

Controlled Thermolysis of Uranium (Alkoxy)siloxy Complexes: A Route to Polymetallic Complexes of Low-Valent Uranium**

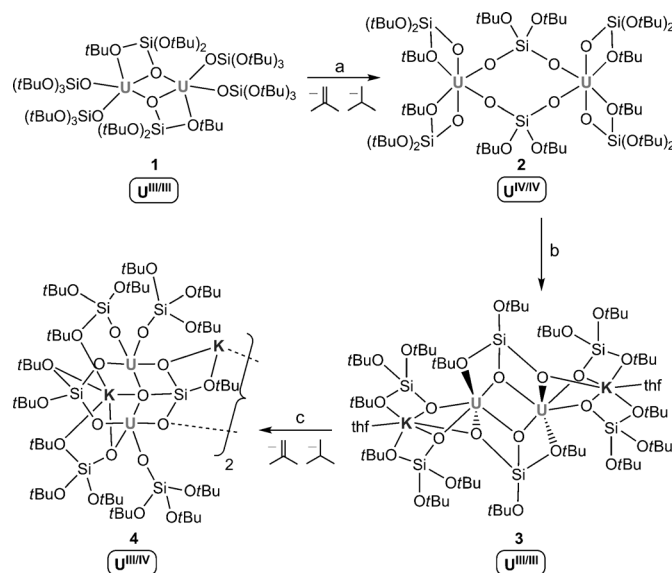
Clément Camp, Christos E. Kefalidis, Jacques Pécaut, Laurent Maron, and Marinella Mazzanti*

The chemistry of metal complexes of siloxy and polysiloxy ligands has attracted high interest in fields ranging from materials science to catalysis^[1] because such compounds find use as efficient precursors for the synthesis of metal oxides and silicates or supported catalysts,^[2] as active catalysts,^[3] and as models for silica-supported heterogeneous catalysts.^[1d,g,3c] Moreover, mono- and polysiloxides serve as versatile ancillary O-donor ligands for the design of stable and highly reactive complexes of low-valent metals.^[1d,h] Monodentate and polydentate N and O donors such as amides and phenolates have recently been used as supporting ligands in uranium chemistry as alternative to the ubiquitous cyclopentadienyl group.^[4] The resulting complexes showed novel and interesting reactivity including CO, CO₂, N₂, azides, arene, chalcogen, and C–H activation.^[5,6] In contrast, the use of siloxide ligands has surprisingly remained extremely rare in uranium chemistry;^[5i,7] complexes of low-valent uranium with polydentate siloxide ligands have proven difficult to obtain.

Besides their potential usefulness for the transformation of small molecules,^[7d] uranium siloxides are attractive precursors for accessing new materials and molecular clusters. In particular, the structure and chemistry of uranium silicates are important in the storage of spent nuclear fuel.^[8] Low-valent uranium silicates are also found in naturally occurring minerals,^[9] and the high-temperature synthesis of a few U^{IV} and U^V silicates has been reported.^[10] Previous studies have shown that the thermolysis of siloxy and polysiloxy complexes of transition metals provides a low-temperature route to homogeneous metal silicates with tailored properties,^[2a,3d,11] but the thermolysis of uranium siloxides has not been investigated.

We recently showed that the tris(*tert*-butoxy)siloxide ligand enables the isolation of a highly reactive U^{III} complex, $[\{U(OSi(OrBu)_3)_2(\mu-OSi(OrBu)_3)_2\}]$ (**1**), which promotes CS₂ reduction, CO₂ disproportionation, and spontaneous arene activation.^[7d] Herein we report the low-temperature thermolysis of **1** to afford the heteroleptic U^{IV} siloxy/silanediolate complex $[\{U(OSi(OrBu)_3)_2(\mu-O_2Si(OrBu)_2)_2\}]$ (**2**) through C–O bond cleavage and the elimination of isobutene (Scheme 1). The reduction of **2** with KC₈ afforded the U^{III}/U^{III} analogue $[\{K(thf)U(OSi(OrBu)_3)_2(\mu-O_2Si(OrBu)_2)_2\}]$ (**3**). In turn, the thermolysis of **3** yielded the tetrametallic mixed-valence U^{III}/U^{IV} siloxy/silanetriolate complex **4**. Complexes **2**, **3**, and **4** are the first reported examples of low-valent uranium complexes containing polysiloxy ligands (silanediolates and silanetriolates). Thus, the thermolysis reaction provides an original route for the synthesis of otherwise inaccessible heteroleptic complexes.

The dinuclear U^{III}–U^{III} complex $[\{U(OSi(OrBu)_3)_2(\mu-OSi(OrBu)_3)_2\}]$ (**1**) is stable in the solid state for several weeks when stored under argon at –40 °C, but it decomposes at room temperature both in the solid state and in solution. The process is faster (less than 30 min) when the solid is heated to 80 °C. The resulting product is highly soluble in hexane and



Scheme 1. Decomposition of the U^{III}/U^{III} complex $[\{U(OSi(OrBu)_3)_2(\mu-OSi(OrBu)_3)_2\}]$ (**1**) to form a U^{IV}/U^{IV} complex $[\{U(OSi(OrBu)_3)_2(\mu-O_2Si(OrBu)_2)_2\}]$ (**2**), and subsequent reduction of **2** to $[\{KU(OSi(OrBu)_3)_2(\mu-O_2Si(OrBu)_2)_2\}]$ (**3**), which yielded the tetranuclear compound $[\{K_2U_2(OSi(OrBu)_3)_4(O_2Si(OrBu)_2)_2(O_2Si(OrBu)_2)_2\}]$ (**4**) upon decomposition: a) solid state, room temperature, 7 days or 80 °C, 30 min; b) KC₈ (2.5 equiv), THF, room temperature, 2 h; c) solid state, 80 °C, 2 h.

[*] C. Camp, Dr. J. Pécaut, Dr. M. Mazzanti
Laboratoire de Reconnaissance Ionique et Chimie de Coordination
SCIB, UMR-E3 CEA-UJF, INAC, CEA-Grenoble
17 rue des Martyrs, F-38054 Grenoble Cedex 09 (France)
E-mail: marinella.mazzanti@cea.fr
Homepage: <http://inac.cea.fr/Pisp/51/marinella.mazzanti.html>
Dr. C. E. Kefalidis, Prof. L. Maron
LPCNO, CNRS and INSA, UPS, Université de Toulouse
135 Avenue de Rangueil, F-31077 Toulouse (France)

[**] We thank Colette Lebrun and Pierre A. Bayle for their help with spectroscopic characterization. We acknowledge support from the Commissariat à l'Energie Atomique, Direction de l'Energie Nucléaire, RBPC program and from the "Agence Nationale de la Recherche" (ANR-10-BLAN-0729). CALMIP and CINES are acknowledged for a generous grant of computing time. L.M. is a member of the Institut Universitaire de France. L.M. also thanks the Humboldt Foundation.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201307291>.

can be recrystallized by cooling a saturated solution to -40°C to yield blue/green crystals of $[\{\text{U}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\mu\text{-O}_2\text{Si}(\text{O}t\text{Bu})_2)_2\}]$ (**2**). The centrosymmetric X-ray crystal structure (Figure 1, top) consists of two uranium cations each coordinated by two bidentate silanolate ligands and two bridging silanediolate $\text{O}_2\text{Si}(\text{O}t\text{Bu})_2$ ligands. The $\text{U}-\text{O}_{\text{siloxide}}$ bond distance (2.17(6) Å) is shorter than in the trivalent complex **1**, in agreement with a higher oxidation state of the metal centers

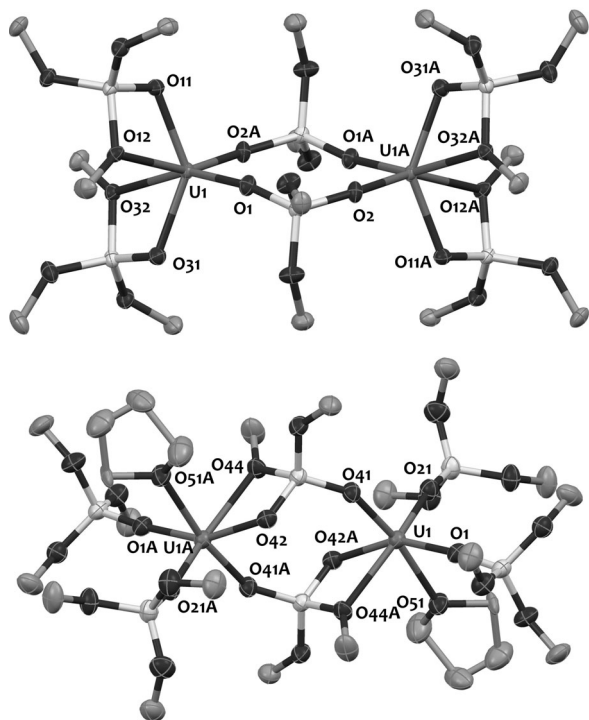


Figure 1. Thermal-ellipsoid drawing for $[\{\text{U}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\mu\text{-O}_2\text{Si}(\text{O}t\text{Bu})_2)_2\}]$ **2** (top) and $[\{\text{U}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\mu\text{-O}_2\text{Si}(\text{O}t\text{Bu})_2)(\text{thf})\}]$ **2·thf** (bottom) crystallized from saturated solutions in hexane; 50% probability. Hydrogen atoms, methyl groups, and interstitial solvent molecules were omitted for clarity. Selected bond distances [Å] for **2**: $\text{U1}-\text{O1}$ 2.1091(18), $\text{U1}-\text{O2A}$ 2.1249(17), $\text{U1}-\text{O11}$ 2.2178(18), $\text{U1}-\text{O31}$ 2.2259(19), $\text{U1}-\text{O}_{\text{tBu,avg}}$ 2.621(3), $\text{U1}-\text{U1A}$ 5.464, $A = -x + 1, -y + 2, -z + 1$; for **2·thf**: $\text{U1}-\text{O21}$ 2.126(4), $\text{U1}-\text{O1}$ 2.166(4), $\text{U1}-\text{O41}$ 2.206(3), $\text{U1}-\text{O42}$ 2.207(4), $\text{U1}-\text{O51}$ 2.513(4), $\text{U1}-\text{O44}$ 2.551(4), $A = -x + 3/2, -y + 3/2, -z + 1$.

in **2**. Bond-valence-sum calculations indicate the presence of two U^{IV} ions. The structure of **1** consists of two UO_6 octahedra, each of which is surrounded by four SiO_4 tetrahedra (see Figure S16 in the Supporting Information). The same uranium coordination environment is found in the only reported synthetic uranium(IV) silicate.^[10a] The formation of **2** from **1** involves the oxidative cleavage of two *t*Bu groups from the $\text{OSi}(\text{O}t\text{Bu})_3$ supporting ligand and is probably driven by the high oxophilicity of the uranium ion and by the high stability of the final U^{IV} complex.

The ESIMS spectra of **2** suggest that the dimeric structure is retained in solution in both toluene and THF. In contrast, as a solution in THF, **1** forms a mononuclear thf solvate.^[7e] The presence of the dianionic bridging $\text{O}_2\text{Si}(\text{O}t\text{Bu})_2$ ligands, which

tightly bind the two uranium centers, results in the isolation of dimeric species even from coordinating solvents. Notably, the solid-state structure obtained by X-ray diffraction of single crystals of the thf solvate **2·thf** grown from a solution of **2** in hexane in the presence of a drop of THF shows the presence of a centrosymmetric dimer (Figure 1, bottom). Each U^{IV} cation in **2·thf** is hexacoordinated by two $\text{OSi}(\text{O}t\text{Bu})_3$ ligands in a terminal monodentate coordination mode, one thf molecule, and two $\text{O}_2\text{Si}(\text{O}t\text{Bu})_2$ ligands, which act as tridentate bridging ligands. Comparison of the structures of **2** and **2·thf** shows the flexibility of the weakly coordinating *O*tBu moieties, which can adjust to stabilize the final compounds in both coordinating and noncoordinating solvents. Two $\text{U}-\text{O}t\text{Bu}$ bonds with the siloxy ligands are disrupted for each uranium center in **2·thf** as compared to the coordination environment in **2** to accommodate in the metal coordination sphere a molecule of THF solvent, which acts as a stronger donor ligand. In the coordination environment of complex **2·thf**, the $\text{O}_2\text{Si}(\text{O}t\text{Bu})_2$ ligands adopt a tridentate bridging mode instead of the bidentate bridging mode adopted in **2**; as a result, the uranium atoms in **2** and **2·thf** have the same coordination number.

^1H NMR spectroscopy of the volatile components formed in the decomposition reaction of **1** to yield **2** revealed the presence of isobutene and isobutane as the major volatile decomposition products of the reaction (see the Supporting Information). The elimination of isobutene from *tert*-butoxide was previously reported for U^{VI} alkoxy derivatives.^[12] A few cases of the activation and reduction of ethers by trivalent uranium to yield oxo complexes are also documented.^[5i,l,13] The elimination of isobutene from d-block metal complexes containing $\text{OSi}(\text{O}t\text{Bu})_3$ ligands has been reported in the thermolysis of siloxy complexes to give metal silicates, and several pathways have been proposed, including heterolytic or homolytic cleavage and $\gamma\text{-H}$ activation.^[2a,3d,11] However, the mechanism of the thermolysis of d-block metal siloxides has not been fully elucidated, and decomposition intermediates have not, to the best of our knowledge, been isolated.

To gain more insight into the reaction mechanism, we carried out DFT studies (B3PW91; see the Supporting Information for computational details). According to the experimental observation that degradation occurs at both uranium centers, the calculations were conducted on a monomeric form of the complex. Of three different decomposition pathways considered, the dissociation of a *t*Bu radical was found to be the energetically most favorable pathway (see the Supporting Information for the other computed profiles from **1**). Homolytic cleavage of the $\text{O}-t\text{Bu}$ bonds occurs with a kinetically accessible barrier (22.9 kcal mol $^{-1}$; Figure 2). The formed *t*Bu radical can then abstract a hydrogen atom from another *t*Bu radical to afford one molecule of isobutene and one molecule of isobutane (see Figure S4a).^[14] This process is in line with the experimental observation of the formation of isobutene and isobutane during the decomposition (see the Supporting Information) and is both thermodynamically and kinetically favored. Thus, the formation of a *t*Bu radical is the rate-determining step of the reaction.

Preliminary studies of the decomposition of complex **2** at a higher temperature showed the formation of an insoluble

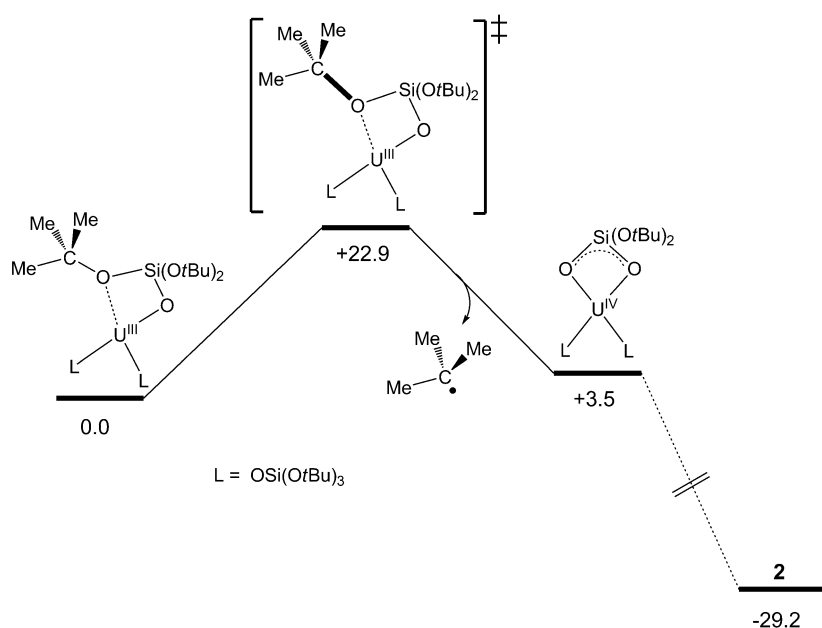


Figure 2. Computed enthalpy profile for the decomposition of complex 1. Enthalpies in kcal mol⁻¹

material as well as H₂O, HOSi(OrBu)₃, and isobutene, similarly to what was observed previously in the decomposition of molecular siloxides of d-block transition metals to give well-defined silicates.^[11a] This result suggests that complex 2 should provide a good molecular precursor for the synthesis of homogenous U^{IV} silicates. Further studies will be directed toward the characterization of the materials obtained from this decomposition.

Complex 2 provides an attractive precursor for accessing heteroleptic dinuclear reduced species bearing siloxy and silanediolate ligands. The reduction of 2 in THF with KC₈ as the reducing agent afforded the new U^{III}–U^{III} complex $[\{K(thf)U(OSi(OrBu)_3)_2(\mu-O_2Si(OrBu)_2)_2\}]$ (**3**) in high yield. The ESIMS spectrum of 3 was in line with the presence of dinuclear species in solution. The UV/Vis absorption spectrum for 3 (see the Supporting Information) exhibited a strong transition centered at 436 nm ($\epsilon = 2360 \text{ L cm}^{-1} \text{ mol}^{-1}$). This band is very similar to that observed in the UV/Vis spectrum of 1 and is characteristic of Laporte-allowed f–d transitions observed in U^{III} complexes.^[5k, 15]

Single crystals suitable for X-ray diffraction were grown by the cooling of a saturated solution of 3 in THF/diisopropyl ether (DIPE) to –40 °C. The solid-state structure of 3 (Figure 3) shows the presence of a dimeric complex in which two O₂Si(OrBu)₂ ligands bridge the two uranium cations in close proximity (U⋯U separation: 3.9619(9) Å) and one potassium cation in an $\eta^2:\eta^2$ fashion. Each potassium cation is also coordinated by four oxygen atoms of two siloxides and one thf molecule.

Complex 3 is the first example of a U^{III} complex containing both siloxide and silanediolate ligands, and provides a new precursor for reactivity studies. In an attempt to form a putative mixed-valent U^{III}–U^{IV} complex, we investigated the reduction of 2 with a single equivalent of

the reducing agent. However, ¹H NMR spectroscopy of the crude mixture showed only the resonances of 2 and 3.

Similarly to 1, the U^{III}–U^{III} complex 3 is unstable at room temperature and decomposes as a solution in THF over a period of 1 week. Decomposition also occurs in the solid state: a purple-brown sample of 3 was transformed into a green solid within 2 h when heated to 80 °C. The resulting solid could be recrystallized from hexane to yield the new tetranuclear complex $[\{K_2U_2(OSi(OrBu)_3)_4(O_2Si(OrBu)_2)(O_3Si(OrBu)_2)\}_2]$ (**4**), which results from the elimination of a *t*Bu group from a bridging O₂Si(OrBu)₂ ligand in 3.

The solid-state structure of 4 is shown in Figure 4. The centrosymmetric structure consists of two dinuclear uranium complexes bridged by two potassium cations coordinated to the siloxide ligands to yield a tetramer. In each dimeric moiety, the two uranium cations are bridged by a trianionic O₃SiOrBu ligand coordinated in a $\mu-\kappa^2:\kappa^2$

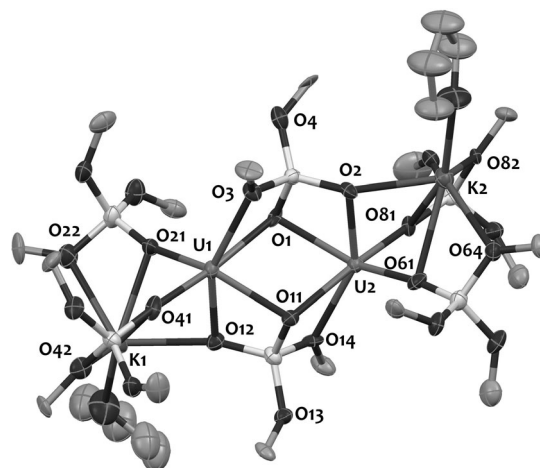


Figure 3. Thermal-ellipsoid drawing for $[\{K(thf)U(OSi(OrBu)_3)_2(\mu-O_2Si(OrBu)_2)_2\}]$ (**3**) crystallized from a saturated solution in THF/DIPE; 50% probability. Hydrogen atoms, methyl groups, and solvent molecules were omitted for clarity. Selected bond distances [Å]: U1–O21 2.281(8), U1–O41 2.284(9), U1–O2 2.373(9), U1–O1 2.425(9), U1–O11 2.489(8), U1–O3 2.742(10), U2–O61 2.257(9), U2–O81 2.275(9), U2–O2 2.364(8), U2–O11 2.451(8), U2–O1 2.507(8), U2–O14 2.755(10), U1⋯U2 3.9619(9).

fashion and a dianionic O₂SiOrBu₂ ligand coordinated in a $\mu-\kappa^1:\kappa^1$ fashion. The U⋯U separation in 4 (3.8393(5) Å) is shorter than in complexes 2 (5.464 Å) and 3 (3.9619(9) Å). The presence of four K⁺ cations and two trianionic, two dianionic, and eight monoanionic siloxide ligands indicates a U^{III}/U^{IV} mixed valence for complex 4, as is also supported by bond-valence-sum calculations. Complex 4 is the first example of a low-valent uranium complex containing a trianionic siloxide ligand and is of interest for both reactivity and magnetism studies.

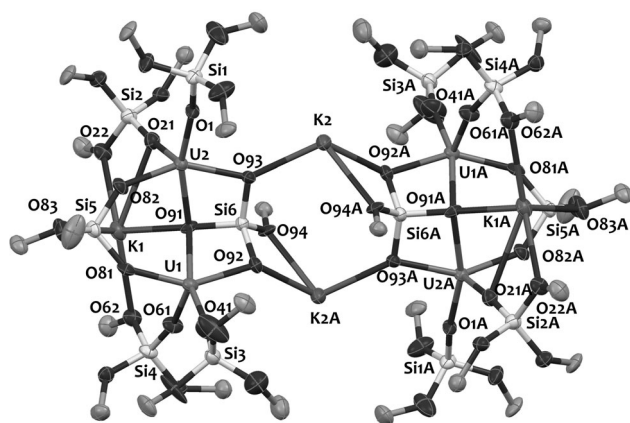


Figure 4. Thermal-ellipsoid drawing for $[(K_2U_2(OSi(OtBu)_3)_4(O_2Si(OtBu)_2)(O_2Si(OtBu)_2))]_2$ (**4**) crystallized from a saturated solution in hexane; 50% probability. Hydrogen atoms and methyl groups were omitted for clarity. Selected bond distances [Å]: U1–O81 2.108(6), U1–O41 2.155(6), U1–O61 2.186(5), U1–O92 2.292(5), U1–O91 2.430(5), U2–O82 2.130(6), U2–O1 2.169(5), U2–O21 2.189(5), U2–O93 2.294(6), U2–O91 2.417(5), U1...U2 3.8392(5), $A = -x + 1, -y + 1, -z + 1$.

In conclusion, we have shown that the (alkoxy)siloxy complexes of trivalent uranium decompose slowly at room temperature and rapidly upon thermal activation at higher temperatures to afford new highly reactive polymetallic complexes. Novel heteroleptic siloxy/silanediolate complexes of U^{III} were isolated and characterized. These complexes can be viewed as attractive precursors for reactivity studies. Thus, the intramolecular U^{III} -mediated C–O bond cleavage presented herein extends the range of reactivity possible with uranium supported by electrodonating ligands and provides a controlled route to polymetallic heteroleptic complexes that would be difficult to obtain by other synthetic methods. These compounds are the first examples of characterized molecular products of the decomposition of siloxy complexes. The structures of these molecular decomposition products provide important unprecedented information on the molecular intermediates involved in the formation of metal silicate materials from molecular precursors. The structures of such intermediates are likely to play a key role in the final stoichiometry and homogeneity of ceramic materials. The isolated compounds may also serve as useful precursors to new uranium ceramics relevant for the storage of spent nuclear fuel and catalysis.

Received: August 19, 2013

Revised: September 12, 2013

Published online: October 9, 2013

Keywords: coordination modes · f-block complexes · polymetallic complexes · siloxide ligands · uranium

- [1] a) V. Lorenz, A. Edelmann, S. Blaurock, C. Hrib, F. T. Edelmann, *C. R. Chim.* **2010**, *13*, 577–583; b) T. J. Boyle, L. A. M. Ottley, *Chem. Rev.* **2008**, *108*, 1896–1917; c) V. Lorenz, A. Fischer, S. Giessmann, J. W. Gilje, Y. Gun'ko, K. Jacob, F. T. Edelmann, *Coord. Chem. Rev.* **2000**, *206*, 321–368; d) R.

- Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, *Chem. Rev.* **1996**, *96*, 2205–2236; e) P. Braunstein, M. Knorr, C. Stern, *Coord. Chem. Rev.* **1998**, *178*, 903–965; f) L. King, A. C. Sullivan, *Coord. Chem. Rev.* **1999**, *189*, 19–57; g) B. Marciniec, H. Maciejewski, *Coord. Chem. Rev.* **2001**, *223*, 301–335; h) P. T. Wolczanski, *Polyhedron* **1995**, *14*, 3335–3362.
- [2] a) K. L. Fajdala, T. D. Tilley, *Chem. Mater.* **2004**, *16*, 1035–1047; b) R. L. Brutchey, C. G. Lugmair, L. O. Schebaum, T. D. Tilley, *J. Catal.* **2005**, *229*, 72–81.
- [3] a) J. Heppekausen, R. Stade, R. Goddard, A. Fürstner, *J. Am. Chem. Soc.* **2010**, *132*, 11045–11057; b) S. Lysenko, J. Volbeda, P. G. Jones, M. Tamm, *Angew. Chem.* **2012**, *124*, 6861–6865; *Angew. Chem. Int. Ed.* **2012**, *51*, 6757–6761; c) F. Blanc, C. Coperet, J. Thivolle-Cazat, J. M. Basset, A. Lesage, L. Emsley, A. Sinha, R. R. Schrock, *Angew. Chem.* **2006**, *118*, 1238–1242; *Angew. Chem. Int. Ed.* **2006**, *45*, 1216–1220; d) J. Jarupatrakorn, J. D. Tilley, *J. Am. Chem. Soc.* **2002**, *124*, 8380–8388.
- [4] a) M. Ephritikhine, *Organometallics* **2013**, *32*, 2464–2488; b) O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green, N. Hazari, *Science* **2006**, *311*, 829–831; c) A. S. P. Frey, F. G. N. Cloke, M. P. Coles, L. Maron, T. Davin, *Angew. Chem.* **2011**, *123*, 7013–7015; *Angew. Chem. Int. Ed.* **2011**, *50*, 6881–6883; d) A. S. Frey, F. G. N. Cloke, P. B. Hitchcock, I. J. Day, J. C. Green, G. Aitken, *J. Am. Chem. Soc.* **2008**, *130*, 13816–13817.
- [5] a) S. M. Mansell, N. Kaltsoyannis, P. L. Arnold, *J. Am. Chem. Soc.* **2011**, *133*, 9036–9051; b) P. L. Arnold, *Chem. Commun.* **2011**, *47*, 9005–9010; c) P. L. Arnold, Z. R. Turner, R. M. Bellabarba, R. P. Tooze, *Chem. Sci.* **2011**, *2*, 77–79; d) I. Castro-Rodríguez, H. Nakai, P. Gantzel, L. N. Zakharov, A. L. Rheingold, K. Meyer, *J. Am. Chem. Soc.* **2003**, *125*, 15734–15735; e) I. Castro-Rodríguez, K. Meyer, *J. Am. Chem. Soc.* **2005**, *127*, 11242–11243; f) I. Castro-Rodríguez, K. Meyer, *Chem. Commun.* **2006**, 1353–1368; g) A. C. Schmidt, A. V. Nizovtsev, A. Scheurer, F. W. Heinemann, K. Meyer, *Chem. Commun.* **2012**, *48*, 8634–8636; h) P. Roussel, P. Scott, *J. Am. Chem. Soc.* **1998**, *120*, 1070–1071; i) I. Korobkov, S. Gambarotta, G. P. A. Yap, *Angew. Chem.* **2002**, *114*, 3583–3586; *Angew. Chem. Int. Ed.* **2002**, *41*, 3433–3436; j) K. R. D. Johnson, P. G. Hayes, *Chem. Soc. Rev.* **2013**, *42*, 1947–1960; k) O. P. Lam, P. L. Feng, F. W. Heinemann, J. M. O'Connor, K. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 2806–2816; l) I. Korobkov, S. Gambarotta, G. P. A. Yap, *Organometallics* **2001**, *20*, 2552–2559; m) B. M. Gardner, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2009**, *131*, 10388–10389; n) J. L. Brown, S. Fortier, R. A. Lewis, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2012**, *134*, 15468–15475; o) O. P. Lam, F. W. Heinemann, K. Meyer, *Chem. Sci.* **2011**, *2*, 1538–1547; p) M. B. Gardner, J. C. Stewart, A. L. Davis, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 9265–9270.
- [6] a) I. Castro-Rodríguez, H. Nakai, L. N. Zakharov, A. L. Rheingold, K. Meyer, *Science* **2004**, *305*, 1757–1759; b) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* **2012**, *337*, 717–720; c) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2013**, *5*, 482–488; d) S. Fortier, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2010**, *132*, 6888–6889.
- [7] a) D. L. Clark, A. P. Sattelberger, W. G. Van Der Sluys, J. G. Watkin, *J. Alloys Compd.* **1992**, *180*, 303–315; b) V. Lorenz, A. Fischer, K. Jacob, W. Bruser, F. T. Edelmann, *Chem. Eur. J.* **2001**, *7*, 848–857; c) V. Lorenz, A. Fischer, K. Jacob, W. Bruser, T. Gelbrich, P. G. Jones, F. T. Edelmann, *Chem. Commun.* **1998**, 2217–2218; d) V. Mougél, C. Camp, J. Pécaut, C. Coperet, L. Maron, C. E. Kefalidis, M. Mazzanti, *Angew. Chem.* **2012**, *124*, 12446–12450; *Angew. Chem. Int. Ed.* **2012**, *51*, 12280–12284; e) C. Camp, J. Pécaut, M. Mazzanti, *J. Am. Chem. Soc.* **2013**, *135*, 12101–12111; f) S. M. Mansell, J. H. Farnaby, A. I. Germeroth,

- P. L. Arnold, *Organometallics* **2013**, 32, 4214–4222; g) C. Camp, V. Mougel, J. Pécaut, L. Maron, M. Mazzanti, *Chem. Eur. J.* **2013**, DOI: 10.1002/chem.201302752.
- [8] P. C. Burns, R. A. Olson, R. J. Finch, J. M. Hanchar, Y. Thibault, *J. Nucl. Mater.* **2000**, 278, 290–300.
- [9] a) L. R. Stieff, T. W. Stern, A. M. Sherwood, *Science* **1955**, 121, 608–609; b) Y. A. Uvarova, E. Sokolova, F. C. Hawthorne, A. A. Agakhanov, L. A. Pautov, *Can. Mineral.* **2004**, 42, 1005–1011.
- [10] a) H. K. Liu, K. H. Lii, *Inorg. Chem.* **2011**, 50, 5870–5872; b) C. S. Chen, S. F. Lee, K. H. Lii, *J. Am. Chem. Soc.* **2005**, 127, 12208–12209; c) C. S. Lee, C. H. Lin, S. L. Wang, K. H. Lii, *Angew. Chem.* **2010**, 122, 4350–4352; *Angew. Chem. Int. Ed.* **2010**, 49, 4254–4256.
- [11] a) K. W. Terry, C. G. Lugmair, T. D. Tilley, *J. Am. Chem. Soc.* **1997**, 119, 9745–9756; b) R. Rulkens, J. L. Male, K. W. Terry, B. Olthof, A. Khodakov, A. T. Bell, E. Iglesia, T. D. Tilley, *Chem. Mater.* **1999**, 11, 2966–2973; c) K. Su, T. D. Tilley, M. J. Sailor, *J. Am. Chem. Soc.* **1996**, 118, 3459–3468; d) K. Su, T. D. Tilley, *Chem. Mater.* **1997**, 9, 588–595; e) K. L. Fajdala, T. D. Tilley, *J. Catal.* **2003**, 216, 265–275.
- [12] S. Fortier, G. Wu, T. W. Hayton, *Inorg. Chem.* **2009**, 48, 3000–3011.
- [13] C. P. Larch, F. G. N. Cloke, P. B. Hitchcock, *Chem. Commun.* **2008**, 82–84.
- [14] J. W. Kraus, J. G. Calvert, *J. Am. Chem. Soc.* **1957**, 79, 5921–5926.
- [15] S. C. Bart, F. W. Heinemann, C. Anthon, C. Hauser, K. Meyer, *Inorg. Chem.* **2009**, 48, 9419–9426.