ChemComm

Quantitative U=O bond activation in uranyl complexes via silyl radical transfer

Journal:	*ChemComm*
Manuscript ID	CC-COM-08-2022-004424.R1
Article Type:	Communication

COMMUNICATION

Quantitative U=O bond activation in uranyl complexes via silyl radical transfer

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Leyla R. Valerio,[a] Brett M. Hakey,[a] William W. Brennessel,[a] and Ellen M. Matson*[a]

Reductive silylation of the uranyl dication with 1,4-bis(trimethylsilyl)dihydropyrazine, or "Mashima's Reagent", is detailed. The substrate simultaneously delivers silylium ions and electrons to multiple uranyl complexes (e.g. pyridine dipyrrolide uranyl complex and a common uranyl-containing starting material, $UO_2Cl_2(OPPh_3)_2$). This results in quantitative activation of thermodynamically robust U=O bonds. The reductive functionalization of environmentally persisent actinyl species with Mashima's reagent is seen as a promising solution for nuclear waste remediation.

The uranyl dication $[UO_2]^{2+}$ is one of the most common forms of uranium that is found in the environment and in nuclear waste.[1] The ubiquity of this ion in the environment is concerning, in part due to the high water solubility and ensuing mobility that this moiety possesses.[2] The uranium–oxygen bonds in uranyl ions are also short and strong, resulting in chemically inert oxo groups that are resistant to activation or functionalization.[1,2] Investigations designed to better understand the bonding and reactivity of these robust bonds has thus become a central point of study in the pursuit of nuclear waste remediation.

Several approaches to functionalize U=O bonds in the uranyl dication have been reported, the most popular being the use of reductive cleavage via reactivity with silylium ions (**Figure 1**).[4,5] One of the first reported examples detailing activation of the uranyl(VI) dioxo moiety was detailed by Ephritikhine in 2006, in upon the addition of excess silylating reagent (Me_3SiX, where X = Cl, Br, or I), $UO_2I_2(THF)_3$ or $UO_2(OTf)_2$ are converted to a tetravalent uranium halide salt, $UX_4(MeCN)_4$.[3] This reactivity leverages the thermodynamic driving force of the formation of strong Si–O bonds, facilitating the reductive cleavage of uranium oxygen bonds through the oxidation of the corresponding halide.[6] Further insight into the mechanism of U=O bond activation via reductive silylation was later reported by Love and co-workers; in this work, coordination of a uranyl ion to a rigid, wedge-shaped macrocyclic "Pacman" ligand results in the generation of a highly oxidizing uranyl complex capable of cleaving N–Si and C–Si bonds to form singly silyl-functionalized pentavalent uranyl complexes.[4] The authors find that insertion of a second metal into the pocket of the "Pacman" ligand facilitates activation of the U=O at the opposite side of the molecule. Hayton later showed the reductive silylation of both oxo groups on uranyl can be accomplished through the addition of an excess of Me_3SiI to $UO_2(^{Ar}acnac)_2$, resulting in the displacement of one $^{Ar}acnac$ ligand and the formation of $U^V(OSiMe_3)_2I_2(^{Ar}acnac)$.[7]

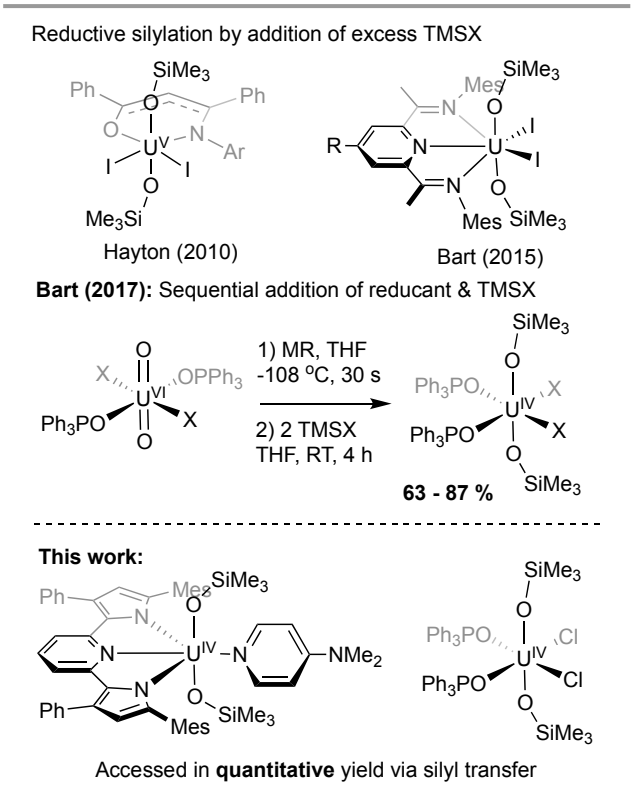
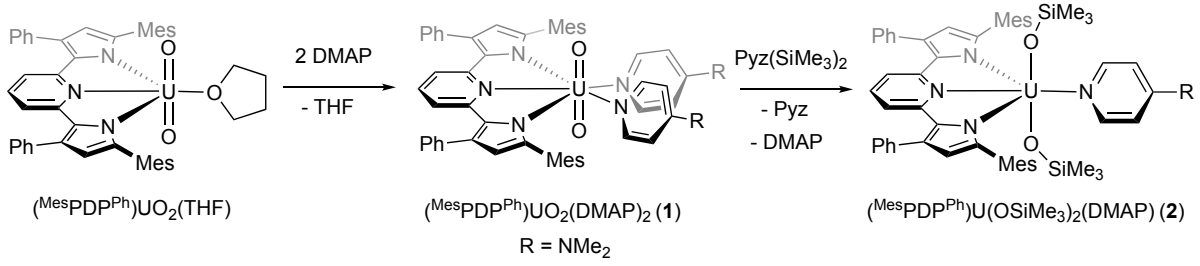


Figure 1. (Top) Previously reported uranium-siloxide complexes accessed through reductive silylation of a uranyl precursor; (Bottom) Summary of this work which describes quantitative formation of uranium(IV) bis-siloxide compounds accessed through silyl radical transfer.

[a] *Department of Chemistry, University of Rochester, Rochester NY 14627 USA*
Electronic Supplementary Information (ESI) available: Synthetic procedures and spectroscopic data (^{1}H NMR, UV-Vis, NIR) for complexes formed in this report. CCDC 2192830-2192831 Crystallographic parameters for complexes **1** and **2**. See DOI: 10.1039/x0xx00000x

Scheme 1. Synthesis of (^{Mes}PDP^{Ph})UO_2(DMAP)$_2$ (**1**) and (^{Mes}PDP^{Ph})U(OSiMe$_3$)$_2$(DMAP) (**2**).

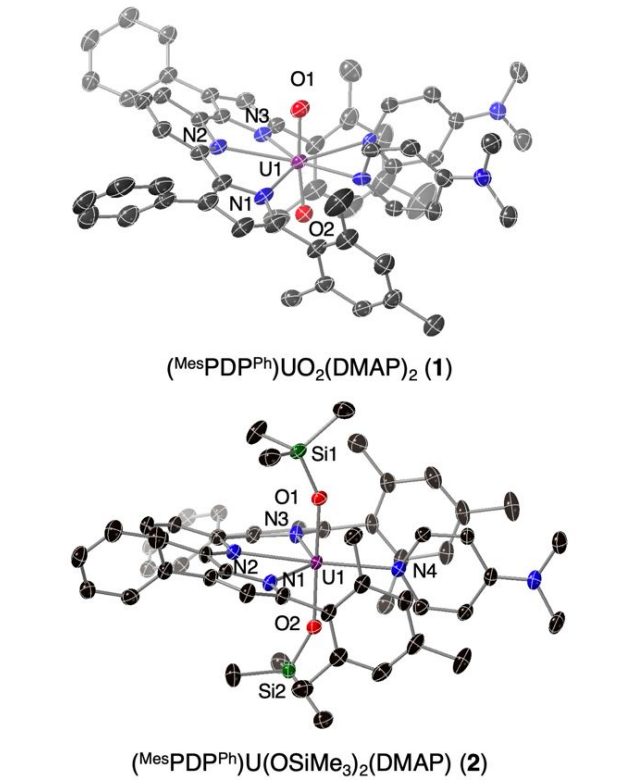


(^{Mes}PDP^{Ph})UO_2(THF) (^{Mes}PDP^{Ph})UO_2(DMAP)$_2$ (**1**) (^{Mes}PDP^{Ph})U(OSiMe$_3$)$_2$(DMAP) (**2**)

In all examples described above, U=O bond activation appears to proceed through a reductive pathway, resulting in the formation of a reduced uranium centre. This redox reaction is essential for U=O bond activation. However, many reports require modification of the reduction potential of the uranyl dication through ligand engineering. For example, in the Pacman complexes published by Love & Arnold, ligation of the uranyl ion to the macrocyclic polypyrrole ligand results in the formation of an easily reduced uranium(VI) centre with a secondary coordination sphere poised for cation binding that assists in the activation of the U=O bond. An exception to this is a report from Bart and co-workers describing a general route for the reductive silylation of the UO_2^{2+} ion.[6] The authors describe the use of stoichiometric amounts of alkylating reagent to transiently generate U^{VI} bis-alkyl complexes. Reductive elimination of these substituents is promoted by the introduction of Me_3SiX (X = Cl, Br, I), resulting in a change in formal oxidation state from $U^{VI} \rightarrow U^{IV}$. The separate addition of reductant and silylium ion invokes the formation of unstable intermediates, limiting the efficiency of U=O bond activation.

As opposed to the separate addition of reductant and substrate that has been reported previously when reducing the uranyl moiety, one can envision a concerted pathway where U=O bond activation is achieved through the addition of a silyl radical. Such a mechanism would be analogous to proton-coupled electron transfer (PCET).[8] PCET is ubiquitous in nature, providing low overpotential pathways for redox reactions.[9,10] More recently, PCET from molecular donors has been used to incorporate hydrogen atom equivalents into metal oxides, allowing for the activation of typically inert substrates by avoiding high-energy intermediates.[11,12] In a similar vein, silylium-coupled electron transfer presents as an intriguing alternative to streamline the mechanism of U=O bond activation. Mashima and co-workers have demonstrated that the silyl transfer reagent, 1,4-bis(trimethylsilyl)dihydropyrazine, $Pyz(SiMe_3)_2$, called "Mashima's reagent", can facilitate the reduction of transition metals in high oxidation states. Initial work focused on the reduction of group 4-6 metal chloride complexes, resulting in the generation of low-valent metal species in a salt-free process.[13] These findings were later extended to the deoxygenation of molecularly defined M=O fragments, leading to the formation of O-atom defects poised for small molecule activation and catalysis.[14,15]

Previously, our research group has reported the synthesis and characterization of a uranyl complex supported by a sterically encumbered pyridine dipyrrolide (PDP) ligand, (^{Mes}PDP^{Ph})UO_2(THF) (**Scheme 1**).[16] This compound exhibits a rich electrochemical profile, including a reversible $U^{VI/V}$ couple centred at -1.22 V (vs. $Fc^{+/0}$ in THF with 0.1 M [^{n}Bu$_4$N][PF$_6$] as supporting electrolyte), suggesting it would make an excellent candidate for the investigation of electron coupled silylium ion transfer for U=O bond activation. Addition of 1 equiv of Mashima's reagent (2 equiv of •SiMe$_3$) to (^{Mes}PDP^{Ph})UO_2(THF) at low temperature results in colour change from dark brown to bright yellow over the course of fifteen minutes (see supporting information for more details). Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy revealed the presence of several paramagnetically shifted and broadened resonances, ranging from +60 to -40 ppm (Figure S1). The presence of these signals suggests successful reduction of the f^0, U^{VI} ion. However, inconsistencies in relative magnitudes of individual resonances were observed on a "batch-to-batch" basis, suggesting the formation of multiple products (Figure S2). We hypothesized



(^{Mes}PDP^{Ph})UO_2(DMAP)$_2$ (**1**)

(^{Mes}PDP^{Ph})U(OSiMe$_3$)$_2$(DMAP) (**2**)

Figure 2. Molecular structures of **1** (top) and **2** (bottom) shown with 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent molecules have been removed for clarity.

that the irregularity in reaction outcomes might be attributed to activation of the coordinated solvent molecule, which has been observed in similar systems.[6,17,18]

To alleviate challenges associated with tetrahydrofuran present in the reaction mixture, ligand exchange of the coordinated solvent molecule with a more basic and less reactive ligand, 4-dimethylaminopyridine (DMAP), was performed. Addition of two equivalents of DMAP to an equivalent of (^{Mes}PDP^{Ph})UO_2(THF) in benzene results in a slight color change of the solution from dark brown to dark red-brown (Scheme 1; see supporting information for details). Characterization of the reaction mixture by ^{1}H NMR spectroscopy reveals a systematic, downfield shift of resonances from that of (^{Mes}PDP^{Ph})UO_2(THF) (Figure S3). Loss of the signals associated with the THF ligand (3.77 and 1.46 ppm), and the presence of three new broadened resonances (8.55, 6.15, and 2.36 ppm) is indicative of successful ligand substitution at the uranyl ion (Figure S4). Interestingly, characterization of the product by single crystal X-ray crystallography reveals coordination of two DMAP molecules to the uranium centre, affording (^{Mes}PDP^{Ph})UO_2(DMAP)$_2$ (**1**; **Figure 2**, Table S1). We believe that this is an artifact of the low temperature of crystallization, as integration of the ^{1}H NMR spectrum of **1** suggests that in solution, only a single DMAP molecule is bound.

With the DMAP-adduct of the uranyl compound isolated, we revisited reductive silylation via Mashima's reagent. The addition of 1 equiv of Pyz($SiMe_3$)$_2$ to **1** results in an immediate color change from dark red-brown to vibrant yellow over the course of fifteen minutes (Scheme 1). Characterization of the product by ^{1}H NMR spectroscopy reveals 13 paramagnetically shifted and broadened resonances, consistent with a C_2v symmetric product (Figure S5). Notably, a signal with a relative integration of 18 H was located at 49.87 ppm, assigned to two trimethylsiloxide ligands, consistent with the reduction of the uranyl fragment to a uranium(IV) bis-siloxide species. The formation of pyrazine in the reaction mixture is evidenced by a signal at 8.5 ppm with a relative integration of ≈4 protons (Figure S5), consistent with the quantitative transfer of silyl radicals. This data suggests successful reduction of **1** by Mashima's reagent with a 90% yield. Formation of a tetravalent uranium center was confirmed by electronic absorption spectroscopy; sharp *f→f* transitions observed in the near infrared region of the spectrum are consistent with reduction of $U^{VI} \rightarrow U^{IV}$ (**Figure 3**).

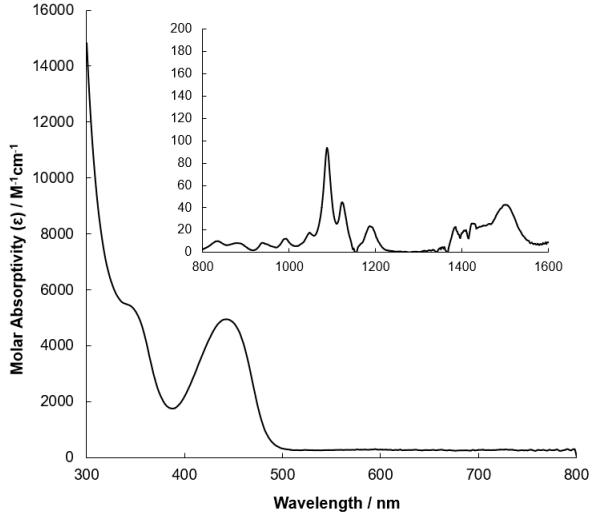


Figure 3. Electronic absorption spectra of (^{Mes}PDP^{Ph})U($OSiMe_3$)$_2$(DMAP) (**2**) in dichloromethane at ambient temperature. Inset shows *f→f* transitions observed the near-infrared region of the spectrum.

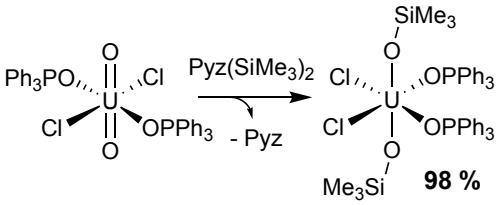
Crystals of the product suitable for X-ray analysis were grown from a concentrated diethyl ether solution of the compound at -30 °C. Structural refinement revealed formation of the desired silylated complex, (^{Mes}PDP^{Ph})U($OSiMe_3$)$_2$(DMAP) (**2**; **Figure 3**, Table S1). The U-O bonds in 2 (2.114(2) Å, 2.123(2) Å) have been significantly elongated from that of the starting material (U-O (1): 1.780(2), 1.781(2) Å), consistent with the reduction of bond order upon activation of the uranyl moiety. These bond distances resemble values reported previously for trans-siloxide uranium(IV) complexes generated via reductive silylation of a uranyl precursor (2.053 – 2.219 Å).[19] Within error, dative interactions between the pyridine substituents and uranium centre remain the same as the higher valent starting material; notably, the U-$N_{pyrrolide}$ bonds (U1-N1, U1-N3) are significantly shorter in **2** (2.369(3), 2.371(3) Å) as compared to the starting material, **1** (2.489(3), 2.493(2) Å). Truncation in uranium-$N_{pyrrolide}$ distances upon reduction of the metal center have been observed, on average, previously.[19-23] However, the U-$N_{pyrrolide}$ bond distances in **2** are amongst the shortest reported for uranium(IV)-pyrrolide species (U^{IV}-$N_{pyrrolide}$ = 2.389 - 2.507 Å).[24-26] We credit the unique coordination environment of the pyridine dipyrrolide pincer ligand for the observed short U-$N_{pyrrolide}$ distances.

To compare reductive silylation of the uranyl fragment via addition of Mashima's reagent to traditional U=O bond activation routes involving the addition of a source of a silylium ion (R_3Si^+), we explored the reactivity of **1** with an excess of TMSI. Reaction conditions mirrored those reported previously for formation of reduced, uranium siloxide assemblies; complex **1** was stirred in dichloromethane with 10 equiv of TMSI. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy revealed an apparent mixture of multiple products (Figure S6). However, a set of paramagnetically shifted and broadened resonances consistent with compound **2** was identified, suggesting that the bis-siloxide complex is indeed one product of the reaction of **1** with TMSI. However, under these reaction conditions, the yield of **2** is limited, due to the generation of at least one other paramagnetic uranium containing product. These results further support our hypothesis that the simultaneous delivery of an electron and a silylium ion is critical for quantitative reduction of the $[UO_2]^{2+}$ ion.

To assess the role the pyridine dipyrrolide ligand plays in facilitating the reduction of the uranyl dication, we next explored the generality of U=O bond activation through the addition of Mashima's reagent to $UO_2Cl_2(OPPh_3)_2$. Previously, Bart and co-workers have reported reductive silylation of this

form of the uranyl dication via the step wise addition of alkylating agent and trimethylsilylhalide.[6] This reaction results in the reduction of the uranyl fragment to a U^{IV} bis-siloxide compound in good yield (73%). It is possible that separate addition of reductant and silylium ion results in the formation of unstable uranyl bis-alkyl intermediates that lower the yield of the overall transformation. Thus, we hypothesized that addition of Mashima's reagent, which is anticipated to deliver an electron and silylium ion in a single concerted step in the form of a silyl radical (•$SiMe_3$), would improve the yield of U=O bond activation. Accordingly, addition of 1 equiv of $Pyz(SiMe_3)_2$ to a yellow dichloromethane solution of $UO_2Cl_2(OPPh_3)_2$ at low temperature yields a clear solution (**Scheme 2**). Characterization of the crude product by ^{1}H NMR spectroscopy reveals four paramagnetically shifted and broadened resonances (δ = 50.33, 4.11, 2.52, -17.54 ppm; Figure S7). The ^{1}H NMR spectrum is identical to that reported by Bart in 2017 for $[(Me_3SiO)_2UCl_2(OPPh_3)_2]$, indicating successful reduction of the uranyl ion. Isolation of the product is consistent with quantitative conversion to the bis-siloxide product (98 % yield) – a significant improvement over that reported by Bart and co-workers, presumably as a result of obviating the need to generate the uranyl/metal alkyl mixture. The mechanism of silyl radical transfer to reduce the uranium centre in these reactions is unclear, but ongoing efforts in our laboratory are focused on understanding this mechanism in full.

Scheme 2. Synthesis of $UCl_2(OSiMe_3)_2(OPPh_3)_2$ via addition of Mashima's reagent to $UO_2Cl_2(OPPh_3)_2$.



A facile method for U=O bond activation by reductive silylation in a pyridine dipyrrolide complex using Mashima's reagent is reported. Importantly, the ability of Mashima's reagent to perform silylium-coupled electron transfer obviates the need to access unstable intermediates that arise from sequential addition of reductant and a silylium ion. Moreover, the utility of Mashima's reagent in this context is also demonstrated to be a general approach for uranyl functionalization; as addition of $Pyz(SiMe_3)_2$ to a common uranyl compound, $UO_2Cl_2(OPPh_3)_2$, results in the quantitative formation of the bis-siloxide uranium(IV) product, $(Me_3SiO)_2U(OPPh_3)_2Cl_2$. In summary, we anticipate that these results may offer a promising strategy for nuclear waste remediation via the reductive functionalization of hazardous and environmentally persistent actinyl species.[27]

This research was funded by the Department of Energy, Office of Basic Energy Sciences Heavy Element Program, under award DE-SC0020436. The authors have no conflicts to declare.

Notes and references

1 R. G. Denning, *J. Phys. Chem. A.,* 2007, **111**, 4125-4143.
2 P. L. Arnold, J. B. Love, and D. Patel, *Coord. Chem. Rev.,* 2009, **253**, 1973-1978.
3 J. Berthet, G. Siffredi, P. Thuery, and M. Ephritikhine, *Eur. J. Inorg*. *Chem*., 2007, 4017-4020.
4 P. L. Arnold, D. Patel, C. Wilson, and J. B. Love*, Nature*, 2008, **451**, 315-318.
5 S. Fortier and T. W. Hayton*, Coord. Chem. Rev.*, 2010, **254**, 197-214.
6 J. J. Kiernicki, M. Zeller, and S. C. Bart, *Angew. Chem. Int. Ed.,* 2017, **56**, 1097-1100.
7 J. L. Brown, G. Wu, and T. W. Hayton, *Inorg. Chem.,* 2010, *132*, 7248-7249.
8 J. Chu, T. G. Carroll, G. Wu, J. Telser, R. Dobrovetsky, and G. Ménard, *J. Am. Chem. Soc.,* 2018, **140, 45,** 14375-15383.
9 E. Odella, S. J. Mora, B. L. Wadsworth, J. J. Goings, M. A. Gervaldo, L. E. Sereno, T. L. Groy, D. Gust, T. A. Moore, G. F. Moore, S. Hammes-Schiffer, and A. L. Moore, *Chem. Sci.,* 2020, **11**, 3820-3828.
10 D. R. Weinberg, C. J. Gagliardi, J. F. Hull, C. F. Murphy, C. A. Kent, B. C. Westlake, A. Paul, D. H. Ess, D. G. McCafferty, and T. J. Meyer, *Chem. Rev.,* 2012, **112**, 4016-4093.
11 E. Schreiber, A. F. Fertig, W. W. Brennessel, and E. M. Matson, *J. Am. Chem. Soc.,* 2022, **144**, 5029-5041.
12 J. N. Schrauben, R. Hayoun, C. N. Valdez, M. Braten, L. Fridley, and J. M. Mayer, *Science*, 2012, **336**, 1298-1301.
13 T. Saito, H. Nishiyama, H. Tanahashi, K. Kawakita, H. Tsurugi, and K. Mashima, *J. Am. Chem. Soc.,* 2014, **136**, 5161-5170.
14 V. Mougel, K. Chan, G. Siddiqi, K. Kawakita, H. Nagae, H. Tsurugi, K. Mashima, O. Safonova, and C. Copéret, *Cent. Sci.,* 2016, **2**, 569-576.
15 S. Chakraborty and E. M. Matson, *Inorg. Chem. Front.,* 2021, **8**, 4507-4516.
16 B. M. Hakey, D. C. Leary, L. M. Lopez, L. R. Valerio, W. W. Brennessel, C. Milsmann, and E. M. Matson, *Inorg. Chem.,* 2022, **61**, 6182-6192.
17 H. C. Brown, S. Krishnamurthy, and R. A. Coleman, *J. Am. Chem. Soc.,* 1972, **94**, **5**, 1750-1751.
18 B. Birkmann, T. Voss, S. J. Geier, M. Ullrich, G. Kehr, G. Erker, and D. W. Stephan, *Organometallics,* 2010, **29**, **21**, 5310-5319.
19 B. E. Cowie, J. M. Purkis, J. Austin, J. B. Love, and P. L. Arnold, *Chem. Rev.,* 2019, **119**, 10595-10637.
20 I. Korobkov, S. Gambarotta, and G. P. A. Yap, *Organometallics*, 2001, **20**, 2552-2559.
21 Z. Bao, H. Zhao, N. Qu, G. Schreckenbach, and Q. Pan, *Dalton Trans.,* 2016, **45**, 15970-15982.
22 M. Suvova, K. T. P. O'Brien, J. H. Farnaby, J. B. Love, N. Kaltsoyannis, and P. L. Arnold, *Organometallics*, 2017, **36**, 4669-4681.
23 K. C. Mullane, Doctoral dissertation, University of Pennsylvania, Philadelphia, 2017.
24 J. L. Brown, G. Wu, and T. W. Hayton, *Inorg. Chem.,* 2011, **50**, 5105-5112.
25 J. J. Kiernicki, D. P. Cladis, P. E. Fanwick, M. Zeller, and S. C. Bart, *J. Am. Chem. Soc.,* 2015, **137**, 11115-11125.
26 J. R. Pankhurst, N. L. Bell, M. Zegke, L. N. Platts, C. A. Lamfsus, L. Maron, L. S. Natrajan, S. Sproules, P. L. Arnold, and J. B. Love, *Chem. Sci.,* 2017, **8**, 108-116.
27 B. R. Mohapatra, O. Dinardo, W. D. Gould, and D. W. Koren, *Miner. Eng.,* 2010, **23**, 591-599.