

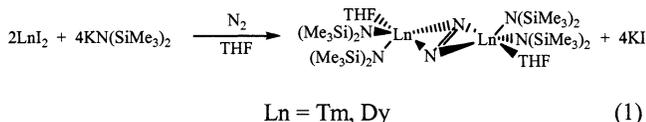
Reduction of Dinitrogen to Planar Bimetallic $M_2(\mu-\eta^2:\eta^2-N_2)$ Complexes of Y, Ho, Tm, and Lu Using the $K/Ln[N(\text{SiMe}_3)_2]_3$ Reduction System

William J. Evans,* David S. Lee, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, California 92697-2025

Received June 26, 2003; E-mail: wevans@uci.edu

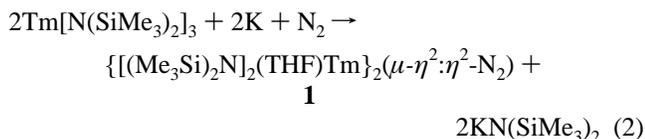
One of the recent advances in dinitrogen reduction chemistry^{1–9} was the discovery that Tm(II), Dy(II), and Nd(II) readily provide access to the formerly rare $M_2(\mu-\eta^2:\eta^2-N_2)$ moiety in complexes with ligands as simple as $[N(\text{SiMe}_3)_2]^-$, eq 1, and $[\text{OC}_6\text{H}_3\text{Bu}_2-2-6]^-$.⁹ This provided the option for the first time of developing the



chemistry of this bimetallic $(N_2)^{2-}$ unit without the constraints of four cyclopentadienyl^{10–12} or polydentate ancillary ligands.^{7,13–15} This approach to dinitrogen reduction chemistry was made possible by the discovery of the first examples of soluble molecular divalent lanthanide reagents: the diiodides of Tm(II),¹⁶ Dy(II),¹⁷ and Nd(II).¹⁸ Although these new reductants will allow the exploration of the $(\mu-\eta^2:\eta^2-N_2)$ moiety with a robust series of ligands, the analysis of the reaction chemistry is complicated by the fact that the Tm(III), Dy(III), and Nd(III) products have magnetic moments of 7.1, 10.4, and 3.5 μ_B , respectively. NMR studies with the first two metal ions are not informative, and Nd(III) spectra are often not definitive.

We now report that the chemistry of eq 1 can be extended to the diamagnetic trivalent metals, yttrium and lutetium, using simple trivalent lanthanide amide precursors that have been known for 30 years.¹⁹ These results raise interesting questions not only about dinitrogen reduction chemistry, but also about f element reduction chemistry in general.

The new chemistry was discovered in connection with efforts to find routes to $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Tm}\}_2\text{N}_2$, **1**, alternative to the synthesis in eq 1. We sought to determine if the putative divalent “Tm $[N(\text{SiMe}_3)_2]_2$ ” intermediate in this reaction could be generated in situ by potassium reduction of the readily available trivalent Tm- $[N(\text{SiMe}_3)_2]_3$ ²⁰ such that the dinitrogen complex could be made from $K/\text{Tm}[N(\text{SiMe}_3)_2]_3$. As shown in reaction 2, this was suc-



cessful: the $(N_2)^{2-}$ complex, **1**, can be synthesized from a trivalent thulium precursor and potassium.²¹ The reaction can be effected with a potassium mirror, solid potassium, and potassium graphite.

Although this $K/\text{Tm}[N(\text{SiMe}_3)_2]_3$ reaction was anticipated to form divalent “Tm $[N(\text{SiMe}_3)_2]_2$ ” which subsequently would reduce N_2 as seen in reaction 1, no evidence of an intensely colored Tm(II) intermediate was observed. Although this could be a transient species difficult to detect, this raised the question of alternative reduction pathways which did not involve Tm(II). For example, was it possible that $\text{Tm}[N(\text{SiMe}_3)_2]_3$ mediated electron transfer from

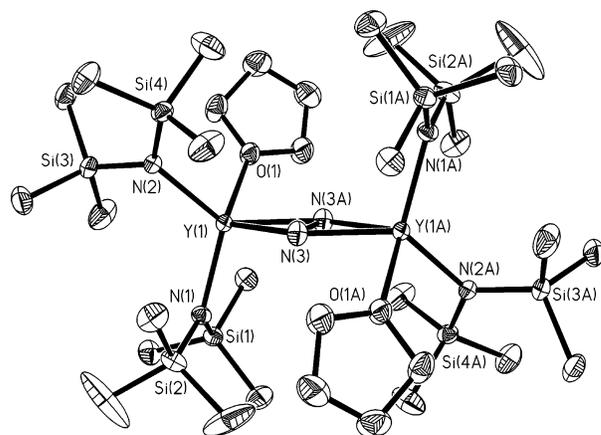
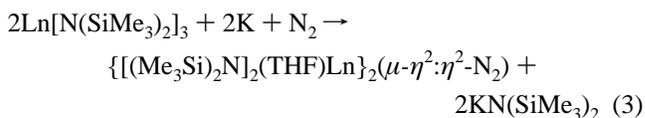


Figure 1. Thermal ellipsoid plot of $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Y}\}_2(\mu-\eta^2:\eta^2-N_2)$ drawn at the 50% probability level. The Tm, Ho, and Lu analogues are isomorphous.

K to N_2 by some undetected “ $\{\text{Tm}[N(\text{SiMe}_3)_2]_3\}_x(N_2)$ ” intermediate in which N_2 is activated to reduction? This is reasonable for transition metals which readily bind N_2 and have good orbital matching,^{4,22} but has not been suggested for f elements.

To test the latter possibility, the $K/\text{Ln}[N(\text{SiMe}_3)_2]_3/N_2$ reaction was examined with Ho. Neither molecular nor solid-state²³ Ln(II) compounds of Ho are known, and the Ln(III)/Ln(II) reduction potential is estimated to be -2.9 V.²⁴ However, as shown in eq 3 (Ln = Ho), this $K/\text{Ln}[N(\text{SiMe}_3)_2]_3$ system also reduces dinitrogen



to an $(N_2)^{2-}$ complex analogous to eq 1, $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Ho}\}_2(\mu-\eta^2:\eta^2-N_2)$, **2**.²⁵ Complex **2** is isomorphous with **1**.⁹

These results led us to examine reaction 3 with the diamagnetic trivalent Y(III) and Lu(III) analogues. To our knowledge, no divalent chemistry has been reported in the literature for these metals: comprehensive reviews of lanthanide reduction potentials do not include Ln(III)/Ln(II) reduction potentials for these metals,²⁴ and the solid-state literature, which includes LnX_2 complexes for most of the lanthanides [as either $\text{Ln}^{2+}(\text{I}^-)_2$ or $\text{Ln}^{3+}(\text{I}^-)_2(\text{e}^-)$], does not include Y and Lu.²³ Nevertheless, the diamagnetic complexes $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Y}\}_2(\mu-\eta^2:\eta^2-N_2)$, **3**, and $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Lu}\}_2(\mu-\eta^2:\eta^2-N_2)$, **4**, are formed via eq 3 (Ln = Y, Lu).²⁶

Characterization of **3** and **4**, Figure 1, showed them to be isomorphous with **1** and **2**. The NN bond distances in **3** and **4** are 1.268(3) and 1.285(4) Å, respectively, which is consistent with the presence of $(N=N)^{2-}$ ligands. The diamagnetic ¹H NMR spectra of **3** and **4** both show conventional $N(\text{SiMe}_3)_2$ resonances at 0.35 and 0.36 ppm, respectively, in C_6D_6 . The 50.67 MHz ¹⁵N NMR

spectra²⁶ revealed a triplet at 513.3 ppm (vs MeNO₂) for the yttrium sample (as expected for a complex containing two spin 1/2 yttrium nuclei) and a singlet at 557.0 ppm for the lutetium analogue.²⁷ The 7 Hz J_{YN} coupling constant is in the 2–15 Hz range found in the two literature reports on yttrium nitrogen coupling.^{28,29}

The K/Ln[N(SiMe₃)₂]₃ reduction system offers a tremendous advantage in the study of dinitrogen reduction because it allows the planar (N₂)²⁻ moiety to be isolated in complexes of simple ligands with the diamagnetic ions Y³⁺ and Lu³⁺. More generally, it offers a method to accomplish with readily available trivalent lanthanide complexes the reductive lanthanide chemistry previously available only from the highly reactive divalent complexes of Tm(II), Dy(II), and Nd(II).⁹

Alkali metal reduction of dinitrogen in the presence of other metals is common with transition metals,^{8,30} but this usually is assumed to involve reduction to lower oxidation states or reduction of transition metal dinitrogen complexes in which good orbital overlap activates the N₂ ligand.^{4,22} If reaction 3 involves divalent lanthanide chemistry, it is the first evidence of Y(II), Ho(II), and Lu(II) chemistry. If these reactions do not involve Ln(II), which is supported by the current literature on their redox chemistry,^{23,24} it means that divalent chemistry can be mimicked simply with alkali metals and trivalent Ln[N(SiMe₃)₂]₃ complexes. In either case, this portends exciting new options in the reductive chemistry of the lanthanides.

We expect that the K/Ln[N(SiMe₃)₂]₃ combination is not the only K/LnZ₃ combination (Z = monoanionic ligand) that will participate in this type of reductive chemistry. In fact, forerunners of this chemistry may already be in the literature. Porphyrinogen complexes of Sm¹⁵ and Pr⁶ have generated reduced dinitrogen products in the presence of alkali metals, and it has been shown that arenes are reduced in the presence of tricyclopentadienyl La and Ce complexes.^{31–34} However, these reactions have been interpreted in terms of divalent lanthanide reductive chemistry. We expect that the extension of the K/LnZ₃ approach to reductive lanthanide chemistry to other metals, ligands, and substrates will be quite productive.

Acknowledgment. We thank the U.S. National Science Foundation for the support of this research.

Supporting Information Available: Experimental details (PDF) and crystallographic information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, 200–202, 379.
- Fryzuk, M. D.; Kozak, C. M.; Bowdridge, M. R.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, 124, 8389.
- Yandulov, D. V.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, 124, 6252.
- Peters, J. C.; Cherry, J. P. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, 121, 10053 and references within.
- Ganesan, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2001**, 40, 766.
- Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *Chem. Commun.* **1998**, 2603.
- Roussel, P.; Scott, P. J. *J. Am. Chem. Soc.* **1998**, 120, 1070.
- Chirik, P. J.; Pool, J. A.; Lobkovsky, E. J. *J. Am. Chem. Soc.* **2003**, 125, 2241.
- Evans, W. J.; Zucchi, G.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, 125, 10.
- Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, 110, 6877.
- Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, 123, 7927.
- Evans, W. J.; Allen, N. T.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2002**, 41, 359.
- Fryzuk, M. D.; Love, J. B.; Rettig, S. T.; Young, V. G. *Science* **1997**, 275, 1445.
- Fryzuk, M. D.; Haddad, T. S.; Rettig, S. T. *J. Am. Chem. Soc.* **1990**, 112, 8185.
- Dube, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, 19, 3716.
- Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Petrovskaya, T. W.; Ziller, J. W.; Broomhall-Dillard, R. N. R.; Evans, W. J. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 133.
- Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, 122, 11749.
- Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Dechert, S.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, 40, 3176.
- Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.
- Edelmann, F. T. *Synth. Methods Organomet. Inorg. Chem.* **1997**, 6, 37.
- {[(Me₃Si)₂N]₂(THF)Tm}₂(μ-η²:η²-N₂), **1**. In a N₂ containing glovebox, a colorless solution of Tm[N(SiMe₃)₂]₃ (0.200 g, 0.31 mmol) in 10 mL of THF was added to a vial containing KC₈ (0.042 g, 0.31 mmol) and a stir bar. The mixture immediately became orange and was allowed to stir for 3 h. The mixture was centrifuged, and evaporation of the supernatant yielded an orange oil. At room temperature over 2–3 days a concentrated sample of the oil in 2 mL of Et₂O produced orange crystals (0.087 g, 49% of **1** which were identified by X-ray crystallography. Anal. Calcd for C₃₂H₈₈N₆O₂Si₈Tm₂: Tm, 29.34. Found: Tm, 30.0.
- O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1998**, 37, 5149.
- Meyer, G.; Wickleder, M. S. *Handb. Phys. Chem. Rare Earths* **2000**, 28, 53.
- Morss, L. R. *Chem. Rev.* **1976**, 76, 827.
- Complex **2** was prepared using the procedure for **1**.²¹ See Supporting Information. Crystallographic data for C₃₂H₈₈N₆O₂Si₈Ho₂. Monoclinic, P₂/n, a = 10.8135(4) Å, b = 23.4721(9) Å, c = 11.5460(4) Å, β = 112.5870(1)°, V = 2705.77(17) Å³, Z = 2, ρ_{calcd} = 1.404 Mg/m³, R₁ = 0.0223 [I > 2σ(I)], wR₂ = 0.0501, GOF = 1.048.
- {[(Me₃Si)₂N]₂(THF)Y}₂(μ-η²:η²-N₂), **3**. A colorless solution of Y[N(SiMe₃)₂]₃ (0.200 g, 0.35 mmol) in 10 mL of THF was added to a vial containing KC₈ (0.047 g, 0.35 mmol) and a stir bar. The mixture immediately became orange and was allowed to stir for 3 h. The mixture was centrifuged, and evaporation of the supernatant yielded an orange oil. A concentrated sample of the oil in 2 mL of Et₂O produced pale blue crystals (0.031 g, 18%) of **3** at room temperature over 2–3 days. NMR spectroscopy showed additional product in solution, but for this study only crystalline samples suitable for X-ray crystallography were used. ¹H NMR (C₆D₆): δ 0.348 (9H, Me), 1.41 (1H, THF), 4.24 (1H, THF). ¹³C NMR (C₆D₆): δ 5.51 (Me), 25.81 (THF), 68.00 (THF). ¹⁵N{¹H} NMR (THF-d₈): δ 513.3 (t, J_{YN} = 7 Hz). Anal. Calcd for C₃₂H₈₈N₆O₂Si₈Y₂: Y, 17.93. Found: Y, 17.4. Samples sent for commercial analysis undergo some desolvation. Anal. Calcd for {[(Me₃Si)₂N]₂Y}₂N₂(THF)₁₅: C, 37.71; H, 8.86; Y, 18.61; N, 8.80; Si, 23.51. Found: C, 37.25; H, 9.02; Y, 18.27; N, 8.57; Si, 23.58. Crystallographic data for C₃₂H₈₈N₆O₂Si₈Y₂. Monoclinic, P₂/n, a = 10.8258(4) Å, b = 23.5068(1) Å, c = 11.5787(5) Å, β = 112.6830(1)°, V = 2718.64(19) Å³, Z = 2, ρ_{calcd} = 1.211 Mg/m³, R₁ = 0.0286 [I > 2σ(I)], wR₂ = 0.0689, GOF = 1.042. The isomorphous Lu analogue was prepared similarly. Crystallographic data for C₃₂H₈₈N₆O₂Si₈Lu₂. P₂/n, a = 10.7686(4) Å, b = 23.4769(9) Å, c = 11.4898(4) Å, β = 112.7590(1)°, V = 2678.61(17) Å³, Z = 2, ρ_{calcd} = 1.443 Mg/m³, R₁ = 0.0207 [I > 2σ(I)], wR₂ = 0.0457, GOF = 1.091. ¹⁵N NMR. The ¹⁵N analogues were prepared similarly by introducing a THF solution of Ln[N(SiMe₃)₂]₃ into a flask containing KC₈ and ¹⁵N₂ gas in an argon containing glovebox. ¹⁵N NMR spectra were measured using an external reference ¹⁵N-formamide in DMSO (–269 ppm with respect to nitromethane at 0.0 ppm).
- For comparison, see: Fryzuk, M. D.; Haddad, T. S.; Mylvaganam, M.; McConville, D. H.; Rettig, S. J. *J. Am. Chem. Soc.* **1993**, 115, 2782.
- Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, 123, 3960.
- Mason, J.; Larkworthy, L. F.; Moore, E. A. *Chem. Rev.* **2002**, 102, 913.
- Fratiello, A.; Kubo-Anderson, V.; Bolanos, E. L.; Haigh, D.; Laghaei, F.; Perrigan, R. D. *J. Magn. Reson., Ser. A* **1994**, 107, 56.
- Lee, S. G. *Bull. Korean Chem. Soc.* **1996**, 17, 589.
- Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, 98, 8351.
- Lappert, M. F.; Cassani, M. C.; Laschi, F. *Chem. Commun.* **1997**, 1563.
- Lappert, M. F.; Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Laschi, F. *Organometallics* **1999**, 18, 5539.
- Lappert, M. F.; Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Laschi, F.; Hulkes, A. G.; Khovstov, A. V.; Protchenko, A. V. *J. Organomet. Chem.* **2002**, 647, 71.
- Lappert, M. F.; Gun'ko, Y. K.; Hitchcock, P. B. *Organometallics* **2000**, 19, 2832.

JA036923M