



Cite this: *Chem. Commun.*, 2015, 51, 16671

Received 27th August 2015,
Accepted 25th September 2015

DOI: 10.1039/c5cc07211e

www.rsc.org/chemcomm

Charge control of the inverse *trans*-influence†

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The synthesis and characterization of uranium(vi) mono(imido) complexes, by the oxidation of corresponding uranium(v) species, are presented. These experimental results, paired with DFT analyses, allow for the comparison of the electronic structure of uranium(vi) mono(oxo) and mono(imido) ligands within a conserved ligand framework and demonstrate that the magnitude of the ground state stabilization derived from the inverse *trans*-influence (ITI) is governed by the relative charge localization on the multiply bonded atom or group.

While terminal oxo (O^{2-}) and imido (RN^{2-}) ligands are formally isolobal and isoelectronic,^{1–3} these ligands differ in the relative energy of their fragment orbitals and in the charge localization at O or N in their respective metal complexes.^{4–8} These subtle differences are most pronounced in the comparison of the reactivity and electronic structure of oxo and imido complexes of the early actinides (Th and U). Andersen's uranium(iv) oxo and imido complexes of $[(\eta^5-1,2,4-(Me_3C)_3C_5H_2)_2U=X]$ ($X = O, NMe$) are principle examples of this divergence.^{5,9,10} In these mid-valent complexes, the uranium oxo bond is significantly stronger, but much more polarized than the uranium imido bond, and, as a result, the imido engages in $[2 + 2]$ reactions with unsaturated substrates. The oxo, in contrast, principally reacts as a nucleophile. Such dramatic differences in oxo and imido reactivity and electronic structure are less common among transition metal complexes within conserved ligand frameworks,

and the variable steric profile afforded by the imido substituent is often employed as a directing group to control reactivity.¹¹

Since the report of the first uranium imido complex by Gilje in 1984,¹² an extensive body of work on uranium-ligand multiple bonding has developed.^{13–16} A major objective of these studies has been to understand the unique bonding in uranyl (and the actinyls) – the most common structural feature of high valent uranium compounds.¹⁷ In uranyl complexes, the two terminal oxo ligands are *trans* to each other and the U–O distances are typically both short at ~ 1.8 Å. The inverse *trans*-influence (ITI) has been proposed as the basis for this geometric preference.^{18–24} In this model charge-induced mixing of the pseudocore 6p orbitals with the valence 5f orbitals leads to contraction and strengthening of the bond *trans* to the oxo ligand.^{25,26} Theoretical and experimental work have established a molecular orbital basis for the ITI,^{6,27–34} but the role that charge localization plays in developing a quadrupolar polarization of the uranium core electrons remains experimentally untested.

Uranium bis(imido) complexes, possessing uranyl-like geometry with two *trans*-imido ligands, $[RN=U=NR]^{n+}$, have been reported by Hayton and Boncella and serve as an excellent synthetic perturbation of the ITI.^{35–38} Surprisingly, in contrast to dioxo uranium complexes, *cis*-bis(imido) complexes (and even tris(imido) complexes)^{39,40} such as $[Cp^*_2U(NPh)_2]$ ($Cp^* = C_5Me_5$) can be prepared.^{41,42} Attempts to isolate analogous *cis*-dioxo complexes supported by Cp^* ($Cp^* = C_5Me_5$) lead only to elimination of Cp^* dimer and precipitation of UO_2 – indicating that deformation of O–U–O angle in uranyl is substantially more energy intensive than in the corresponding *trans*-bis(imido) complexes.⁹

However, appropriate complexes to disentangle the difference in high-valent uranium oxo and imido bonding have yet to be prepared. Complexes in which the highest uranium oxidation states (v) and (vi) are stabilized by a mono(imido) (or mono(oxo)) moiety are still scarce.^{43–51} Recently, we demonstrated that the ITI was key feature in determining geometry of the two C_5 tacn-supported uranium(vi) mono(oxo) complexes $[(^RArO)_3-tacn]U^{VI}(O)SbF_6$ ($(^RArO)_3tacn^{3-} = 1,4,7$ -tris(3-*R*-5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane, $R = t$ -Bu, adamantyl)

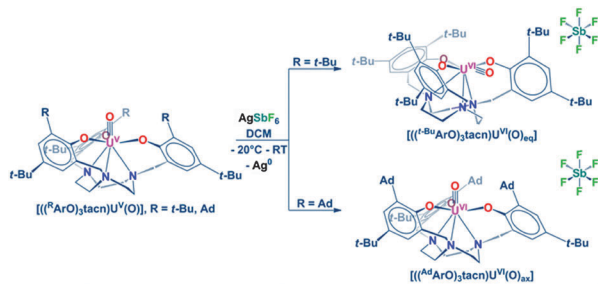
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† Electronic supplementary information (ESI) available: General considerations, synthetic and spectroscopic as well as crystallographic and computational details for **2-t-Bu**, **2-Ad**, and crystallographic details for **3-Ad**. CCDC 894627, 894628, and 747048. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc07211e



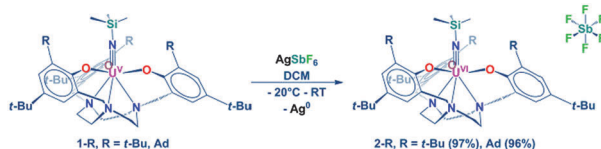


Scheme 1 Oxidation of $[[(\text{R}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{V}}(\text{O})]$ with 1 equiv. AgSbF_6 to give the complexes $[[(\text{t-Bu}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{VI}}(\text{O})_{\text{eq}}]\text{SbF}_6$ and $[[(\text{Ad}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{VI}}(\text{O})_{\text{ax}}]\text{SbF}_6$ (eq. = equatorial, ax. = axial with respect to the tris(aryloxo) coordination).⁴³

obtained *via* oxidation of the corresponding C_3 uranium(V) oxo compounds with silver(I) salts (Scheme 1).⁴³ Herein we report the synthesis of uranium(VI) mono(imido) complexes supported by the conserved ligand framework $(\text{R}^{\text{ArO}})_3\text{tacn}^{3-}=1,4,7\text{-tris}(3\text{-}R\text{-}5\text{-}tert\text{-butyl-}2\text{-hydroxybenzyl)-}1,4,7\text{-triazacyclononane}$, $\text{R} = t\text{-Bu}$, adamantyl). These C_3 complexes retain an axially ligated metal-ligand multiple bond in contrast to their oxo analogues. Theoretical modelling of these complexes demonstrates that charge localization at the multiply-bonded ligand (either O^{2-} or (TMSN^{2-})) is an essential component of the ITI.

The uranium(V) trimethylsilylimido complexes $[[(\text{R}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{V}}(\text{NSiMe}_3)]$ ⁵² (**1-R**, with $\text{R} = t\text{-Bu}$, Ad) can be oxidized with AgSbF_6 to yield the uranium(VI) imido complexes $[[(\text{R}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{VI}}(\text{NSiMe}_3)]\text{SbF}_6$ (**2-R**, see Scheme 2). Addition of one equivalent of AgSbF_6 to cold, dark-brown methylene chloride solutions of **1-R** results in an immediate colour change to black. After filtration through celite and removal of the solvent *in vacuo*, the uranium(VI) compounds **2-t-Bu** and **2-Ad** are obtained in near quantitative yields. In contrast to the previously reported C_s U(VI) mono(oxo) species, an exclusively axial coordination mode of the imido ligands is observed in both the *tert*-butyl as well as the sterically more encumbered adamantyl derivatized uranium(VI) imido complexes. The coordination modes were established by ¹H NMR spectroscopy, showing the C_3 symmetry to be present in solution (see ESI[†]), and confirmed by X-ray diffraction on single crystals of both compounds.

The structures of the imido complexes **2-t-Bu** (Fig. 1) and **2-Ad** (see ESI[†]) are very similar. Their U–N_{imido} bond distances are short, measuring 1.911(9) and 1.917(9) Å in **2-t-Bu** (two independent molecules) and 1.921(4) Å in **2-Ad**, consistent with previously reported U(VI)–N_{imido} distances.^{44,45} The N–Si bond lengths are 1.750(10) Å for the *t*-Bu (both independent molecules) and 1.745(4) Å for the adamantyl imido, and the U–N–Si angles for both complexes are essentially linear for both



Scheme 2 Oxidation of $[[(\text{R}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{V}}(\text{NSiMe}_3)]$ (**1-R**) with 1 equiv. AgSbF_6 to form $[[(\text{R}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{VI}}(\text{NSiMe}_3)]\text{SbF}_6$ (**2-R**).

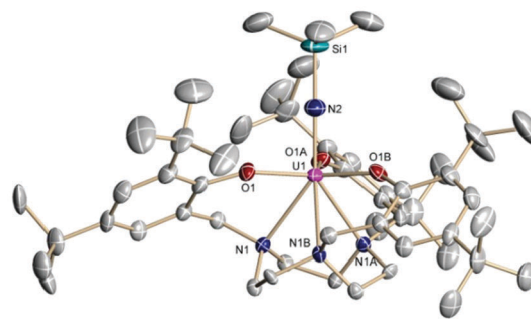


Fig. 1 Molecular structure of one of the two independent cations of $[[(\text{t-Bu}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{VI}}(\text{NSiMe}_3)]\text{SbF}_6$ in crystals of $[[(\text{t-Bu}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{VI}}(\text{NSiMe}_3)]\text{-SbF}_6 \cdot 0.5 [\text{Na}(\text{DME})_3]\text{SbF}_6 \cdot 1.5\text{DME}$ (**2-t-Bu**). Counter anion, co-crystallized solvent and NaSbF_6 , as well as hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 50% probability. Selected bond lengths (Å) and angles ($^\circ$): U–N_{imido}: 1.911(9)/1.917(9); N–Si: 1.752(10)/1.750(10); U–O: 2.137(3)/2.134(4); U–N_{tacn}: 2.617(4)/2.619(4); U–N–Si: 180.

complexes (**2-t-Bu**, 180.0° and **2-Ad**, 175.8(3)°). The slight deviation from linearity in **2-Ad** is due to the increased steric clash with the *ortho*-adamantyl ligand substituents. The uranium center lies 0.195 and 0.189 Å below the plane of the three aryloxo oxygen atoms for **2-t-Bu**, while the out-of-plane shift of **2-Ad** is smaller at 0.139 Å. This trend was found previously for isostructural complexes of the same chelating ligand system, *e.g.* $[[(\text{R}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{IV}}(\text{OME})]$ ⁵³ or $[[(\text{R}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{V}}(\text{O})]$,⁴⁷ and is related to the greater steric demand of the adamantyl *vs.* *tert*-butyl groups in the *ortho* position of the aryloxo ligand pendant arms. The isoelectronic oxo ligand leads to a markedly different geometry at the uranium center in contrast to the axially bound imido ligands of the uranium(VI) complexes **2-R**. In the compound with the sterically less encumbered *t*-Bu derivatized ligand, $[[(\text{t-Bu}^{\text{ArO}})_3\text{tacn}]\text{U}^{\text{VI}}(\text{O})]\text{SbF}_6$, the terminal oxo is coordinated within the equatorial plane, along with the three aryloxo arms of the chelating ligand and the U–O_{aryloxo} bond *trans* to the oxo ligand is shortened.⁴³

In order to understand these observed differences, and to compare the electronic structures of the U(VI) imido and U(VI) oxo complexes, restricted DFT calculations were carried out, employing a ZORA/TZP all-electron basis set on the axial and hypothetical equatorial isomers of **2-t-Bu** and **2-Ad**. While the calculation of **2-Ad** with an imido ligand hypothetically bound in the equatorial plane did not converge, suggesting instability of this geometrical isomer, calculations for both axial and equatorial imido coordination converged for **2-t-Bu**. However, for the axially bound imido ligand in **2-t-Bu_{ax}**, the U–N distance is calculated to be slightly shorter by 0.017 Å compared to the equatorial derivative. The calculated energy of **2-t-Bu_{ax}** is approximately 11 kcal mol^{−1} lower in absolute energy than **2-t-Bu_{eq}**, which fully agrees with the experimentally observed axial coordination of the imido ligand. For the respective oxo complexes the equatorial coordination was calculated to be more stable than the axial by approximately 6 kcal mol^{−1}. These data suggest that the ITI is weaker for the imido compound than for the oxo counterpart. Additionally, a simple consideration of the calculated Mulliken charge to oxidation number ratio for the experimentally observed isomers of **2-t-Bu_{ax}** (0.44 for 2.61/6) and



Table 1 Selected calculated bond lengths, Nalewajski–Mrozek bond indices, and Mulliken charges for **2-t-Bu_{ax}**, **2-t-Bu_{eq}**, **2-Ad_{ax}**, $[[(\text{}^t\text{-BuArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{O})_{\text{eq}}]^{+43}$ and $[[(\text{}^t\text{-BuArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{O})_{\text{ax}}]^{+43}$

Complex	Calc. bond length (and indice) ^a	Calc. Mulliken charge on U	Calc. Mulliken charge on TMSN _{nitrene} or O _{oxo}
2-t-Bu_{ax}	1.9122 (2.71)	+2.61	−0.52
2-t-Bu_{eq}	1.9294 (2.67)	+2.58	−0.57
2-Ad_{ax}	1.9143 (2.70)	+2.68	−0.65
$[[(\text{}^t\text{-BuArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{O})_{\text{eq}}]^{+43}$	1.8273 (2.67)	+2.52	−0.63
$[[(\text{}^t\text{-BuArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{O})_{\text{ax}}]^{+43}$	1.8348 (2.69)	+2.59	−0.61

^a Nalewajski–Mrozek bond indices.

$[[(\text{}^t\text{-BuArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{O})_{\text{eq}}]^{+43}$ (0.42 for 2.52/6) indicates that the U–O is slightly more covalent than the U–N bond in **2-t-Bu_{ax}**. This result is in contrast to the mid-valent uranium oxo and imido complexes studied by Maron, Eisenstein, and Andersen,^{5,9,10} and suggests that the increased oxidation state and accompanied decrease in energy of the 5f orbitals leads to better energy parity with O 2p orbitals than the N 2p orbitals.

While the steric demands of the trimethylsilylimido ligand are greater than for the oxo ligand, and thus steric influences should not be overlooked, DFT calculations clearly show that the U=O bond is more polarized than the U≡NR bond and that the charge localized at O (in the oxo) is substantially greater than that localized at N (in the imides) (Table 1). Specifically, for the model complexes of the experimentally observed isomers – **2-t-Bu_{ax}** and $[[(\text{}^t\text{-BuArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{O})_{\text{eq}}]^{+43}$ – the calculated charge on the TMSN^{2−} is substantially lower in magnitude than on the oxo (−0.52 *versus* −0.63). In line with this observation, the calculated charge on the TMSN^{2−} in the hypothetical imide isomer, **2-t-Bu_{eq}**, is of insufficient magnitude (−0.57) to induce a stabilizing ITI; and hence, is higher in energy than the axial isomer, **2-t-Bu_{ax}**. It should be noted that increased covalency with increased bond polarity are not conflicting trends. Covalency is driven both by valence orbital degeneracy and orbital overlap: the importance of both of these trends for determining the magnitude of covalent bonding is particularly pronounced in the f-elements.⁵⁴

Since the molecular orbital description of the ITI primarily,²⁵ but not exclusively, invokes involvement of a 6p orbital directed along the σ-bond axis we conclude that the oxo group induces the greater polarization of the metal atom core electrons. Mixing the 6p and the 5f orbitals induces a quadrupolar polarization because the orbitals are the same parity. This phenomenon leads to the observed shortening and strengthening of the bond to the *trans* disposed ligand. Consequently, the observed demand for a strong ligand coordinated *trans* to the terminal ligand (O^{2−} *vs.* TMSN^{2−}) is more pronounced in the oxo species, $[[(\text{}^t\text{-BuArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{O})_{\text{eq}}]\text{SbF}_6$.

In summary, we have synthesized terminal U(vi) imido complexes $[[(\text{}^R\text{ArO})_3\text{tacn})\text{U}^{\text{VI}}(\text{NSiMe}_3)]\text{SbF}_6$ **2-R**, with a conserved ligand framework, *via* oxidation of the U(v) compounds with AgSbF₆. Unlike the *t*-Bu derivative of the U(vi) complex with equatorial oxo coordination, for which ITI was shown previously to be a key feature, we find a different behaviour for the terminal imido complex **2-t-Bu**, with the imido group coordinating exclusively in the axial position. While DFT calculations suggest that coordination of the imido ligand in the equatorial position of the

2-t-Bu derivative (but not in **2-Ad**) would be sterically possible, this structure is higher in absolute energy and therefore is a disfavoured ground state geometry. These results show that polarization of the metal–ligand bond (and the resultant quadrupolar polarization of the metal core electrons) is a key factor in determining the magnitude of the ITI in actinide complexes.

This research was supported by the German Bundesministerium für Bildung und Forschung (BMBF 2020+, 02NUK012C), the Deutsche Forschungsgemeinschaft (DFG) within SFB 583 and ME1754/2-1. The FAU Erlangen-Nürnberg is gratefully acknowledged for financial support, as is COST Action CM1006. S.T.L. thanks the Royal Society, EPSRC, ERC, and University of Nottingham for support. This work is dedicated to the 60th birthday of Prof. Manfred Scheer (University of Regensburg).

Notes and references

- W. A. Nugent and J. A. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988.
- D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
- H. S. La Pierre, S. G. Minasian, M. Abubekurov, S. A. Kozimor, D. K. Shuh, T. Tylliszczak, J. Arnold, R. G. Bergman and F. D. Toste, *Inorg. Chem.*, 2013, **52**, 11650.
- W. A. Nugent, R. J. McKinney, R. V. Kasowski and F. A. Vancatledge, *Inorg. Chim. Acta*, 1982, **65**, L91.
- N. Barros, D. Maynau, L. Maron, O. Eisenstein, G. F. Zi and R. A. Andersen, *Organometallics*, 2007, **26**, 5059.
- L. P. Spencer, P. Yang, S. G. Minasian, R. E. Jilek, E. R. Batista, K. S. Boland, J. M. Boncella, S. D. Conradson, D. L. Clark, T. W. Hayton, S. A. Kozimor, R. L. Martin, M. M. MacInnes, A. C. Olson, B. L. Scott, D. K. Shuh and M. P. Wilkerson, *J. Am. Chem. Soc.*, 2013, **135**, 2279.
- T. L. Gianetti, H. S. La Pierre and J. Arnold, *Eur. J. Inorg. Chem.*, 2013, 3771.
- H. S. La Pierre, J. Arnold, R. G. Bergman and F. D. Toste, *Inorg. Chem.*, 2012, **51**, 13334.
- G. F. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen and R. A. Andersen, *Organometallics*, 2005, **24**, 4251.
- G. F. Zi, L. L. Blossch, L. Jia and R. A. Andersen, *Organometallics*, 2005, **24**, 4602.
- S. J. Meek, R. V. O'Brien, J. Lloveria, R. R. Schrock and A. H. Hoyveda, *Nature*, 2011, **471**, 461.
- R. E. Cramer, K. Panchanatheswaran and J. W. Gilje, *J. Am. Chem. Soc.*, 1984, **106**, 1853.
- T. W. Hayton, *Chem. Commun.*, 2013, **49**, 2888.
- T. W. Hayton, *Dalton Trans.*, 2010, **39**, 1145.
- S. T. Liddle, *Angew. Chem., Int. Ed.*, 2015, **54**, 8604.
- H. S. La Pierre and K. Meyer, *Prog. Inorg. Chem.*, 2014, **58**, 303.
- Z. Y. Zhang and R. M. Pitzer, *J. Phys. Chem. A*, 1999, **103**, 6880.
- R. G. Denning, in *Electronic Structure and Bonding in Actinyl Ions, in Structure and Bonding*, ed. D. M. P. Mingos, Springer-Verlag, Berlin, 1992, p. 215.
- K. Tatsumi and R. Hoffmann, *Inorg. Chem.*, 1980, **19**, 2656.
- W. R. Wadt, *J. Am. Chem. Soc.*, 1981, **103**, 6053.
- P. Pyykkö, L. J. Laakkönen and K. Tatsumi, *Inorg. Chem.*, 1989, **28**, 1801.



- 22 N. Kaltsoyannis, *Inorg. Chem.*, 2000, **39**, 6009.
- 23 R. G. Denning, J. C. Green, T. E. Hutchings, C. Dallera, A. Tagliaferri, K. Giarda, N. B. Brookes and L. Braicovich, *J. Chem. Phys.*, 2002, **117**, 8008.
- 24 S. Matsika and R. M. Pitzer, *J. Phys. Chem. A*, 2001, **105**, 637.
- 25 E. O'Grady and N. Kaltsoyannis, *J. Chem. Soc., Dalton Trans.*, 2002, 1233.
- 26 H. S. La Pierre and K. Meyer, *Inorg. Chem.*, 2013, **52**, 529.
- 27 D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717.
- 28 T. Vitova, J. C. Green, R. G. Denning, M. Loeble, K. Kvashnina, J. J. Kas, K. Jorissen, J. J. Rehr, T. Malcherek and M. A. Denecke, *Inorg. Chem.*, 2015, **54**, 174.
- 29 S. G. Minasian, J. L. Krinsky and J. Arnold, *Chem. – Eur. J.*, 2011, **17**, 12234.
- 30 A. J. Lewis, P. J. Carroll and E. J. Schelter, *J. Am. Chem. Soc.*, 2013, **135**, 13185.
- 31 A. J. Lewis, K. C. Mullane, E. Nakamaru-Ogiso, P. J. Carroll and E. J. Schelter, *Inorg. Chem.*, 2014, **53**, 6944.
- 32 D. M. King, F. Tuna, J. McMaster, W. Lewis, A. J. Blake, E. J. L. McInnes and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2013, **52**, 4921.
- 33 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.
- 34 D. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake and S. T. Liddle, *J. Am. Chem. Soc.*, 2014, **136**, 5619.
- 35 T. W. Hayton, J. M. Boncella, B. L. Scott, P. D. Palmer, E. R. Batista and P. J. Hay, *Science*, 2005, **310**, 1941.
- 36 T. W. Hayton, J. M. Boncella, B. L. Scott and E. R. Batista, *J. Am. Chem. Soc.*, 2006, **128**, 12622.
- 37 T. W. Hayton, J. M. Boncella, B. L. Scott, E. R. Batista and P. J. Hay, *J. Am. Chem. Soc.*, 2006, **128**, 10549.
- 38 R. E. Jilek, L. P. Spencer, R. A. Lewis, B. L. Scott, T. W. Hayton and J. M. Boncella, *J. Am. Chem. Soc.*, 2012, **134**, 9876.
- 39 N. H. Anderson, S. O. Odoh, Y. Yao, U. J. Williams, B. A. Schaefer, J. J. Kiernicki, A. J. Lewis, M. D. Goshert, P. E. Fanwick, E. J. Schelter, J. R. Walensky, L. Gagliardi and S. C. Bart, *Nat. Chem.*, 2014, **6**, 919.
- 40 N. H. Anderson, H. Yin, J. J. Kiernicki, P. E. Fanwick, E. J. Schelter and S. C. Bart, *Angew. Chem., Int. Ed.*, 2015, **54**, 9386.
- 41 D. S. J. Arney, C. J. Burns and D. C. Smith, *J. Am. Chem. Soc.*, 1992, **114**, 10068.
- 42 J. L. Kiplinger, D. E. Morris, B. L. Scott and C. J. Burns, *Chem. Commun.*, 2002, 30.
- 43 B. Kosog, H. S. La Pierre, F. W. Heinemann, S. T. Liddle and K. Meyer, *J. Am. Chem. Soc.*, 2012, **134**, 5284.
- 44 D. S. J. Arney and C. J. Burns, *J. Am. Chem. Soc.*, 1993, **115**, 9840.
- 45 D. S. J. Arney and C. J. Burns, *J. Am. Chem. Soc.*, 1995, **117**, 9448.
- 46 J. F. de Wet and J. G. H. du Preez, *J. Chem. Soc., Dalton Trans.*, 1978, 592.
- 47 S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein and K. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 12536.
- 48 S. Fortier, N. Kaltsoyannis, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 14224.
- 49 D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake and S. T. Liddle, *J. Am. Chem. Soc.*, 2012, **134**, 10047.
- 50 C. R. Graves, B. L. Scott, D. E. Morris and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2007, **129**, 11914.
- 51 C. R. Graves, P. Yang, S. A. Kozimor, A. E. Vaughn, D. L. Clark, S. D. Conradson, E. J. Schelter, B. L. Scott, J. D. Thompson, P. J. Hay, D. E. Morris and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2008, **130**, 5272.
- 52 I. Castro-Rodriguez, K. Olsen, P. Gantzel and K. Meyer, *J. Am. Chem. Soc.*, 2003, **125**, 4565.
- 53 B. Kosog, H. S. La Pierre, M. A. Denecke, F. W. Heinemann and K. Meyer, *Inorg. Chem.*, 2012, **51**, 7940.
- 54 M. W. Löble, J. M. Keith, A. B. Altman, S. C. E. Steiber, E. R. Batista, K. S. Boland, S. D. Conradson, D. L. Clark, J. Lezama Pacheco, S. A. Kozimor, R. L. Martin, S. G. Minasian, A. C. Olson, B. L. Scott, D. K. Shuh, T. Tyliczszak, M. P. Wilkerson and R. A. Zehnder, *J. Am. Chem. Soc.*, 2015, **137**, 2506.

