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Dioxygen reacts with metal-carbon bonds in thorium dialkyls to produce bis(alkoxides)

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Exposure of bis-amidinate and -guanidinate supported thorium dialkyl complexes to dioxygen results in facile oxygen atom insertion and formation of the corresponding thorium dialkoxide species. Preliminary mechanistic studies suggest a radical propagation mechanism is operative. All new complexes were fully characterized by ¹H and ¹³C NMR spectroscopy, IR, EA and X-ray crystallography.

The chemical oxidation of inert C-H bonds in hydrocarbons to produce value-added products is a major goal of academic and industrial research for its implications in a variety of commercial processes.^{1,2} Molecular oxygen presents itself as an ideal oxidant, due to its natural availability, non-existent environmental impact, and low cost. As a result, many industries have adapted to use molecular oxygen as their oxidant of choice.¹ However, the use of expensive and environmentally hazardous oxidants still persists in many industries,³ as oxidation with molecular oxygen can be difficult to control, often leading to undesirable side reactions such as overoxidation.⁴ While late transition metal complexes and catalysts have generally proven themselves to be powerful tools for generating value-added products,^{3,5} their utility in processes involving molecular oxygen remains unrealized due to a poor understanding of how oxygen reacts with these species.⁶ The Goldberg group has made great progress to address this and have investigated a number of mechanistic steps in the reaction of oxygen with various late transition metal complexes.⁷⁻¹² However, a major drawback to these systems is the high cost of the precious metals involved.

While the use of early transition metals to facilitate such reactions would have the added benefit of low cost due to the

relative earth abundance of these metals, even less is known about how oxygen reacts with d⁰ transition metal complexes.¹³⁻²⁰ Wolczanski and co-workers were able to observe insertion of molecular oxygen into titanium and zirconium dialkyl species supported by the tritox ligand (tritox = (tBu)₃CO) and formation of the corresponding alkoxide complexes.¹³ Mechanistic investigations on this system indicated a radical propagation mechanism, was responsible for the observed reactivity, and the poorly electron-donating nature of the tritox ligand (and increased electrophilicity of the metal center) was partly responsible for the inner sphere attack by either oxygen or the propagating radical species.¹⁴

Intrigued by the results observed with group IV metals, we were curious to see if appropriately tailored thorium complexes would undergo similar molecular oxygen reactivity, as the debate regarding whether thorium behaves more like a group IV transition metal or actinide is still ongoing.²¹ While there have been studies regarding the reactivity of thorium and oxygen in argon and neon matrices at 10 and 4 K, respectively,²² to the best of our knowledge no accounts describing molecular thorium species are known that report similar reactivity to that observed in early transition metal systems. Our group has previously described the reactivity of a thorium monoalkyl complex supported by a tris-amidinate framework with chalcogen-atom transfer reagents²³ and a variety of small molecules;²⁴ we envisioned a similar, bis-amidinate, dialkyl thorium system may be suitable for reactivity with molecular oxygen. Additionally, the more electron-donating guanidinate ligand,^{25,26} of which there are currently no thorium complexes known, would serve as a useful comparison regarding the effect of metal electrophilicity on reaction kinetics. Herein, we present the synthesis and characterization of thorium dialkyl amidinate and guanidinate complexes, as well as their reactivity towards molecular oxygen.

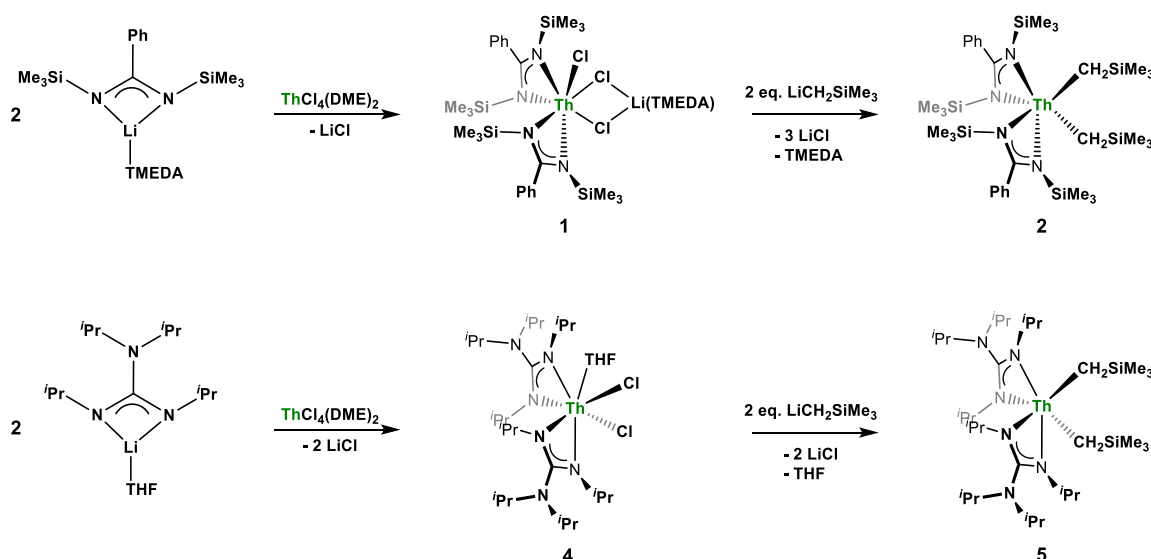
Although our previous studies employed the bis(isopropyl)methylamidinate (BIMA) ligand, attempted syntheses of a ThX₂(BIMA)₂ complex (where X = halide) were

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^c Dedicated to Professor Geoff Cloke – a master in the art of synthetic chemistry – on the occasion of his 65th birthday.

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Scheme 1 Syntheses of analogous amidinate (**1** and **2**) and guanidinate (**4** and **5**) thorium complexes.

unsuccessful. Eisen and co-workers were successful utilizing a bulkier *N,N'*-bis(trimethylsilyl)-2-pyridylamidinate ligand,²⁷ so we turned to *N,N'*-bis(trimethylsilyl)benzamidinate (BTBA), for its ease of synthesis and prior use with actinide metals.^{28–30} Salt metathesis of $\text{ThCl}_4(\text{DME})_2$ ³¹ with 2 equiv. of $\text{Li}(\text{BTBA})(\text{TMEDA})$ ³² (TMEDA = tetramethylethylenediamine) afforded $\text{Th}(\text{BTBA})_2\text{Cl}(\mu\text{-Cl})_2\text{Li}(\text{TMEDA})$ (**1**) as large, colorless blocks in 78% yield (Scheme 1). The ¹H NMR spectrum of **1** exhibits equivalent amidinate ligands in solution, with only one observable resonance for the -SiMe₃ protons at δ 0.34 ppm and phenyl resonances appearing at δ 7.35 and 7.03 ppm, as well as two singlets at δ 2.07 and 1.72 ppm corresponding to the TMEDA-methyl and methylene protons, respectively. The molecular structure of **1** was determined by single-crystal X-ray diffraction studies (Figure S17). The Th-N_{amid} bond distances are typical of that observed with previous thorium amidinate complexes,^{24,25,27,29} while the terminal Th-Cl1 bond length of 2.7030(8) Å is, as expected, noticeably shorter than those observed for the bridging chlorides (2.8148(8) and 2.7999(6) Å for Th-Cl2 and Th-Cl3, respectively). The thorium, lithium and two bridging chlorides exhibit a dihedral angle of ~9° and form a nearly flat metallacycle, and is similar to that seen with the 2-pyridyl system reported by Eisen (dihedral angle of ~5°).²⁷ Electron delocalization is observed throughout the amidinate ligands, as all the C-N bond lengths fall between 1.33–1.34 Å.

With **1** in hand, we looked to synthesize the corresponding dialkyl complex; addition of 2 equiv. of $\text{LiCH}_2\text{SiMe}_3$ to a stirred solution of **1** in toluene resulted in immediate precipitation of LiCl, followed by a gradual color change from colorless to orange. This orange color could be avoided by decreasing the reaction time to only a few minutes. Nonetheless, standard workup followed by crystallization from hexane afforded the dialkyl complex $\text{Th}(\text{BTBA})_2(\text{CH}_2\text{SiMe}_3)_2$ (**2**) as colorless crystals in 76% yield (Scheme 1). ¹H NMR spectroscopy of **2** confirms the incorporation of alkyl moieties as indicated by the presence of new singlets arising from the methylene and -SiMe₃ protons at δ 0.42 and 0.51 ppm, respectively. The molecule exhibits

averaged C₂-symmetry in solution, as there is only a single set of peaks corresponding to the alkyl and amidinate ligands. Interestingly, the alkyl methylene resonance is significantly more downfield than that observed in $\text{Th}(\text{CH}_2\text{SiMe}_3)(\text{BIMA})_3$ (δ -0.08 ppm),²³ and may be indicative of a more electrophilic thorium center in **2**. The methylene singlet serves as a diagnostic NMR handle for determining the success of insertion reactions. Single-crystals of **2** were grown from a concentrated hexane solution, and the molecular structure was determined by X-ray diffraction studies (Figure S18). Two molecules crystallize in the asymmetric unit, thus the metrics discussed henceforth are an average of the two. Although the thorium center is six-coordinate, the ligand geometry around the metal center is pseudo-tetrahedral, similar to that seen in $\text{Th}(\text{BIMA})_4$.²⁴ The average Th-C bond length of 2.492(5) Å is shorter than that seen in $\text{Th}(\text{CH}_2\text{SiMe}_3)(\text{BIMA})_3$ (2.557(3) Å), but is typical of those of other thorium (IV) complexes bearing the -CH₂SiMe₃ ligand.^{33–38} The Th-C-Si bond angle of 125.1(2)° is ~10° more acute than in $\text{Th}(\text{CH}_2\text{SiMe}_3)(\text{BIMA})_3$, which may be due to the less congested nature of the bis-amidinate system. Th-N_{amid} bond distances range from 2.440(3) to 2.566(3) Å while the C-N bonds within the amidinates fall between 1.32–1.35 Å and are typical of that seen with other thorium amidinate complexes.^{23,24,39–41}

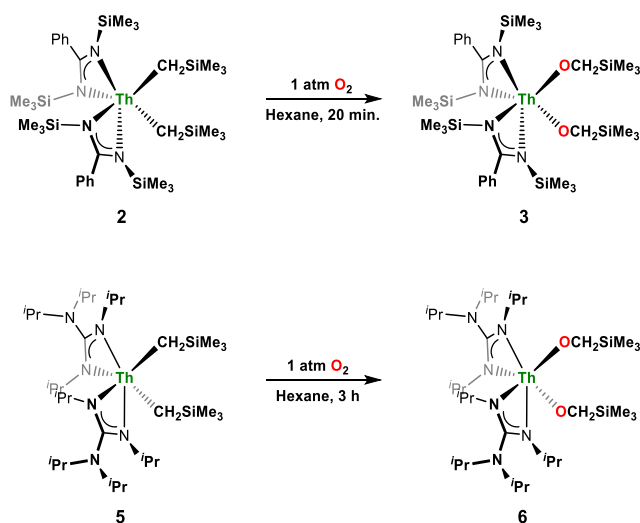
With **2** synthesized, we sought to see if this complex would mimic the reactivity seen by group IV tritox systems with molecular oxygen.^{13,14} Exposure of a C₆D₆ solution of **2** to dry oxygen resulted in conversion to a new product in less than five minutes. The most striking change in the ¹H NMR spectrum is the methylene resonance of the alkyl substituents, which shifts downfield from δ 0.42 to δ 4.18 ppm. We attribute this dramatic shift to the deshielding nature of the oxygen atom on the methylene protons. This new product was tentatively assigned as $\text{Th}(\text{BTBA})_2(\text{OCH}_2\text{SiMe}_3)_2$ (**3**, Scheme 2). Scaling up the reaction revealed the highly soluble nature of **3**, which had to be isolated from minimal amounts of hexamethyldisiloxane (HMDSO). Fortuitously, X-ray quality crystals were obtained

from a highly concentrated HMDSO solution of **3** stored at -35°C for 24 h, which confirmed the identity of **3** as the O_2 insertion product (Figure 1). The Th-O1 and Th-O2 bond distances of 2.133(4) and 2.127(4) Å, respectively, are similar to the Th-O bond length of 2.1663(15) Å seen in $\text{Th}(\text{OCH}_2\text{NMe}_2)(\text{BIMA})_3$ ²³ and fall in the range observed for known thorium alkoxide and aryloxide species.⁴²⁻⁴⁵ The near linear Th-O1-C27 and Th-O2-C31 bond angles of $175.4(3)^{\circ}$ and $169.4(3)^{\circ}$, respectively, are also consistent with these similar complexes. The Th-N_{amid} bond distances range from 2.508(4) to 2.577(4) Å, while the C-N bond distances in the amidinate fall in between 1.32-1.34 Å. Next, we were curious if this insertion reaction was operating by a radical mechanism analogous to Wolczanski's group IV tritox complexes. However, carrying out the conversion of **2** to **3** in the presence of 1,4-cyclohexadiene did not produce an appreciable amount of tetramethylsilane (the product expected to form if the $\bullet\text{CH}_2\text{SiMe}_3$ radical species was present), and the rate of formation of **3** was not noticeably affected. This does not disprove the radical-based mechanism, though, as the kinetics of formation of **3** may be significantly faster than radical abstraction by 1,4-cyclohexadiene.

With the amidinate dialkyl complex successfully able to insert O_2 to form the dialkoxide, we turned our attention to the analogous thorium guanidinate complex to probe what effect the more electron-donating guanidates would have on O_2 insertion. The similar steric profile combined with our success using the *N, N, N', N''*-tetraisopropylguanidinate (TIG) ligand with uranium²⁶ prompted us to utilize this ligand for the synthesis of our analogous thorium complex. Salt metathesis of $\text{ThCl}_4(\text{DME})_2$ with 2 equiv. of $\text{Li}(\text{TIG})(\text{THF})$ ⁴⁶ afforded $\text{Th}(\text{TIG})_2\text{Cl}_2(\text{THF})$ (**4**) in 56% yield (Scheme 1). Slow addition of $\text{Li}(\text{TIG})(\text{THF})$ is critical for the clean formation of the target bis-guanidinate species **4**, as the tris-guanidinate complex $\text{Th}(\text{TIG})_3\text{Cl}$ is readily formed in the presence of excess $\text{Li}(\text{TIG})(\text{THF})$.

The bound THF molecule in **4** is important for crystallization but can be removed under dynamic vacuum. The ^1H NMR spectrum of **4** exhibits two different isopropyl environments on the TIG ligand, with two septets and two doublets observed in total, and indicates averaged C_2 -symmetry of the molecule in solution. The solid-state structure of **4** features two Th-Cl distances of 2.673(1) and 2.746(1) Å, a Cl1-Th-Cl2 bond angle of $115.19(3)^{\circ}$, and a Th-O1 bond length of 2.564(3) Å; these values are typical of those seen in similar thorium dichloride complexes with a bound THF molecule (Figure S19).^{47,48} Exposing **4** to 2 equiv. of $\text{LiCH}_2\text{SiMe}_3$ produced the desired bis-guanidinate thorium dialkyl complex $\text{Th}(\text{TIG})_2(\text{CH}_2\text{SiMe}_3)_2$ (**5**, Scheme 1) in 96% yield. The ^1H NMR spectrum of **5** contains one new set of peaks attributable to the alkyl moieties; however, the methylene singlet is now seen further upfield at δ 0.21 ppm (compared to δ 0.42 in **2**), possibly indicating a more electron-rich metal center. The molecular structure of **5** was determined by X-ray diffraction studies (Figure S20); **5** crystallizes in the monoclinic space group $\text{C}2/c$, with half of the molecule in the asymmetric unit. The Th-C14 bond length of 2.528(2) Å is similar to that seen in $\text{Th}(\text{CH}_2\text{SiMe}_3)(\text{BIMA})_3$ and **2**, and the Th-C14-Si1 bond angle of $126.22(10)^{\circ}$ is only 1° larger than that observed in **2**. All other crystallographic metrics are unremarkable.

Exposing a C_6D_6 solution of **5** to 1 atm of O_2 resulted in the formation of a new product with a downfield singlet appearing in the ^1H NMR spectrum at δ 4.22 ppm, along with shifted resonances corresponding to the TIG ligand and $-\text{SiMe}_3$ protons on the alkyl moieties. Based on these results, we concluded that O_2 insertion had been achieved and $\text{Th}(\text{TIG})_2(\text{OCH}_2\text{SiMe}_3)_2$ (**6**) had been formed (Scheme 2). This transformation occurred more slowly than that seen with **2**, with completion times routinely taking >3 h when monitored by ^1H NMR spectroscopy. We postulated that the kinetics of O_2 insertion had indeed been slowed due to the increased electron-richness of the thorium metal center caused by the guanidinate ligands, although the role of the different steric profile of TIG vs. BTBA cannot be discounted. Due to the poorer solubility of the TIG framework, **6** could be isolated as colorless, block crystals in 89% yield from hexane. The molecular structure of **6** was determined by X-ray diffraction studies (Figure 1); like that observed with **5**, complex **6** crystallizes in the monoclinic space group $\text{C}2/c$, with half of the molecule in the asymmetric unit. Perhaps the most noticeable feature of this structure is the orientation of the alkyl groups, with the moieties almost eclipsed; the dihedral angle between the SiMe_3 groups (defined by the Si- CH_2 - CH_2 -Si atoms of the two SiMe_3 moieties) is $21.9(1)^{\circ}$ in **6** (compared to $164.8(3)^{\circ}$ in **3**). Although this kind of packing was not observed



Scheme 2 Syntheses of dialkoxide thorium species (**3** and **6**) by reaction of amidinate and guanidinate alkyl complexes with O_2 .

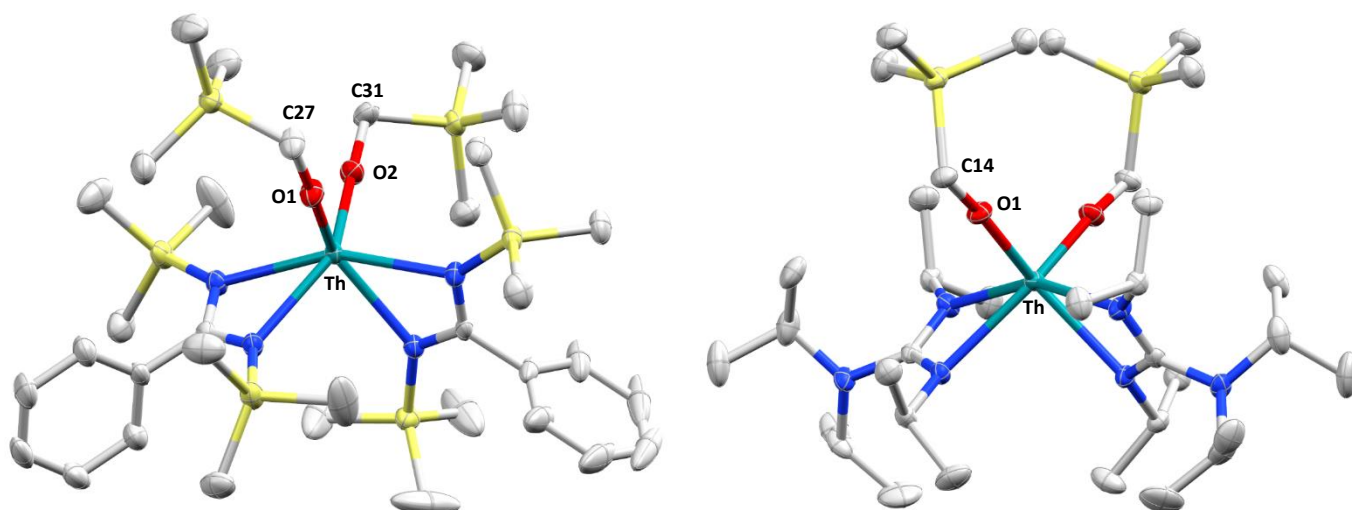


Fig. 1 Molecular structures of **3** (left) and **6** (right). Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity.

in **3**, it is presumably the lowest energy conformation for this molecule, and not the result of additional intramolecular interactions. The Th-O1 bond length of 2.1525(18) Å and Th-O1-C14 bond angle of 170.52(16)° are all consistent with those observed in **3**.

With the kinetics of O₂ insertion slowed for **5** compared to that of **2**, we looked to see if we could perform the same trapping experiment we had attempted using 1,4-cyclohexadiene to find evidence for a radical-based mechanism (Scheme S1). Three NMR-scale experiments were run in Teflon-capped J-Young NMR tubes simultaneously and monitored over a period of 5 days to test this: first, as a control, a sample of **5** was subjected to 1,4-cyclohexadiene in C₆D₆, which brought about no observable change to the ¹H NMR spectrum. Second, a sample of **5** in C₆D₆ was subjected to dry O₂, and the rate of conversion to **6** was monitored as judged by the ratio of **6**:**5**. Lastly, a sample of **5** in C₆D₆ containing 1,4-cyclohexadiene was subjected to dry O₂ and the rate of conversion to **6** was monitored similarly. All samples contained an internal standard of hexamethylbenzene. When the O₂ experiment was carried out in the presence of 1,4-cyclohexadiene, the generation of tetramethylsilane increased and the rate of formation of **6** decreased (Figures S13-16). Additional experiments showed that increasing the amount of 1,4-cyclohexadiene decreased the amount of **6** formed and increased the amount of tetramethylsilane generated. However, in the presence of excess 1,4-cyclohexadiene the conversion of **5** to **6** did not proceed cleanly, and this increase in SiMe₄ cannot be conclusively stated to be the result of hydrogen abstraction by •CH₂SiMe₃ radicals, as it may be the result of decomposition of **5**. Considering this evidence and prior literature precedent,¹⁴ we hypothesize that a radical-based mechanism similar to that observed with group IV tritox species is operative in the formation of **3** and **6** (Scheme S1), and that the greater electron-donating nature of the guanidinate ligand plays a role in affecting the kinetics of the reaction. This is consistent with Wolczanski's assertion that the electrophilicity of the metal center is important in synthesizing systems capable of this

reactivity. However, these results are very preliminary and the possibility of an α-O insertion mechanism¹⁸ cannot be ruled out; more thorough investigations are necessary to give credence to the proposed mechanism for these amidinate and guanidinate systems.

In summary, the amidinate- and guanidinate-supported thorium dialkyl complexes **2** and **5** undergo oxygen atom insertion to form the corresponding dialkoxide species. This type of reactivity is seldom seen with early metal systems and, until now, has not been reported with the oxophilic actinides. Probing the mechanism of this reactivity provided initial evidence for a radical-based mechanism, although further experiments are necessary to confirm this theory. This is consistent with the mechanism likely operative with group IV metal systems. The electrophilicity of the metal center plays an important role in the ability of O₂ to react with these actinide systems, as was evidenced by the kinetic differences in the amidinate and guanidinate frameworks.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 F. Cavani and J. H. Teles, *ChemSusChem*, 2009, **2**, 508-534.
- 2 L. Boisvert and K. I. Goldberg, *Acc. Chem. Res.*, 2012, **45**, 899-910.
- 3 R. A. Sheldon, I. Arends and U. Hanefeld, *Green Chemistry and Catalysis*; Wiley-VCH: Weinheim, Germany, 2007; Chapter 4.
- 4 *Active Oxygen in Chemistry*; C. S. Foote, J. S. Valentine, A. Greenberg and J. F. Liebman, Eds.; Blackie Academic & Professional: London, 1995.
- 5 H.-J. Arpe, *Industrial Organic Chemistry*, 5th ed.; Wiley-VCH: Weinheim, Germany, 2010.
- 6 T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.*, 2005, **105**, 2329-2363.
- 7 D. D. Wick and K. I. Goldberg, *J. Am. Chem. Soc.*, 1997, **119**, 10235-10236.
- 8 B. S. Williams and K. I. Goldberg, *J. Am. Chem. Soc.*, 2001, **123**, 2576-2587.
- 9 M. P. Jensen, D. D. Wick, S. Reinartz, P. S. White, J. L. Templeton and K. I. Goldberg, *J. Am. Chem. Soc.*, 2003, **125**, 8614-8624.
- 10 N. A. Smythe, K. A. Grice, B. S. Williams and K. I. Goldberg, *Organometallics*, 2009, **28**, 277-288.
- 11 G. R. Fulmer, R. P. Muller, R. A. Kemp and K. I. Goldberg, *J. Am. Chem. Soc.*, 2009, **131**, 1346-1347.
- 12 G. R. Fulmer, A. N. Herndon, W. Kaminsky, R. A. Kemp and K. I. Goldberg, *J. Am. Chem. Soc.*, 2011, **133**, 17713-17726.
- 13 T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1985, **107**, 701-703.
- 14 T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1987, **109**, 424-435.
- 15 C. Stanciu, M. E. Jones, P. E. Fanwick and M. M. Abu-Omar, *J. Am. Chem. Soc.*, 2007, **129**, 12400-12401.
- 16 T. D. Tilley, *Organometallics*, 1985, **4**, 1452-1457.
- 17 S. C. Hunter, S.-J. Chen, C. A. Stern, M. G. Richmond and Z.-L. Xue, *Organometallics*, 2015, **34**, 5687-5696.
- 18 S.-J. Chen and Z.-L. Xue, *Organometallics*, 2010, **29**, 5579-5584.
- 19 R. Wang, X.-H. Zhang, S.-J. Chen, X. Yu, C.-S. Wang, D. B. Beach, Y.-D. Yu and Z.-L. Xue, *J. Am. Chem. Soc.*, 2005, **127**, 5204-5211.
- 20 A. Van Asselt, M. S. Trimmer, L. M. Henling and J. E. Bercaw, *J. Am. Chem. Soc.*, 1988, **110**, 8254-8255.
- 21 A. Yahia and L. Maron, *Organometallics*, 2009, **28**, 672-679.
- 22 L. Andrews, Y. Gong, B. Liang, V. E. Jackson, R. Flamerich, S. Li and D. A. Dixon, *J. Phys. Chem. A*, 2011, **115**, 14407-14416.
- 23 N. S. Settineri, M. E. Garner and J. Arnold, *J. Am. Chem. Soc.*, 2017, **139**, 6261-6269.
- 24 N. S. Settineri and J. Arnold, *Chem. Sci.*, 2018, **9**, 2831-2841.
- 25 A. K. Maity, A. J. Metta-Magaña and S. Fortier, *Inorg. Chem.*, 2015, **54**, 10030-10041.
- 26 N. S. Settineri, A. A. Shiao and J. Arnold, *Chem. Commun.*, 2018, **54**, 10913-10916.
- 27 E. Rabinovich, S. Aharonovich, M. Botoshansky and M. S. Eisen, *Dalton Trans.*, 2010, **39**, 6667-6676.
- 28 M. Wedler, H. W. Roesky and F. T. Edelman, *J. Organomet. Chem.*, 1988, **345**, C1-C3.
- 29 M. Wedler, F. Knösel, M. Noltemeyer and F. T. Edelman, *J. Organomet. Chem.*, 1990, **388**, 21-45.
- 30 C. Camp, N. Settineri, J. Lefèvre, A. R. Jupp, J. M. Goicoechea, L. Maron and J. Arnold, *Chem. Sci.*, 2015, **6**, 6379-6384.
- 31 T. Cantat, B. L. Scott and J. L. Kiplinger, *Chem. Commun.*, 2010, **46**, 919-921.
- 32 V. Volkis, E. Nelkenbaum, A. Lisovskii, G. Hasson, R. Semiat, M. Kapon, M. Botoshansky, Y. Eishen and M. S. Eisen, *J. Am. Chem. Soc.*, 2003, **125**, 2179-2194.
- 33 C. M. Fendrick, E. A. Mintz, L. D. Schertz and T. J. Marks, *Organometallics*, 1984, **3**, 819-821.
- 34 R. J. Butcher, D. L. Clark, S. K. Grumbine, B. L. Scott and J. G. Watkin, *Organometallics*, 1996, **15**, 1488-1496.
- 35 C. A. Cruz, D. J. H. Emslie, L. E. Harrington, J. F. Britten and C. M. Robertson, *Organometallics*, 2007, **26**, 692-701.
- 36 D. L. Clark, S. K. Grumbine, B. L. Scott and J. G. Watkin, *Organometallics*, 1996, **15**, 949-957.
- 37 C. A. Cruz, D. J. H. Emslie, C. M. Robertson, L. E. Harrington, H. A. Jenkins and J. F. Britten, *Organometallics*, 2009, **28**, 1891-1899.
- 38 J. W. Bruno, G. M. Smith, T. J. Marks, C. K. Fair, A. J. Schultz and J. M. Williams, *J. Am. Chem. Soc.*, 1986, **108**, 40-56.
- 39 W. J. Evans, J. R. Walensky, J. W. Ziller and A. L. Rheingold, *Organometallics*, 2009, **28**, 3350-3357.
- 40 I. S. R. Karmel, T. Elkin, N. Fridman and M. S. Eisen, *Dalton Trans.*, 2014, **43**, 11376-11387.
- 41 I. S. R. Karmel, N. Fridman and M. S. Eisen, *Organometallics*, 2015, **34**, 636-643.
- 42 C. E. Hayes, Y. Sarazin, M. J. Katz, J.-F. Carpentier and D. B. Leznoff, *Organometallics*, 2013, **32**, 1183-1192.
- 43 J. M. Berg, D. L. Clark, J. C. Huffman, D. E. Morris, A. P. Sattelberger, W. E. Streib, W. G. Van Der Sluys and J. G. Watkin, *J. Am. Chem. Soc.*, 1992, **114**, 10811-10821.
- 44 D. L. Clark, J. C. Huffman and J. G. Watkin, *J. Chem. Soc., Chem. Commun.*, 1992, 266-268.
- 45 D. L. Clark and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 1766-1772.
- 46 X.-A. Pang, Y.-M. Yao, J.-F. Wang, H.-T. Sheng, Y. Zhang and Q. Shen, *Chin. J. Chem.*, 2005, **23**, 1193-1197.
- 47 D. J. Wilson, A. Sebastian, F. G. N. Cloke, A. G. Avent and P. B. Hitchcock, *Inorg. Chim. Acta*, 2003, **345**, 89-94.
- 48 A. Arunachalampillai, P. Crewdson, I. Korobkov and S. Gambarotta, *Organometallics*, 2006, **25**, 3856-3866.

Reaction of molecular O_2 with thorium alkyl complexes supported by amidinates and guanidines generates thorium alkoxides via O_2 insertion into thorium-carbon bonds.

