N−C Bond Formation

International Edition: DOI: 10.1002/anie.201600158
German Edition: DOI: 10.1002/ange.201600158

Nucleophilic Reactivity of a Nitride-Bridged Diuranium(IV) Complex: CO_2 and CS_2 Functionalization

*Marta Falcone, Lucile Chatelain, and Marinella Mazzanti**

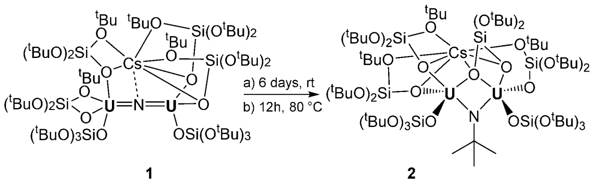
Abstract: *Thermolysis of the nitride-bridged diuranium(IV) complex* $Cs\{(\mu\text{-}N)[U(OSi(O^tBu)_3)_3]_2\}$ (***1***) *showed that the bridging nitride behaves as a strong nucleophile, promoting N−C bond formation by siloxide ligand fragmentation to yield an imido-bridged siloxide/silanediolate diuranium(IV) complex,* $Cs\{(\mu\text{-}N^tBu)(\mu\text{-}O_2Si(O^tBu)_2)U_2(OSi(O^tBu)_3)_5\}$*. Complex **1** displayed reactivity towards* CS_2 *and* CO_2 *at room temperature that is unprecedented in f-element chemistry, affording diverse N-functionalized products depending on the reaction stoichiometry. The reaction of **1** with two equivalents of* CS_2 *yielded the thiocyanate/thiocarbonate complex* $Cs\{(\mu\text{-}NCS)(\mu\text{-}CS_3)[U(OSi(O^tBu)_3)_3]_2\}$ *via a putative* NCS^-/S^{2-} *intermediate. The reaction of **1** with one equivalent of* CO_2 *resulted in deoxygenation and N−C bond formation, yielding the cyanate/oxo complex* $Cs\{(\mu\text{-}NCO)(\mu\text{-}O)[U(OSi(O^tBu)_3)_3]_2\}$*. Addition of excess* CO_2 *to **1** led to the unprecedented dicarbamate product* $Cs\{(\mu\text{-}NC_2O_4)[U(OSi(O^tBu)_3)_3]_2\}$*.*

Uranium nitrides are attractive candidates for both stoichiometric and catalytic nitrogen-transfer reactions and small-molecule transformations.[1] Understanding the reactivity of uranium nitrides is also of great interest because of their importance in many fields of science and engineering (e.g., as nuclear fuels).[2] In recent years, an increasing number of molecular nitride compounds of uranium have been prepared and characterized,[2b,3] but their reactivity has remained virtually unexplored. The activation of a C−H bond by a transient terminal uranium nitride, which resulted in the formation of new N−H and N−C bonds, was first reported by Kiplinger and co-workers.[3j] More recently, the two-electron reduction of terminal U^V and U^{VI} nitrides to cyanates by carbon monoxide has also been described.[3n] Although most previously reported uranium nitride complexes contain a bridging nitride, the reactivity of the U=N=U fragment has thus far only been studied for a diuranium(V) complex in which the nitride reacted as a masked metallonitrene to afford a cyanoimide diuranium(IV/IV) complex.[3g]

N−C bond-formation reactions are very important in the construction of value-added chemical compounds, such as amino acids, pharmaceuticals, or agrochemicals,[4] and synthetic methods that use inexpensive and largely available feedstocks, such as carbon dioxide, are particularly desirable.[5] A few examples of N−C bond formation from the reaction of carbon dioxide with activated nitride-bridged complexes[6] or terminal nitride complexes[7] have been reported for transition metals but thus far, the reactivity of molecular nitride compounds of f-block elements with CO_2 has not been investigated.

Herein, we have investigated the ability of a previously described nitride-bridged diuranium(IV) complex, $Cs\{(\mu\text{-}N)[U(OSi(O^tBu)_3)_3]_2\}$ (**1**),[3h] to promote N−C bond formation, and we have studied its reactivity with CO_2 and CS_2. We found that the temperature-induced decomposition of complex **1** induced N−C bond formation by fragmentation of a siloxide ligand. We also report the isolation and characterization of the products obtained from the room-temperature reactions of **1** with CO_2 and CS_2. In these reactions, the bridging nitride group acts as a strong nucleophile, which leads to N−C bond formation yielding cyanate and thiocyanate species and the unprecedented construction of a dicarbamate.

The nitride-bridged diuranium(IV) complex $Cs\{(\mu\text{-}N)[U(OSi(O^tBu)_3)_3]_2\}$ (**1**) is stable in solution at −40 °C for several months but undergoes decomposition at higher temperatures. Notably, the overnight thermolysis of **1** at 80 °C in toluene solution resulted in the complete transformation of **1** to afford a new imido-bridged siloxide/silanediolate diuranium(IV) complex, $Cs\{(\mu\text{-}N^tBu)(\mu\text{-}O_2Si(O^tBu)_2)U_2(OSi(O^tBu)_3)_5\}$ (**2**), in 65 % yield (Scheme 1). The solid-state crystal structure of **2** was determined by single-crystal X-ray diffraction (Figure 1).



Scheme 1. *tert*-Butyl transfer from a ligand of $Cs\{(\mu\text{-}N)[U(OSi(O^tBu)_3)_3]_2\}$ (**1**) to the bridging nitride to form $Cs\{(\mu\text{-}N^tBu)(\mu\text{-}O_2Si(O^tBu)_2)U_2(OSi(O^tBu)_3)_5\}$ (**2**).

The structure of **2** shows the presence of a tris(siloxide) U^{IV} moiety, $[U(OSi(O^tBu)_3)_3]$, and of a bis(siloxide)/mono(silanediolate) U^{IV} moiety, $[U(O_2Si(O^tBu)_2)(OSi(O^tBu)_3)_2]$. The two uranium ions are bridged by a *tert*-butylimido group and by one of the oxygen atoms of the silanediolate moiety, affording a non-symmetric structure. This result shows that the thermolysis of complex **1** leads to C−O cleavage in one of the siloxide ligands with concomitant transfer of the *tert*-butyl

---

[*] M. Falcone, L. Chatelain, Dr. M. Mazzanti
Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne (EPFL)
1015 Lausanne (Switzerland)
E-mail: marinella.mazzanti@epfl.ch

Supporting information for this article can be found under http://dx.doi.org/10.1002/anie.201600158.

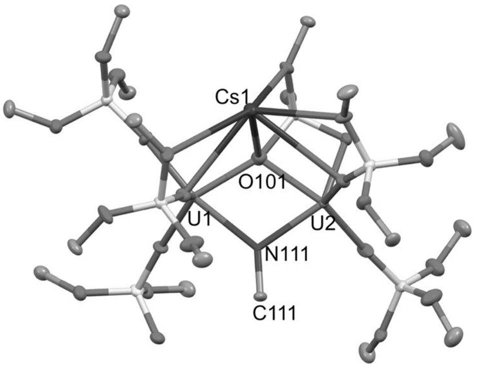


Figure 1. Crystal structure of Cs{(μ-N^{t}Bu)(μ-O_2Si(O^{t}Bu)$_2$)U_2(OSi(O^{t}Bu)$_3$)$_5$} (**2**). Thermal ellipsoids set at 50% probability. Hydrogen atoms and methyl groups were omitted for clarity. Selected bond lengths [Å]: U1–N111 2.300(3), U2–N111 2.398(3), N111–C111 1.461(6), U2–O101 2.223(4), U1–O101 2.323(4), Cs1–O101 3.340(4).

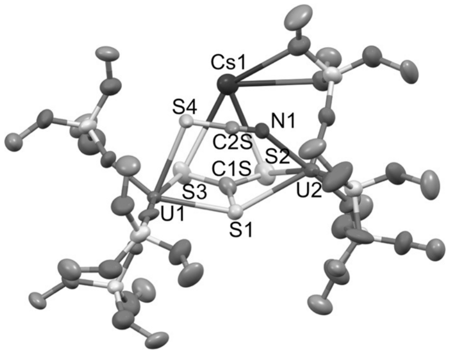
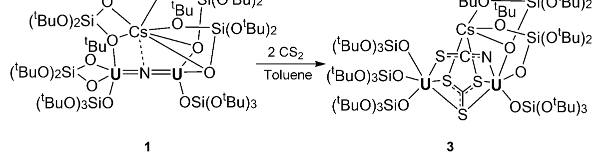


Figure 2. Crystal structure of Cs{(μ-NCS)(μ-CS_3)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$} (**3a**) in **3**. Thermal ellipsoids set at 50% probability. Hydrogen atoms, methyl groups, and lattice solvent molecules were omitted for clarity. Selected bond lengths [Å] for **3a**: U1–S1 2.9792(18), U1–S4 3.029(4), U1–S3 2.885(3), U2–S1 3.0411(18), U2–S2 2.881(4), U2–N1 2.501(15), S4–C2S 1.639(15), N1–C2S 1.07(2), S1–C1S 1.740(12), S2–C1S 1.682(9), S3–C1S 1.712(10), Cs1–S3 3.525(3), Cs1–S4 4.170(6), Cs1–S2 3.408(3), U2–Cs1 4.7200(9).

group to the nitride, giving a dianionic silanediolate ligand that bridges the two uranium centers. C–O cleavage in a *tert*-butoxysiloxide ligand with concomitant elimination of isobutene has previously been observed in the thermolysis of the diuranium(III) complex [U(OSi(O^{t}Bu)$_3$)$_2$(μ-OSi(O^{t}Bu)$_3$)]$_2$.[8] The strongly nucleophilic character of the bridging nitride in **1** results in the formation of a new N–C bond with the *tert*-butyl group from the siloxide ligand, yielding the *tert*-butylimido bridging group. The *tert*-butylimide bridges the two uranium centers in a non-symmetric fashion with U–N_{imido} bond lengths of 2.300(3) and 2.398(3) Å, which are slightly longer than those found in the few reported examples of dinuclear imido-bridged U^{IV} complexes (2.156(8)–2.378(3) Å).[9]

The high nucleophilic reactivity of the bridging nitride, as evidenced by the slow decomposition of complex **1** at room temperature, inspired us to investigate the reactivity of this complex with the electrophiles CS_2 and CO_2. The addition of two equivalents of CS_2 to **1** resulted in an immediate color change of the solution to green. Storing the solution at −40 °C resulted in the isolation of Cs{(μ-NCS)(μ-CS_3)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$} (**3**) in 58% yield (Scheme 2).

The solid-state structure of **3** is disordered with an occupancy of 0.85 for the Cs atom in one position (**3a**, Figure 2) and an occupancy of 0.15 in the other position (**3b**; see the Supporting Information). The structure of **3a** consists of a diuranium(IV) complex in which two [U(OSi(O^{t}Bu)$_3$)$_3$] fragments are bridged by a thiocyanate unit and a trithiocarbonate unit that binds the two uranium cations and the cesium cation in a μ_3-κ^2:κ^2:κ^2 fashion. The C–S bond lengths (1.740(12), 1.682(9), 1.712(10) Å) are consistent with electronic delocalization of the negative charge over the CS_3^{2-} unit, and are similar to those found in the two other reported uranium trithiocarbonate complexes.[10] The bridging thiocyanate is disordered over two positions: one with N bound to U2 and S bound to U1, and one with N bound to U1 and S bound to U2. Only the structure with N1 bound to U2 is shown in Figure 2.



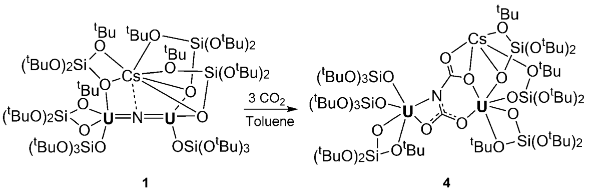
Scheme 2. Reaction of Cs{(μ-N)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$} (**1**) with CS_2 to form Cs{(μ-NCS)(μ-CS_3)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$} (**3**).

The U–N bonds (U1–N1 2.501(15) Å, U2–N1 2.62(2) Å) are longer than those reported for terminal N-bound U^{IV} thiocyanate complexes (2.385(4) Å).[11] No examples of uranium complexes containing bridging thiocyanate or S-bound thiocyanate ligands were found in the Cambridge Structural Database.

The ^{13}C NMR spectrum of **3** in [D_8]toluene shows a resonance at $\delta = 124.0$ ppm for the bridging NCS^- ligand and one at 195.8 ppm for the bridging CS_3^{2-} ligand. The ^{13}C NMR spectrum of **3** in [D_6]DMSO shows a resonance at 129.3 ppm that was assigned to the NCS^- anion. The presence of two $\nu(^{13}CN)$ stretches at 2006 and 2085 cm^{-1} in the IR spectrum of a sample of **3** that was prepared with $^{13}CS_2$ is consistent with the presence of a bridging thiocyanate ligand.[12]

The addition of an equimolar amount of CS_2 to complex **1** led to a mixture of unreacted complex **3** and an additional species (**a**), which was transformed into **3** after addition of a second equivalent of CS_2. The ^{13}C NMR spectrum in [D_6]DMSO of the residue obtained after drying of the reaction mixture allowed us to confirm the presence of the free NCS^- group. This finding suggests that the formation of the trithiocarbonate- and thiocyanate-bridged complex **3** is most likely the result of the reaction of a sulfide- and thiocyanate-bridged intermediate, "Cs{(μ-NCS)(μ-S)[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$}" (**a**), with a second molecule of CS_2. The formation of a trithiocarbonate-bridged diuranium(IV) complex by the nucleophilic addition of a sulfide-bridged diuranium(IV) complex to CS_2 has previously been described by Meyer et al.[10a] Moreover, the formation of sulfide and thiocyanate species from the nucleophilic addition of CS_2 to a nitride via a dithiocarbamate intermediate has been described for a terminal V^V nitride.[7b]

Rather different reactivity was observed with CO_2. The addition of three equivalents of CO_2 to **1** in toluene at low temperature (below −70 °C) resulted in an immediate color change to yield a blue solution. Storing the solution at −40 °C gave $Cs\{(\mu\text{-}NC_2O_4)[U(OSi(O^tBu)_3)_3]_2\}$ (**4**) in 72 % yield (Scheme 3). Complex **4** is stable in toluene solution at room temperature for up to two weeks. The solid-state structure of **4** (Figure 3) shows the presence of a unique dicarbamate ligand bridging two $[U(OSi(O^tBu)_3)_3]$ fragments in an asymmetric fashion and a cesium cation. One uranium cation is bound by the nitrogen atom and a carboxylate oxygen atom, while the second uranium cation is bound by two oxygen atoms from two different carbamate units. The $U_2NC_2O_4$ core comprises two fused rings, with one six-membered ring (UOCNCO) and one four-membered ring (UNCO). The two rings share the N−C bond and are arranged in a planar fashion. A carbamate oxygen atom that is not bound to the uranium ion is located above this plane, and it is bound to the Cs cation. The U−N bond length (2.467(3) Å) is longer than those usually found in U^{IV} amide complexes (ca. 2.3 Å)[13] but similar to the U^{IV}−N bond reported for a sterically demanding amide (2.415 Å)[14] and in the range of U−N bond lengths reported for amido-bridged diuranium(IV) complexes (2.4–2.57 Å).[15] The similar values of the O121−C121 and C121−O122 bond lengths (1.292(5) and 1.282(4) Å) are consistent with delocalization of the negative charge. The C122−O124 bond (1.229(6) Å) is shorter than the C122−O123 bond (1.317(4) Å), which suggests a localized C=O bond.



Scheme 3. Reaction of $Cs\{(\mu\text{-}N)[U(OSi(O^tBu)_3)_3]_2\}$ (**1**) with CO_2 to form $Cs\{(\mu\text{-}NC_2O_4)[U(OSi(O^tBu)_3)_3]_2\}$ (**4**).

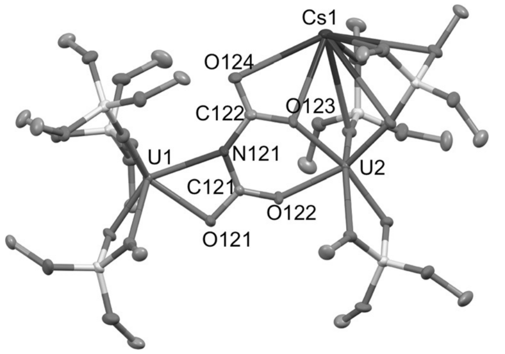


Figure 3. Crystal structure of $Cs\{(\mu\text{-}NC_2O_4)[U(OSi(O^tBu)_3)_3]_2\}$ (**4**). Thermal ellipsoids set at 50% probability. Hydrogen atoms, methyl groups, and solvent molecules were omitted for clarity. Selected bond lengths [Å]: U1–O121 2.360(3), U1–N121 2.467(3), O121–C121 1.292(5), C121–N121 1.347(5), C121–O122 1.282(4), N121–C122 1.396(6), C122–O124 1.229(6), C122–O123 1.317(4), U2–O123 2.252(3), U2–O122 2.283(3), O124–Cs1 3.206(3), O123–Cs1 3.045(3). Torsion angles [°]: O121-C121-N121-C122 178.11, O124-C122-N121-C121 158.03.

The ^{13}C NMR spectrum of the crude reaction mixture obtained from the reaction of **1** with three equivalents of $^{13}CO_2$ in $[D_8]$toluene only shows one peak at −134.1 ppm, which was assigned to the bridging dicarbamate ligand. This result suggests that complex **4** is the only product formed in this reaction. In contrast, ^1H and ^{13}C NMR studies showed that the addition of smaller amounts of carbon dioxide (1–2 equiv) led to a mixture of **4**, unreacted **1**, and an additional species that cannot be transformed into **4** by the subsequent addition of excess CO_2. X-ray diffraction analysis of crystals obtained from this reaction mixture showed the presence of two co-crystallized complexes, $Cs\{(\mu\text{-}NCO)(\mu\text{-}O)[U(OSi(O^tBu)_3)_3]_2\}$ (**5**; Figure 4) and $Cs_2\{(\mu\text{-}O)_2[U(OSi(O^tBu)_3)_3]_2\}$ (**6**; Figure S27), in a ratio of 1:0.5. The ^{13}C NMR spectrum of these crystals in $[D_6]$DMSO shows the presence of free isocyanate, indicating that NCO^- is released when the crystals are dissolved in DMSO. The structure of **5** shows the presence of two tris(siloxide) U^{IV} moieties that are bridged by an oxo ligand and an N-bound isocyanate. The U−N bonds (2.535(9) and 2.582(9) Å) are longer than those found in terminally bound isocyanates (around 2.3 Å)[11] but similar to those reported for an isocyanatodioxouranate(VI) (2.58(1) Å), in which the cyanate group adopted a similar bridging mode.[16]

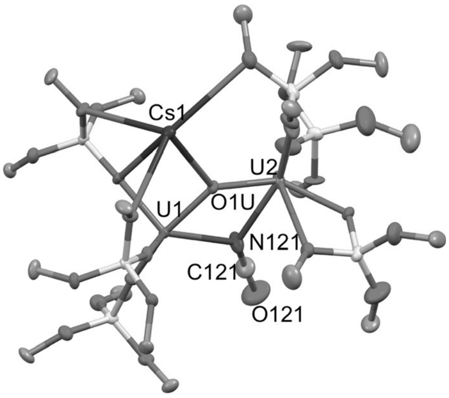


Figure 4. Crystal structure of $Cs\{(\mu\text{-}NCO)(\mu\text{-}O)[U(OSi(O^tBu)_3)_3]_2\}$ (**5**) in $\mathbf{5}\cdot\mathbf{6}_{0.5}$. Thermal ellipsoids set at 50% probability. Hydrogen atoms, methyl groups, and lattice solvent molecules were omitted for clarity. Selected bond lengths [Å] of **5**: U1–N121 2.535(9), U2–N121 2.582(9), U1–O1U 2.118(5), U2–O1U 2.127(5), N121–C121 1.178(2), C121–O121 1.180(2).

The isolation of compound **5** indicates that at substoichiometric ratios of CO_2, the reaction of **1** with CO_2 proceeds with deoxygenation and N−C bond formation to yield the cyanate/oxo complex, which is probably formed via a bridging carbamate intermediate. Analogous reactivity has been reported for a terminal niobium carbamate, which undergoes intramolecular metathesis to afford a terminal oxo complex and free isocyanate, but only after heating at 80 °C.[7c] The presence of the co-crystallized bis(oxo) complex **6** also suggests that scrambling of the isocyanate and oxo ligands occurs in solution, which is in agreement with the observation of only one peak for this complex in the ^{1}H NMR spectrum of crystals of $\mathbf{5}\cdot\mathbf{6}_{0.5}$. In the presence of excess CO_2, the addition of a second equivalent of CO_2 to the monocarbamate intermediate is faster than the isocyanate formation that affords the stable complex **4**.

The formation of a dicarbamate from the reaction of a metal nitride with CO_2 is unprecedented and points to the presence of a highly nucleophilic nitride in complex **1**. Moreover, complexes of the $N(CO_2)_2^{3-}$ ligand have never been reported, which is probably due to the difficulty of preparing the parent triprotic species.[17] Only a few examples of the reactivity of the U–N bond with CO_2 have been previously described. Insertion of CO_2 into $U^{III}{-}N_{amide}$ or $U^{IV}{-}N_{amide}$ bonds resulted in the formation of O-bound carbamate complexes of U^{III} or U^{IV}[13c,18] or U^{IV} isocyanate complexes,[19] and the reaction of CO_2 with U^{V} imido complexes led to isocyanate extrusion and formation of a terminal U^{V} oxo complex by multiple metathesis.[18d,20] However, we have herein described the first example of the insertion of CO_2 into a $U{-}N_{nitride}$ bond. The high reactivity of **1** with electrophiles is in stark contrast to the often inert character of nitride-bridged transition-metal complexes,[21] which require activation of the nitride group for further functionalization,[6] and this result highlights the potential of uranium nitrides in promoting N–C bond-formation reactions. The results presented in this work open up new pathways for the selective synthesis of new organic molecules from metal nitrides and the abundant and inexpensive feedstock CO_2, and demonstrate that nitride functionalization with heteroallenes is readily feasible with uranium. This novel reactivity of uranium nitrides will certainly inspire new approaches to both stoichiometric and catalytic N–C bond-formation reactions.

Acknowledgements

We acknowledge support from the Swiss National Science Foundation and the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank Euro Solari for carrying out the elemental analyses, Rosario Scopelliti for collecting X-ray data, and Jacques Pécaut for solving the crystal structures.

Keywords: carbon dioxide · carbon disulfide · cyanates · nitrides · uranium

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4074–4078
Angew. Chem. **2016**, *128*, 4142–4146

[1] a) F. Haber, DE 229126, **1909**; b) A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* **2008**, *455*, 341–349; c) M. S. Eisen, *Top. Organomet. Chem.* **2010**, *31*, 157–184.

[2] a) G. W. C. Silva, C. B. Yeamans, A. P. Sattelberger, T. Hartmann, G. S. Cerefice, K. R. Czerwinski, *Inorg. Chem.* **2009**, *48*, 10635–10642; b) D. M. King, S. T. Liddle, *Coord. Chem. Rev.* **2014**, *266–267*, 2–15.

[3] a) T. W. Hayton, *Chem. Commun.* **2013**, *49*, 2956–2973; b) W. J. Evans, S. A. Kozimor, J. W. Ziller, *Science* **2005**, *309*, 1835–1838; c) I. Korobkov, S. Gambarotta, G. P. A. Yap, *Angew. Chem. Int. Ed.* **2002**, *41*, 3433–3436; *Angew. Chem.* **2002**, *114*, 3583–3586; d) T. K. Todorova, L. Gagliardi, J. R. Walensky, K. A. Miller, W. J. Evans, *J. Am. Chem. Soc.* **2010**, *132*, 12397–12403; e) G. Nocton, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed.* **2008**, *47*, 3040–3042; *Angew. Chem.* **2008**, *120*, 3082–3084; f) S. Fortier, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2010**, *132*, 6888–6889; g) A. R. Fox, P. L. Arnold, C. C. Cummins, *J. Am. Chem. Soc.* **2010**, *132*, 3250–3251; h) C. Camp, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2013**, *135*, 12101–12111; i) L. Maria, I. C. Santos, V. R. Sousa, J. Marcalo, *Inorg. Chem.* **2015**, *54*, 9115–9126; j) R. K. Thomson, T. Cantat, B. L. Scott, D. E. Morris, E. R. Batista, J. L. Kiplinger, *Nat. Chem.* **2010**, *2*, 723–729; k) 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; l) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* **2012**, *337*, 717–720; m) D. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2014**, *136*, 5619–5622; n) P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2014**, *53*, 10412–10415; *Angew. Chem.* **2014**, *126*, 10580–10583.

[4] S. D. Roughley, A. M. Jordan, *J. Med. Chem.* **2011**, *54*, 3451–3479.

[5] M. Aresta, A. Dibenedetto, *J. Chem. Soc. Dalton Trans.* **2007**, 2975–2992.

[6] a) S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2013**, *135*, 11373–11383; b) S. P. Semproni, P. J. Chirik, *Angew. Chem. Int. Ed.* **2013**, *52*, 12965–12969; *Angew. Chem.* **2013**, *125*, 13203–13207.

[7] a) J. M. Smith, *Prog. Inorg. Chem.* **2014**, *58*, 417–470; b) J. K. Brask, V. Dura-Vila, P. L. Diaconescu, C. C. Cummins, *Chem. Commun.* **2002**, 902–903; c) J. S. Silvia, C. C. Cummins, *J. Am. Chem. Soc.* **2010**, *132*, 2169–2170.

[8] C. Camp, C. E. Kefalidis, J. Pecaut, L. Maron, M. Mazzanti, *Angew. Chem. Int. Ed.* **2013**, *52*, 12646–12650; *Angew. Chem.* **2013**, *125*, 12878–12882.

[9] a) J. G. Brennan, R. A. Andersen, A. Zalkin, *J. Am. Chem. Soc.* **1988**, *110*, 4554–4558; b) J. L. Stewart, R. A. Andersen, *New J. Chem.* **1995**, *19*, 587–595; c) R. C. Schnabel, B. L. Scott, W. H. Smith, C. J. Burns, *J. Organomet. Chem.* **1999**, *591*, 14–23.

[10] a) O. P. Lam, L. Castro, B. Kosog, F. W. Heinemann, L. Maron, K. Meyer, *Inorg. Chem.* **2012**, *51*, 781–783; b) C. Camp, O. Cooper, J. Andrez, J. Pecaut, M. Mazzanti, *J. Chem. Soc. Dalton Trans.* **2015**, *44*, 2650–2656.

[11] C. Camp, N. Settineri, J. Lefevre, A. R. Jupp, J. M. Goicoechea, L. Maron, J. Arnold, *Chem. Sci.* **2015**, *6*, 6379–6384.

[12] M. A. S. Goher, *Collect. Czech. Chem. Commun.* **1977**, *42*, 1478.

[13] a) S. M. Franke, M. W. Rosenzweig, F. W. Heinemann, K. Meyer, *Chem. Sci.* **2015**, *6*, 275–282; b) L. P. Spencer, P. Yang, S. G. Minasian, R. E. Jilek, E. R. Batista, K. S. Boland, J. M. Boncella, S. D. Conradson, D. L. Clark, T. W. Hayton, S. A. Kozimor, R. L. Martin, M. M. MacInnes, A. C. Olson, B. L. Scott, D. K. Shuh, M. P. Wilkerson, *J. Am. Chem. Soc.* **2013**, *135*, 2279–2290; c) J. A. Higgins Frey, G. N. Cloke, S. M. Roe, *Organometallics* **2015**, *34*, 2102–2105.

[14] C. A. P. Goodwin, F. Tuna, E. J. L. McInnes, S. T. Liddle, J. McMaster, I. J. Vitorica-Yrezabal, D. P. Mills, *Chem. Eur. J.* **2014**, *20*, 14579–14583.

[15] a) J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, *Inorg. Chem.* **1977**, *16*, 599–603; b) J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, L. K. Templeton, *Inorg. Chem.* **1976**, *15*, 2498–2502.

[16] M. J. Crawford, P. Mayer, H. Noth, M. Suter, *Inorg. Chem.* **2004**, *43*, 6860–6862.

[17] R. B. MacMullin, US 43178, **1935**.

[18] a) P. J. Fagan, J. M. Manriquez, S. H. Vollmer, C. S. Day, V. W. Day, T. J. Marks, *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220; b) E. M. Matson, P. E. Fanwick, S. C. Bart, *Organometallics* **2011**, *30*, 5753–5762; c) A. L. Arduini, J. D. Jamerson, J. Takats, *Inorg. Chem.* **1981**, *20*, 2474–2479; d) S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein, K. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 12536–12546.

[19] C. Camp, L. Chatelain, C. E. Kefalidis, J. Pécaut, L. Maron, M. Mazzanti, *Chem. Commun.* **2015**, *51*, 15454–15457.

[20] A.-C. Schmidt, F. W. Heinemann, L. Maron, K. Meyer, *Inorg. Chem.* **2014**, *53*, 13142–13153.

[21] B. A. MacKay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385–401.

Received: January 6, 2016