

Dinitrogen Reduction by Tm(II), Dy(II), and Nd(II) with Simple Amide and Aryloxy Ligands

William J. Evans,* Gaël Zucchi, and Joseph W. Ziller

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

Received September 11, 2002; E-mail: wevans@uci.edu

Reduction of dinitrogen has been a challenging problem for decades.¹ Although many approaches have been taken, the use of lanthanide complexes was not investigated for many years because it was thought that these metals did not have the appropriate orbitals to bind dinitrogen. Interestingly, when the first lanthanide dinitrogen complex, $[(C_5Me_5)_2Sm]_2N_2$,² was discovered, it had a planar $M_2(\mu-\eta^2:\eta^2-N_2)$ structure not previously observed in dinitrogen chemistry. Both metals were interacting with dinitrogen in the same plane. When this structure was isolated, it seemed possible that the unusual M_2N_2 geometry was the result of the steric environment generated by the four C_5Me_5 ligands.³ Subsequently, this structural type was observed with tridentate $[(Pr_2PCH_2SiMe_2)_2N]$ and tetradentate $[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]$ complexes of zirconium,^{1,4,5} with polydentate porphyrinogen complexes of lanthanides,^{6,7} and with a tetradentate amine complex of uranium.⁸ Recently, additional examples of this M_2N_2 arrangement have been discovered with the cyclopentadienyl lanthanide systems, $[(C_5Me_5)_2Tm]_2N_2$,⁹ $\{[C_5H_3(SiMe_3)_2Ln]_2N_2$ ($Ln = Tm$,⁹ Dy ,¹⁰), and $\{[C_5H_4(SiMe_3)]_2(THF)-Tm\}_2N_2$ ⁹ and with a cyclopentadienyl uranium pentalene complex.¹¹

We now report that these M_2N_2 moieties readily form without the necessity of four ancillary cyclopentadienyl ligands,^{2,9,10} specialized multidentate ligands,^{1,4-8} or even very electron-donating ligands. This result occurs using as starting materials the highly reactive Tm(II),¹² Dy(II),¹³ and Nd(II)¹⁴ ions, whose first molecular complexes were recently discovered.¹²⁻¹⁴ The M_2N_2 unit forms from dinitrogen and these ions with ligands as simple as the commonly used amide, $N(SiMe_3)_2$, and aryloxy, $OC_6H_3tBu_{2-6}$.

Addition of 2 equiv of $NaN(SiMe_3)_2$ to an emerald-green solution of $TmI_2(THF)_3$ ⁹ in THF generates a dark brown-green solution, which turns yellow upon exposure to nitrogen. Recrystallization of this solution yields yellow $\{[(Me_3Si)_2N]_2(THF)Tm\}_2(\mu-\eta^2:\eta^2-N_2)$, **1**,¹⁵ Figure 1.¹⁶ Attempts to isolate the putative reductant, $[(Me_3Si)_2N]_2Tm(THF)_x$, before reaction with nitrogen led to a highly reactive purple solid which has not yet been obtained in pure form.

Similar solutions of the more reactive DyI_2 ^{13,17} and 2 equiv of $NaN(SiMe_3)_2$ in THF are unstable even at -30 °C, and the analogous dysprosium reaction was conducted at -78 °C. A purple solution develops in this case which gradually changes to brown upon exposure to nitrogen. From this mixture, orange $\{[(Me_3Si)_2N]_2(THF)Dy\}_2(\mu-\eta^2:\eta^2-N_2)$, **2**, is obtained.^{18,19}

X-ray crystallography revealed that complexes **1** and **2** are isomorphous. Each metal is formally five-coordinate and there are no obvious agostic $Ln\cdots Me_3Si$ interactions as often occur in lanthanide $N(SiMe_3)_2$ complexes.²⁰ The NN distances in **1** and **2** are 1.264(7) Å and 1.305(6) Å, respectively. These are in the double bond region²¹ and are close to the values in $\{[C_5H_3(SiMe_3)_2]_2Tm\}_2N_2$, **3**, 1.259(4) Å, and $\{[C_5H_4(SiMe_3)]_2(THF)Tm\}_2N_2$, **4**, 1.236(8) Å.⁹ The N–Ln–N angles in **1** and **2**, 32.11(18)° and 32.97(14)°, respectively, are within experimental error of those in **3** and **4**, 32.16(10)° and 31.34(18)°, respectively.

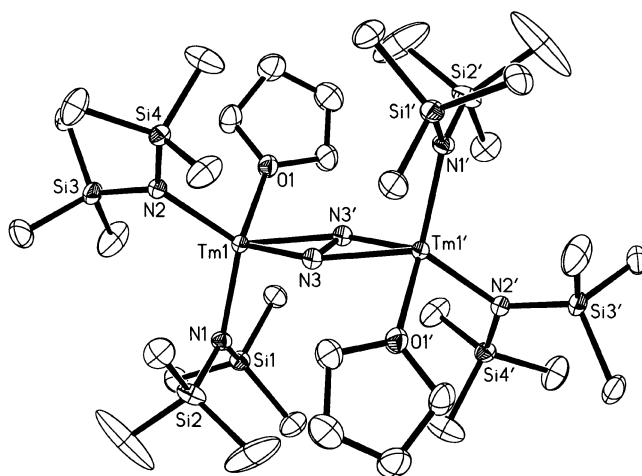


Figure 1. Thermal ellipsoid plot of **1** drawn at the 50% probability level.

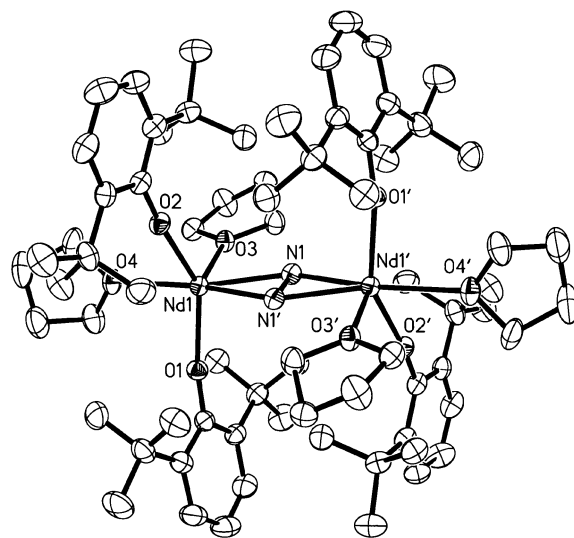


Figure 2. Thermal ellipsoid plot of **5** drawn at the 50% probability level.

THF solutions of the most strongly reducing diiodide of this series, NdI_2 ,^{14,17} are not stable at room temperature. Isolation of a dinitrogen reduction product directly from NdI_2 , in the absence of other ancillary ligands has not yet been accomplished, but in the presence of 2 equiv of $KOC_6H_3tBu_{2-6}$ (KOAr), the light blue-green dinitrogen complex $[(ArO)_2(THF)_2Nd]_2(\mu-\eta^2:\eta^2-N_2)$, **5**, is generated, Figure 2.^{22,23} This is the first successful use of the highly reactive NdI_2 as a starting material for productive Nd(II)-based reduction.

The structure of **5** has an M_2N_2 unit similar to those of **1–4**. The NN distance is 1.242(7) Å, and the N–Nd–N and Nd–N–Nd angles are 30.0(2)° and 150.0(2)°, respectively (see Table 1).

Table 1. Selected Bond Lengths (Å) and Angles (deg) in $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Tm}\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)$, **1**, $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Dy}\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)$, **2**, and $\{[(2,6\text{-tBu}_2\text{C}_6\text{H}_3\text{O})_2(\text{THF})_2\text{Nd}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)$, **5**

	1	2	5
Tm(1)–N(1)	2.216(4)	Dy(1)–N(1)	2.250(2)
Tm(1)–N(2)	2.234(4)	Dy(1)–N(2)	2.267(2)
Tm(1)–N(3)	2.275(4)	Dy(1)–N(3)	2.287(3)
Tm(1)–N(3)′	2.296(4)	Dy(1)–N(3)′	2.312(3)
Tm(1)–O(1)	2.361(4)	Dy(1)–O(1)	2.405(2)
Tm(1)–N(3)–Tm(1)′	147.9(2)	Dy(1)–N(3)–Dy(1)′	147.0(1)
N(3)–Tm(1)–N(3)′	32.1(2)	N(3)–Dy(1)–N(3)′	33.0(1)
		Nd(1)–O(1)	2.234(3)
		Nd(1)–O(2)	2.203(3)
		Nd(1)–N(1)	2.401(3)
		Nd(1)–N(1)′	2.397(4)
		Nd(1)–O(3)	2.505(3)
		Nd(1)–O(4)	2.582(3)
		Nd(1)′–N(1)–Nd(1)	150.0(2)
		N(1)′–Nd(1)–N(1)	30.0(2)

Complex **5** differs from **1–4** in that it contains *two* THF molecules solvated to each metal. Since this collection of ligands on neodymium is likely to generate a flexible coordination environment, it appears that the structure of the M_2N_2 unit is not enforced by the ancillary ligands, but is a favored geometry for dinitrogen with two lanthanide metal ions.

The results reported here suggest that there should be an extensive dinitrogen chemistry with the Tm(II), Dy(II), and Nd(II) ions. Many combinations of these metals and ligands should yield $(\text{N}_2)^{2-}$ complexes, and these in turn significantly expand the opportunities to study further reduction of the N_2 unit. The opportunity to use ligands as robust as aryloxides for dinitrogen reduction also suggests that cyclic processes for dinitrogen conversions may be possible with these metals. These results also indicate that the formerly unusual planar M_2N_2 geometry does not require any special ancillary ligand environment to form.

The facile reduction of dinitrogen in the presence of a variety of ligand types may explain why these strongly reducing ions¹⁷ have been difficult to handle in the past.^{14,24,25} The neodymium reaction demonstrates that this highly reducing ion in its +2 oxidation state can be tamed with the proper ligand set to do productive divalent lanthanide reduction chemistry.

Acknowledgment. We thank the U.S. National Science Foundation for support of this research and the Swiss National Science Foundation for a postdoctoral fellowship for G.Z.

Supporting Information Available: Experimental details (PDF). 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 and references therein; Fryzuk, M. D.; Kozak, C. M.; Bowdridge, M. R.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 8389.
- Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
- Evans, W. J. *J. Alloys Compd.* **1993**, *192*, 205.
- Fryzuk, M. D.; Haddad, T. S.; Rettig, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 8185.
- Fryzuk, M. D.; Love, J. B.; Rettig, S. T.; Young, V. G., Jr. *Science* **1997**, *275*, 1445.
- Dubé, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716 and references therein.
- Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *Chem. Commun.* **1998**, 2603.
- Roussel, P.; Scott, P. J. *Am. Chem. Soc.* **1998**, *120*, 1070.
- 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.
- Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **2002**, *124*, 9352.
- 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.
- Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11749.
- Bochkarev, M. N.; Fedushkin, I. L.; Dechert, S.; Fagin, A. A.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3176.
- $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Tm}\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)$, **1**. In an argon-filled glovebox, a solution of $\text{NaN}(\text{SiMe}_3)_2$ (109 mg, 0.59 mmol) in 5 mL of THF was added to an emerald green solution of $\text{TmI}_2(\text{THF})_3$ (192 mg, 0.30 mmol) in 5 mL of THF at -30°C in a 50-mL round-bottom flask fitted with a high-vacuum stopcock adapter. The solution immediately darkened and was stirred for 30 min. The flask was connected to a high-vacuum line, cooled in a liquid nitrogen bath, and evacuated. N_2 (1 atm) was introduced, and the solution was allowed to warm to room temperature. The frozen solution turned dark yellow as it melted. The mixture was stirred for 30 min, and the solvent was evaporated under vacuum. The residue was extracted with 5 mL of hexane and centrifuged. After 2 days at -35°C , yellow crystals of **1** (94 mg, 0.08 mmol, 54%) were isolated. Anal. Calcd for $\text{Tm}_2\text{C}_{32}\text{H}_{88}\text{N}_6\text{O}_2\text{Si}_8$: C, 33.37; H, 7.70; N, 7.30; Si, 19.51; Tm, 29.34. Found: C, 32.99; H, 7.53; N, 6.98; Si, 19.36; Tm, 29.50. μ_{eff} (298 K) = $6.9 \mu_B$ (Evans method; Evans, D. F. *J. Chem. Soc.* **1959**, 2003; Beccossall, J. K. *Mol. Phys.* **1968**, *15*, 129).
- Crystallographic data for 1.** $\text{C}_{32}\text{H}_{88}\text{N}_6\text{O}_2\text{Si}_8\text{Tm}_2$, monoclinic, space group $P2_1/n$, $a = 10.7744(4)$ Å, $b = 23.479(1)$ Å, $c = 11.5031(5)$ Å, $\beta = 112.671(1)^\circ$, $V = 2685.18(19)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.427$ Mg/m³, $R_1 = 0.0228$, $wR_2 = 0.0554$, GOF = 1.086.
- Aqueous $\text{Ln}^{\text{III}}/\text{Ln}^{\text{II}}$ reduction potentials (vs NHE): Tm (-2.3 V); Dy (-2.5 V); Nd (-2.6 V). See: Morss, L. R. *Chem. Rev.* **1976**, *76*, 827.
- $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Dy}\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)$, **2**. In an argon-filled glovebox, a 50-mL round-bottom flask fitted with a high-vacuum stopcock adapter was charged with DyI_2 (199 mg, 0.48 mmol) and $\text{NaN}(\text{SiMe}_3)_2$ (175 mg, 0.95 mmol). The flask was connected to a high-vacuum line and approximately 10 mL of THF was added under vacuum. N_2 (1 atm) was introduced into the flask while the solvent was frozen. The mixture was allowed to warm to -78°C with stirring, and a dark purple solution formed. After 15 min, the color slowly changed to dark brown. The solution was stirred for 30 min more at -78°C and then allowed to warm to rt. After 1 h, the solvent was evaporated under vacuum. The dark yellow-brown residue was extracted with 10 mL of hexane, centrifuged, and concentrated to 1 mL. After 1 week at -35°C , **2** was isolated as orange crystals (80 mg, 0.07 mmol, 30%). Anal. Calcd for $\text{Dy}_2\text{C}_{32}\text{H}_{88}\text{N}_6\text{O}_2\text{Si}_8$: 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. μ_{eff} (298K) = $9.9 \mu_B$.
- Crystallographic data for 2.** $\text{C}_{32}\text{H}_{88}\text{N}_6\text{O}_2\text{Si}_8\text{Dy}_2$, monoclinic, space group $P2_1/n$, $a = 10.8445(4)$ Å, $b = 23.4461(9)$ Å, $c = 11.5625(4)$ Å, $\beta = 112.6310(10)^\circ$, $V = 2713.53(17)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.394$ Mg/m³, $R_1 = 0.0236$, $wR_2 = 0.0599$, GOF = 1.085.
- Evans, W. J.; Johnston, M. A.; Clark, R. D.; Anwander, R.; Ziller, J. W. *Polyhedron* **2001**, *20*, 2483 and references therein.
- Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, *12*, S1.
- $\{[(2,6\text{-tBu}_2\text{C}_6\text{H}_3\text{O})_2(\text{THF})_2\text{Nd}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)$, **5**. Following the procedure described for **2**, NdI_2 (240 mg, 0.60 mmol) and $\text{KOC}_6\text{H}_3\text{Bu}_2\text{-2,6}$ (370 mg, 1.51 mmol) were combined in THF under nitrogen. After one week at -35°C , **5** was obtained from a THF/hexane (1/1) solution as blue-green crystals of the tetrasolvate, **5**·4THF (154 mg, 0.09 mmol, 31%). Anal. Calcd for **5**·3THF, i.e., $\text{Nd}_2\text{C}_{84}\text{H}_{40}\text{N}_2\text{O}_{11}$: Nd, 17.56. Found: Nd, 17.89. ¹H NMR: (THF-*d*₆) δ 10.18 (Ar, d, 2H), 7.97 (Ar, t, 1H), 3.61 (THF, br, 16H), 1.78 (THF, br, 16H), 0.02 (Bu, br, 18 H). ¹³C NMR (THF-*d*₆) δ 153.68 (Ar), 127.86 (Ar), 121.30 (Ar), 68.41 (THF), 36.41 (CMe₃), 26.66 (THF), 24.15 (CH₃). μ_{eff} (298 K) = $3.5 \mu_B$.
- Crystallographic data for 5**·4THF. $\text{C}_{72}\text{H}_{116}\text{N}_2\text{O}_8\text{Nd}_2$, triclinic, space group $P1$, $a = 12.2314(9)$ Å, $b = 12.9321(10)$ Å, $c = 15.1594(11)$ Å, $\alpha = 74.0530(10)^\circ$, $\beta = 82.6520(10)^\circ$, $\gamma = 74.0600(10)^\circ$, $V = 2213.4(3)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.286$ Mg/m³, $R_1 = 0.0506$, $wR_2 = 0.1329$, GOF = 1.085.
- Fedushkin, I. L.; Bochkarev, M. N.; Dechert, S.; Schumann, H. *Chem. Eur. J.* **2001**, *7*, 3558.
- Evans, W. J.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *Polyhedron* **1998**, *17*, 3361.

JA0211712