Santos, J. Pecault, M. Almeida, J. Marcalo, M. Mazzanti, *Chem. Sci.* 2014, **5**, 841;
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 24](#) |
 - [Go here for SFX](#)
- 17cE. Lu, O. J. Cooper, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* 2014, **53**, 6696;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 26](#) |
 - [Go here for SFX](#)

Angew. Chem. 2014, **126**, 6814;

 - [Wiley Online Library](#) |
 - [Go here for SFX](#)
- 17dD. M. King, F. Tuna, J. McMaster, W. Lewis, A. J. Blake, E. J. L. McInnes, S. T. Liddle, *Angew. Chem. Int. Ed.* 2013, **52**, 4921;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 47](#) |
 - [Go here for SFX](#)

Angew. Chem. 2013, **125**, 5021;

 - [Wiley Online Library](#) |
 - [Go here for SFX](#)
- 17eJ. L. Brown, S. Fortier, G. Wu, N. Kaltsoyannis, T. W. Hayton, *J. Am. Chem. Soc.* 2013, **135**, 5352;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 29](#) |
 - [Go here for SFX](#)
- 17fD. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* 2012, **134**, 10047;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 79](#) |
 - [Go here for SFX](#)
- 17gS. Fortier, J. L. Brown, N. Kaltsoyannis, G. Wu, T. W. Hayton, *Inorg. Chem.* 2012, **51**, 1625;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 54](#) |
 - [Go here for SFX](#)
- 17hC. R. Graves, J. L. Kiplinger, *Chem. Commun.* 2009, 3831;
 - [CrossRef](#) |
 - [Web of Science® Times Cited: 89](#) |
 - [Go here for SFX](#)
- 17iI. Castro-Rodríguez, H. Nakai, K. Meyer, *Angew. Chem. Int. Ed.* 2006, **45**, 2389;
 - [Wiley Online Library](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 66](#) |

- [Go here for SFX](#)
Angew. Chem. 2006, **118**, 2449;
- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 17jD. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* 1995, **117**, 9448;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 162](#) |
- [Go here for SFX](#)
- 17kD. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* 1993, **115**, 9840;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 111](#) |
- [Go here for SFX](#)
- 17lD. S. J. Arney, C. J. Burns, D. C. Smith, *J. Am. Chem. Soc.* 1992, **114**, 10068;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 97](#) |
- [Go here for SFX](#)
- 17mJ. G. Brennan, R. A. Andersen, *J. Am. Chem. Soc.* 1985, **107**, 514.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 160](#) |
- [Go here for SFX](#)
- 18J. Selbin, J. D. Ortego, *Chem. Rev.* 1969, **69**, 657.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 147](#) |
- [Go here for SFX](#)
- 19D. R. Kindra, W. J. Evans, *Chem. Rev.* 2014, **114**, 8865.
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 33](#) |
- [Go here for SFX](#)
- 20D. Patel, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* 2013, **42**, 5224.
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 19](#) |
- [Go here for SFX](#)
- 21B. M. Gardner, S. T. Liddle, *Chem. Commun.* 2015, **51**, 10589.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 8](#) |
- [Go here for SFX](#)
- 22
- 22aH. S. La Pierre, M. Rosenzweig, B. Kosog, C. Hauser, F. W. Heinemann, S. T. Liddle, K. Meyer, *Chem. Commun.* 2015, **51**, 16671;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 4](#) |

- [Go here for SFX](#)
- 22bH. S. La Pierre, K. Meyer, *Inorg. Chem.* 2013, **52**, 529;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 35](#) |
- [Go here for SFX](#)
- 22cA. J. Lewis, P. J. Carroll, E. J. Schelter, *J. Am. Chem. Soc.* 2013, **135**, 13185;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 20](#) |
- [Go here for SFX](#)
- 22dB. Kosog, H. S. La Pierre, F. W. Heinemann, S. T. Liddle, K. Meyer, *J. Am. Chem. Soc.* 2012, **134**, 5284;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 46](#) |
- [Go here for SFX](#)
- 22eE. O'Grady, N. Kaltosyannis, *J. Chem. Soc. Dalton Trans.* 2002, 1233;
- [CrossRef](#) |
- [Web of Science® Times Cited: 40](#) |
- [Go here for SFX](#)
- 22fR. G. Denning, *J. Phys. Chem. A* 2007, **111**, 4125;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 277](#) |
- [ADS](#) |
- [Go here for SFX](#)
- 22gR. G. Denning, *Struct. Bonding*, Springer, Berlin 1992, **79**, 215.
- [Go here for SFX](#)
- 23A. Schulz, T. M. Klapötke, *Inorg. Chem.* 1996, **35**, 4791.
- [CrossRef](#) |
- [Web of Science® Times Cited: 18](#) |
- [Go here for SFX](#)
- 24B. Ruscic, J. Berkowitz, *Chem. Sci.* 1994, **100**, 4498.
- [Web of Science® Times Cited: 54](#) |
- [Go here for SFX](#)
- 25Recorded at 145 K (b.p. 296 K), the N–H IR frequency of HNCO is 2254 cm⁻¹ (ν₂). See: M. S. Lowenthal, R. K. Khanna, M. H. Moore, *Spectrochim. Acta Part A* 2002, **58**, 73.
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 38](#) |
- [ADS](#) |
- [Go here for SFX](#)
- 26A. R. Amell, *J. Am. Chem. Soc.* 1956, **78**, 6234.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 38](#) |
- [Go here for SFX](#)
- 27

- 27aC. Camp, N. Settineri, J. Lefèvre, A. R. Jupp, J. M. Goicoechea, L. Maron, J. Arnold, *Chem. Sci.* 2015, **6**, 6379;
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 10](#) |
 - [Go here for SFX](#)
- 27bE. Hashem, J. A. Platts, F. Hartl, G. Lorusso, M. Evangelisti, C. Schulzke, R. J. Baker, *Inorg. Chem.* 2014, **53**, 8624;
 - [CrossRef](#) |
 - [PubMed](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 8](#) |
 - [Go here for SFX](#)
- 27cA. J. Lewis, E. Nakamaru-Ogiso, J. M. Kikkawa, P. J. Carroll, E. J. Schelter, *Chem. Commun.* 2012, **48**, 4977.
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 26](#) |
 - [Go here for SFX](#)
- 28See for instance: P. Liu, B. L. H. Taylor, J. Garcia-Lopez, and K. N. Houk, *Computational Studies of Ruthenium-Catalyzed Olefin Metathesis*, in *Handbook of Metathesis* (Eds: R. H. Grubbs, A. G. Wenzel, D. J. O'Leary, E. Khosravi), Wiley-VCH, Weinheim, **2015**, DOI: [10.1002/9783527674107.ch7](https://doi.org/10.1002/9783527674107.ch7).
- 29C. E. Kefalidis, A. Stasch, C. Jones, L. Maron, *Chem. Commun.* 2014, **50**, 12318.
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 10](#) |
 - [Go here for SFX](#)
- 30C. E. Kefalidis, L. Maron, *Chem. Eur. J.* 2016, **22**, 4743.
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science®](#) |
 - [Go here for SFX](#)
- 31L. Watson, O. Eisenstein, *J. Chem. Educ.* 2002, **79**, 1269.
 - [CrossRef](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 64](#) |
 - [ADS](#) |
 - [Go here for SFX](#)
- 32
- 32aB. M. Gardner, G. Balázs, M. Scheer, A. J. Wooles, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* 2015, **54**, 15250;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Web of Science® Times Cited: 6](#) |
 - [Go here for SFX](#)
- *Angew. Chem.* 2015, **127**, 15465;
 - [Wiley Online Library](#) |
 - [CAS](#) |
 - [Go here for SFX](#)
- 32bB. M. Gardner, G. Balázs, M. Scheer, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* 2015, **7**, 582;
 - [CrossRef](#) |

- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 16](#) |
- [ADS](#) |
- [Go here for SFX](#)
- 32cB. M. Gardner, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* 2015, **54**, 7068;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 8](#) |
- [Go here for SFX](#)
Angew. Chem. 2015, **127**, 7174;

- [Wiley Online Library](#) |
- [CAS](#) |
- [Go here for SFX](#)
- 32dB. M. Gardner, P. A. Cleaves, C. E. Kefalidis, J. Fang, L. Maron, W. Lewis, A. J. Blake, S. T. Liddle, *Chem. Sci.* 2014, **5**, 2489;
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 20](#) |
- [Go here for SFX](#)
- 32eB. M. Gardner, G. Balázs, M. Scheer, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* 2014, **53**, 4484;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 32](#) |
- [Go here for SFX](#)
Angew. Chem. 2014, **126**, 4573;

- [Wiley Online Library](#) |
- [Go here for SFX](#)
- 32fD. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* 2014, **136**, 5619.
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 38](#) |
- [Go here for SFX](#)
- 33For examples of sterically compressed complexes, see:
- 33aN. A. Siladke, K. R. Meihaus, J. W. Ziller, M. Fang, F. Furche, J. R. Long, W. J. Evans, *J. Am. Chem. Soc.* 2012, **134**, 1243;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 31](#) |
- [Go here for SFX](#)
- 33bW. J. Evans, S. A. Kozimor, J. W. Ziller, *J. Am. Chem. Soc.* 2003, **125**, 14264;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 89](#) |
- [Go here for SFX](#)
- 33cW. J. Evans, S. A. Kozimor, G. W. Nyce, J. W. Ziller, *J. Am. Chem. Soc.* 2003, **125**, 13831;
- [CrossRef](#) |

- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 82](#) |
- [Go here for SFX](#)
- 33dW. J. Evans, B. L. Davis, *Chem. Rev.* 2002, **102**, 2119;
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 222](#) |
- [Go here for SFX](#)
- 33eW. J. Evans, G. W. Nyce, M. A. Johnston, J. W. Ziller, *J. Am. Chem. Soc.* 2000, **122**, 12019.
- [CrossRef](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 59](#) |
- [Go here for SFX](#)
- 34C. E. Kefalidis, A. S. P. Frey, S. M. Roe, F. G. N. Cloke, L. Maron, *Dalton Trans.* 2014, **43**, 11202.
- [CrossRef](#) |
- [PubMed](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 7](#) |
- [Go here for SFX](#)
- 35
- 35aL. Castro, S. Labouille, D. R. Kindra, J. W. Ziller, F. Nief, W. J. Evans, L. Maron, *Chem. Eur. J.* 2012, **18**, 7886;
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 19](#) |
- [Go here for SFX](#)
- 35bL. Castro, L. Maron, *Chem. Eur. J.* 2012, **18**, 6610.
- [Wiley Online Library](#) |
- [CAS](#) |
- [Web of Science® Times Cited: 10](#) |
- [Go here for SFX](#)
- 36CCDC 1486563 (**3**), 1486564 (**6**), and 1486565 (**8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by [The Cambridge Crystallographic Data Centre](#).