ChemComm

Lewis Acid Capping of a Uranium(V) Nitride via a Uranium(III) Azide Molecular Square

COMMUNICATION

Lewis Acid Capping of a Uranium(V) Nitride via a Uranium(III) Azide Molecular Square

Michael A. Boreen,[a,b] Guodong Rao,[c] David Villarreal,[c] Fabian A. Watt,[d] R. David Britt,[c] Stephan Hohloch,[e,*] and John Arnold[a,b,*]

Reaction of (CpiPr4)2UI with NaN3 resulted in formation of tetrameric uranium(III) azide-bridged 'molecular square' [(CpiPr4)2U(μ-η^1:η^1-N3)]4 (1). Addition of B(C6F5)3 to 1 induced loss of N2 at room temperature, yielding the uranium(V) borane-capped nitrido (CpiPr4)2U(μ-N)B(C6F5)3 (2).

Studies of uranium nitrido complexes, LnU≡N, have been motivated by their ability to provide insight into the fundamental nature of actinide-ligand multiple bonds[1–3] and their potential to act as molecular models for uranium nitride (UN, U2N3, and UN2) materials, which are of considerable interest in the context of next-generation nuclear fuels.[4–12] Our group and others are interested in discovering new ways to convert molecules containing uranium into materials, and while considerable progress has been made towards uranium oxide materials,[13–20] much less is known about potential uranium nitride precursors.

Uranium azides have received considerable attention for their ability to act as precursors to uranium nitrido complexes,[1,2,21] however, it remains an outstanding challenge to predict the products of reactions of low-valent uranium species with small molecules and ions, such as N3−, as relatively subtle structural differences in supporting ligands have been shown in multiple cases to exert a large effect on factors such as product nuclearity and oxidation state.[22–27]

Evans and coworkers showed that reaction between [(C5Me4R)2U][(μ-Ph)2BPh2] (R = H, Me) and NaN3 led to the formation of octa-uranium(IV) complexes [(C5Me4R)2U(μ-N)Cp*2U(μ-η^1:η^1-N3)]4, molecules with alternating bridging nitrido and azide ligands.[28] The metallocene uranium(III) azide (C5Me4R)2U(N3) can be implicated as an intermediate, but it is unclear if the subsequent loss of N2 occurs from mononuclear or multi-metallic azide-bridged species,[28] especially because both terminal[29] and bridging[30,31] uranium(III) azides have been isolated with different supporting ligand systems.

Here we report the effect of using the CpiPr4 ligand (CpiPr4 = tetra(isopropyl)cyclopentadienyl) on the reactivity of metallocene uranium(III) azides and reveal significant differences compared to earlier reports using Cp* or C5Me4H. In particular, we isolated a much lower molecularity tetrameric bis-CpiPr4 uranium(III) azide-bridged 'molecular square' that could be directly converted to a mononuclear, uranium(V) borane-capped nitrido using the strong Lewis acid B(C6F5)3.

Reaction of one equivalent of NaN3 with (CpiPr4)2UI[32] in THF overnight led to green oily solids after removal of solvent. Single crystals suitable for X-ray crystallographic analysis (see below) were grown by recrystallization of the crude material from pentane and revealed the green crystalline product to be the tetrameric uranium(III) azide 'molecular square' [(CpiPr4)2U(μ-η^1:η^1-N3)]4 (1) (Scheme 1). A sharp, strong azide stretch observed at 2100 cm−1 is almost identical to that seen in the precursor material NaN3 (2104 cm−1). Importantly, there is a large difference in both the nuclearity and oxidation state between 1 and the octa-uranium(IV) complex [(C5Me4R)2U(μ-N)Cp*2U(μ-η^1:η^1-N3)]4 (R = H, Me) formed under related conditions with less bulky Cp ligands.[28]

While extremely uncommon, an example of this square motif has been reported by Liddle and coworkers in a tetra-uranium(IV) complex [(TrenDMBS)U(μ-η^1:η^1-N3)]4 (TrenDMBS = N(CH2CH2NSiMe2tBu)3), which has both a different uranium oxidation state and an entirely different supporting ligand scaffold from 1.[33] A trimeric metallocene uranium(IV) 'molecular triangle' [Cp*2U(N3)(μ-η^1:η^1-N3)]3 has also been isolated, further illustrating the challenge in predicting the structures and aggregation of uranium azides.[34]

a. Department of Chemistry, University of California, Berkeley, California 94720, USA.
b. Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.
c. Department of Chemistry, University of California, Davis, California 95616, USA.
d. University of Paderborn, Warburger Straße 100, 33098 Paderborn, Germany.
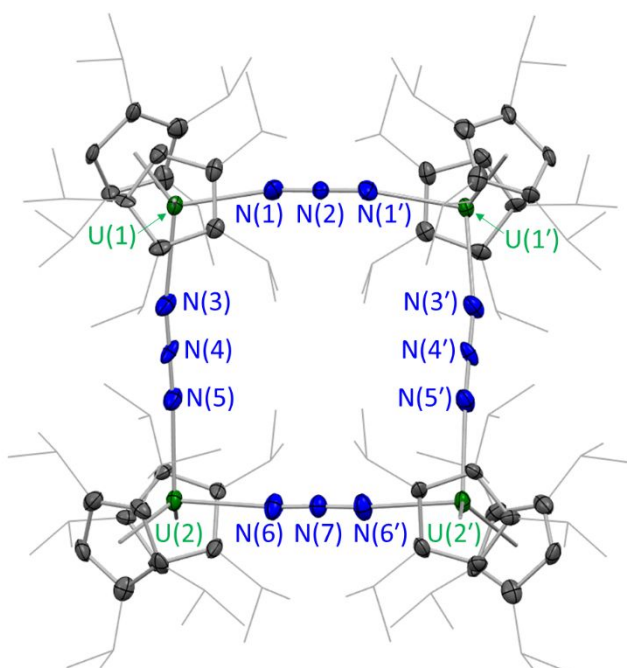e. ΔLeopold-Franzens-University Innsbruck, Faculty of Chemistry and Pharmacy, Institute of General, Inorganic and Theoretical Chemistry, Innrain 80-82, 6020 Innsbruck, Austria.
Email: J.A.: arnold@berkeley.edu, S.H.: stephan.hohloch@uibk.ac.at
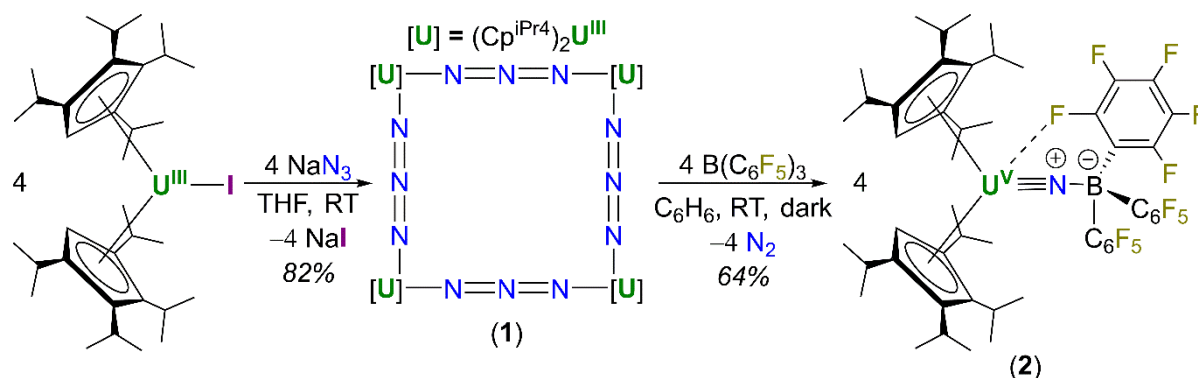
Scheme 1 Synthesis of complexes **1** and **2**.

The solid-state structure of **1** is shown in Fig. 1, and selected structural metrics are provided in Table S1 (ESI†). **Fig. 1** X-ray crystal structure of $[(Cp^{iPr4})_2U(\mu\text{-}\eta^1{:}\eta^1\text{-}N_3)]_4$ (**1**) with 50% probability ellipsoids. Isopropyl groups are displayed as wireframes; hydrogen atoms and positional disorder are omitted for clarity. Selected structural metrics are listed in Table S1 (ESI†).

Complex **1** crystallizes in the space group $P4_22_12$ with individual molecules of **1** lying on a crystallographic 2-fold axis. The average U–N distance in **1** is 2.508(8) Å, much longer than the U–N_{azide} bond length of 2.321(4) Å in the uranium(III) terminal azide complex $Tp^*_2U(N_3)$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate), as would be expected for a bridging species.[29] Furthermore, a U–N_{azide} distance of 2.298(8) Å was found in the azide-bridged uranium(III/IV) complex $[\{(^{t\text{-}Bu}ArO)_3tacn\}U]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_3)$ (($^{t\text{-}Bu}$ArO)$_3$tacn = 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzylate)-1,4,7-triazacyclononane),[31] and a U–N_{azide} distance of 2.40(2) Å was found in the azide-bridged uranium(III/III) complex $[Na(18\text{-crown-}6)][(C_5H_4SiMe_3)_3U]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_3)$.[30] The long U–N distances in **1** are presumably a result of the bulky Cp^{iPr4} groups. Notably, however, U–N_{azide} distances in the uranium(IV) species $[(C_5Me_4R)_2U(\mu\text{-}N)Cp^*_2U(\mu\text{-}\eta^1{:}\eta^1\text{-}N_3)]_4$ (R = H, Me) were found to range from 2.449(14) to 2.525(7) Å;[28] this similarity is surprising given that uranium(IV)

has an effective ionic radius roughly 0.135 Å smaller than that of uranium(III).[35]

While **1** is stable when stored in the dark at room temperature, it was found to turn brown over days when exposed to room light. Photolysis of **1** as a suspension in pentane led to complete conversion to a dark red-orange solution after a week, but no products could be isolated from the resulting mixture. Similarly, toluene suspensions of **1** rapidly changed color to dark red-orange between 90–100 °C, producing intractable mixtures. If terminal nitrido species form in these reactions, they undergo rapid intramolecular decomposition pathways, such as addition of C(sp³)–H bonds.[36,37]

With these findings in mind, we sought to use a protection strategy to trap a nitride species. The strong Lewis acid $B(C_6F_5)_3$ has been found to form stable metal azidoborates,[36,38,39] but the reactivity of this moiety appears to vary by metal and oxidation state. The niobium(V) azidoborate $(BDI)Nb(N^tBu)(Ph)[(\mu\text{-}\eta^1{:}\eta^1\text{-}N_3)B(C_6F_5)_3]$ (BDI = *N,N′*-bis(2,6-diisopropylphenyl)-3,5-dimethyl-*β*-diketiminate) could be photolyzed to form a borane-capped nitrido,[38] while loss of N_2 via azide photolysis was deactivated in the uranium(IV) complexes $(C_5Me_4R)_2U[N(SiMe_3)_2](N_3)$ (R = Me, Et) upon capping of the azides with $B(C_6F_5)_3$.[36]

In contrast to these earlier reports, we found that addition of $B(C_6F_5)_3$ to **1** induced loss of N_2 at room temperature without the necessity of light, leading to the isolation of the borane-capped nitrido complex $(Cp^{iPr4})_2U(\mu\text{-}N)B(C_6F_5)_3$ (**2**) as dark red crystals in 64% yield (Scheme 1). The IR spectrum of **2** showed no azide stretching bands, and the identity of the product was confirmed through X-ray crystallographic studies (see below). A related borane-capped nitrido species, $([N(^nBu)_4][\{N(^tBu)(3,5\text{-}Me_2C_6H_3)\}_3U(\mu\text{-}N)B(C_6F_5)_3])$, albeit prepared via a quite different synthetic pathway, was described by Cummins and coworkers.[40]

The solid-state structure of **2** is shown in Fig. 2, and selected structural metrics are shown in Table S2 (ESI†). The U–N bond length of 1.893(2) Å in **2** is slightly shorter than those of the only other two structurally characterized uranium(V) borane-capped nitrido complexes, $[N(^nBu)_4][\{N(^tBu)(3,5\text{-}Me_2C_6H_3)\}_3U(\mu\text{-}N)B(C_6F_5)_3]$ (1.914(4) Å)[40] and $[K(benzo\text{-}15\text{-crown-}5)][(Tren^{TIPS})U(\mu\text{-}N)BPh_3]$ (1.911(6) Å) ($Tren^{TIPS}$ = $N(CH_2CH_2NSi^iPr_3)_3$)[41] but longer than the U–$N_{nitrido}$

distances generally observed in terminal or alkali metal-capped uranium(V) nitrido complexes.[22,42–45] Notably, a close contact of 2.597(2) Å is observed in **2** between the uranium center and one
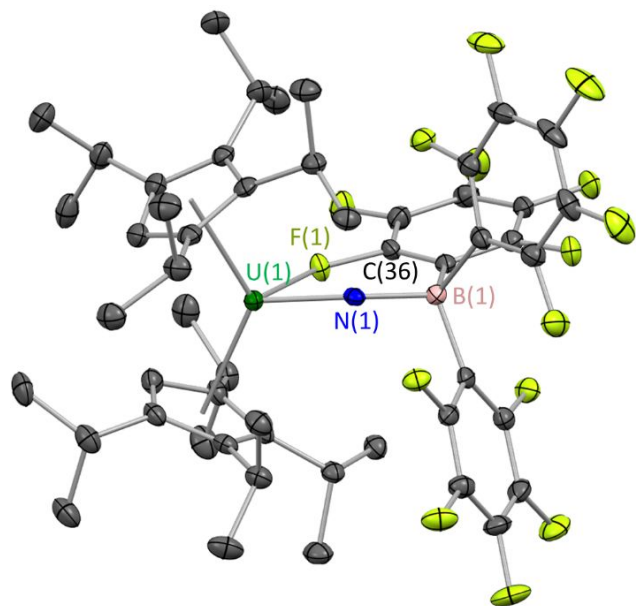

Fig. 2 X-ray crystal structure of $(Cp^{iPr4})_2U(\mu\text{-}N)B(C_6F_5)_3$ (**2**) with 50% probability ellipsoids. Hydrogen atoms and positional disorder are omitted for clarity. Selected structural metrics are listed in Table S2 (ESI†).

of the fluorine atoms on the coordinated $B(C_6F_5)_3$ (F(1) in Fig. 2). The presence of only one nitrogen atom between the uranium center and the borane along with the C–F→U close contact enables the $B(C_6F_5)_3$ molecule to exert considerable steric pressure on the $(Cp^{iPr4})_2U$ fragment in **2**; one effect of this is the quite small (for the $(Cp^{iPr4})_2U$ fragment) Cp(cent)–U–Cp(cent) angle, 129.60(4)°.

While uncommon, C–F→U close contacts have been observed in the solid-state structures of several uranium(IV) complexes: U–F distances of 2.648(1) and 2.599(1) Å were determined in $U[N(C_6F_5)_2]_4$,[46] and U–F distances of 2.762(6) and 2.789(5) Å were found in $[Cp^*_2Co][U\{OB(C_6F_5)_3\}_2(^{Ar}acnac)(OEt_2)]$ ($^{Ar}acnac$ =

ArNC(Ph)CHC(Ph)O, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$)[47]. The C–F bond making a close contact with the uranium center in **2** is

Fig. 3 X-band EPR spectrum of **2** (black trace) simulated with an effective S = ½ spin system with g_{eff} = [3.38, 1.01, 0.79] (red trace). Conditions: frequency = 9.4 GHz; temperature = 10 K; modulation amplitude = 0.5 mT. The residual features near the baseline likely arise from spin-spin dipolar interactions in the powder sample.

longer (1.394(3) Å) than any of the other C–F bonds in **2** (1.338(3) to 1.354(4) Å); a comparable slight elongation was observed in the C–F bonds interacting with the cerium(III) center in $Ce[N(C_6F_5)_2]_3$.[48] While NMR spectroscopy has been used to study a variety of C–F→Ln/An interactions in the solution-state,[49] such analysis was not possible for **2** due to poor solubility and solution-state instability.
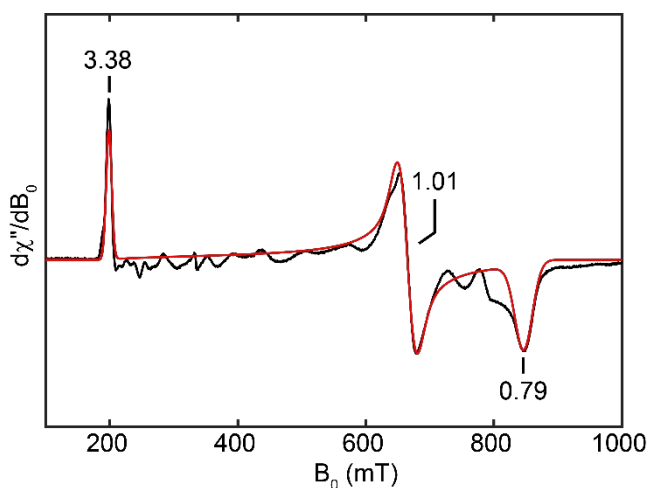
The powder continuous-wave (CW) X-band EPR spectrum of **2** shows a rhombic system with effective g-values of [3.38, 1.01, 0.79], giving g_{avg} = 1.72 (Fig. 3). The g-values are deviated significantly from g_e (2.0023), which is consistent with the 5f^1 electronic configuration of **2**. Similar g-values have been observed in another uranium(V) systems with a pseudotetrahedral ligand field.[50] Despite the relatively small C–F→U close contact in the solid-state of **2**, no clear hyperfine coupling to fluorine was observed in the CW EPR spectrum, possibly due to the broad spectral line shape.

To summarize, reaction of $(Cp^{iPr4})_2UI$ with NaN_3 yields the unusual uranium(III) azide-bridged tetramer $[(Cp^{iPr4})_2U(\mu\text{-}\eta^1{:}\eta^1\text{-}N_3)]_4$ (**1**), a rare example of a 'molecular square'. Isolation of a uranium(III) azide species using Cp^{iPr4} stands in contrast to previous octa-uranium(IV) complexes formed using less bulky Cp^* or C_5Me_4H, a finding that further demonstrates the importance of supporting ligand effects in actinide chemistry. Reaction of **1** with $B(C_6F_5)_3$ results in loss of N_2 and formal trapping of a nitride fragment as the uranium(V) nitridoborate $(Cp^{iPr4})_2U(\mu\text{-}N)B(C_6F_5)_3$ (**2**). Future work will seek to elucidate the properties that govern the conversion of low-valent uranium azides to nitrides.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1   D. M. King and S. T. Liddle, *Coord. Chem. Rev.*, 2014, **266–267**, 2.
2   M. A. Boreen and J. Arnold, Multiple Bonding in Actinide Chemistry, In *Encyclopedia of Inorganic and Bioinorganic Chemistry*, ed. R. A. Scott, Wiley, Hoboken, 2018. DOI: 10.1002/9781119951438.eibc2535.
3   T. W. Hayton, *Chem. Commun.*, 2013, **49**, 2956.
4   K. Liu, X. Wang, J. Liu, Y. Hu, Y. Zhong, Q. Pan, L. Luo, S. Chen, Y. Zhang and Z. Long, *Prog. Surf. Sci.*, 2018, **93**, 47.
5   S. J. Zinkle, K. A. Terrani, J. C. Gehin, L. J. Ott and L. L. Snead, *J. Nucl. Mater.*, 2014, **448**, 374.
6   M. Streit and F. Ingold, *J. Eur. Ceram. Soc.*, 2005, **25**, 2687.
7   B. J. Jaques, B. M. Marx, A. S. Hamdy and D. P. Butt, *J. Nucl. Mater.*, 2008, **381**, 309.
8   L. Black, F. Miserque, T. Gouder, L. Havela, J. Rebizant and F. Wastin, *J. Alloys Compd.*, 2001, **315**, 36.
9   T. M. Besmann, D. Shin and T. B. Lindemer, *J. Nucl. Mater.*, 2012, **427**, 162.
10 S. J. Zinkle and G. S. Was, *Acta Mater.*, 2013, **61**, 735.
11 L. H. Ortega, B. J. Blamer, J. A. Evans and S. M. McDeavitt, *J. Nucl. Mater.*, 2016, **471**, 116.
12 K. Shrestha, D. Antonio, M. Jaime, N. Harrison, D. S. Mast, D. Safarik, T. Durakiewicz, J.-C. Griveau and K. Gofryk, *Sci. Rep.*, 2017, **7**, 6642.
13 M. D. Straub, J. Leduc, M. Frank, A. Raauf, T. D. Lohrey, S. G. Minasian, S. Mathur and J. Arnold, *Angew. Chem. Int. Ed.*, 2019, **58**, 5749.
14 M. D. Straub, S. Hohloch, S. G. Minasian and J. Arnold, *Dalton Trans.*, 2018, **47**, 1772.
15 H. Wu, Y. Yang and Y. C. Cao, *J. Am. Chem. Soc.*, 2006, **128**, 16522.
16 T. M. Nenoff, B. W. Jacobs, D. B. Robinson, P. P. Provencio, J. Huang, S. Ferreira and D. J. Hanson, *Chem. Mater.*, 2011, **23**, 5185.
17 J. Leduc, J. I. Pacold, D. K. Shuh, C.-L. Dong and S. Mathur, *Z. Anorg. Allg. Chem.*, 2018, **644**, 12.
18 C. Falaise, H. A. Neal and M. Nyman, *Inorg. Chem.*, 2017, **56**, 6591.
19 T. T. Meek, B. von Roedern, P. G. Clem and R. J. Hanrahan Jr., *Mater. Lett.*, 2005, **59**, 1085.
20 S. R. Qiu, C. Amrhein, M. L. Hunt, R. Pfeffer, B. Yakshinskiy, L. Zhang, T. E. Madey and J. A. Yarmoff, *Appl. Surf. Sci.*, 2001, **181**, 211.
21 M. Yadav, A. Metta-Magaña and S. Fortier, *Chem. Sci.*, 2020, Advance Article. DOI: 10.1039/C9SC05992J.
22 N. Tsoureas, A. F. R. Kilpatrick, C. J. Inman and F. G. N. Cloke, *Chem. Sci.*, 2016, **7**, 4624.
23 O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *J. Am. Chem. Soc.*, 2006, **128**, 9602.
24 O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *Science*, 2006, **311**, 829.
25 N. Tsoureas, O. T. Summerscales, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2013, **32**, 1353.
26 O. T. Summerscales, A. S. P. Frey, F. G. N. Cloke and P. B. Hitchcock, *Chem. Commun.*, 2009, 198.
27 N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. G. N. Cloke and L. Maron, *Chem. Sci.*, 2014, **5**, 3777.
28 W. J. Evans, S. A. Kozimor and J. W. Ziller, *Science*, 2005, **309**, 1835.
29 C. J. Tatebe, S. A. Johnson, M. Zeller and S. C. Bart, *J. Organomet. Chem.*, 2018, **857**, 152.
30 J.-C. Berthet, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Organomet. Chem.*, 1991, **420**, C9.
31 I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 11242.
32 M. A. Boreen, D. J. Lussier, B. A. Skeel, T. D. Lohrey, F. A. Watt, D. K. Shuh, J. R. Long, S. Hohloch and J. Arnold, *Inorg. Chem.*, 2019, **58**, 16629.
33 J. Du, D. M. King, L. Chatelain, E. Lu, F. Tuna, E. J. L. McInnes, A. J. Wooles, L. Maron and S. T. Liddle, *Chem. Sci.*, 2019, **10**, 3738.
34 W. J. Evans, K. A. Miller, J. W. Ziller and J. Greaves, *Inorg. Chem.*, 2007, **46**, 8008.
35 R. D. Shannon, *Acta Cryst.*, 1976, **A32**, 751.
36 R. K. Thomson, T. Cantat, B. L. Scott, D. E. Morris, E. R. Batista and J. L. Kiplinger, *Nat. Chem.*, 2010, **2**, 723.
37 K. C. Mullane, H. Ryu, T. Cheisson, L. N. Grant, J. Y. Park, B. C. Manor, P. J. Carroll, M.-H. Baik, D. J. Mindiola and E. J. Schelter, *J. Am. Chem. Soc.*, 2018, **140**, 11335.
38 C. Camp, L. N. Grant, R. G. Bergman and J. Arnold, *Chem. Commun.*, 2016, **52**, 5538.
39 D. E. Herbert, N. C. Lara and T. Agapie, *Chem. Eur. J.*, 2013, **19**, 16453.
40 A. R. Fox and C. C. Cummins, *J. Am. Chem. Soc.*, 2009, **131**, 5716.
41 L. Chatelain, E. Louyriac, I. Douair, E. Lu, F. Tuna, A. J. Wooles, B. M. Gardner, L. Maron and S. T. Liddle, *Nat. Commun.*, 2020, **11**, 337.
42 D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717.
43 D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2013, **5**, 482.
44 D. M. King, P. A. Cleaves, A. J. Wooles, B. M. Gardner, N. F. Chilton, F. Tuna, W. Lewis, E. J. L. McInnes and S. T. Liddle, *Nat. Commun.*, 2016, **7**, 13773.
45 P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem. Int. Ed.*, 2014, **53**, 10412.
46 H. Yin, A. J. Lewis, U. J. Williams, P. J. Carroll and E. J. Schelter, *Chem. Sci.* 2013, **4**, 798.
47 D. D. Schnaars, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2009, **131**, 17532.
48 H. Yin, A. J. Lewis, P. Carroll and E. J. Schelter, *Inorg. Chem.*, 2013, **52**, 8234.
49 H. Yin, A. V. Zabula and E. J. Schelter, *Dalton Trans.*, 2016, **45**, 6313.
50 A. M. Tondreau, T. J. Duignan, B. W. Stein, V. E. Fleischauer, J. Autschbach, E. R. Batista, J. M. Boncella, M. G. Ferrier, S. A. Kozimor, V. Mocko, M. L. Neidig, S. K. Cary and P. Yang, *Inorg. Chem.*, 2018, **57**, 8106.