Dinitrogen Activation

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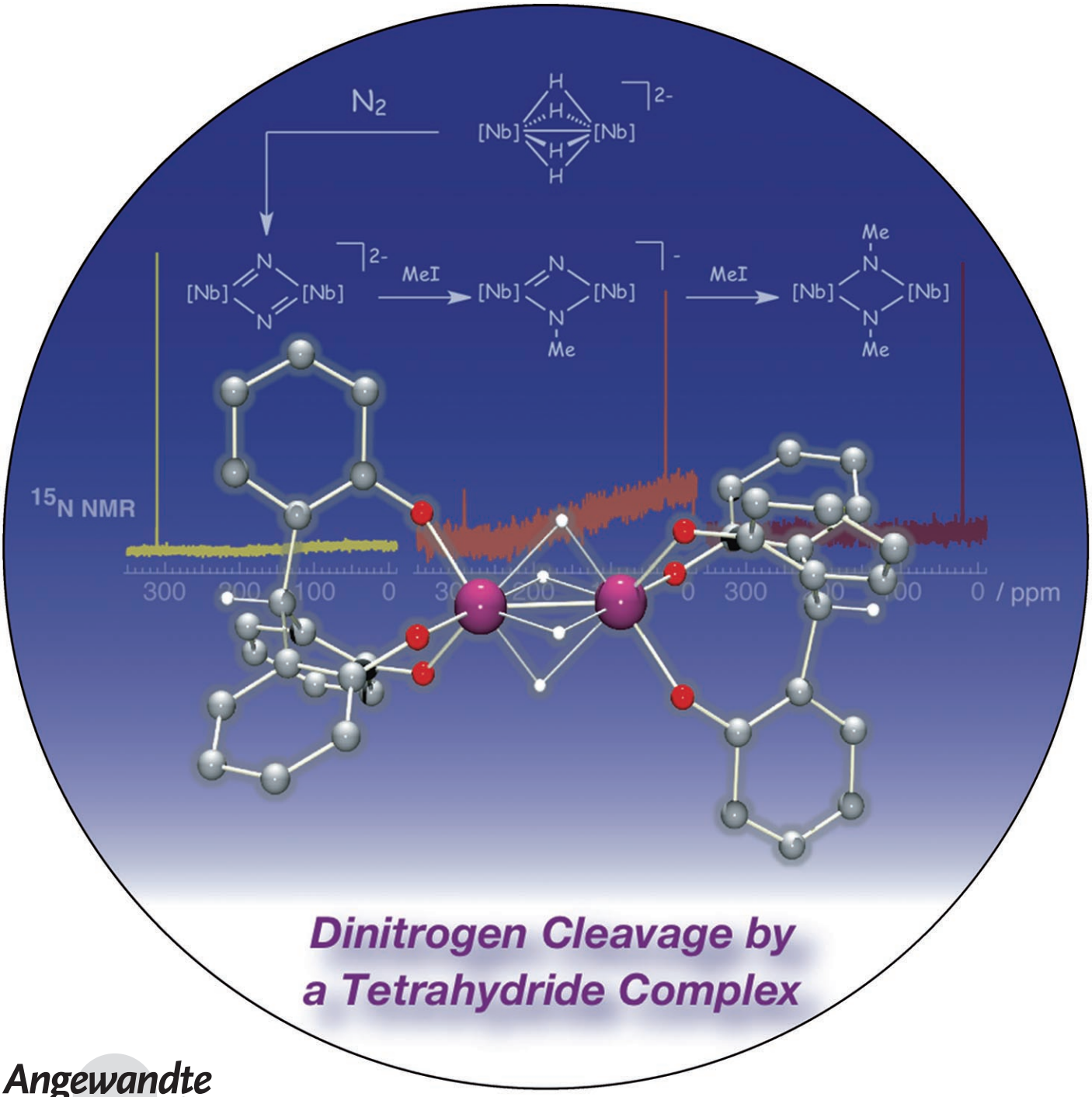
Dinitrogen Cleavage by a Diniobium Tetrahydride Complex: Formation of a Nitride and Its Conversion into Imide Species**

*Fumio Akagi, Tsukasa Matsuo, and Hiroyuki Kawaguchi**

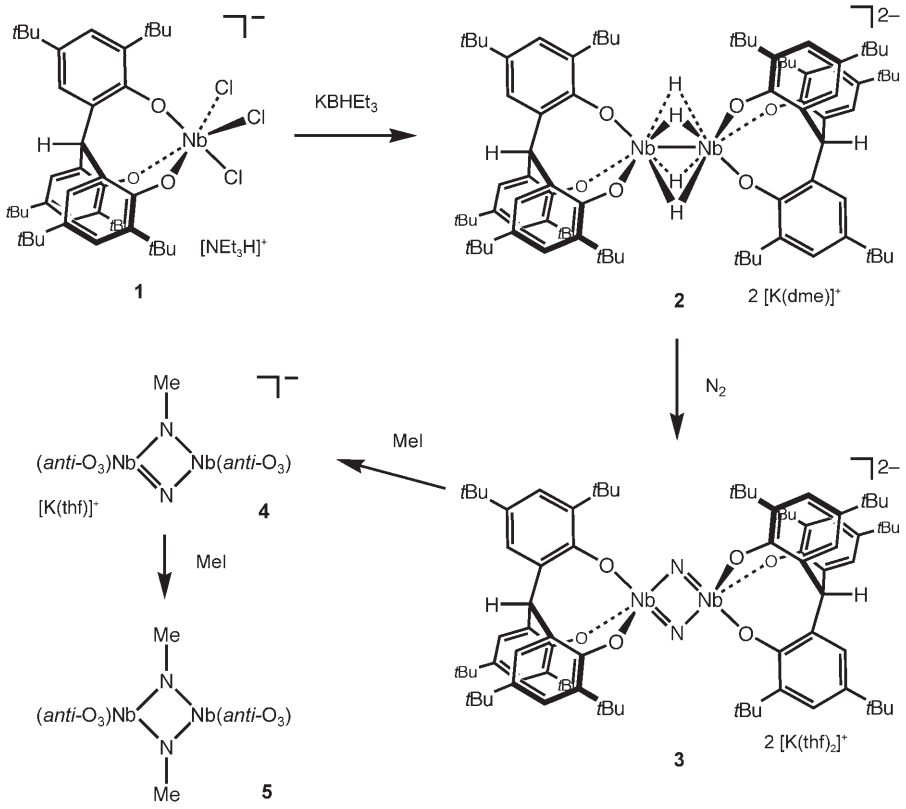


Activation and functionalization of molecular nitrogen by soluble metal complexes has attracted widespread attention from both fundamental and practical points of view.[1,2] Typically, metal complexes capable of strongly activating N_2 and cleaving the N≡N bond are formed from low-valent early-transition-metal precursors[2b,3] or using strong reducing reagents, such as alkali metals.[4,5] Another method is the use of metal hydride complexes. Dinitrogen cleavage by hydride species could be important in a catalytic system and is relevant to the Harber–Bosch process, in which a mixture of N_2 and H_2 is catalytically converted to NH_3.[6] Although late-transition-metal hydride complexes are often found to weakly bind dinitrogen with concomitant elimination of H_2,[7] conversion of an early-transition-metal hydride to a dinitrogen complex is a rarely documented phenomenon.[8,9]

We reported that a niobium complex bearing a linear triaryloxide ligand generates a nitride complex when treated with $LiBHEt_3$ under dinitrogen.[10] Although we speculated that the reaction proceeds through a hydride intermediate that binds and cleaves N_2 with reductive elimination of H_2, attempts to isolate any hydride species capable of activating N_2 have met with difficulties. As part of our investigations of ancillary ligand effects in metal aryloxide chemistry, we recently described the first examples of Group 4 metal complexes with a tripodal triaryloxide ligand (abbreviated $[O_3]^{3-}$, Scheme 1).[11] The O_3 ligand provides a rigid, facial donor environment, and it can coordinate a metal in two forms, which differ in the relative orientation of the methine C–H bond.[11] In the context of dinitrogen activation, we were interested in extending this chemistry to niobium. Herein we report the preparation of a hydride complex $[K(dme)]_2[\{(anti\text{-}O_3)Nb\}_2(\mu\text{-}H)_4]$ (**2**, dme = dimethoxyethane), which yielded $[K(thf)_2]_2[\{(anti\text{-}O_3)Nb\}_2(\mu\text{-}N)_2]$ (**3**) upon reaction with N_2. This transformation is a rare example of N_2 dissociation induced by a hydride complex alone.[9c]

Coordination of the tripodal triaryloxide ligand to niobium may be achieved by a two-step sequence involving the initial reaction of $NbCl_5$ with $H_3(O_3)$ in CH_3CN to give $[\{H(O_3)\}NbCl_3(CH_3CN)]$ in 77% yield. The nitrile adduct features a bidentate $[H(O_3)]^{2-}$ ligand in which only two of the aryloxide donors coordinate to niobium, with the uncoordinated aryloxide fragment remaining protonated. The remaining hydroxy group was deprotonated by NEt_3 in toluene at 80 °C, yielding $[NEt_3H][(anti\text{-}O_3)NbCl_3]$ (**1**) as a red powder in 92%. An X-ray structure analysis of **1** reveals that the tridentate O_3 ligand coordinates to Nb facially, and its methine proton is oriented away from the metal center.[12]

Slow addition of four equivalents of $KBHEt_3$ in THF to a cooled toluene solution of **1** led to isolation of **2** as yellow crystals in 66% yield after the solution was warmed to room temperature and the product was recrystallized from dme (Scheme 1). During the reaction, $KBHEt_3$ partially acts as a reductant, and the metal center is reduced from Nb^V to Nb^{IV}. The synthesis of **2** must occur under an argon atmosphere to avoid further reaction (see below). The deuterated analogue was quantitatively prepared by treatment of **2** under D_2 gas for three days at room temperature and was characterized by NMR spectroscopy.



Scheme 1.

An X-ray crystal structure determination of **2** reveals a dimeric structure with two $\{(anti\text{-}O_3)Nb\}$ units bridged by four hydride ligands (Figure 1).[12] The hydrides were located in the Fourier difference map and refined isotropically. The dimer possesses a center of inversion about a central $\{Nb_2(\mu\text{-}H)_4\}$

[*] Dr. F. Akagi, Dr. T. Matsuo, Dr. H. Kawaguchi
Coordination Chemistry Laboratories
Institute for Molecular Science
Myodaiji, Okazaki 444-8787 (Japan)
Fax: (+81) 564-59-5589
E-mail: hkawa@ims.ac.jp

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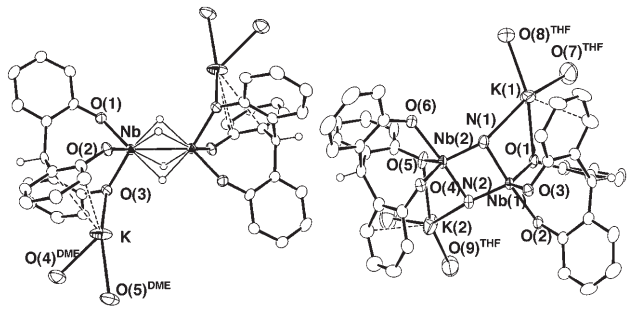

Figure 1. Molecular structures of **2** (left) and **3** (right). Thermal ellipsoids are set at the 50% probability level; the solvate molecules (except for their oxygen atoms) and *tert*-butyl groups have been omitted for clarity.

core. The environment around potassium includes an aryloxide oxygen atom, one dme molecule, and η^3-aryl complexation, with K–C_{aryl} distances averaging 3.145 Å. The short Nb–Nb distance of 2.5690(5) Å indicates metal–metal bonding,[5a,13] thus accounting for the observed diamagnetism. The NMR spectra of **2** are consistent with its solid-state structure if a fluxional process is invoked to explain the observed equivalence of the aryloxide groups on the NMR timescale at 25 °C. The bridging hydrides are observed as a broad signal at $\delta = 6.29$ ppm in the ^{1}H NMR spectrum. Upon cooling the sample, we did not detect any significant change in the hydride region.

Complex **2** appears to be thermally stable in solution under argon (3 h at 80 °C), while exposure of a toluene solution of **2** to an atmosphere of N_2 at room temperature resulted in a gradual color change from maroon to yellow-brown. As monitored by ^{1}H NMR spectroscopy at room temperature in a sealed NMR tube, the reaction required three days for completion and gave the nitride complex **3** in greater than 70% yield. Coupled with ^{1}H NMR spectroscopy, the GC analysis of the headspace above the reaction confirmed elimination of H_2. The preparative-scale synthesis of the nitride complex was accomplished at higher temperature (80 °C) and allowed isolation of **3** as yellow crystals in 37% yield after recrystallization from THF/pentane. The isotopically labeled complex [^{15}N]**3** was prepared analogously under $^{15}N_2$ and exhibits a single resonance at 311 ppm in the ^{15}N NMR spectrum. This result confirms that the origin of the nitride ligands is added N_2. The ^{1}H NMR spectrum of **3** displays no resonances indicative of hydride ligands. Complex **3** possesses high symmetry in solution, as equivalent aryloxide groups are observed.

An X-ray crystal structure determination of **3** has shown it to be dimeric, constructed around a $\{Nb_2N_2\}$ four-membered ring that resides on a pseudo-two-fold axis (Figure 1).[12] Reduction of dinitrogen by **2** results in cleavage of the N≡N bond, as evidenced by the N···N separation of 2.589(5) Å. Each niobium center displays five-coordinate, distorted trigonal-bipyramidal coordination, with N(1) and O(2) in the axial positions of Nb(1) [N(2) and O(6) for Nb(2)]. The $\{Nb_2N_2\}$ core is nearly planar with a Nb(1)-N(2)-Nb(2)-N(1) torsion angle of 6.2(1)°. Dinuclear complexes with four-membered $\{M_2N_2\}$ cores are somewhat rare. Of the few example, some were derived from N_2 activation.[5,10,14] The geometrical parameters within the $\{Nb_2N_2\}$ unit of **3** are similar to those found in the known diniobium nitrides.[5a,10]

The nitride complex **3** occurs as an ion pair. The potassium cations are tightly associated with the nitride ligands, which are possibly the most nucleophilic sites in the anionic complex.[15] The nucleophilic behavior of the nitride groups was observed in the reaction of **3** with excess methyl iodide. Methylation was found to proceed in a stepwise fashion (Scheme 1). One of the nitride ligands was readily methylated to afford a nitride imide complex, [K(thf)][{(*anti*-O_3)Nb}$_2$(μ-N)(μ-NMe)] (**4**). Prolonged heating (five days, 60 °C) resulted in clean formation of a bis-imide complex, [{(*anti*-O_3)Nb}$_2$(μ-$NMe)_2$] (**5**). The ^{15}N NMR spectrum of the isotopically labeled complex [^{15}N]**4** exhibits the nitride and imide signals at $\delta = 290$ and 29.6 ppm, respectively, while the imide groups of [^{15}N]**5** appear as a singlet at 20.2 ppm. Although bridging nitride complexes are known to react with hydrosilanes to give silylimide ligands,[5c,16] the dianionic nitride complex **3** was found to be unreactive toward hydrosilanes and H_2.

In summary, the hydride complex **2** was found to react with dinitrogen, giving the nitride complex **3**. The nitride complex underwent stepwise methylation to produce the bis-imide complex **5**. Reduction of N_2 utilizing the hydride complex **2** is closely related to work by Fryzuk et al., who used the tantalum(IV) hydride complex [{(NPN)Ta}$_2$(μ-H)$_4$] ([NPN] = PhP($CH_2SiMe_2NPh)_2$).[8] This complex was found to react with N_2 through partial loss of H_2 to give the dinitrogen complex [{(NPN)Ta}$_2$(μ-η^1:η^2-N_2)(μ-H)$_2$], in which two hydride ligands remain coordinated. Subsequent treatment with boranes, silanes, and zirconium hydrides resulted in N–N bond cleavage of the coordinated N_2 molecule.[16,17] For **2**, the cleavage proceeded spontaneously and did not require external reducing agent. This process corresponds to an overall six-electron reduction of N_2, in which two electrons are initially stored in a metal–metal bond, and four additional electrons are provided by H_2 elimination. Further studies on the mechanism of dinitrogen activation by **2** and the reactivity of **2** and **3** are underway.

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[1] a) *Catalytic Ammonia Synthesis* (Ed.: J. R. Jennings), Plenum, New York, **1991**; b) H.-J. Himmel, M. Reiher, *Angew. Chem.* **2006**, *118*, 6412 – 6437; *Angew. Chem. Int. Ed.* **2006**, *45*, 6264 – 6288.

[2] a) D. V. Yandulov, R. R. Schrock, *Science* **2003**, *301*, 76 – 78; b) C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 861 – 863; c) J. S. Figueroa, N. A. Piro, C. R. Clough, C. C. Cummins, *J. Am. Chem. Soc.* **2006**, *128*, 940 – 950; d) M. D. Fryzuk, J. B. Love, S. J. Rettig, V. G. Young, *Science* **1997**, *275*, 1445 – 1447; e) J. A. Pool, E. Lobkovsky, P. J. Chirik, *Nature* **2004**, *427*, 527 – 530; f) Y. Ohki, M. D. Fryzuk, *Angew. Chem.* **2007**, *119*, 3242 – 3245; *Angew. Chem. Int. Ed.* **2007**, *46*, 3180 – 3183; g) S. Gambarotta, J. Scott, *Angew. Chem.* **2004**, *116*, 5412 – 5422; *Angew. Chem. Int. Ed.* **2004**, *43*, 5298 – 5308.

[3] a) T.-C. Tsai, M. J. A. Johnson, D. J. Mindiola, C. C. Cummins, W. T. Klooster, T. F. Koetzle, *J. Am. Chem. Soc.* **1999**, *121*, 10426 – 10427; b) J. A. Pool, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2003**, *125*, 2241 – 2251.

[4] a) U. J. Kilgore, X. Yang, J. Tomaszewski, J. C. Huffman, D. J. Mindiola, *Inorg. Chem.* **2006**, *45*, 10712 – 10721; b) J. R. Hagadorn, J. Arnold, *J. Am. Chem. Soc.* **1996**, *118*, 893 – 894; c) W. H. Monillas, G. P. A. Yap, L. A. MacAdams, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 8090 – 8091.

[5] a) A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli, A. Chiesi-Villa, *J. Am. Chem. Soc.* **2000**, *122*, 3652 – 3670; b) G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock, F. G. N. Cloke, *J. Am. Chem. Soc.* **1999**, *121*, 10444 – 10445; c) M. Hirotsu, P. P. Fontaine, A. Epshteyn, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2007**, *129*, 9284 – 9285.

[6] R. Schlögl, *Angew. Chem.* **2003**, *115*, 2050 – 2055; *Angew. Chem. Int. Ed.* **2003**, *42*, 2004 – 2008.

[7] a) B. Chaudret, J. Devillers, R. Poilblanc, *Organometallics* **1985**, *4*, 1727 – 1732; b) M. H. G. Prechtl, Y. Ben-David, D. Giunta, S. Busch, Y. Taniguchi, W. Wisniewski, H. Görls, R. J. Mynott, N. Theyssen, D. Milstein, W. Leitner, *Chem. Eur. J.* **2007**, *13*, 1539 – 1546.

[8] M. D. Fryzuk, S. A. Johnson, B. O. Patrick, A. Albinati, S. A. Mason, T. F. Koetzle, *J. Am. Chem. Soc.* **2001**, *123*, 3960 – 3973.

[9] a) J. M. de Wolf, R. Blaauw, A. Meetsma, J. H. Teuben, R. Gyepes, V. Varga, K. Mach, N. Veldman, A. L. Spek, *Organometallics* **1996**, *15*, 4977 – 4983; b) P. J. Chirik, L. M. Henling, J. E. Bercaw, *Organometallics* **2001**, *20*, 534 – 544; c) P. Avenier, M. Taoufik, A. Lesage, X. Solans-Monfort, A. Baudouin, A. de Mallmann, L. Veyre, J.-M. Basset, O. Eisenstein, L. Emsley, E. A. Quadrelli, *Science* **2007**, *317*, 1056 – 1060.

[10] H. Kawaguchi, T. Matsuo, *Angew. Chem.* **2002**, *114*, 2916 – 2918; *Angew. Chem. Int. Ed.* **2002**, *41*, 2792 – 2794.

[11] F. Akagi, T. Matsuo, H. Kawaguchi, *J. Am. Chem. Soc.* **2005**, *127*, 11936 – 11937.

[12] CCDC-655242 (**2**), 655243 (**3**), and 655244 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] a) M. Tayebani, K. Feghali, S. Gambarotta, C. Bensimon, *Organometallics* **1997**, *16*, 5084 – 5088; b) B.-L. Ooi, I. Søtofte, J. J. Vittal, *Inorg. Chim. Acta* **2004**, *357*, 625 – 629.

[14] T. S. Haddad, A. Aistars, J. W. Ziller, N. M. Doherty, *Organometallics* **1993**, *12*, 2420 – 2422.

[15] a) J. K. Brask, M. G. Fickes, P. Sangtrirutnugul, V. Durà-Vilà, A. L. Odom, C. C. Cummins, *Chem. Commun.* **2001**, 1676 – 1677; b) K. Dehnicke, J. Strähle, *Angew. Chem.* **1992**, *104*, 978 – 1000; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 955 – 978.

[16] B. A. MacKay, R. F. Munha, M. D. Fryzuk, *J. Am. Chem. Soc.* **2006**, *128*, 9472 – 9483.

[17] L. P. Spencer, B. A. MacKay, B. O. Patrick, M. D. Fryzuk, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17094 – 17098.

