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Expanding Dinitrogen Reduction Chemistry to Trivalent Lanthanides via the LnZ_3/Alkali Metal Reduction System: Evaluation of the Generality of Forming $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Complexes via LnZ_3/K

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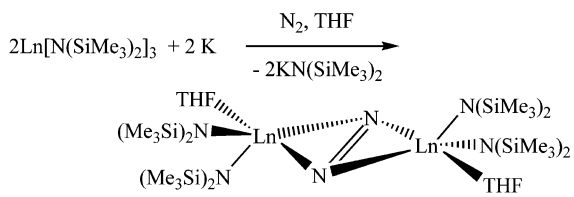
Abstract: The $Ln[N(SiMe_3)_2]_3$/K dinitrogen reduction system, which mimicks the reactions of the highly reducing divalent ions Tm(II), Dy(II), and Nd(II), has been explored with the entire lanthanide series and uranium to examine its generality and to correlate the observed reactivity with accessibility of divalent oxidation states. The $Ln[N(SiMe_3)_2]_3$/K reduction of dinitrogen provides access from readily available starting materials to the formerly rare class of $M_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes, $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **1**, that had previously been made only from TmI_2, DyI_2, and NdI_2 in the presence of $KN(SiMe_3)_2$. This LnZ_3/alkali metal reduction system provides crystallographically characterizable examples of **1** for Nd, Gd, Tb, Dy, Ho, Er, Y, Tm, and Lu. Sodium can be used as the alkali metal as well as potassium. These compounds have NN distances in the 1.258(3) to 1.318(5) Å range consistent with formation of an $(N{=}N)^{2-}$ moiety. Isolation of **1** with this selection of metals demonstrates that the $Ln[N(SiMe_3)_2]_3$/alkali metal reaction can mimic divalent lanthanide reduction chemistry with metals that have calculated Ln(III)/Ln(II) reduction potentials ranging from −2.3 to −3.9 V vs NHE. In the case of Ln = Sm, which has an analogous Ln(III)/Ln(II) potential of −1.55 V, reduction to the stable divalent tris(amide) complex, $K\{Sm[N(SiMe_3)_2]_3\}$, is observed instead of dinitrogen reduction. When the metal is La, Ce, Pr, or U, the first crystallographically characterized examples of the tetrakis[bis(trimethylsilyl)amide] anions, $\{M[N(SiMe_3)_2]_4\}^-$, are isolated as THF-solvated potassium or sodium salts. The implications of the LnZ_3/alkali metal reduction chemistry on the mechanism of dinitrogen reduction and on reductive lanthanide chemistry in general are discussed.

Introduction

Among the recent advances in dinitrogen reduction chemistry[1−7] was the discovery that simple lanthanide bis(trimethylsilyl)amide complexes, $Ln[N(SiMe_3)_2]_3$, reported by Bradley over 30 years ago,[8] could be combined with alkali metals to reduce N_2 to form $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes, eq 1.[7] This result was unusual in several respects as discussed in the following paragraphs.

For many years, the lanthanides were not expected to have the appropriate orbital characteristics to interact with dinitrogen,[9] much less to form the $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ structural arrangement



(1)

that was formerly rare in dinitrogen chemistry.[9−12] The special properties of divalent Sm(II)[9,13] and the recently discovered, structurally characterizable, molecular divalent diiodide complexes of Tm(II),[14] Dy(II),[15] and Nd(II),[16] allowed a significant number of $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes to be prepared with a

(1) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385−401.
(2) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76−78.
(3) 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*, 10053−10067.
(4) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4958−4961.
(5) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527−530.
(6) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 10782−10783.
(7) Evans, W. J.; Lee, D. S.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 454−455.
(8) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021−1023.
(9) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877−6879.
(10) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445−1447.
(11) Guan, J.; Dube, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 4820−4827.
(12) Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *Chem. Commun.* **1998**, 2603−2604.
(13) Evans, W. J. *J. Organomet. Chem.* **2002**, *652*, 61−68.
(14) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Petrovskaya, T. V.; Ziller, J. W.; Broomhall-Dillard, R. N. R.; Evans, W. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 133−135.
(15) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11749−11750.
(16) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Dechert, S.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3176−3178.

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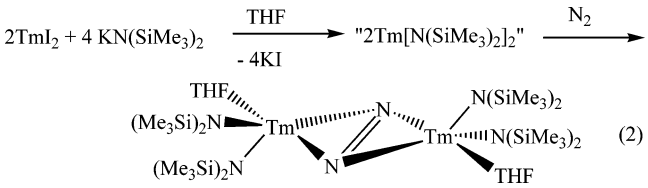
Table 1. Calculated Values of the $Ln^{3+} + e^- \rightarrow Ln^{2+}$ Half Reaction vs NHE[22]

Ln	$Ln^{3+} + e^- \rightarrow Ln^{2+}$ $E_{1/2}$ vs NHE, V
Eu	−0.35
Yb	−1.15
Sm	−1.5
Tm	−2.3
Dy	−2.5
Nd	−2.6
Pr	−2.7
Ho	−2.9
Er	−3.1
La	−3.1
Ce	−3.2
Tb	−3.7
Gd	−3.9
Lu	a
Y	a

[a] No values calculated.

variety of ligands including cyclopentadienyls,[9,17,18] amides,[19] aryloxides,[19] and porphyrinogens.[12,20,21] However, it appeared that this lanthanide-based dinitrogen reduction would require accessible divalent states.

Equation 1 was originally explored[7] with Ln = Tm to determine if the presumed divalent "$Ln[N(SiMe_3)_2]_2$" intermediates thought to be responsible for the formation of the dinitrogen complexes in the synthesis from LnI_2 and $KN(SiMe_3)_2$, eq 2,[19]



(2)

could be generated in situ from the readily accessible $Ln[N(SiMe_3)_2]_3$ and potassium. As shown in eq 1, this reaction succeeded as expected for Ln = Tm, which has a −2.3 V (vs NHE) calculated Ln(III)/Ln(II) reduction potential (Table 1).[22] However, surprisingly this reaction also was successful with Ho, which has a −2.9 V Ln(III)/Ln(II) reduction potential, and Y and Lu, for which no molecular divalent chemistry has previously been reported.[23,24]

These results suggested several mechanistic possibilities. If the reactions proceeded through divalent $Ln[N(SiMe_3)_2]_2$ intermediates, they represent the first examples of molecular Ho(II), Y(II), and Lu(II) chemistry. This seemed unlikely although there recently have been many breakthroughs in molecular divalent lanthanide chemistry.[25,26] Alternatively, if the trivalent $Ln[N(SiMe_3)_2]_3$ complexes were activating dinitrogen for reduction by potassium in THF, e.g., by formation of a "$(N_2)Ln[N(SiMe_3)_2]_3$" complex, this would be the first evidence of dinitrogen complexation to a trivalent lanthanide. Although this type of dinitrogen activation is common with transition metals,[27−30] formation of a dinitrogen complex of a trivalent lanthanide in the presence of a much larger concentration of a better ligand for lanthanides, namely THF, is not precedented.

An additional possibility involves activation of dinitrogen by potassium with the lanthanide amides facilitating electron transfer and reduction. Since none of these options were expected, this reaction deserved further study.

To determine the generality of the LnZ_3/alkali metal reduction system and the correlation, if any, with Ln(III)/Ln(II) reduction potentials, we have examined (a) the full range of lanthanides including those with calculated Ln(III)/Ln(II) reduction potentials as negative as −3.9 V vs NHE (Table 1),[22] (b) uranium, to examine if 5f metals as well as 4f metals participate in this chemistry, and (c) sodium (−2.7 V vs NHE) as well as potassium (−2.9 V vs NHE) to see if the reactions were also successful with a less reducing alkali metal.

Concomitantly, we have examined the variation of the LnZ_3/alkali metal reaction with the ionic radius of the lanthanides. Ionic radius is traditionally used as an important parameter with which to optimize trivalent lanthanide chemistry.[31] Size optimization of divalent chemistry is usually not an option because only a few divalent ions are accessible in solution and their significantly different reduction potentials give them different chemistry. If the LnZ_3/alkali reduction system was found to be general across the lanthanide series, then it could allow size optimization of reductive chemistry as well as trivalent chemistry.

This study has generated several new lanthanide dinitrogen complexes as well as the first crystallographically characterized tetrakis[bis(trimethylsilyl)amide] complexes, $\{M[N(SiMe_3)_2]_4\}^{1-}$. The implications of these results in dinitrogen reduction chemistry and f element reduction chemistry in general are discussed along with connections to previous alkali metal reduction chemistry, which has a long history in both the dinitrogen[27−30] and lanthanide[12,20,21,26,32−35] areas.

Experimental Section

The manipulations described below were performed under nitrogen with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Sodium and potassium were purchased from Aldrich, washed with hexanes,

(17) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7927−7928.
(18) Evans, W. J.; Allen, N. T.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 359−361.
(19) Evans, W. J.; Zucchi, G.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 10−11.
(20) Ganesan, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 766−769.
(21) Dube, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716−3721.
(22) Morss, L. R. *Chem. Rev.* **1976**, *76*, 827−841.
(23) Meyer, G.; Wickleder, M. S. *Handbook on the Physics and Chemistry of Rare Earths* **2000**, *28*, 53−129.
(24) Meyer, G.; Morss, L. R., Eds. *Synthesis of Lanthanide and Actinide Compounds* **1991**, 159−173.
(25) Evans, W. J. *Coord. Chem. Rev.* **2000**, *206−207*, 263−283.
(26) Cassani, M. C.; Gun′ko, Y. K.; Hitchcock, P. B.; Hulkes, A. G.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. *J. Organomet. Chem.* **2002**, *647*, 71−83.
(27) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351−8357.
(28) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R.; Reiff, W. M. *Inorg. Chem.* **1999**, *38*, 243−252.
(29) Fryzuk, M. D.; Love, J. B.; Rettig, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 8185−8186.
(30) Fryzuk, M. D.; Kozak, C. M.; Bowridge, M. R.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 8389−8397.
(31) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119−2136.
(32) Cassani, M. C.; Lappert, M. F.; Laschi, F. *Chem. Commun.* **1997**, 1563−1564.
(33) Cassani, M. C.; Duncalf, D. J.; Lappert, M. F. *J. Am. Chem. Soc.* **1998**, *120*, 12958−12959.
(34) Lappert, M. F.; Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Laschi, F. *Organometallics* **1999**, *18*, 5539−5547.
(35) Lappert, M. F.; Gun'ko, Y. K.; Hitchcock, P. B. *Organometallics* **2000**, *19*, 2832−2834.

and scraped to provide shiny pieces before use. KC_8 was prepared according to literature methods.[36] KH under mineral oil was purchased from Aldrich and used after washing with hexanes. Potassium bis(trimethylsilyl)amide was prepared by mixing 1 equiv of KH with 1 equiv of 1,1,1,3,3,3-hexamethyldisilazane in THF. $Ln[N(SiMe_3)_2]_3$[37] and $U[N(SiMe_3)_2]_3$[38] compounds were prepared according to literature methods. Solvents were sparged with argon and dried over columns containing Q-5 and sieves. NMR solvents were dried over sodium potassium alloy, degassed, and vacuum transferred before use. ^{1}H NMR, ^{13}C NMR, ^{15}N NMR spectra were recorded with Bruker DRX 400 MHz or Bruker DRX 500 MHz spectrometers. ^{15}N NMR spectra were measured using as an external reference ^{15}N-formamide in DMSO (−269 ppm with respect to nitromethane at 0 ppm). Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany). Complexometric analyses were carried out as previously described.[39] A variety of protocols were successful in providing complexes of **1**. All are based on the procedure reported earlier for Tm, Ho, Y and Lu.[7] Representative examples of experimental variations are given here.

{[(Me$_3$Si)$_2$N]$_2$(THF)Dy}$_2$(μ-η^2:η^2-N$_2$), 1-Dy. In a nitrogen glovebox, $Dy[N(SiMe_3)_2]_3$ (100 mg, 0.16 mmol) and KC_8 (25 mg, 0.18 mmol) are combined in 10 mL of THF and stirred. The mixture immediately became orange and was allowed to stir for 3 h. The mixture was centrifuged to remove dark insoluble material and evaporation of the supernatant yielded an orange oil. At −38 °C over 2−3 d a concentrated sample of the oil in toluene produced yellow crystals of **1** (40 mg, 45%). Anal. Calcd. for $C_{32}H_{88}N_6O_2Si_8Dy_2$: C, 33.75; H, 7.79; N, 7.38; Si, 19.73; Dy, 28.54. Found: C, 33.57; H, 7.64; N, 7.36; Si, 19.84; Dy, 28.60. This complex was found to be isomorphous with the structure previously prepared from DyI_2 and $KN(SiMe_3)_2$.[19]

{[(Me$_3$Si)$_2$N]$_2$(THF)Nd}$_2$(μ-η^2:η^2-N$_2$), 1-Nd. Following the protocol previously reported,[19] THF was condensed onto a mixture of NdI_2 (0.200 g, 0.50 mmol) and $KN(SiMe_3)_2$ (0.200 g, 1.0 mmol), and a stir bar in a tube fitted with a high vacuum stopcock. The mixture was warmed to −78° C and stirred under N_2 (1 atm) for 1 h and then allowed to stir for an additional hour at room temperature. The mixture was extracted with hexanes and concentrated to 1 mL. After 1 week at −35° C, **1-Nd** was isolated as blue green crystals (0.011 g, 4%). ^{1}H NMR (C_6D_6): δ −0.46 (9H, Me), 1.03 (1H, THF), 3.17 (1H, THF). ^{13}C NMR (C_6D_6): δ −0.26 (Me), THF resonances could not be located. Anal. Calcd. for $C_{32}H_{88}N_6O_2Si_8Nd_2$: Nd, 26.17. Found: Nd, 26.3. **1-Nd** can also be synthesized using $Nd[N(SiMe_3)_2]_3$ and K, KC_8, or Na.[7] However, the yields have been variable.

{[(Me$_3$Si)$_2$N]$_2$(THF)Er}$_2$(μ-η^2:η^2-N$_2$), 1-Er. In a nitrogen glovebox, pink $Er[N(SiMe_3)_2]_3$ (90 mg, 0.14 mmol) in 10 mL of THF was added dropwise to a >5-fold excess of sodium smeared on the bottom of a flask. The mixture immediately changed to a peach color and after stirring for 3 h, the solution was golden brown. The mixture was centrifuged to remove any insoluble materials and evaporation of the supernatant yielded a dark pink solid. At −38 °C over 2−3 days a concentrated sample in Et_2O produced pink crystals of **1-Er** (35 mg, 22%). Anal. Calcd. for $C_{32}H_{88}N_6O_2Si_8Er_2$: Er, 29.13. Found: Er, 28.4.

{[(Me$_3$Si)$_2$N]$_2$(THF)Tb}$_2$(μ-η^2:η^2-N$_2$), 1-Tb. As described for **1-Er**, pale blue crystals of **1-Tb** (27 mg, 0.02 mmol, 25%) were obtained from $Tb[N(SiMe_3)_2]_3$ (123 mg, 0.19 mmol) with initial color changes from yellow-brown to golden brown. Anal. Calcd. for $C_{32}H_{88}N_6O_2Si_8Tb_2$: Tb, 28.09. Found: Tb, 27.6.

{[(Me$_3$Si)$_2$N]$_2$(THF)Gd}$_2$(μ-η^2:η^2-N$_2$), 1-Gd. As described for **1-Er**, pale blue crystals of **1-Gd** (22 mg, 0.02 mmol, 20%) were obtained from colorless $Gd[N(SiMe_3)_2]_3$ (127 mg, 0.20 mmol) with an initial color change to dark greenish bronze. Anal. Calcd. for $C_{32}H_{88}N_6O_2Si_8Gd_2$: Gd, 27.87. Found: Gd, 27.1.

{[(Me$_3$Si)$_2$N]$_2$(THF)La}$_2$(μ-η^2:η^2-N$_2$), 1-La and {[(Me$_3$Si)$_2$N]$_4$La}{K(THF)$_6$}, 2-La. In a nitrogen glovebox, $La[N(SiMe_3)_2]_3$ (252 mg, 0.41 mmol) dissolved in 10 mL of THF was added dropwise to a flask containing KC_8 (55 mg, 0.41 mmol) and a stir bar. The mixture immediately became yellow orange and was allowed to stir for 3 h. The mixture was centrifuged to remove insoluble material and evaporation of the supernatant yielded a yellow tacky solid. ^{1}H NMR (C_6D_6): δ 0.15 [$KN(SiMe_3)_2$], 0.31 (9H, Me), 1.40 (1H, THF), 3.60 (1H, THF). ^{13}C NMR (C_6D_6): δ 7.53 [$KN(SiMe_3)_2$], 4.26 (Me), 26.10 (THF), 68.44 (THF). No crystals were obtained from this system. To obtain ^{15}N NMR data, THF was condensed onto a mixture of $La[N(SiMe_3)_2]_3$ (780 mg, 1.26 mmol), KC_8 (170 mg, 1.26 mmol), and a stir bar in a tube fitted with a high vacuum stopcock. The mixture was warmed to room temperature under $^{15}N_2$ and stirred for 3 h. The ^{1}H NMR spectrum of this sample was more complicated, but the 0.31 ppm resonance was prominent. $^{15}N\{^1H\}$ NMR (THF-d_8): δ 516 (s). At −35° C over 2−3 days a concentrated sample in Et_2O produced colorless X-ray quality crystals of **2-La**. Anal. Calcd. for $C_{24}H_{72}N_4Si_8KLa$: La, 16.95. Found: La, 16.67.

{[(Me$_3$Si)$_2$N]$_4$Pr}{K(THF)$_6$}, 2-Pr. In a nitrogen glovebox, $Pr[N(SiMe_3)_2]_3$ (300 mg, 0.48 mmol) in 10 mL of THF was added to a flask containing K (19 mg, 0.49 mmol) and a stir bar. The mixture immediately became green and was allowed to stir for 3 h. The mixture was centrifuged to remove insoluble material and evaporation of the supernatant yielded a green yellow powder. At −35 °C over 2−3 days a concentrated sample of the powder in Et_2O produced yellow X-ray quality crystals of **2-Pr**.

{U[N(SiMe$_3$)$_2$]$_4$}{K(THF)$_6$}, 2-U. In a nitrogen glovebox, $U[N(SiMe_3)_2]_3$ (86 mg, 0.12 mmol) in THF was added slowly to a flask containing freshly made K sand (5 mg, 0.13 mmol) in THF. After the mixture was stirred for 12 h at ambient temperature, excess potassium was separated by centrifugation and the solvent was removed by rotary evaporation to afford a purple solid. At −35° C over 2−3 days a concentrated sample in toluene produced purple X-ray quality crystals of **2-U**.

{[(Me$_3$Si)$_2$N]$_4$Ce}{Na(THF)$_4$(Et$_2$O)}, 3-Ce. In a nitrogen glovebox, yellow $Ce[N(SiMe_3)_2]_3$ (90 mg, 0.15 mmol) in 10 mL of THF was added to a >5-fold excess of sodium smeared on the bottom of a flask. The mixture immediately became orange and was allowed to stir for 3 h. The mixture was centrifuged to remove any residual pieces of sodium and

(36) Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2126−2134.
(37) Edelmann, F. T. *Synthetic Methods of Organometallic and Inorganic Chemistry* **1997**, *6*, 37−40.
(38) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248−2256.
(39) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672−6677.

Table 2. X-ray Data Collection Parameters for the $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **1**, Complexes

empirical formula	$C_{32}H_{88}N_6O_2Si_8Nd_2$ **1-Nd**	$C_{32}H_{88}N_6O_2Si_8Gd_2$ **1-Gd**	$C_{32}H_{88}N_4O_3Si_8Tb_2$ **1-Tb**	$C_{32}H_{88}N_4O_3Si_8Er_2$ **1-Er**
formula weight	1102.28	1128.30	1131.64	1148.32
T (K)	175(2)	163(2)	163(2)	168(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
A (Å)	10.8970(5)	10.8414(18)	10.8206(8)	10.7711(12)
B (Å)	23.5933(10)	23.469(4)	23.4274(16)	23.420(3)
C (Å)	11.6870(5)	11.5946(19)	11.5654(8)	11.5021(12)
α (deg)	90	90	90	90
β (deg)	112.6870(10)	112.585(3)	112.6410(10)	112.638(2)
γ (deg)	90	90	90	90
volume Å^3	2772.2(2)	2723.9(8)	2705.9(3)	2678.0(5)
Z	2	2	2	2
ρ_{calcd} (Mg/m^3)	1.321	1.376	1.389	1.424
μ (mm^{-1})	2.055	2.620	2.800	3.322
$R1$ [$I > 2.0\sigma(I)$]	0.0186	0.0223	0.0234	0.0315
w$R2$ (all data)	0.0461	0.0500	0.0507	0.0817

Table 3. X-ray Data Collection Parameters for the $\{Ln[N(SiMe_3)_2]_4\}^-$ Complexes, **2** and **3**

empirical formula	$C_{48}H_{120}N_4O_6Si_8KU$ **2-U**	$C_{48}H_{120}N_4O_6Si_8KLa$ **2-La**	$C_{48}H_{120}N_4O_6Si_8KPr$ **2-Pr**	$C_{44}H_{114}N_4O_5Si_8NaCe$ **3-Ce**
formula weight	1351.33	1252.21	1254.21	1167.22
T (K)	173(2)	163(2)	183(2)	163(2)
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$C2/c$	$C2/c$	$C2/c$	$Pbcn$
A (Å)	26.630(5)	26.623(3)	26.627(3)	47.804(5)
B (Å)	30.601(5)	30.624(3)	30.590(3)	23.067(2)
C (Å)	17.379(3)	17.3572(17)	17.3452(19)	24.033(3)
α (deg)	90	90	90	90
β (deg)	91.613(3)	91.339(2)	91.169(2)	90
γ (deg)	90	90	90	90
volume Å^3	14157(4)	14147(2)	14125(3)	26502(5)
Z	8	8	8	16
ρ_{calcd} (Mg/m^3)	1.268	1.176	1.180	1.170
μ (mm^{-1})	2.528	0.839	0.925	0.876
$R1$ [$I > 2.0\sigma(I)$]	0.0578	0.0662	0.0904	0.0608
w$R2$ (all data)	0.1785	0.2144	0.2878	0.1657

evaporation of the supernatant yielded a yellow solid. At −35 °C over 1−2 days, a concentrated sample in Et_2O produced colorless X-ray quality crystals of **3-Ce**.

$KSm[(Me_3Si)_2N]_3$, 4. In a nitrogen containing glovebox, $Sm[N(SiMe_3)_2]_3$ (0.262 g, 0.41 mmol) in 10 mL of THF was added to a flask containing KC_8 (0.056 g, 0.41 mmol) and a stir bar. The mixture immediately became purple and was allowed to stir for 3 h. The mixture was centrifuged to remove insoluble material and evaporation of the supernatant yielded a purple powder which was placed under high vacuum for 2 days (0.150 g, 54%). ^{1}H NMR spectroscopy in C_6D_6 shows this product to be the previously characterized $KSm[(Me_3Si)_2N]_3$.[40]

X-ray Data Collection, Structure Solution, and Refinement. The SMART[41] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[42] and SADABS[43] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[44] program. The analytical scattering factors[45] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

$\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, 1. The diffraction symmetry was 2/m and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct. The structures of **1-Er**, **1-Tb**, and **1-Gd** were solved using the coordinates of an isomorphous complex followed by refinement on F^2 by full-matrix least-squares techniques. Data are given in Table 2.

$\{[(Me_3Si)_2N]_4M\}\{K(THF)_6\}$, 2. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that the centrosymmetric space group $C2/c$ was correct. The structures of **2-La**, **2-U**, and **2-Pr** were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The SHELXTL[44] restraints SAME and EADP were employed to refine the THF ligands. Data are given in Table 3.

$\{[(Me_3Si)_2N]_4Ce\}\{Na(THF)_4(Et_2O)\}$, 3-Ce. The diffraction symmetry was mmm and the systematic absences were consistent with the orthorhombic space group Pbcn which was later determined to be correct. The structure **3-Ce** was solved by direct methods and refined on F^2 by full-matrix least squares techniques. There were two $\{Cc[N(SiMe_3)_2]_4\}^-$ anions and two ions of $[Na(THF)_4(OEt)_2]^+$ per unit cell (one ion was located

(40) Evans, W. J.; Johnston, M. A.; Clark, R. D.; Anwander, R.; Ziller, J. W. *Polyhedron* **2001**, *20*, 2483−2490.
(41) SMART Software Users Guide, Version 5.1, Bruker Analytical X-ray Systems, Inc.; Madison, WI 1999.
(42) SAINT Software Users Guide, Version 6.34A, Bruker Analytical X-ray Systems, Inc.; Madison, WI 2003.
(43) Sheldrick, G. M. SADABS, Version 2.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI 2001.
(44) Sheldrick, G. M. SHELXTL Version 6.12; Bruker Analytical X-ray Systems, Inc.: Madison, WI 2001.
(45) International Tables for X-ray Crystallography; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **1**

	1-Nd	1-Gd	1-Tb	1-Dy[19]	1-Y[7]
Ln(1)−N(1)	2.3276(14)	2.2782(19)	2.2599(19)	2.250(2)	2.2443(15)
Ln(1)−N(2)	2.3470(14)	2.2964(19)	2.2742(19)	2.267(2)	2.2640(15)
Ln(1)−N(3)	2.3758(16)	2.326(2)	2.301(2)	2.287(3)	2.2958(17)
Ln(1)−N(3)#1	2.3938(16)	2.353(2)	2.328(2)	2.312(3)	2.3170(16)
Ln(1)−O(1)	2.5182(13)	2.4408(17)	2.4220(18)	2.405(2)	2.3898(14)
N(3)−N(3)#1	1.258(3)	1.278(4)	1.271(4)	1.305(6)	1.268(3)
N(3)−Ln(1)−N(3)#1	30.59(7)	31.70(10)	31.87(10)	32.97(14)	31.90(8)
N(3)#1−N(3)−Ln(1)	75.49(14)	75.28(19)	75.23(19)	74.6(3)	74.97(14)
N(3)#1−N(3)−Ln(1)#1	73.92(14)	73.01(18)	72.89(19)	72.5(2)	73.13(14)
Ln(1)−N(3)−Ln(1)#1	149.41(7)	148.30(10)	148.13(10)	147.03(14)	148.10(8)

	1-Ho[7]	1-Er	1-Tm[7,19]	1-Lu[7]
Ln(1)−N(1)	2.237(2)	2.224(3)	2.211(2)	2.1930(19)
Ln(1)−N(2)	2.252(2)	2.239(2)	2.228(2)	2.2136(19)
Ln(1)−N(3)	2.296(2)	2.271(3)	2.271(2)	2.241(2)
Ln(1)−N(3)#1	2.315(2)	2.302(3)	2.296(2)	2.272(2)
Ln(1)−O(1)	2.3875(18)	2.366(2)	2.355(2)	2.3214(18)
N(3)−N(3)#1	1.264(4)	1.276(5)	1.261(4)	1.285(4)
N(3)−Ln(1)−N(3)#1	31.81(9)	32.39(13)	32.06(11)	33.08(10)
N(3)#1−N(3)−Ln(1)	74.92(19)	75.2(3)	75.1(2)	74.76(19)
N(3)#1−N(3)−Ln(1)#1	73.27(18)	72.4(2)	72.87(19)	72.16(18)
Ln(1)−N(3)−Ln(1)#1	148.19(9)	147.61(13)	147.94(11)	146.92(10)

Table 5. Selected Bond Distances (Å) and Angles (deg) for $\{Ln[N(SiMe_3)_2]_4\}^-$, in **2** and **3**

compound	2-La	3-Ce [Ce(1)]	3-Ce [Ce(2)][a]	2-U	2-Pr
Ln−N(1)	2.469(5)	2.444(6)	2.435(7)	2.430(6)	2.423(8)
Ln−N(2)	2.472(5)	2.437(6)	2.434(6)	2.430(6)	2.430(8)
Ln−N(3)	2.468(5)	2.448(6)	2.445(6)	2.430(7)	2.431(8)
Ln−N(4)	2.471(5)	2.440(6)	2.446(6)	2.438(6)	2.427(8)
N(1)−Ln−N(2)	103.77(16)	115.3(2)	112.3(2)	102.5(2)	104.4(3)
N(1)−Ln−N(3)	111.64(17)	113.3(2)	114.2(2)	112.3(2)	111.2(3)
N(1)−Ln−N(4)	115.01(18)	100.0(2)	102.3(2)	115.3(2)	115.7(3)
N(2)−Ln−N(3)	112.96(17)	100.8(2)	101.0(2)	113.4(2)	113.0(3)
N(2)−Ln−N(4)	111.54(19)	113.2(2)	113.4(2)	112.2(2)	110.5(3)
N(3)−Ln−N(4)	102.27(18)	115.0(2)	114.2(2)	101.7(2)	102.4(3)

[a] Two $\{[(Me_3Si)_2N]_4Ce\}^-$ anions are present in each unit cell. For Ce(2), N(5) through N(8) replace N(1) through N(4), respectively.

in a general position; two-half ions were located on 2-fold rotation axes). The $[Na(THF)_4(OEt_2)]$ ions were disordered and included using multiple components with partial site-occupancy-factors. Hydrogen atoms associated with the $[Na(THF)_4(OEt_2)]$ ions were not included in the refinement. It was necessary to include SHELXTL[44] restraints (SAME, EADP) in order to refine the THF and OEt_2 ligands. Data are given in Table 5.

Results

LnZ_3/Alkali Metal Synthesis of $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 1. Dysprosium and Neodymium. Reaction of $Dy[N(SiMe_3)_2]_3$ with potassium graphite in THF under N_2 according to eq 1 gave the identical orange colored product, $\{[(Me_3Si)_2N]_2(THF)Dy\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **1-Dy**, obtained from the reaction of 2 equiv of $KN(SiMe_3)_2$ with DyI_2 under dinitrogen according to eq 2.[19] This was anticipated in analogy with the successful Tm reaction and the calculated Dy(III)/Dy(II) reduction potential of −2.5 V, Table 1.[22] The yield of **1-Dy** via eq 1 was 45% compared to a 30% yield via DyI_2 and eq 2. Hence, not only was the $Dy[N(SiMe_3)_2]_3$ precursor of this dysprosium reaction easier to synthesize, the yield was superior.

The synthesis of the Nd analogue of **1** was expected to be as straightforward as the syntheses for Tm and Dy for the following reasons. A molecular divalent neodymium complex, $NdI_2(THF)_5$, has been fully characterized by X-ray crystallography,[16] the calculated −2.6 V Nd(III)/Nd(II) reduction potential should be accessible by alkali metal reduction, and a $Nd_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complex has been synthesized from NdI_2 and aryloxide ligands, $[(ArO)_2(THF)_2Nd]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (Ar = $C_6H_3{}^tBu_2$-2,6).[19] However, the $Nd[N(SiMe_3)_2]_3$/alkali metal/N_2 reaction was not as facile a route to **1-Nd** as with the smaller metals dysprosium and thulium. **1-Nd** could be synthesized from both $NdI_2/2KN(SiMe_3)_2$, according to eq 2, and $Nd[N(SiMe_3)_2]_3/KC_8$, according to eq 1, but the yields were variable and low. Crystallographically characterizable samples of **1-Nd** were obtained from both $Nd[N(SiMe_3)_2]_3/Na/N_2$ and $NdI_2/2KN(SiMe_3)_2/N_2$ reactions.

Erbium, Terbium, and Gadolinium. Since Ho and Y had given the isolable products **1-Ho** and **1-Y**, the analogous reaction with the similarly sized Er was examined. As shown in Table 1, the Er(III)/Er(II) reduction potential is calculated to be −3.1 V (vs NHE), a value more negative than the reduction potential of K, −2.9 V (vs NHE). As in the other reactions, an analogous $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ product, the pale pink **1-Er**, was isolated, this time in 22% yield. Extension of eq 1 to Tb and Gd, the two metals which have the most negative Ln(III)/Ln(II) calculated reduction potentials in Table 1, −3.7 and −3.9 V, respectively, was also successful. These reactions provided the first dinitrogen derivatives of Gd, Tb, and Er, metals that usually are not involved in reductive chemistry and that are valued for their magnetic and optical properties.[46−48]

Structural Data. Each of the $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes described above was definitively characterized by X-ray crystallography and found to be isomorphous with the previously characterized examples.[7,19] Figure 1 shows the structure of **1-Gd**. Comparative crystallographic data for all of the known examples of **1** are given in Table 4.

The NN distances for **1-Nd**, **1-Gd**, **1-Tb**, **1-Dy**, and **1-Er** are 1.258(3), 1.278(4), 1.271(4), 1.305(6), and 1.276(5) Å, respectively. These are similar to the 1.264(7)-1.305 (6) Å values

(46) Caravan, P.; Ellison, J. J.; McMurry, T. J.; Lauffer, R. B. *Chem. Rev.* **1999**, *99*, 2293−2352.
(47) Adam, J. L. *Chem. Rev.* **2002**, *102*, 2461−2476.
(48) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357−2368.

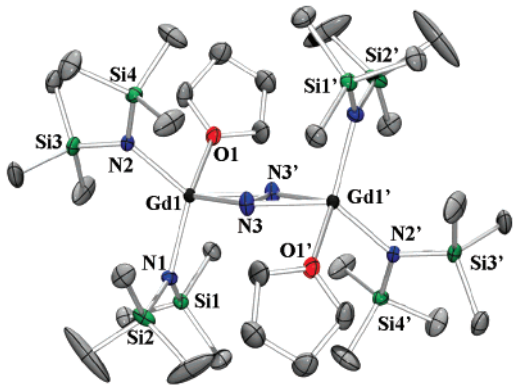


Figure 1. Thermal ellipsoid plot of $\{[(Me_3Si)_2N]_2(THF)Gd\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **1-Gd**, drawn at the 50% probability level.

found previously for other examples of **1**. Each of these NN distances is consistent with formation of a doubly reduced dinitrogen ligand containing a double bond, i.e., $(N{=}N)^{2-}$. Table 2 shows the variation in other structural parameters in the **1** series as a function of the metal. As expected, Ln−N and Ln−O bond distances vary in a periodic fashion commensurate with the varying radial size of the ions. This is illustrated graphically in Figure 2.

Sodium vs Potassium. The use of Na, which has a −2.7 V (vs NHE) reduction potential, instead of K was examined in the above $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reactions to determine if the weaker reductant would also accomplish this reaction. $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes were obtainable with sodium as well as potassium and no obvious correlation in yield of the desired products was observed using Na vs K vs KC_8. The reactions are likely to be favored by reductants with high surface areas, but no single type of reductant or reaction protocol has been found which appears to be generally superior for all of the systems examined. This suggests that there is considerable flexibility in using the LnZ_3/alkali metal reduction system.

Lanthanum, Cerium, Praseodymium, and Uranium. In contrast to the reactions above, attempts to make crystallographically characterizable $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes from $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reactions with the three largest metals in the lanthanide series, La, Ce, and Pr, have not been successful. Conducting these reactions under the same conditions successful with the smaller lanthanides has not provided any crystalline analogues of **1** for the larger metals. However, for each of these three large metals, the products that crystallized most readily from solution were the tetrakis(amide) products, $\{Ln[N(SiMe_3)_2]_4\}\{K(THF)_6\}$, **2-La** and **2-Pr**, and $\{[(Me_3Si)_2N]_4Ce\}\{Na(THF)_4(Et_2O)\}$, **3-Ce**, described below.

Attempts were also made to extend the $M[N(SiMe_3)_2]_3$/K/N_2 reaction to the 5f metals since a variety of uranium dinitrogen complexes have been reported[49−52] and $U[N(SiMe_3)_2]_3$[38] is readily available. However, treatment of $U[N(SiMe_3)_2]_3$ with potassium in THF under N_2 gave $\{U[N(SiMe_3)_2]_4\}\{K(THF)_6\}$,

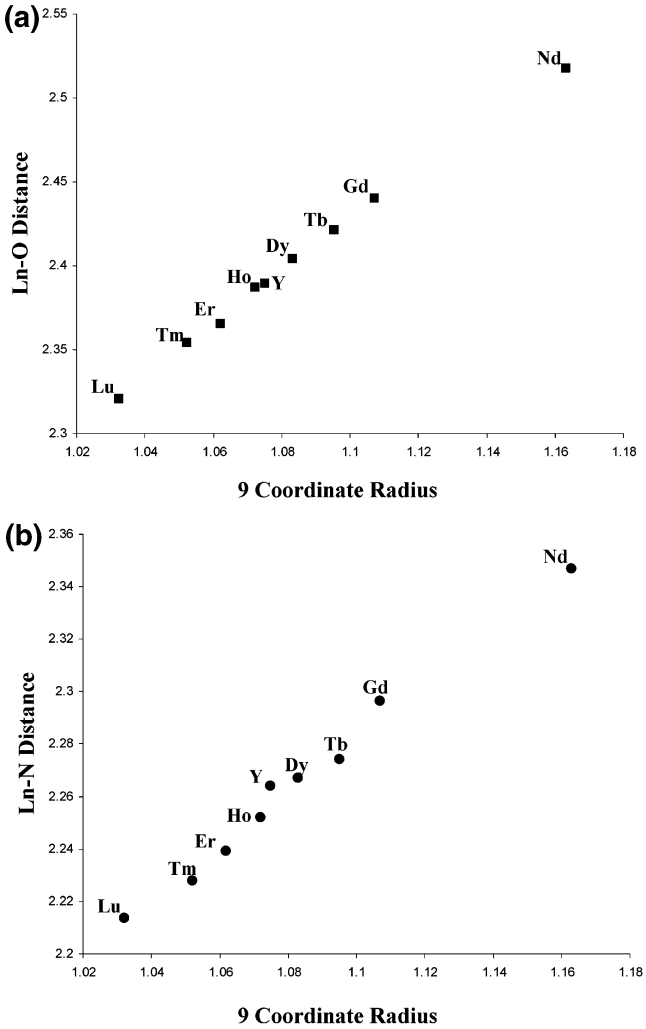


Figure 2. (a) Lanthanide-oxygen distances (Å) in **1-Ln** vs 9 coordinate ionic radii[53] (Å). (b) Lanthanide−nitrogen $[N(SiMe_3)_2]$ distances (Å) in **1-Ln** vs 9 coordinate ionic radii[53] (Å).

2-U, isomorphous with the La and Pr complexes just described. It is interesting to note that this analogous result occurs with a metal which is similar in size to the large lanthanides: six coordinate U(III) has a 1.025 Å radius close to that of La(III), 1.032 Å.[53]

Structural Data on $\{M[N(SiMe_3)_2]_4\}^-$ Complexes of 2-La, 2-Pr, 2-U, and 3-Ce. The $\{M[N(SiMe_3)_2]_4\}^{1-}$ complexes, **2** and **3**, were identified by X-ray crystallography, Figure 3, and are the first crystallographically characterized tetrakis[bis(trimethylsilyl)amide] metal complexes to our knowledge. We are aware of only two examples in the literature of compounds containing four $[N(SiMe_3)_2]^{1-}$ ligands around a single metal, but in each case no crystallographic evidence was available. The U(VI) uranyl salt, $\{UO_2[N(SiMe_3)_2]_4\}\{Na(THF)_2\}_2$,[54] is postulated to have a square planar arrangement of four $N(SiMe_3)_2$ groups around the linear O=U=O moiety and a mixed ligand bimetallic lanthanum complex is postulated to be $[(fluorenyl)Me_2SiC_5H_4]La[\mu\text{-}N(SiMe_3)_2]_2La[N(SiMe_3)_2]_2$[55] on the basis of NMR spectroscopy. Examples of lanthanides

(49) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070−1071.
(50) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836−5837.
(51) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **2002**, *124*, 9352−9353.
(52) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 14264−14265.
(53) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.
(54) Burns, C. J.; Clark, D. L.; Donohoe, R. J.; Duval, P. B.; Scott, B. L.; Tait, C. D. *Inorg. Chem.* **2000**, *39*, 5464−5468.
(55) Dash, A. K.; Razavi, A.; Mortreux, A.; Lehmann, C. W.; Carpentier, J. F. *Organometallics* **2002**, *21*, 3238−3249.

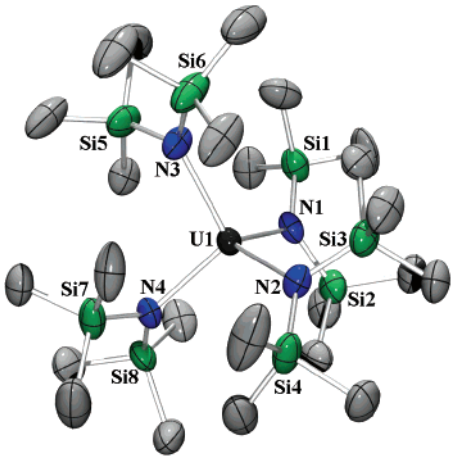


Figure 3. Thermal ellipsoid plot of the anion in **2-U**, $\{U[N(SiMe_3)_2]_4\}^-$, drawn at the 50% probability level. The anions in the La and Pr analogues, **2-La** and **2-Pr**, are isomorphous.

surrounded by four amide ligands are known, but not with four $[N(SiMe_3)_2]^{1-}$ ligands. The closest related examples include $[Na(THF)_6]\{[(Me_3Si)_2N]_2Lu(\mu\text{-}NH_2)(\mu\text{-}NSiMe_3)Lu[N(SiMe_3)_2]_2\}$,[56] $[(THF)_2Na(\mu\text{-}NPh_2)Ln[N(SiMe_3)_2]_2$ (Ln = Gd, Yb)[57] $Ln_3[N(SiMe_2H)_2]_6(THF)_2$ (Ln = Sm,[58] Yb[59]) and $(THF)LiLn(N^iPr_2)_4$ (Ln = La, Y, Yb,[60] Pr[61]).

Complexes **2-La, 2-Pr**, and **2-U** are isomorphous. **3-Ce** has a similar $\{M[N(SiMe_3)_2]_4\}^{1-}$ anion, but it is not isomorphous. The cerium complex also differs in that the alkali metal is Na not K and both THF and Et_2O solvate the cation. This complicates the structural analysis of the two crystallographically independent solvated cations in **3-Ce**, but the other aspects of the structure are not significantly perturbed.

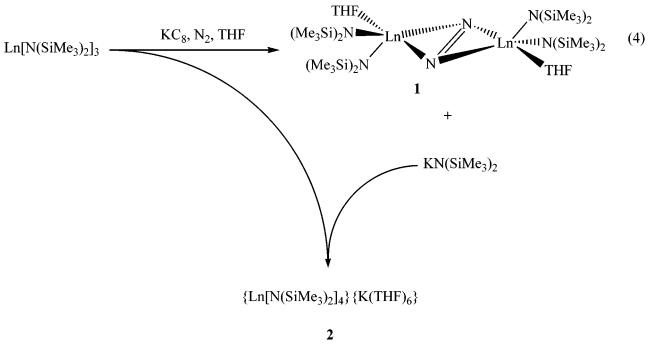
Overall the $\{M[N(SiMe_3)_2]_4\}^{1-}$ anions in **2** and **3** have distorted tetrahedral geometries with N−M−N angles in the 100.0(2)−115.7(3)° range, Table 5. The 2.420(7)−2.438(6) Å U−N[N(SiMe$_3$)$_2$] distances in **2-U** are significantly longer than the 2.320(4) Å U−N[N(SiMe$_3$)$_2$] distance in U[N(SiMe$_3$)$_2$]$_3$.[62] This is expected for a higher coordinate complex although the increase with coordination number is generally 0.04−0.07 Å.[53] The U−N distances are even larger than the 2.352(2) Å U−N[N(SiMe$_3$)$_2$] length in $(C_5Me_5)_2U[N(SiMe_3)_2]$.[63] The 2.468(5)−2.472(5) Å La−N[N(SiMe$_3$)$_2$] distances in **2-La** are similarly longer than the 2.29(2) Å distance in Nd[N(SiMe$_3$)$_2$]$_3$,[64] the closest lanthanide analogue which has been structurally characterized. The distances in **2-La** are closer to the 2.40(3) and 2.41(2) Å La−N[N(SiMe$_3$)$_2$] distances in four coordinate La[N(SiMe$_3$)$_2$]$_3$[OPPh$_3$].[65] Because no M−C(Me) contacts smaller than 3.46 Å were found in the structures, there was no evidence found for agostic interactions of the type common for f element $[N(SiMe_3)_2]^{1-}$ complexes.[66−69]

Formation of 2 and 3. It should be noted that in all of the syntheses of the Ln_2N_2 complexes, **1**, the compounds are isolated exclusively by crystallization to insure separation of the byproducts and the yields reported are only of the amount of **1** that crystallized. In particular, the stoichiometric byproduct of a successful Ln[N(SiMe$_3$)$_2$]$_3$/K/N$_2$ reaction, namely KN(SiMe$_3$)$_2$, must be separated. If there is a problem crystallizing the larger lanthanide analogues of **1**, it will be difficult to identify a successful reaction. Since the radii of the lanthanides vary in size over a 0.17 Å range, it is quite possible that not all of the elements in the series will have the ideal ratio of metal radius to size of this $\{[(Me_3Si)_2N]_2(THF)\}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ ligand set for crystallization. Since U(III) has an ionic radius similar to that of La(III), it could suffer from a similar problem. Isolation of the $\{Ln[N(SiMe_3)_2]_4\}^{1-}$ compounds with the larger metals is reasonable, since these metals have more room to fit four $[N(SiMe_3)_2]^{1-}$ ligands in their coordination sphere.

Formation of **2** could occur via complexation of the KN(SiMe$_3$)$_2$ byproduct of a successful M[N(SiMe$_3$)$_2$]$_3$/K/N$_2$ reaction with the M[N(SiMe$_3$)$_2$]$_3$ starting material according to eq 3.

$$M[N(SiMe_3)_2]_3 + KN(SiMe_3)_2 \xrightarrow{THF} \{M[N(SiMe_3)_2]_4\}\{K(THF)_6\} \quad (3)$$

This may be one reason for the relatively low yields of crystalline **1**. As soon as some **1** is formed, the KN(SiMe$_3$)$_2$ byproduct can start to react with the M[N(SiMe$_3$)$_2$]$_3$ starting material and compete with the dinitrogen reduction reaction, eq 4. Indeed, the reason for the experimental arrangement of



(4)

adding a M[N(SiMe$_3$)$_2$]$_3$ solution slowly to K under N$_2$[7] is to keep the concentration of M[N(SiMe$_3$)$_2$]$_3$ in the solution to a minimum so that it cannot be depleted by attack by KN(SiMe$_3$)$_2$.

Interestingly, attempts to make **2** by direct reaction of M[N(SiMe$_3$)$_2$]$_3$ with bulk KN(SiMe$_3$)$_2$ according to eq 3 have not been successful. Crystallizable samples of **2** have only been isolated from M[N(SiMe$_3$)$_2$]$_3$/K/N$_2$ reactions in which the KN(SiMe$_3$)$_2$ is generated in situ. To our knowledge, the only remotely related reaction in the literature is the reaction of Ln[N(SiMe$_3$)$_2$]$_3$ with NaN(SiMe$_3$)$_2$ in THF at reflux over 2 d.

(56) Karl, M.; Seybert, G.; Massa, W.; Harms, K.; Agarwal, S.; Maleika, R.; Stelter, W.; Greiner, A.; Heitz, W.; Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1301−1309.
(57) Karl, M.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1774−1776.
(58) Nagel, I.; Scherer, W.; Tafipolsky, M.; Anwander, R. *Eur. J. Inorg. Chem.* **1999**, 1405−1407.
(59) Lee, L.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem.* **1994**, *33*, 5302−5308.
(60) Aspinall, H. C.; Tillotson, M. R. *Polyhedron* **1994**, *13*, 3229−3234.
(61) Evans, W. J.; Anwander, R.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1995**, *34*, 5927−5930.
(62) Stewart, J. L.; Andersen, R. A. *Polyhedron* **1998**, *17*, 953−958.
(63) Evans, W. J.; Nyce, G. W.; Forrestal, K. J.; Ziller, J. W. *Organometallics* **2002**, *120*, 1050−1055.
(64) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317−2319.
(65) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *J. Chem. Soc., Dalton* **1977**, 1166−1172.
(66) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725−3727.
(67) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271−2276.
(68) Boncella, J. M.; Andersen, R. A. *Organometallics* **1985**, *4*, 205−206.
(69) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575−579.

Under these conditions, $HN(SiMe_3)_2$ is eliminated and the metalated product, $[(Me_3Si)_2N]_2Ln[N(SiMe_3)(SiMe_2CH_2)][Na(THF)_3]$ is isolated for Ln = Sc, Yb, and Lu.[70]

^{15}N NMR Identification of 1-La. If the $\{M[N(SiMe_3)_2]_4\}^-$ complexes **2-La**, **2-Pr**, **2-U**, and **3-Ce**, are formed by reaction of the $M[N(SiMe_3)_2]_3$ starting materials with $KN(SiMe_3)_2$ or $NaN(SiMe_3)_2$ generated in situ via eq 1, then this implies that the $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes **1-La**, **1-Pr**, **1-U**, and **1-Ce** could have also been synthesized. If the tetrakis(amide) salts crystallized preferentially, then the dinitrogen reduction products would not be identified. This possibility was probed with the largest of these metals, La, since La(III) is diamagnetic. By ^{1}H NMR spectroscopy, the reaction of $La[N(SiMe_3)_2]_3$ with KC_8 forms $KN(SiMe_3)_2$ and only one other product with a resonance at 0.31 ppm that is similar to those of diamagnetic **1-Y** and **1-Lu**, 0.35 and 0.36 ppm, respectively. Extensive attempts to crystallize the lanthanum product have been unsuccessful. However, when this reaction was run under $^{15}N_2$, the 0.31 ppm product is again formed and a ^{15}N NMR resonance at 516 ppm is observed. This resonance is similar to those found for **1-Y** and **1-Lu**, 513 and 557 ppm, respectively. This is strong evidence for the formation of a complex of the general type $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ for even the largest member of the lanthanide series.

$KSm[N(SiMe_3)_2]_3$. When the $Ln[N(SiMe_3)_2]_3/K/N_2$ reaction was examined with Ln = Sm, a different result from those above was obtained. The pale yellow solution of the trivalent starting material immediately turned a deep purple color of the type found with many types of Sm(II) complexes. ^{1}H NMR analysis of the reaction mixture matched the NMR spectrum of the divalent tris[bis(trimethylsilyl)amide] complex, $KSm[N(Me_3Si)_2]_3$, previously prepared from SmI_2 and 3 equiv of $KN(SiMe_3)_2$.[40] Hence, with Sm, which has a −1.55 V calculated Sm(III)/Sm(II) reduction potential, simple reduction to a divalent tris(amide) salt occurs, eq 5.

$$Sm[N(SiMe_3)_2]_3 + KC_8 \xrightarrow[\text{- graphite}]{\text{THF, } N_2} KSm[N(SiMe_3)_2]_3 \qquad (5)$$

$K/Ln[N(SiMe_3)_2]_3/Ar$. Attempts to isolate divalent intermediates by treating the $Ln[N(SiMe_3)_2]_3$ complexes with K under argon has not yet been successful. Transient colors are observed, but in all cases only the starting material, the trivalent $Ln[N(SiMe_3)_2]_3$ complexes, are isolated upon work up.

Discussion

The results of these $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reactions will be discussed in the order of increasing difficulty in making the divalent lanthanide oxidation states.

In the case of samarium, treatment of $Sm[N(SiMe_3)_2]_3$ with an alkali metal under N_2 results in reduction of Sm(III) to Sm(II) and no dinitrogen reduction. This is as expected: previous studies have shown that Sm(III) complexes can be reduced to Sm(II) with alkali metals[71,72] and none of the Sm(II) bis(trimethylsilyl)amide complexes[40,73] have been found to react with dinitrogen. This $Ln[N(SiMe_3)_2]_3/K$ reaction clearly goes by reduction of the trivalent precursor to a Sm(II) compound.

In the case of Tm, Dy, and Nd, the $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reactions generate the same products, $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **1**, obtained from their molecular diiodides, LnI_2 and 2 equiv of $KN(SiMe_3)_2$. The formation of **1** from the trivalent tris(amide) precursors could occur via transient formation of divalent intermediates on the basis of the Ln(III)/Ln(II) reduction potentials, the reduction potentials of K, −2.9 V, and Na, −2.7 V, and the prior chemistry demonstrated with the divalent precursors.[19] No specific evidence for the formation of the Ln(II) intermediates is observed. For example, highly colored intermediates of the type generated from TmI_2, DyI_2, and NdI_2 in THF are not observed. However, if the divalent intermediates reacted quickly with dinitrogen, these might not be detected. Interestingly, the largest metal of these three, Nd, proved to be the most problematic in generating a reduced dinitrogen complex, although it has the most reducing divalent state.

Although divalent intermediates are possible for the four metals just discussed, it is more difficult to attribute a $Ln[N(SiMe_3)_2]_3/K$ to "$Ln[N(SiMe_3)_2]_2$" reaction pathway for any of the other metals for which eq 1 is successful, namely Gd, Tb, Ho, Er, Y, and Lu. The fact that this $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reaction can be extended to the lanthanides with the most negative calculated Ln(III)/Ln(II) reduction potentials, Tb (−3.7 V) and Gd (−3.9 V) and can be done with the less reducing Na as well as K, makes it more difficult to argue for a divalent intermediate in these reactions.

Since these reduction potentials are only calculated values estimated in aqueous solution and do not apply specifically to $M^{III}[N(SiMe_3)_2]_3/[M^{II}[N(SiMe_3)_2]_x]^{n-}$ redox couples, they cannot be used directly in this system. Certainly, different reduction potentials have been reported for Ln(III)/Ln(II) couples in the few reports in the literature on lanthanide electrochemistry in nonaqueous solution.[74−76] These studies show that it is more difficult to do the Ln(III) to Ln(II) reduction in nonaqueous media. Hence, nonaqueous reduction potentials might indicate that it is even more unlikely that Na and K can effect Ln(III) reduction in these systems. In any case, the fact that lanthanides with a wide range of reduction potentials can be used in the $Ln[N(SiMe_3)_2]_3/K/N_2$ reaction with both Na and K suggests that there is no obvious correlation between this dinitrogen reduction and the lanthanide ion reduction potential. Consistent with this, the three metals, La, Ce, and Pr, which have not yielded crystalline $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes from $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reactions, are metals which have more accessible divalent states than several of the metals which are successful in this reaction, Gd, Tb, Y, and Lu.

If divalent lanthanide oxidation states are involved in the $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reactions, this is the first evidence of Ho(II), Er(II), Tb(II), Gd(II), Y(II), and Lu(II) in a molecular system. However, it seems that more evidence than the possible existence of a transient unobserved intermediate is needed before the divalent states of these metals can be claimed. Solid-state

(70) Karl, M.; Harms, K.; Seybert, G.; Massa, W.; Fau, S.; Frenking, G.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2055−2063.
(71) Evans, W. J. *The Chemistry of the Metal−Carbon Bond* **1982**, *1*, 489−537.
(72) Watt, G. W.; Gillow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 775−776.
(73) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575−579.
(74) Bond, A. M.; Deacon, G. B.; Newnham, R. H. *Organometallics* **1986**, *5*, 2312−2316.
(75) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A. *Organometallics* **1986**, *5*, 598−601.
(76) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999−2009.

compounds of formula LnI_2 are known for La, Pr, and Gd, but these exist as $Ln^{3+}(I^{1-})_2(e^{1-})$ species rather than as $Ln^{2+}(I^{1-})_2$ complexes.[23,24] No crystallographically characterized LnI_2 species are known for Ho, Er, Tb, Y, and Lu, to our knowledge, but a mixed valence Ho_5X_{11}[77] has been reported and Ln_2Cl_3 compounds are known for Y and Tb.[24] A variety of LnI_x species in which x ranges from 1.86 to 2.77 have been made for Y, Ce, Pr, Gd, Ho, Er, and Lu[78] and are assigned $Ln^{3+}(I^{1-})_y(e^{1-})_z$ structures based on solubility and reaction chemistry.

Instead of correlating with Ln(III)/Ln(II) reduction potential, the success of the $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reaction seems to have a dependence on the radial size of the metal. Hence, it is the largest of the lanthanides, La, Ce, and Pr, that have not given isolable $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **1**, products. Neither has the reaction with U, which has a size similar to lanthanum.[53] In the case of each of these metals, La, Ce, Pr, and U, only $\{M[N(SiMe_3)_2]_4\}^{1-}$ products are isolated. Although this implies dinitrogen reduction, since this would provide the source of in situ $KN(SiMe_3)_2$, eq 4, it does not prove it. Isolation of these sterically crowded tetrakis(amide) complexes with the larger metals is reasonable, since larger metals early in the series can better accommodate four of these amide ligands. It is possible that for the larger metals, the tetrakis(amide) species predominates as the most crystallizable complex in the reaction mixture and this may mask the isolation of a dinitrogen reduction product.

Consistent with this view, the reaction between $La[N(SiMe_3)_2]_3$ and KC_8 and $^{15}N_2$ gives a ^{15}N NMR resonance in the same region observed for $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ and $\{[(Me_3Si)_2N]_2(THF)Lu\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.[7] This suggests that the dinitrogen reduction is successful with the larger metals, but that this ligand set is not ideal for isolating crystalline examples.

Although the $Ln[N(SiMe_3)_2]_3$/alkali metal/N_2 reaction is more successful with the later, smaller lanthanides than the earlier, larger ones in terms of providing crystalline products, there is no regular correlation between the size of the metal and the yield, as is often found with the lanthanides. In this reaction, the order of the yields is Tm > Dy > Lu > Ho > Tb > Er > Gd > Y > Nd ≫ La, Ce, Pr. This is neither periodic nor in the order of reduction potentials. The irregularity may occur because the yield depends on the isolation of crystals and since small changes can affect the crystallinity of similar lanthanide complexes.[79] However, there may also be other factors that are not yet obvious.

If the $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ products are not formed through a divalent intermediate, then the $Ln[N(SiMe_3)_2]_3$/K/N_2 reaction could be envisioned to involve activation of N_2 by coordination to $Ln[N(SiMe_3)_2]_3$. Formation of a "$(N_2)Ln[N(SiMe_3)_2]_3$" complex in THF solution seems unlikely since the solvent is both a better ligand and in much greater concentration than the dinitrogen. Isolation of a simple end-on dinitrogen coordination complex of an f element has been observed recently, but this species, $(C_5Me_5)_3U(\eta^1\text{-}N_2)$, is only stable under N_2 pressure and in the absence of coordinating solvents.[52] The formation of a $(N_2)M[N(SiMe_3)_2]_3$ complex which is activated for reduction by Na or K would not be unusual if M were a transition metal. Indeed, bimetallic complexes in which the reductant is attached to the N_2 attached to the transition metal are known.[3,28] Postulating the existence of such a complex for a 4f element is much more speculative considering the known coordination chemistry of these ions.

It is possible that eq 1 does not proceed through either of the alternatives mentioned above and involves alkali metal activation of the dinitrogen which gets triggered by the $Ln[N(SiMe_3)_2]_3$ complexes. Since lithium (−3.1 V vs NHE) is known to reduce dinitrogen, the possibility that potassium and sodium reduce dinitrogen with the proper activators is reasonable. If this alkali metal activation mechanism is operable, then it would appear to work with Na, K, and KC_8.

In any case, it is clear that the $Ln[N(SiMe_3)_2]_3$/alkali metal reaction system is of general synthetic utility for reducing dinitrogen to form $M_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes. With the expansion of this formerly rare structural motif to an increasing number of lanthanide metals, it now appears that this is the preferred mode for dinitrogen lanthanide coordination. As a compact, anionic, nitrogen donor atom ligand, the $(N{=}N)^{2-}$ unit seems ideal for making bimetallic lanthanide complexes with a variety of ancillary ligands.

More generally, it appears that the $Ln[N(SiMe_3)_2]_3$/alkali metal reducing system is not limited to lanthanides that have accessible divalent states or to K as the alkali metal. It is likely that the LnZ_3/alkali metal reduction system will also be applicable to substrates other than dinitrogen. For example, the many substrates activated by $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$[31] are all appropriate targets with this approach. As a wider range of substrates is explored, more information on the possible modes of reactivity will become available, particularly in terms of pre-coordination of substrate.

Conclusion

The LnZ_3/alkali metal reduction system when applied to dinitrogen as a substrate using $N(SiMe_3)_2$ as the monoanionic Z ligand generates a series of isomorphous $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes for Nd, Gd−Tm, Y and Lu. These metals have a wide range of Ln(III)/Ln(II) reduction potentials, −2.3 to −3.9 V which suggest that accessibility of a divalent state is not a prerequisite for this reduction system. In fact, the success of the LnZ_3/alkali metal reduction system in providing reduced dinitrogen products seems to depend more on the size of the metal and the ability to crystallize the product. Hence, variation of the Z ligands in this system may provide access to crystalline dinitrogen reduction products for the larger metals. In any case, the LnZ_3/alkali metal/substrate approach has extended reductive lanthanide dinitrogen chemistry to a much wider range of metals and is also likely to provide extensive reductive chemistry to other metal/substrate combinations as well.

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Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, complete bond distances, and angles (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(77) Lochner, U.; Barnighausen, H.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2134−2135.
(78) Khoroshenkov, G. V.; Petrovskaya, T. V.; Fedushkin, I. L.; Bochkarev, M. N. *Z. Anorg. Allg. Chem.* **2002**, *628*, 699−702.
(79) Evans, W. J.; Shreeve, J. L.; Ziller, J. W. *Inorg. Chem.* **1994**, *33*, 6435−6437.