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Synthesis and Characterization of an f-Block Terminal Parent Imido [U=NH] Complex: A Masked Uranium(IV) Nitride

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S Supporting Information

ABSTRACT: Deprotonation of [U(Tren^{TIPS})(NH₂)] (**1**) [Tren^{TIPS} = N(CH₂CH₂NSiPrⁱ)₃] with organoalkali metal reagents MR (M = Li, R = Bu^t; M = Na–Cs, R = CH₂C₆H₅) afforded the imido-bridged dimers [{U(Tren^{TIPS})(μ-N[H]M)}₂] [M = Li–Cs (**2a–e**)]. Treatment of **2c** (M = K) with 2 equiv of 15-crown-5 ether (15C5) afforded the uranium terminal parent imido complex [U(Tren^{TIPS})(NH)][K(15C5)₂] (**3c**), which can also be viewed as a masked uranium(IV) nitride. The uranium–imido linkage was found to be essentially linear, and theoretical calculations suggested σ²π⁴ polarized U–N multiple bonding. Attempts to oxidize **3c** to afford the neutral uranium terminal parent imido complex [U(Tren^{TIPS})(NH)] (**4**) resulted in spontaneous disproportionation to give **1** and the uranium–nitride complex [U(Tren^{TIPS})(N)] (**5**); this reaction is a new way to prepare the terminal uranium–nitride linkage and was calculated to be exothermic by –3.25 kcal mol^{–1}.

An important class of metal–ligand multiple bonds is metal–imido linkages, L_nM=NR (L_n = coligands).¹ The R groups in L_nM=NR complexes are overwhelmingly bulky alkyl, silyl, or aryl substituents since these groups afford kinetic stabilization for the L_nM=NR linkage and impart crystallinity to the resulting complexes. Indeed, it is notable that in over 1800 crystallographically authenticated terminal metal–imido complexes the sterically undemanding metal terminal parent imido linkage L_nM=NH remains rare, accounting for less than 1% of structurally characterized terminal metal–imido bonds, with all examples confined to the d block.² In recent years there has been a surge of interest in terminal metal–ligand multiple bonds in the f block,³ in particular with uranium,⁴ for which examples of terminal U–imido^{4,5} and even U–nitride⁶ complexes are now known. However, despite the burgeoning nature of U–N multiple bonds, there is yet to be any report of a metal terminal parent imido linkage in the f block, presumably because large R groups are usually needed to afford kinetic stabilization at large f-element centers. Such complexes are of interest since they represent benchmarks for f-block–nitrogen multiple bonding and can also be considered to be protonated, masked nitrides, which is of note since molecular uranium nitrides remain relatively rare.^{7,8}

We recently reported the inadvertent formation of the uranium amide [U(Tren^{TIPS})(NH₂)] (**1**) [Tren^{TIPS} = N(CH₂CH₂NSiPrⁱ)₃].^{6b} We have now prepared **1** deliberately in high yield, making it an attractive precursor from which to target U–N multiple bonds. Here we show that deprotonation of **1** affords several uranium imido-bridged dimers, one of which can be converted into a uranium terminal parent imido complex. We also describe attempts to oxidize this complex that resulted in disproportionation to give **1** and a uranium(VI) nitride.

Complex **1** was previously isolated from the reaction of [U(Tren^{TIPS})] with [N₃][NBuⁿ]₄ in low yield (29%).^{6b} We have now found that **1** can be routinely prepared from [U(Tren^{TIPS})(Cl)]^{6a} and NaNH₂ and isolated in >90% yield,⁹ which renders **1** an attractive precursor to U–N multiple bonds. Noting that a terminal molybdenum carbide was successfully prepared from its conjugate base by deprotonation and alkali metal sequestration¹⁰ and that closely related uranium nitrides are dimeric,^{6a} we anticipated that deprotonation of **1** would give [{U(Tren^{TIPS})(N[H]M)}_n] (M = alkali metal), which could then undergo abstraction of M. Accordingly, treatment of **1** with *tert*-butyllithium or benzylsodium, -potassium, -rubidium, or -cesium afforded the alkali metal imido-bridged dimer complexes [{U(Tren^{TIPS})(μ-N[H]M)}₂] [M = Li–Cs (**2a–e**)] in yields varying from 22 to 89% as pale-pink crystalline solids after workup and recrystallization (Scheme 1). The characterization data for **2a–e** fully support the proposed formulations.⁹

To confirm the molecular structures of **2a–e**, we determined their structures by X-ray crystallography and found that the whole series adopts an essentially isostructural dimeric formulation constructed around centrosymmetric M₂N₂ rings; the structure of the representative potassium complex **2c** is illustrated in Figure 1.⁹ In **2a–e** the imido centers adopt distorted tetrahedral geometries, and other than the expected expansion of the M₂N₂ ring size as the group-1 metal becomes larger, the basic structural unit varies little over the entire size range of the group-1 metals. The imido H atoms could be located in the Fourier transform difference maps but were then restrained during refinement of these heavy-atom structures. The U1–N5 bond lengths in **2a–e** span the range 2.042(3) to 2.135(3) Å, with the longer U–N_{imido} bond lengths observed in the lighter alkali metal complexes. This can be rationalized on the basis that lithium and

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Scheme 1. Synthesis of 2a–e, 3c, and 5

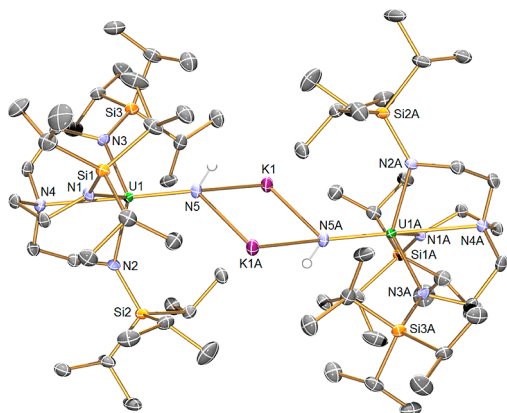
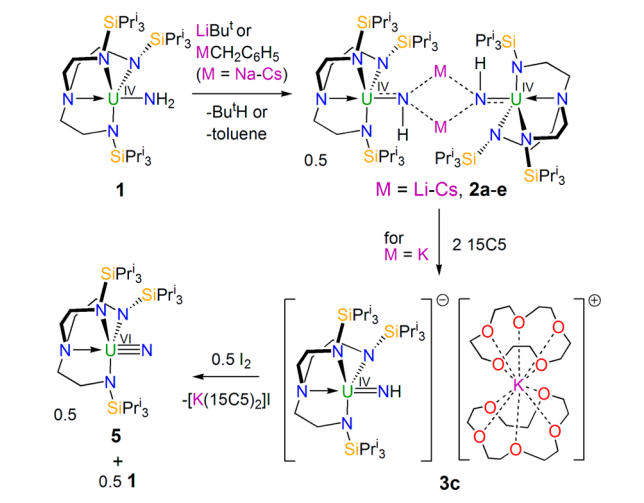


Figure 1. Structure of 2c (40% displacement ellipsoids; non-imido H atoms and agostic-type M...HC interactions omitted for clarity). Complexes 2a, 2b, 2d, and 2e are essentially isostructural.

sodium are more polarizing than the heavier alkali metals. Thus, the former polarize and lessen the electron density in the U–N_{imido} linkage more than the latter, resulting in the observed trend. Notably, however, the U–N_{imido} bond lengths in 2a–e are significantly shorter than the U–NH₂ bond length of 2.228(4) Å in 1,^{6b} reflecting the imido character of 2a–e compared with the amide character of 1. The U–N_{amide}, U–N_{amine}, and M–N bond lengths in 2a–e are unexceptional.¹¹

With 2a–e in-hand, we attempted to abstract the alkali metal cations. Attempts to remove the Li, Na, Rb, and Cs ions from 2a, 2b, 2d, and 2e with crown ethers and cryptands gave intractable, oily product mixtures that could not be conclusively identified. However, treatment of 2c with 2 equiv of 15-crown-5 ether (15C5) and stirring of the resulting oil in hexane afforded [U(Tren^{TIPS})(NH)][K(15C5)₂] (3c) as a pale-brown powder in 91% yield.⁹ The ¹H NMR spectrum exhibits four resonances, consistent with a C_{3v}-symmetric [U(Tren^{TIPS})(NH)][−] anion; however the imido hydrogen resonance could not be located. The UV/vis/NIR electronic absorption spectrum of 3c exhibits strong ligand-to-metal charge transfer bands that tail in from the UV region to around 15 000 cm^{−1} and weak ($\epsilon \leq 100$ M^{−1} cm^{−1}) absorptions in the 15000–5000 cm^{−1} range that are characteristic of Laporte-forbidden f–f transitions of U(IV).¹² The magnetic moment of 3c was found to be 2.8μ_B at 298 K; this decreased slowly upon cooling to ca. 80 K before falling more

precipitously, reaching 1.5μ_B at 1.8 K and continuing to decrease. Although this is not classical U(IV) magnetism,¹³ similar behavior has been observed before for U(IV) in C_{3v} symmetry with strongly donating axial ligands.¹⁴

The solid-state structure of 3c was determined by X-ray crystallography to confirm the separated ion pair formulation (Figure 2). The U1–N5 bond length was determined to be

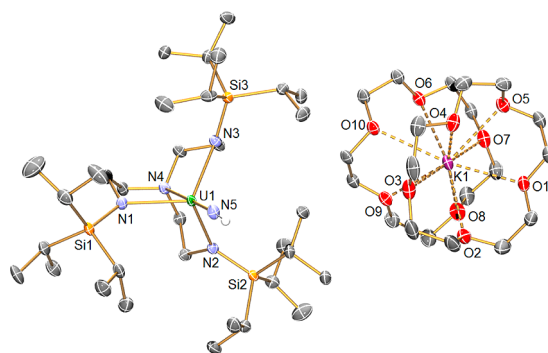
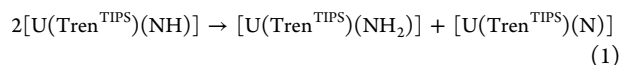


Figure 2. Structure of 3c (40% displacement ellipsoids; non-imido H atoms and minor disorder components omitted for clarity).

2.034(3) Å, which most likely reflects the anionic nature of [U(Tren^{TIPS})(NH)][−] in part counteracting the abstraction of an alkali metal to give a terminal U=NH linkage. However, the U–N_{imido} distance in 3c is 0.2 Å shorter than the U–NH₂ bond length in 1,^{6b} is only 0.07 Å longer than the sum of the double additive covalent radii of uranium and nitrogen,¹⁵ and compares well to terminal U(IV)=NR bond lengths (1.95–2.01 Å).¹⁶ The U–N_{amide} distances in 3c are indistinguishable from those of 2a–e, but the anionic and terminal nature of [U(Tren^{TIPS})(NH)][−] in 3c is apparent upon inspection of the U–N_{amine} bond, which is trans to the imido group and notably longer [2.749(3) Å] than the analogous distances in 2a–e [av 2.674(4) Å]. The imido H atom was located in the Fourier transform difference map and was refined with restraints, giving a U=N–H angle of 172(3)°.

With 3c isolated, we reasoned that it might be straightforward to oxidize because of its “ate” formulation. This would in principle enable isolation of the unknown U(V) terminal parent imido linkage in [U(Tren^{TIPS})(NH)] (4). We therefore treated 3c with 0.5 equiv of I₂, since this method previously afforded a uranium(VI) nitride from a uranium(V) nitride separated ion pair precursor.^{6b} However, although the I₂ was consumed, [K(15C5)₂]I was eliminated, and oxidation of 3c appeared to occur, we found that spontaneous disproportionation occurred, as evidenced by inspection of the ¹H NMR spectrum recorded within 10 min of a freshly prepared reaction between 3c and I₂, which showed only 1 and [U(Tren^{TIPS})(N)] (5) in a 1:1 ratio. Despite numerous attempts to trap 4 by performing reactions and workup at low temperature or adding potential Lewis acid traps, we could not isolate it.⁹ Nevertheless, this reaction represents a new way to prepare terminal uranium(VI) nitrides, although it is intrinsically limited to a 50% maximum yield.



In order to probe further the disproportionation reaction of 4 to give 1 and 5, we calculated the gas-phase enthalpy change (ΔH_{rxn}) for the reaction in eq 1 from single-point energy calculations on the geometry-optimized coordinates of 1, 4, and 5 and determined that this reaction is exothermic with $\Delta H_{\text{rxn}} =$

Table 1. Selected DFT, NBO, and QTAIM Data for the U–N (Primary Amide, Imido, or Nitride) Linkages in **1**, **3c**, **4**, and **5**

complex ^a	bond lengths and bond indices		atomic spin densities and charges			NBO σ component ^g			NBO π components ^g			QTAIM data ^h			
	U–N ^b	BI ^c	m_U^d	q_U^e	q_N^f	%N	%U	U 5f:6d	%N	%U	U 5f:6d	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$\epsilon(r)$
1	2.2443	0.64	2.32	2.36	–1.53	100	–	–	89.6	10.4	70:30	0.10	0.27	–0.03	0.38
3c	2.0022	1.75	2.34	2.33	–1.53	90.3	9.7	36:59	82.9	17.2	63:37	0.16	0.53	–0.08	0.04
4	1.9487	1.77	1.29	3.02	–1.69	88.2	11.8	40:56	77.0	23.1	78:22	0.18	0.57	–0.11	0.04
5	1.7795	2.92	–	3.79	–1.35	59.0	41.0	89:9	70.0	30.0	81:19	0.39	0.21	–0.30	0.06

^aAll of the complexes were geometry-optimized at the LDA VWN BP TZP/ZORA level. ^bCalculated U–N (primary amide, imido, or nitride) distances (Å). ^cMayer bond indices. ^dMDC-m α -spin densities on uranium. ^eMDC-q charges on uranium. ^fMDC-q charges on the primary amide, imido, or nitride. ^gNBO analyses; for the σ bonds, the remaining contributions are 7s/7p and $\leq 5\%$, and for **3c**–**5** the π components are the averages. ^hQTAIM topological electron density [$\rho(r)$], Laplacian [$\nabla^2\rho(r)$], electronic energy density [$H(r)$], and ellipticity [$\epsilon(r)$] BCP data for the U–N primary amide, imido, or nitride bonds. Except for $\epsilon(r)$, the data for **5** were taken from ref 6b.

–3.25 kcal mol^{–1}. This value suggests that disproportionation of **4** to **1** and **5** is thermodynamically favorable, consistent with our experimental observations, and it is germane to note that although U(V) can be kinetically stabilized, it is fundamentally unstable with respect to disproportionation to U(IV) and U(VI);¹⁷ these observations may suggest one reason why the U(V)=NH linkage has never been isolated, since there is not a kinetically stabilizing NR group.

In order to probe the electronic structure of the uranium–imido linkage in **3c**, we carried out density functional theory (DFT), natural bond orbital (NBO), and quantum theory of atoms in molecules (QTAIM) calculations on the anion of **3c** and models of **1**, **4**, and **5** (Table 1). Known experimental structural data compare very well to the computed gas-phase data, indicating that the calculations provide qualitative models.

The calculated MDC-q charges and MDC-m spin densities for **1**–**5** are typical of Tren complexes of U(IV)–U(VI).¹⁸ The Mayer bond indices (BIs) increase in going from **1** to **5**, reflecting the progression from amide to U(IV)–imido to U(V)–imido and finally to U(VI)–nitride. Although the BI for **5** is clearly consistent with a U≡N triple bond, the U–N_{imido} BIs in **3c** and **4** are substantially lower and are more consistent with the presence of formal double bonds. However, the linear U=N–H linkages in **3c** and **4** are suggestive of triple-bonding interactions. Inspection of the Kohn–Sham frontier molecular orbitals (FMOs) for **1** and **3c**⁹ reveal the HOMO and HOMO–1 orbitals to be of essentially pure 5f character, consistent with the ³H₄ ground state of U(IV). For **4**, only the HOMO is of essentially pure 5f character, consistent with the ²F_{5/2} ground state of U(V). For the U–NH₂ linkage in **1**, a $\sigma^2\pi^2$ bonding combination could be identified. For **3c** and **4**, $\sigma^2\pi^4$ bonding combinations could be found for the U–N_{imido} bonds, analogous to the U≡N triple-bond $\sigma^2\pi^4$ bonding interaction in **5**. For **3c** and **4**, the expected orbital energy trend of $\pi > \sigma$ was found, whereas this is reversed in **5**⁶ because of the very short U≡N bond in this compound. The MOs representing the principal interactions that constitute the U–imido bonds in **3c** and **4** are delocalized with significant Tren–N_{amide} contributions, and thus, we turned to NBO analysis to provide a chemically more intuitive description of the U–N_{imido} bonds in **3c** and **4** (Table 1).

The formal U–NH₂ σ bond of **1** was returned by NBO as a N lone pair; however, a highly polarized π bond was reported. NBO identified one σ - and two π -bonding interactions for **3c**–**5**. The imido N dominates the NBO breakdown of the U–N_{imido} bonding interactions in **3c** and **4**, which suggests the presence of highly polarized U–N_{imido} bonds, consistent with the calculated Mayer BIs. For the π bonds of **3c** and **4**, NBO suggests that the 5f orbitals dominate the U contribution, with

the 6d orbitals playing only a modest role; in contrast, for the σ -bonding components, the 6d contribution dominates. The oxidation of **3c** to **4** impacts on the nature of the U–N_{imido} bond; specifically, upon moving from **3c** to **4** the percentage contribution of U increases in both the σ and π bonds, and this trend continues upon moving to **5**. However, since this trend could reflect an adjustment of the relative energies of the parent atomic orbitals in the U–N_{imido} bonds in **3c** and **4** rather than an increase in covalent overlap of the FMOs,¹⁹ we examined these linkages using QTAIM.

For **1**–**5**, the calculations identified 3,–1 bond critical points (BCPs) for the U–amide, U–imido, and U–nitride linkages (Table 1). The topological electron densities [$\rho(r)$] of these BCPs vary from covalent (**5**) to polarized covalent (**3c** and **4**) to predominantly electrostatic with a minor covalent contribution (**1**). The Laplacians of these BCP electron densities [$\nabla^2\rho(r)$] for **1**–**5** are dominated by the heavy U center and consequently are uninformative. However, the increasingly negative BCP electronic energy density of the charge distribution [defined as $H(r) = G(r) + V(r)$, where $G(r)$ is the kinetic energy density and $V(r)$ is the potential energy] in moving from **1** to **5** supports the increase in covalency in going from **1** to **5** as revealed by the $\rho(r)$ data. The calculated BCP ellipticity parameters [$\epsilon(r)$] for **3c**–**5** are close to zero, confirming the triple-bonding U–N_{imido} and U–N_{nitride} interactions in these linkages;¹⁹ σ bonds and triple ($\sigma +$ two π) bonds present a spherical distribution of electron density perpendicular to the bond path ($\epsilon = 0$), whereas a double ($\sigma + \pi$) bond is asymmetric ($\epsilon > 0$). The ellipticity of the U–NH₂ BCP in **1** is consistent with a $\sigma + \pi$ bond and is comparable to that of the C=C BCP in ethylene (0.45).²⁰ Thus, the computational results suggest polarized, linear U–N triple bonding interactions in **3c** and **4**, in contrast to [U(Tren^{TIPS})(PH)][K(B15C5)₂] (B15C5 = benzo-15-crown-5 ether), which exhibits a bent U(IV)=PH double-bond interaction.²¹

We have reported the first f-block terminal parent imido complex, which can be viewed as a masked uranium(IV) nitride, and attempts to oxidize this complex to the neutral U(V) derivative resulted in disproportionation to the parent uranium(IV) amide and a uranium(VI) nitride. This reaction represents a new route to uranium nitrides and suggests one reason why U(V)=NH linkages are unknown to date. Calculations suggested that $\sigma^2\pi^4$ triple-bonding interactions are present in the U–N_{imido} linkages of **3c** and putative **4**.

■ ASSOCIATED CONTENT

📄 Supporting Information

Procedures and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988.
- (2) (a) Chatt, J.; Choukroun, R.; Dilworth, J. R.; Hyde, J.; Vella, P.; Zubieta, J. *Transition Met. Chem.* **1979**, *4*, 59. (b) Dilworth, J. R.; Henderson, R.; Dahlstrom, P.; Hutchinson, J.; Zubieta, J. *Cryst. Struct. Commun.* **1982**, *11*, 1135. (c) Dilworth, J. R.; Dahlstrom, P.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *71*, 21. (d) Herrmann, W. A.; Bogdanovic, S.; Poli, R.; Priermeier, T. *J. Am. Chem. Soc.* **1994**, *116*, 4989. (e) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448. (f) Dilworth, J. R.; Lewis, J. S.; Miller, J. R.; Zheng, Y. *J. Chem. Soc., Dalton Trans.* **1995**, 1357. (g) Hermann, W. A.; Stumpf, A. W.; Priermeier, T.; Bogdanovic, S.; Dufaud, V.; Basset, J.-M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2803. (h) McKarns, P. J.; Yap, G. P. A.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1996**, *35*, 5968. (i) Haug, A.; Strahle, J. Z. *Anorg. Allg. Chem.* **1998**, *624*, 1746. (j) Leung, W.-H.; Chim, J. L. C.; Williams, I. D.; Wong, W.-T. *Inorg. Chem.* **1999**, *38*, 3000. (k) Davies, S. C.; Hughes, D. L.; Janas, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sanders, J. R.; Silverston, J. E.; Sobota, P. *Inorg. Chem.* **2000**, *39*, 3485. (l) Huynh, M. H. V.; White, P. S.; John, K. D.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4049. (m) Blanc, F.; Chabanas, M.; Coperet, C.; Fenet, B.; Herdweck, E. *J. Organomet. Chem.* **2005**, *690*, 5014. (n) Yandulov, D. V.; Schrock, R. R. *Inorg. Chem.* **2005**, *44*, 1103. (o) Cugny, J.; Schmale, H. W.; Fox, T.; Blacque, O.; Alfonso, M.; Berke, H. *Eur. J. Inorg. Chem.* **2006**, 540. (p) Watanabe, D.; Gondo, S.; Seino, H.; Mizobe, Y. *Organometallics* **2007**, *26*, 4909. (q) Tran, B. L.; Washington, M. P.; Henckei, D. A.; Gao, X.; Park, H.; Pink, M.; Mindiola, D. J. *Chem. Commun.* **2012**, *48*, 1529.
- (3) (a) Giesbrecht, G. R.; Gordon, J. C. *Dalton Trans.* **2004**, 2387. (b) Summerscales, O. T.; Gordon, J. C. *RSC Adv.* **2013**, *3*, 6682.
- (4) (a) Ephritikhine, M. *Dalton Trans.* **2006**, 2501. (b) Hayton, T. W. *Dalton Trans.* **2010**, *39*, 1145. (c) Hayton, T. W. *Chem. Commun.* **2013**, *49*, 2956.
- (5) Selected examples: (a) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853. (b) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514. (c) Zalkin, A.; Brennan, J. G.; Andersen, R. A. *Acta Crystallogr.* **1988**, *C44*, 1553. (d) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237. (e) Arney, D. S.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068. (f) Arney, D. S.; Burns, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 9840. (g) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959. (h) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 4565. (i) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941. (j) Castro-Rodriguez, I.; Nakai, H.; Meyer, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2389. (k) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R.; Hay, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10549. (l) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 11914. (m) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536. (n) Evans, W. J.; Traina, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 17473. (o) Korobkov, I.; Gambarotta, S. *Inorg. Chem.* **2010**, *49*, 3409.
- (6) (a) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Science* **2012**, *337*, 717. (b) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Nat. Chem.* **2013**, *5*, 482.
- (7) (a) Green, D. W.; Reedy, G. T. *J. Chem. Phys.* **1976**, *65*, 2921. (b) Hunt, R. D.; Yustein, J. T.; Andrews, L. *J. Chem. Phys.* **1993**, *98*, 6070. (c) Pyykkö, P.; Li, J.; Runeberg, N. *J. Phys. Chem.* **1994**, *98*, 4809. (d) Heinemann, C.; Schwarz, H. *Chem.—Eur. J.* **1995**, *1*, 7. (e) Zhou, M.; Andrews, L. *J. Chem. Phys.* **1999**, *111*, 11044. (f) Kaltsoyannis, N. *Inorg. Chem.* **2000**, *39*, 6009. (g) Andrews, L.; Wang, X.; Lindh, R.; Roos, B. O.; Marsden, C. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 5366.
- (8) (a) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 3433. (b) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Science* **2005**, *309*, 1835. (c) Evans, W. J.; Miller, K. A.; Ziller, J. W.; Greaves, J. *Inorg. Chem.* **2007**, *46*, 8008. (d) Nocton, G.; Pécaut, J.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3040. (e) Fox, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 5716. (f) Fox, A. R.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2010**, *132*, 3250. (g) Fortier, S.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 6888. (h) Todorova, T. K.; Gagliardi, L.; Walensky, J. R.; Miller, K. A.; Evans, W. J. *J. Am. Chem. Soc.* **2010**, *132*, 12397. (i) Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista, E. R.; Kiplinger, J. L. *Nat. Chem.* **2010**, *2*, 723. (j) Camp, C.; Pécaut, J.; Mazzanti, M. *J. Am. Chem. Soc.* **2013**, *135*, 12101.
- (9) See the Supporting Information for full details.
- (10) Peters, J. C.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1995.
- (11) (a) Berthet, J. C.; Ephritikhine, M. *Coord. Chem. Rev.* **1998**, *178–180*, 83. (b) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.
- (12) Mills, D. P.; Moro, F.; McMaster, J.; Van Slageren, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Nat. Chem.* **2011**, *3*, 454.
- (13) Castro-Rodriguez, I.; Meyer, K. *Chem. Commun.* **2006**, 1353.
- (14) (a) Patel, D.; Tuna, F.; McInnes, E. J. L.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem., Int. Ed.* **2013**, *52*, 13334. (b) Brown, J. L.; Fortier, S.; Lewis, R. A.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2012**, *134*, 15468. (c) Patel, D.; Moro, F.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 10388.
- (15) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770.
- (16) (a) Arney, D. S.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448. (b) Zi, G.; Jia, L.; Werkema, E. L.; Walter, M. D.; Gottfriedsen, J. P.; Andersen, R. A. *Organometallics* **2005**, *24*, 4251. (c) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272. (d) Jilek, R. E.; Spencer, L. P.; Kuiper, D. L.; Scott, B. L.; Williams, U. J.; Kikkawa, J. M.; Schelter, E. J.; Boncella, J. M. *Inorg. Chem.* **2011**, *50*, 4235. (e) Matson, E. M.; Crestani, M. G.; Fanwick, P. E.; Bart, S. C. *Dalton Trans.* **2012**, *41*, 7952.
- (17) (a) Selbin, J.; Ortego, J. D. *Chem. Rev.* **1969**, *69*, 657. (b) Graves, C. R.; Kiplinger, J. L. *Chem. Commun.* **2009**, 3831.
- (18) (a) Gardner, B. M.; McMaster, J.; Lewis, W.; Liddle, S. T. *Chem. Commun.* **2009**, 2851. (b) Liddle, S. T.; McMaster, J.; Mills, D. P.; Blake, A. J.; Jones, C.; Woodul, W. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1077. (c) Gardner, B. M.; McMaster, J.; Moro, F.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Chem.—Eur. J.* **2011**, *17*, 6909. (d) Gardner, B. M.; Patel, D.; Cornish, A. D.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Chem.—Eur. J.* **2011**, *17*, 11266. (e) Gardner, B. M.; Patel, D.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 10440. (f) Gardner, B. M.; Stewart, J. C.; Davis, A. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 9265. (g) King, D. M.; Tuna, F.; McMaster, J.; Lewis, W.; Blake, A. J.; McInnes, E. J. L.; Liddle, S. T. *Angew. Chem., Int. Ed.* **2013**, *52*, 4921.
- (19) (a) Walensky, J. R.; Martin, R. L.; Ziller, J. W.; Evans, W. J. *Inorg. Chem.* **2010**, *49*, 10007. (b) Kaltsoyannis, N. *Inorg. Chem.* **2013**, *52*, 3407. (c) Neidig, M. L.; Clark, D. L.; Martin, R. L. *Coord. Chem. Rev.* **2013**, *257*, 394.
- (20) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.
- (21) Gardner, B. M.; Balázs, G.; Scheer, M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem., Int. Ed.* **2014**, DOI: 10.1002/anie.201400798.