

# Expanding Yttrium Bis(trimethylsilylamide) Chemistry Through the Reaction Chemistry of $(N_2)^{2-}$ , $(N_2)^{3-}$ , and $(NO)^{2-}$ Complexes

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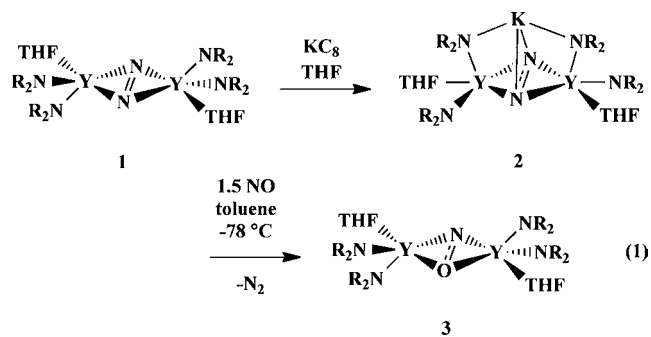
## Supporting Information

**ABSTRACT:** The reaction chemistry of the side-on bound  $(N_2)^{2-}$ ,  $(N_2)^{3-}$ , and  $(NO)^{2-}$  complexes of the  $[(R_2N)_2Y]^+$  cation ( $R = SiMe_3$ ), namely,  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)$ , **1**,  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)K$ , **2**, and  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-NO)$ , **3**, with oxidizing agents has been explored to search for other  $(E_2)^{n-}$  ( $E = N, O$ ), species that can be stabilized by this cation. This has led to the first examples for the  $[(R_2N)_2Y]^+$  cation of two fundamental classes of  $[(\text{monoanion})_2Ln]^+$  rare earth systems ( $Ln = Sc, Y, \text{lanthanides}$ ), namely, oxide complexes and the tetraphenylborate salt. In addition, an unusually high yield reaction with dioxygen was found to give a peroxide complex that completes the  $(N_2)^{2-}$ ,  $(NO)^{2-}$ ,  $(O_2)^{2-}$  series with **1** and **3**. Specifically, the  $(\mu-O)^{2-}$  oxide-bridged bimetallic complex,  $[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**, is obtained as a byproduct from reactions of either the  $(N_2)^{2-}$  complex, **1**, or the  $(N_2)^{3-}$  complex, **2**, with  $NO$ , while the oxide formed from **2** with  $N_2O$  is a polymeric species incorporating potassium,  $\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**. Reaction of **1** with 1 atm of  $O_2$  generates the  $(O_2)^{2-}$  bridging side-on peroxide  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-O_2)$ , **6**. The  $O-O$  bond in **6** is cleaved by  $KC_8$  to provide an alternative synthetic route to **5**. Attempts to oxidize the  $(NO)^{2-}$  complex, **3**, with  $AgBPh_4$  led to the isolation of the tetraphenylborate complex,  $[(R_2N)_2Y(THF)_3][BPh_4]$ , **7**, that was also synthesized from **1** and  $AgBPh_4$ . Oxidation of the  $(N_2)^{2-}$  complex, **1**, with the radical trap (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, TEMPO, generates the  $(TEMPO)^-$  anion complex,  $(R_2N)_2(THF)Y(\eta^2-ONC_5H_6Me_4)$ , **8**.

## INTRODUCTION

$Y[N(SiMe_3)_2]_3$ , originally reported by Bradley in 1973,<sup>1</sup> has proven to be an extremely important precursor in the  $LnA_3/M$  rare earth reduction system ( $Ln = Sc, Y, \text{lanthanides}$ ;  $A = \text{anion}$ ;  $M = \text{alkali metal}$ ) that reduces  $N_2$  and  $NO$ .<sup>2–5</sup> Of all the possible  $Ln(NR_2)_3$  precursors ( $R = SiMe_3$ ), the yttrium variant has provided the most information as yttrium has  $I = 1/2$  nuclear spin that is useful in NMR and EPR studies.<sup>6</sup> In addition, this metal appears to be of the appropriate size with  $(NR_2)^-$  ligands to readily yield crystalline products characterizable by X-ray crystallography. The  $Y(NR_2)_3/KC_8$  reactions have provided not only an  $(N_2)^{2-}$  complex,  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)$ , **1**, but also the first examples of complexes of the  $(N_2)^{3-}$  and  $(NO)^{2-}$  radicals,  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)K$ , **2**, and  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-NO)$ , **3**, eq 1. This bis(amide) yttrium system also provided the first EPR evidence of  $Y^{2+}$  in solution as well as the first  $^{15}N$  NMR information on rare earth  $(N_2)^{2-}$  and  $(N_2H_2)^{2-}$  complexes.<sup>5</sup>

In efforts to expand the scope of small molecule activation with the  $Y[N(SiMe_3)_2]_3/M$  system, reactions of **1–3** with oxidizing agents have been explored. Among the targets of these reactions were the  $(E_2)^{n-}$  ions  $(O_2)^{2-}$ ,  $(O_2)^-$ , and  $(NO)^-$ . These known anions were conspicuous by their absence in the series of  $Ln_2(\mu-\eta^2:\eta^2-E_2)$  planar, side-on bound, reduced diatomic complexes, **1–3**, where  $(E_2)^{n-} = (N_2)^{2-}$ ,  $(N_2)^{3-}$ , and  $(NO)^{2-}$ , respectively. Since the  $(N_2)^{3-}$  ligand has proven to be especially effective in coupling paramagnetic lanthanide ions to form single molecule magnets,<sup>7</sup> expansion in this area is desirable.



Since the rare earths are so oxophilic, the oxo, peroxy, and even the superoxo complexes might be expected to be the most stable of this series. It was also expected that a  $(NO)^-$  complex would be discovered before  $(NO)^{2-}$  since the monoanion is the common anionic reduced form of nitric oxide. On the other hand, it is unknown, in contrast to rare earth metallocene chemistry, if a monoanionic  $(E_2)^-$  ligand can electrostatically stabilize bimetallic species with a  $Ln_2(\mu-\eta^2:\eta^2-E_2)$  core when  $(NR_2)^-$  is the ancillary ligand.

Although rare earth complexes are highly reactive with oxygen-containing species, these reactions are often complicated and can produce mixtures of inseparable products including the insoluble oxides. This has also been the case in this study of the reactions of **1–3** with oxidizing agents and only reactions that have provided

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reproducible, crystallographically characterizable products are reported in detail. Although only one of the three  $(E_2)^n$  targets has been obtained in this study, the reactions of 1–3 have provided the first yttrium bis(trimethylsilylamide) examples of some common classes of compounds important for the development of any type of bis(anionic ligand) rare earth complex.

Specifically, structural data on the first examples of oxides and tetraphenylborate salts of the  $[(R_2N)_2Y]^+$  cation are reported. The importance of these classes can be seen in metallocene chemistry. For example, the identification of  $[(C_5Me_5)_2Ln](\mu-O)$  complexes that are commonly observed byproducts of many reactions provides a good gauge of the reactivity of the rare earth metallocene complex and of availability of oxygen contaminants in the reaction system.<sup>8</sup> Previously, the only reported bimetallic oxide of a  $[(R_2N)_2Ln]^+$  cation is the samarium complex  $[(R_2N)_2(THF)-Sm](\mu-O)$ .<sup>9</sup> The metallocene tetraphenylborates,  $[(C_5Me_5)_2Ln]-[(\mu-Ph)_2BPh_2]$  have proven to be an important class through their utility as precursors to  $(C_5Me_5)_2LnX^{10}$  compounds ( $X =$  alkyl, pseudohalide) and to the mixed metallocene complexes  $(C_5Me_5)_n(C_5Me_4H)_{3-n}Ln$ .<sup>11</sup> Analogous complexes in these common classes have not been identified for the  $[(R_2N)_2Y]^+$  system until now.

There is also precedent for  $(TEMPO)^-$  anion and peroxide rare earth complexes, but specific  $[(R_2N)_2Y]^+$  derivatives were not known. Complexes of the  $(TEMPO)^-$  anion with rare earths were known only with samarium,  $[(\eta^1-ONC_5H_6Me_4)_2Sm-(\mu-\eta^1:\eta^2-ONC_5H_6Me_4)]_2$  and  $[(C_5Me_5)(\eta^2-ONC_5H_6Me_4)-SmCl]_2$ .<sup>12</sup> That study found the  $(TEMPO)^-$  ligand to be comparable in steric bulk to large alkoxide ligands. Crystallographically characterized bis(amide) rare earth peroxide complexes  $\{[(Me_3Si)_2N]_2Ln(L)\}_2(\mu-\eta^2:\eta^2-O_2)$  ( $Ln = La, L = OPPh_3$ ;<sup>13</sup>  $Ln = Yb, L = THF$ <sup>14</sup>) are known, but the lanthanum complex was made from  $H_2O_2$  and the ytterbium complex from an  $Yb^{2+}$  precursor. The peroxide synthesis reported here involving an  $Y^{3+}$  complex of  $(N=N)^{2-}$  and  $O_2$  is more unusual and expands the reduced dianion chemistry of  $[(R_2N)_2Y]^+$  in terms of both reactivity and composition.

## EXPERIMENTAL SECTION

All syntheses and manipulations described below were conducted under nitrogen or argon with rigorous exclusion of air and water using glovebox, Schlenk, and vacuum line techniques. Solvents were dried over columns containing Q-5 and molecular sieves. Benzene- $d_6$  and THF- $d_8$  were dried over sodium-potassium alloy, degassed using three freeze–pump–thaw cycles, and vacuum transferred before use. Potassium and sodium were purchased from Aldrich, washed with hexanes, and scraped to provide fresh surfaces before use. NO gas was purchased from Aldrich (98.5%) and passed through two U-shaped glass columns connected in series and cooled to  $-78^\circ C$ .  $N_2O$  gas (99%) and  $^{18}O_2$  gas (99%) were purchased from Aldrich and used as received. Compressed  $O_2$  gas was purchased from Airgas and was passed through a U-shaped glass column cooled to  $-78^\circ C$  prior to use. (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was purchased from Aldrich and sublimed in vacuo prior to use. The complexes  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)$ , **1**,<sup>2</sup>  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)K$ , **2**,<sup>3</sup>  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-NO)$ , **3**,<sup>4</sup>  $AgBPh_4$ ,<sup>15</sup> and  $KC_8$ <sup>16</sup> were synthesized according to the literature.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra were obtained on a Bruker CRYO 500 MHz spectrometer at  $25^\circ C$ . IR samples were prepared as KBr pellets on a Varian 1000 FT-IR system. Elemental analyses were performed on a PerkinElmer Series II 2400 CHNS analyzer. Raman experiments were performed on crystalline samples in a quartz cell sealed with a Teflon stopcock with a Renishaw inVia confocal Raman Microscope using 532 nm laser excitation (laser power 10%, laser focus 50% at 200 s exposure) and a 5 X objective lens.

$[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**. Crystals of **4** were obtained by recrystallization of a hexane solution at  $-35^\circ C$  from the reaction of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)K$ , **2**, with 1.5 equiv of NO or from the reaction of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)$ , **1**, with 2 equiv of NO.  $^1H$  NMR (500 MHz, benzene- $d_6$ ):  $\delta$  0.40 (s, 72H, N(SiMe<sub>3</sub>)<sub>2</sub>).  $^{13}C\{^1H\}$  NMR (126 MHz, benzene- $d_6$ ):  $\delta$  6.8 (s, N(SiMe<sub>3</sub>)<sub>2</sub>). Numerous attempts to prepare **4** from **1** with oxidants such as  $N_2O$ ,  $O_2$ , pyridine *N*-oxide, trimethylamine *N*-oxide, 1,2-epoxybutane,  $Ag_2O$ , and  $K_2O$ , in reactions of **2** with  $N_2O$ , in the reaction of **3** with 1,2-epoxybutane, and in reactions of **7** (see below) with  $Ag_2O$ , pyridine *N*-oxide, and  $Na_2O_2$  were unsuccessful.

$\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**. Crystals of **5** were obtained from cooling a toluene solution to  $-35^\circ C$  of the reaction of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)K$ , **2**, with  $N_2O$ .  $^1H$  NMR (500 MHz, benzene- $d_6$ ):  $\delta$  0.41 (N(SiMe<sub>3</sub>)<sub>2</sub>).  $^{13}C\{^1H\}$  NMR (126 MHz, benzene- $d_6$ ):  $\delta$  6.8 (s, N(SiMe<sub>3</sub>)<sub>2</sub>). Complex **6** (below) provided a preparative route. A solution of **6** (83 mg, 0.08 mmol) in THF (3 mL) was added to a suspension of  $KC_8$  (22 mg, 0.16 mmol) in tetrahydrofuran (THF, 2 mL) at room temperature and stirred vigorously for 15 min. The colorless solution was centrifuged and filtered to remove graphite, and the solvent was removed in vacuo to yield 94 mg of a white solid from which complex **5** (43 mg, 25%) was isolated by recrystallization from toluene at  $-35^\circ C$ . IR: 2947s, 2877m, 1240s, 1185w, 1054m, 1005s, 937w, 870m, 828s, 769w, 749w, 694w, 662m, 599w, 549s, 485m  $cm^{-1}$ . Anal. Calcd for **5**(–0.5 toluene)  $C_{27.5}H_{76}K_2N_4O_2Si_8Y_2$ : C, 33.85; H, 7.85; N, 5.74. Found: C, 33.57; H, 7.98; N, 5.09.

$[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-O_2)$ , **6**. A pale blue, frozen,  $N_2$ -saturated solution of **1** (220 mg, 0.22 mmol) in THF (7 mL) was exposed to  $O_2$  (1 atm) and stirred at ambient temperature for 40 min. On thawing there was an immediate color change to bright yellow. This color persisted for 2 min and then the solution became colorless. The solution was centrifuged and filtered to exclude a white precipitate, and the solvent was removed in vacuo to yield **6** as a white powder (185 mg, 84%). Crystals suitable for X-ray diffraction were grown from toluene at  $-35^\circ C$ .  $^1H$  NMR (500 MHz, benzene- $d_6$ ):  $\delta$  0.41 (s, 72H, N(SiMe<sub>3</sub>)<sub>2</sub>).  $^{13}C\{^1H\}$  NMR (126 MHz, benzene- $d_6$ ):  $\delta$  6.1 (s, N(SiMe<sub>3</sub>)<sub>2</sub>). IR: 2952s, 2897m, 1595m, 1413w, 1248s, 974s, 867sh, 831s, 774m, 753m, 670m, 609m, 477m  $cm^{-1}$ . Raman ( $^{16}O_2$ ): 767  $cm^{-1}$ ; ( $^{18}O_2$ ): 730  $cm^{-1}$  (calcd 723  $cm^{-1}$ ). Anal. Calcd for **6**(–0.5 THF)  $C_{30}H_{84}N_4O_{3.5}Si_8Y_2$ : C, 37.57; H, 8.77; N, 5.85. Found: C, 37.14; H, 9.36; N, 5.41. Complexes **1** and **6** have been observed to undergo partial desolvation under vacuum.<sup>2</sup>

$[(R_2N)_2(THF)_3Y][BPh_4]$ , **7**. A cold ( $-35^\circ C$ ) solution of **1** (40 mg, 0.04 mmol) in toluene (20 mL) was added to a pre-cooled, light-protected vial containing  $AgBPh_4$  (34 mg, 0.08 mmol) and stirred at room temperature for 48 h. The mixture was centrifuged and filtered to remove dark solids, the solvent was removed in vacuo from the pale yellow solution, and the product was washed with hexane to yield **7** as a white powder (35 mg, 45%). Crystals suitable for X-ray diffraction were grown from a THF solution at  $-35^\circ C$ .  $^1H$  NMR (500 MHz, THF- $d_8$ ):  $\delta$  0.19 (s, 36H, N(SiMe<sub>3</sub>)<sub>2</sub>), 6.73 (br m, 4H, B(*p*-C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>), 6.87 (br m, 8H, B(*m*-C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>), 7.28 (br s, 8H, B(*o*-C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>).  $^{13}C\{^1H\}$  NMR (126 MHz, THF- $d_8$ ):  $\delta$  6.0 (N(SiMe<sub>3</sub>)<sub>2</sub>), 122.1 (BPh<sub>4</sub>), 125.9 (BPh<sub>4</sub>), 129.8 (BPh<sub>4</sub>), 137.3 (BPh<sub>4</sub>). IR: 3056m, 3039m, 2955s, 2899m, 1945w, 1884w, 1820w, 1764w, 1580m, 1480m, 1458w, 1427m, 1340w, 1250s, 1183w, 1136w, 1069m, 1032w, 998m, 959s, 900s, 844s, 774m, 734s, 706s, 669m, 613s  $cm^{-1}$ . Anal. Calcd for **7**(–THF)  $C_{44}H_{72}BN_2O_2Si_4Y$ : C, 60.53; H, 8.31; N, 3.21. Found: C, 60.41; H, 8.13; N, 2.95.

$(R_2N)_2(THF)Y(\eta^2-ONC_5H_6Me_4)$ , **8**. Addition of an orange solution of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (25 mg, 0.16 mmol) in toluene (2 mL) dropwise to a stirred pale blue solution of **1** (81 mg, 0.08 mmol) in toluene (5 mL) caused the immediate formation of a colorless solution. The volume of the solution was reduced to about 2 mL, and **8**-THF (48 mg, 83%) was isolated as colorless crystals at  $-35^\circ C$ . Crystals suitable for X-ray diffraction were grown from another toluene solution at  $-35^\circ C$ .  $^1H$  NMR (500 MHz, benzene- $d_6$ ):  $\delta$  0.43 (s, 36H, N(SiMe<sub>3</sub>)<sub>2</sub>), 1.20 (s, 12H, ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>), 1.35 (m, 14H, ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>, THF), 3.71 (m, 8H, THF).  $^{13}C\{^1H\}$  NMR (126 MHz, benzene- $d_6$ ):  $\delta$  6.7 (s, N(SiMe<sub>3</sub>)<sub>2</sub>), 17.6 (ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>),

**Table 1.** X-ray Data Collection Parameters for  $[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**,  $\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**,  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2-\eta^2-O_2)$ , **6**,  $[(R_2N)_2(THF)_3Y][BPh_4]$ , **7**, and  $(R_2N)_2(THF)Y(\eta^2-ONC_5H_6Me_4)$ , **8**

	4	5	6	7	8
empirical formula	$C_{32}H_{88}N_4Si_8O_3Y_2$	$[C_{31}H_{80}K_2N_4O_2Si_8Y_2]_n$	$C_{32}H_{88}N_4O_4Si_8Y_2 \cdot C_7H_8$	$C_{48}H_{80}BN_2O_3Si_4Y_2$	$C_{25}H_{62}N_3O_2Si_4Y \cdot C_7H_8$
formula weight	979.60	1021.73	1087.74	945.22	730.18
T(K)	143(2)	148(2)	143(2)	143(2)	103(2)
crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1$
a (Å)	10.8326(6)	11.7914(6)	11.2181(17)	21.6041(17)	12.2932(7)
b (Å)	11.9799(6)	12.0827(6)	12.922(2)	12.7933(10)	12.8887(7)
c (Å)	12.1523(6)	20.3900(10)	13.156(2)	21.7958(17)	13.2122(7)
$\alpha$ (deg)	60.6233(6)	98.8969(7)	107.0028(18)	90	90
$\beta$ (deg)	76.3438(6)	106.6799(7)	108.8235(17)	118.0084(10)	102.6215(6)
$\gamma$ (deg)	89.1598(6)	103.1034(7)	109.3789(18)	90	90
volume (Å <sup>3</sup> )	1325.85(12)	2634.1(2)	1522.9(4)	5318.5(7)	2042.80(19)
Z	1	2	1	4	2
$\rho_{\text{calcd}}$ (Mg/m <sup>3</sup> )	1.227	1.288	1.186	1.180	1.187
$\mu$ (mm <sup>-1</sup> )	2.389	2.561	2.088	1.225	1.574
R1 <sup>a</sup> [ $I > 2.0\sigma(I)$ ]	0.0256	0.0324	0.0333	0.0437	0.0175
wR2 <sup>a</sup> (all data)	0.0666	0.0762	0.0897	0.1075	0.0435

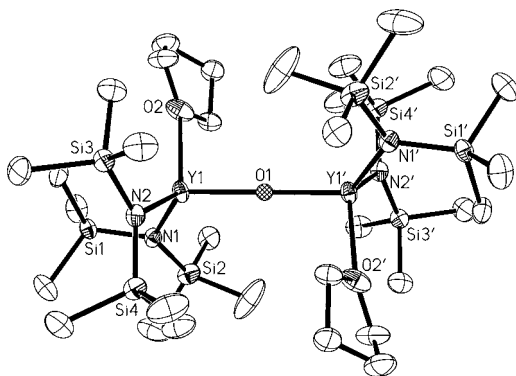
<sup>a</sup>Definitions:  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

25.7 (ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>), 40.5 (ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>), 60.4 (ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>). IR: 2949s, 1462w, 1360w, 1251s, 1180w, 1132w, 1013sh, 974s, 941s, 887sh, 843s, 779m, 665m, 604m, 517m cm<sup>-1</sup>. Anal. Calcd for 8-THF C<sub>29</sub>H<sub>70</sub>N<sub>3</sub>O<sub>3</sub>Si<sub>4</sub>Y: C, 49.05; H, 9.94; N, 5.92. Found: C, 49.19; H, 9.77; N, 5.93.

**X-ray Data Collection, Structure Solution, and Refinement for 4–8.** A summary of the X-ray data collection parameters is presented in Table 1. Full information is available in the Supporting Information.

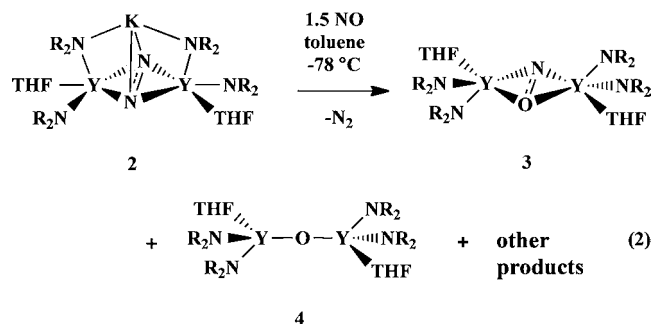
## RESULTS

**Oxide Complexes  $[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**, and  $\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5** (R = SiMe<sub>3</sub>).** The oxide  $[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**, was initially identified as a crystalline byproduct, Figure 1, in the reaction of the  $(N_2)^{3-}$  complex,



**Figure 1.** Thermal ellipsoid plot of  $[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**, showing the calculated average position of the two disordered (O)<sup>2-</sup> positions, drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.

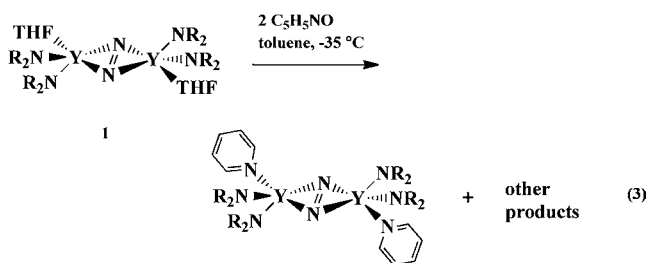
$[(R_2N)_2(THF)Y]_2(\mu-\eta^2-\eta^2-N_2)K$ , **2**,<sup>3</sup> with NO that was previously reported to form the (NO)<sup>2-</sup> complex,  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2-\eta^2-NO)$ , **3**,<sup>4</sup> as the main product, eq 2. Crystals of **4** were also obtained as a byproduct from the reaction of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2-\eta^2-N_2)$ , **1**, with two equiv of NO that forms the (ON=NO)<sup>2-</sup> complex  $[(R_2N)_2Y]_4(\mu_3-ON=NO)_2(THF)_2$  as the main



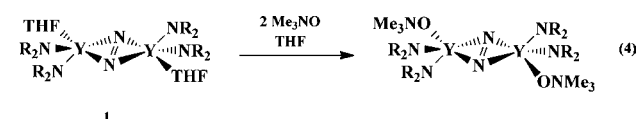
product.<sup>4</sup> The isolation of **4** was the first evidence that a bridging oxide of the  $[Y(NR_2)_2]^+$  cation was accessible, analogous to the ubiquitous  $[(C_5Me_5)_2Ln]_2(\mu-O)$  byproducts in rare earth metallocene reactions.

After complex **4** was identified from both reaction mixtures described above by X-ray crystallography, it was identified in other reaction mixtures containing  $[(R_2N)_2Y]^+$  by its characteristic <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR shifts. However, numerous attempts to generate **4** deliberately were unsuccessful. This is not unlike the situation with the metallocene oxides: the compounds are often observed by NMR spectroscopy, but direct high yield syntheses are either not known or non-trivial, as in the case of the most studied system  $[(C_5Me_5)_2Sm]_2(\mu-O)$ .<sup>17–19</sup> Hence, variations in the conditions of the NO reactions that initially gave **4** as a byproduct were not successful in generating high yields of **4**. In addition, **4** was not obtained in reactions of **1** with oxidants such as N<sub>2</sub>O, O<sub>2</sub>, pyridine *N*-oxide, trimethylamine *N*-oxide, 1,2-epoxybutane, Ag<sub>2</sub>O, and K<sub>2</sub>O, in reactions of **2** with N<sub>2</sub>O, in the reaction of **3** with 1,2-epoxybutane, and in reactions of the cationic complex  $[(R_2N)_2(THF)_3Y][BPh_4]$ , **7** (see below), with Ag<sub>2</sub>O, pyridine *N*-oxide, and Na<sub>2</sub>O<sub>2</sub>. No fully characterizable new oxide or oxygen-containing complexes were isolated from these reactions, except in the case of the synthesis of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2-\eta^2-O_2)$ , **6**, from the reaction of **1** with O<sub>2</sub> (see later section). The reaction of **1** with pyridine *N*-oxide gave  $[(R_2N)_2(C_5H_5N)Y]_2(\mu-\eta^2-\eta^2-N_2)$ ,<sup>20</sup> eq 3, by NMR and X-ray crystallography, which indicated that oxygen had been delivered by the *N*-oxide reagent, but the oxide product was not identified. In contrast to the pyridine *N*-oxide reaction in eq 3, only THF





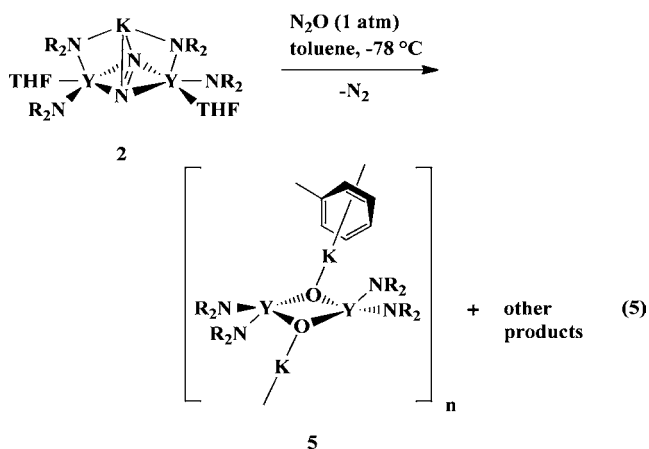
substitution occurred when **1** was treated with trimethylamine *N*-oxide to yield the adduct  $[(R_2N)_2(Me_3NO)Y]_2(\mu-\eta^2:\eta^2-N_2)$ ,<sup>20</sup> eq 4.



Since oxides like **4** are usually unwanted decomposition products and are not commonly used as precursors, it was more important to identify **4** than to find a high yield synthesis for it. Interestingly, the synthesis of the related samarium oxide,  $[(R_2N)_2(THF)Sm]_2(\mu-O)$ ,<sup>9</sup> also proved challenging. Although the samarium oxide can be made from the isolable  $Sm^{2+}$  precursor,  $(R_2N)_2Sm(THF)_2$ ,<sup>21</sup> with nitrosobenzene or 1,2,3,4-di(epoxy)butane, isolation of the product proved problematic. Neither yields nor elemental analysis were reportable since the compound readily loses THF and decomposes when removed from the mother liquor of the reaction.<sup>9</sup>

The reaction of **2** with  $N_2O$  mentioned above did not form **4**, but gave crystals of another yttrium amide oxide, namely, the potassium bridged species,  $\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**, which when recrystallized from toluene exists as a polymer in the solid state, eq 5, Figures 2 and 3. Multi-metallic bridged oxides containing alkali metals are well-known for the lanthanides and actinides,<sup>22</sup> but there are few examples either with the  $[N(SiMe_3)_2]^-$  ligand<sup>23,24</sup> or with yttrium.<sup>25</sup>

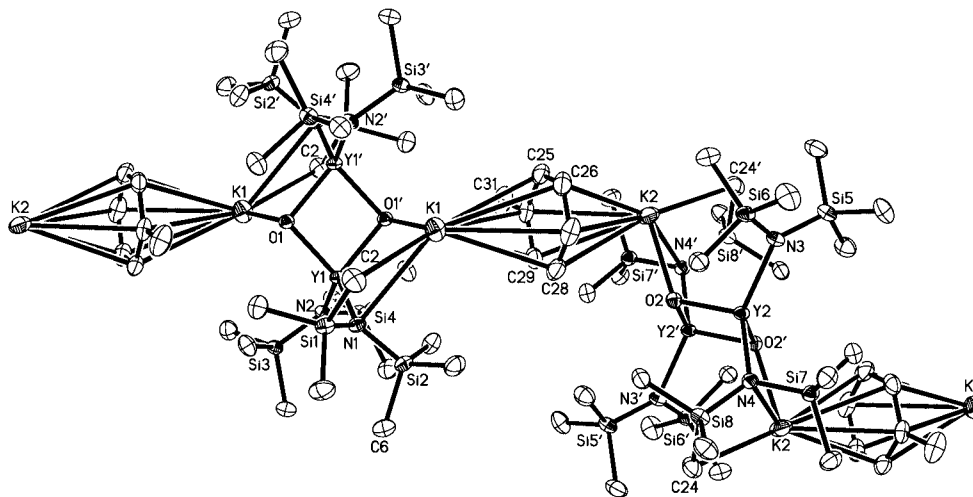
**Structures of  $[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**, and  $\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**.** Complex **4** crystallizes with one THF of solvation per yttrium such that each metal is four coordinate



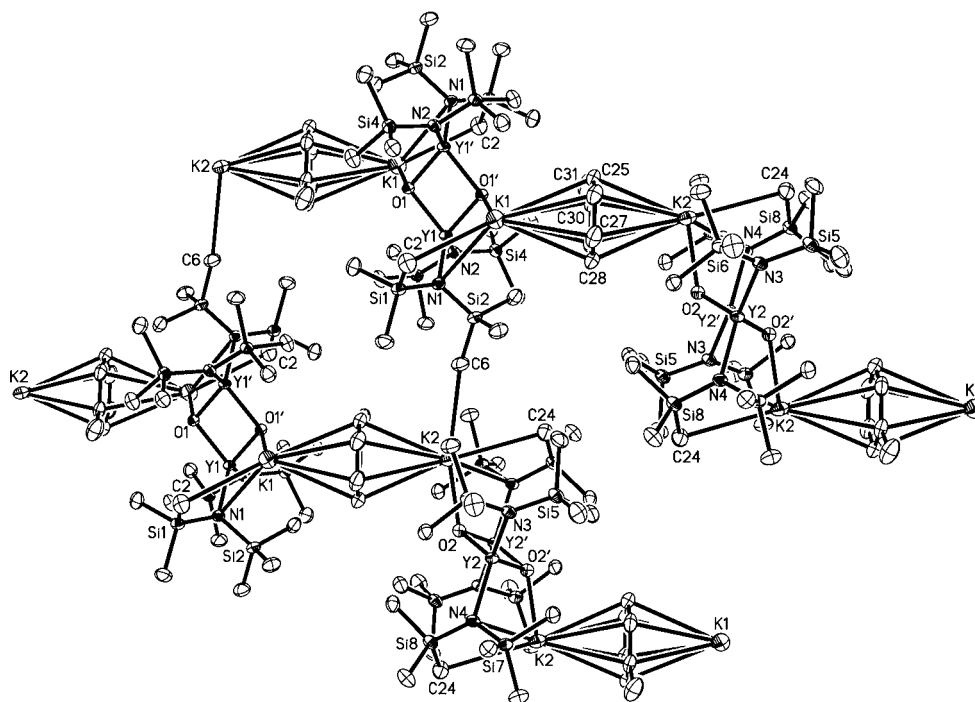
like the previously reported samarium analogue,  $[(R_2N)_2(THF)Sm]_2(\mu-O)$ .<sup>9</sup> Although **4** crystallizes in the same space group as its samarium analogue, the complexes are not isomorphous. The samarium compound has a  $180^\circ$  Sm–O–Sm linkage, the most compact arrangement for two  $[(R_2N)_2Ln]^+$  cations around a bridging  $(O)^{2-}$  ion, with equivalent  $2.0819(2)$  Å Sm–O distances. The related complex,  $[(C_5Me_5)_2Y]_2(\mu-O)$ ,<sup>26</sup> has a Y–O distance of  $2.053(1)$  Å and a linear Y–O–Y angle.<sup>27</sup> Large variations in Ln–O–Ln angles have been observed in analogous bimetallic rare earth metallocenes.<sup>8,17,18,23</sup>

The oxide ligand in **4**, on the other hand, is disordered such that it is not possible to determine from the X-ray data whether the Y–O–Y angle is linear or whether the Y–O distances are symmetric. The model used to describe the disorder involves the displacement of the  $(O)^{2-}$  atom to either side of the inversion center with 0.5 site occupancy in each position (see Supporting Information). Figure 1 is a representation of the structure of **4** that shows the average of those two disordered oxide positions and therefore the Y–O–Y angle appears linear. However, the actual angle cannot be determined from the data.

The  $2.257(1)$  Å and  $2.266(2)$  Å Y–N(amide) distances in **4** are normal for bis(trimethylsilyl)amide yttrium complexes<sup>2,20</sup> and comparable to the  $2.322(3)$  and  $2.333(3)$  Å distances in  $[(R_2N)_2(THF)Sm]_2(\mu-O)$ <sup>9</sup> given the  $0.058$  Å larger ionic radius of samarium.<sup>28</sup> However, the  $2.367(2)$  Å Y–O(THF) bond is shorter than the  $2.468(3)$  Å samarium analogue. Hence, **4**



**Figure 2.** Thermal ellipsoid plot of a dimeric unit of  $\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



**Figure 3.** Thermal ellipsoid plot of  $\{[(R_2N)_2Y](\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**, showing the intermolecular interactions in the polymeric structure, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

and its samarium analogue do not match as well structurally as many analogous compounds in series of rare earth species.

The solid-state structure of **5**, Figure 2, is complicated by two types of orthogonal bridging networks. The fundamental formula of **5** is just  $[(R_2N)_2YO][K]$ , that is, it is formally a potassium “ate salt” variant of **4**. In the solid state structure of **5**, two  $[(R_2N)_2YO]^-$  moieties combine to form a bis(oxo) bridged  $\{[(R_2N)_2Y](\mu-O)_2[Y(NR_2)_2]\}^{2-}$  bimetallic unit; there are two types of these in the repeat unit that generates the extended structure as described below. Each oxide ligand has a potassium within bonding distance, but each potassium also has additional interactions with a nearby  $[N(SiMe_3)_2]^-$  ligand, which is a common feature of rare earth complexes of the bis(trimethylsilyl) amide ligand.<sup>14,29</sup> The coordination sphere of the potassium ion also contains a toluene molecule that functions as a bridge between the  $K_2[(R_2N)_2Y](\mu-O)_2[Y(NR_2)_2]$  units. Additional long-range potassium-amide interactions are present perpendicular to the bridging toluene chain that lead to a two-dimensional network (Figure 3).

The structure of **5** has additional complexity in that there are two types of  $\{[(R_2N)_2Y](\mu-O)_2[Y(NR_2)_2]\}^{2-}$  units, one formed from Y1 and its symmetry equivalent Y1' and the other composed of Y2 and Y2'. K1 is associated with the  $Y_2O_2$  unit made of Y1 and K2 is associated with the  $Y_2O_2$  unit made of Y2. Both K ions attach to bridging toluene molecules in an  $\eta^6$ -mode. The unique crystallographic repeat unit has one Y1 from one-half of one bimetallic unit and one Y2 from one-half of the other and includes K1 and K2 and the bridged toluene in between.

Despite this complicated solid state structure, each Y atom is simply four coordinate with distorted tetrahedral geometry formed by two  $[N(SiMe_3)_2]^-$  ligands and two  $(\mu-O)^{2-}$  ligands (Table 2). The 2.319(2)–2.346(2) Å range of Y–N distances is longer than the Y–N distances in **4** and at the longer end of the range observed for yttrium bis(trimethylsilylamide) complexes in the literature.<sup>24,30–32</sup> The 2.103(2)–2.113(2) Å Y–O distances

**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) for  $\{[(R_2N)_2Y](\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**

parameter	length	parameter	angle
Y1–O1	2.103(2)	O1–Y1–O1'	81.33(6)
Y1–O1'	2.113(2)	N2–Y1–N1	120.17(7)
Y2–O2	2.104(2)	O1–Y1–N2	105.79(6)
Y2–O2'	2.109(2)	O1'–Y1–N2	122.95(6)
		O1–Y1–N1	119.66(6)
Y1–N2	2.337(2)	O1'–Y1–N1	101.57(7)
Y1–N1	2.346(2)		
Y2–N3	2.319(2)	O2–Y2–O2'	81.24(7)
Y2–N4	2.325(2)	O2–Y2–N3	109.21(7)
		O2'–Y2–N3	123.48(7)
K1–O1	2.561(2)	O2–Y2–N4	118.42(7)
K2–O2	2.504(2)	O2'–Y2–N4	102.31(7)
		N3–Y2–N4	117.53(7)
K1–C2	3.403(3)		
K1–N1	3.373(2)	O1–Y1–Y1'	40.78(4)
K2–C6	3.447(3)	O1'–Y1–Y1'	40.55(4)
K2–C24	3.536(3)	O2–Y2–Y2'	40.68(4)
K2–N4	3.478(2)	O2'–Y2–Y2'	40.56(4)

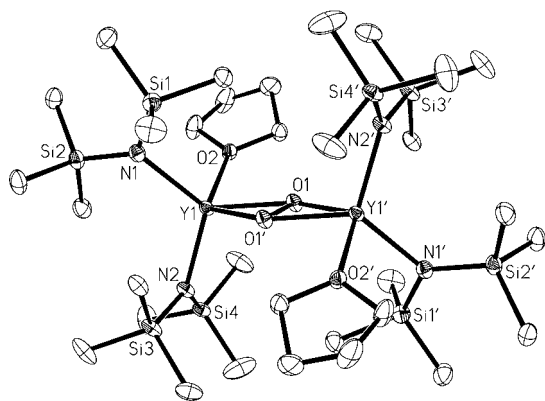
in **5** are longer than the Y–O(oxo) distances in **4** as expected since they are coordinated to three metals rather than two in **5**. The 2.562(2) Å and 2.504(2) K–O distances are significantly shorter than the range of K–O distances 2.661(6)–2.945(4) Å found in bridging alkoxide or salen potassium salts of yttrium.<sup>33–35</sup>

The K–C(toluenes) distances in **5** range from 3.393(3)–3.474(3) Å. These values are on average longer than those observed in ate salt complexes of the lanthanides, for example, in  $\{K(C_7H_8)[Ln(tBu_2pz)_4]\}$  (Ln = La, Sm, Tb, Ho, Yb, Lu),<sup>36</sup> involving terminal toluene  $\eta^6$ -bound to potassium, but they are comparable to the average values of 3.275–3.59 Å found in  $\{K[Ln(O-2,6-i-Pr_2C_6H_3)_4]\}_n$  (Ln = La, Nd, Er), which form extended chain structures.<sup>37</sup> A two-dimensional polymeric structure

is also observed in  $\{K(\text{THF})_x[\text{Sc}(\text{CH}_2\text{Ph})_4]\}_n$  which has potassium interactions with the aryl rings of the benzyl ligands,<sup>38</sup> but the structure of **5** is unusual in that the  $\eta^6$ -arene-bridged polymer is formed by interaction of potassium with toluene solvent, rather than with an arene of a ligand.

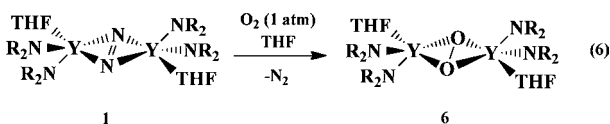
The shortest  $K-(\text{NR}_2)$  contacts are the 3.373(2) Å  $K1-N1$  and 3.403(3) Å  $K1-C2(\text{Me})$  distances. The distances to  $K2$  are longer: 3.478(2) Å for  $K2-N4$ , and 3.536(3) Å for  $K2-C24(\text{Me})$ . In comparison, the cyclometalated bis(trimethylsilyl) amide yttrium complex,  $\{(\text{R}_2\text{N})_2\text{Y}[\text{CH}_2\text{Si}(\text{Me})_2\text{NR}]\}[\text{K}(\text{C}_6\text{H}_6)_2]$ , has an intramolecular  $K-C(\text{Me})$  distance of 3.000(4) Å and an intermolecular  $K-C(\text{Me})$  distance of 3.228(4) Å.<sup>29a,b</sup> The benzene-free Yb analogue,  $\{(\text{R}_2\text{N})_2\text{Yb}[\text{CH}_2\text{Si}(\text{Me})_2\text{NR}]\}\text{K}$ , is even more similar to **5** in that it has multiple  $K-C(\text{Me})$  contacts and a polymeric layer structure.<sup>29a,b</sup>

**Peroxide Complex  $[(\text{R}_2\text{N})_2(\text{THF})\text{Y}]_2(\mu-\eta^2-\eta^2-\text{O}_2)$ , **6**.** The reaction of  $[(\text{R}_2\text{N})_2(\text{THF})\text{Y}]_2(\mu-\eta^2-\eta^2-\text{N}_2)$ , **1**, with oxygen was attempted as part of this study. The reaction was initially run at  $-78^\circ\text{C}$  in toluene with 0.5 equiv of  $\text{O}_2$  and produced a single new diamagnetic product by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy in a 50% yield. Subsequent reactions with up to 1 atm  $\text{O}_2$  in either toluene or THF at temperatures up to ambient temperature generated the same product in good yields. An 84% yield was found for the reaction in THF, in which 1 atm of  $\text{O}_2$  was added to a previously frozen solution of **1** with fast warming to room temperature. The reaction is not sensitive to the concentration of nitrogen in solution and proceeds irrespective of whether the solvent is degassed or not. The structure of the product was determined to be the  $(\text{O}_2)^{2-}$  peroxide species,  $[(\text{R}_2\text{N})_2(\text{THF})\text{Y}]_2(\mu-\eta^2-\eta^2-\text{O}_2)$ , **6**, by single crystal X-ray analysis, Figure 4, eq 6. The peroxide unit in **6** has the same bridging



**Figure 4.** Thermal ellipsoid plot of  $[(\text{R}_2\text{N})_2(\text{THF})\text{Y}]_2(\mu-\eta^2-\eta^2-\text{O}_2)$ , **6**, drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

$\eta^2-\eta^2$ -coordination mode as the  $(\text{N}_2)^{2-}$ ,  $(\text{NO})^{2-}$ , and  $(\text{N}_2)^{3-}$  complexes previously synthesized from the  $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3/\text{K}$  reduction system.<sup>1–5</sup> Hence, crystallographic data are now available for all three variations of the  $(\text{E}_2)^{2-}$  unit in  $\text{Y}_2\text{E}_2$  complexes where  $\text{E} = \text{N}$  and  $\text{O}$ .



Raman spectroscopy experiments were performed on **6** and  $6-^{18}\text{O}_2$ , the analogue prepared from  $^{18}\text{O}_2$ . Since the  $\nu_{\text{O-O}}$  is

one of the least intense features of the overall spectrum, single crystalline samples were required to obtain definitive data. The Raman spectrum of **6** displayed a resonance at  $767\text{ cm}^{-1}$  that was absent in the spectrum of  $6-^{18}\text{O}_2$ , which had a resonance at  $730\text{ cm}^{-1}$  (calculated,  $723\text{ cm}^{-1}$ ). In comparison, for most transition metal peroxides the range of  $\nu_{\text{O-O}}$  bands is  $800-930\text{ cm}^{-1}$ ; metal superoxide complexes have  $\nu_{\text{O-O}}$  at  $1050-1200\text{ cm}^{-1}$ .<sup>39,40</sup> In cases of  $\mu-\eta^2-\eta^2-\text{O}_2$  transition metal binding, the peroxide  $\nu_{\text{O-O}}$  has been found to shift to lower wavenumbers ( $\nu_{\text{O-O}} < 750\text{ cm}^{-1}$ ).<sup>41,42</sup> In the closely related complex,  $[(\text{R}_2\text{N})_2(\text{THF})\text{Yb}]_2(\mu-\eta^2-\eta^2-\text{O}_2)$ , **9**,<sup>14</sup> which has a 1.543(4) Å  $\text{O-O}$  distance by X-ray crystallography, a Raman resonance at  $775\text{ cm}^{-1}$  was assigned as  $\nu_{\text{O-O}}$ . However, density functional theory (DFT) predicted a shorter  $\text{O-O}$  bond of 1.519 Å with a  $\nu_{\text{O-O}}$  resonance at  $853\text{ cm}^{-1}$ , and the  $^{18}\text{O}_2$  isotopomer was not synthesized. Recently Lappert et al. reported a  $[\text{Ce}(\text{NR}_2)_3]_2(\mu-\text{O}_2)$  complex believed to be a peroxide rather than a superoxide, but neither X-ray or Raman data were definitive.<sup>23</sup>

Attempts to oxidize **6** to a superoxo species with  $\text{AgBPh}_4$  were unsuccessful. Complex **6** is also stable toward excess  $\text{O}_2$ , as the reaction is run at 1 atm, and no reaction was observed with  $\text{NO}$  (1 equiv) in contrast to **1** (see earlier section). The reaction of **6** with  $\text{KC}_8$  (1 equiv) in cold THF and recrystallization from toluene resulted in the isolation of the bridged species  $\{[(\text{R}_2\text{N})_2\text{Y}]_2(\mu-\text{O})_2\text{K}_2(\mu-\text{C}_7\text{H}_8)\}_n$ , **5**, the product of complete reduction of the  $\text{O-O}$  bond. The reaction of **6** with  $\text{KC}_8$  (2 equiv) in THF resulted in the quantitative conversion, by  $^1\text{H}$  NMR spectroscopy, to a new diamagnetic species. Recrystallization from toluene at  $-35^\circ\text{C}$  yielded **5** in 25% yield. This improved synthetic route allowed full characterization of complex **5**. To date there is only one example of a superoxide complex of a rare earth metal,  $[(\text{Tp}^{\text{Me}_2})_2\text{Sm}(\eta^2-\text{O}_2)]$ .<sup>43</sup>

**Structure of  $[(\text{R}_2\text{N})_2(\text{THF})\text{Y}]_2(\mu-\eta^2-\eta^2-\text{O}_2)$ , **6**.** Complex **6** crystallized in the same space group as the yttrium analogue,  $[(\text{R}_2\text{N})_2(\text{THF})\text{Yb}]_2(\mu-\eta^2-\eta^2-\text{O}_2)$ , **9**,<sup>14</sup> but the complexes are not isomorphous. The structures are similar, however, with analogous  $\text{Ln}_2(\mu-\eta^2-\eta^2-\text{O}_2)$  cores with trans THF ligands. The 1.535(3) Å  $\text{O-O}$  distance in **6** matches the 1.543(4) Å value in **9** and is normal for a peroxide (superoxide: 1.2–1.3 Å; peroxide: 1.4–1.5 Å).<sup>36,37</sup> The 2.206(2) Å and 2.240(2) Å  $\text{Y-O}(\text{O}_2)$  distances are slightly larger than the 2.186(2) and 2.219(2) Å values of **9** as expected for the slightly larger yttrium. The  $\text{O-Ln-O}$  angle of  $40.38(7)^\circ$  in **6** also matches the  $41.00(9)^\circ$  analogue in **9**.

**Tetraphenylborate Complex  $[(\text{R}_2\text{N})_2(\text{THF})_3\text{Y}][\text{BPh}_4]$ , **7**.** When the  $(\text{NO})^{2-}$  complex  $[(\text{R}_2\text{N})_2(\text{THF})\text{Y}]_2(\mu-\eta^2-\eta^2-\text{NO})$ ,<sup>4</sup> **3**, was initially discovered, there were no  $(\text{NO})^-$  complexes of the rare earth metals.<sup>44</sup> In efforts to synthesize such a complex, the oxidation of **3** was examined. Treatment of **3** with  $\text{AgBPh}_4$  did not give an isolable  $(\text{NO})^-$  complex, but instead formed the tetraphenylborate salt of the  $[\text{Y}(\text{NR}_2)_2]^+$  cation,  $[(\text{R}_2\text{N})_2(\text{THF})_3\text{Y}][\text{BPh}_4]$ , **7**, Figure 5. Like the oxide **4** above, cationic salts of this type are another basic type of rare earth complex that had not been identified for the yttrium bis(trimethylsilylamide) system. The isolation of **7** showed that an analogue of the metallocene cation was available for yttrium amides.

The isolation of **7** spurred attempts to find more direct routes to this compound. Simple reactions like that of  $\text{Y}(\text{NR}_2)_3$  with  $[\text{HNET}_3][\text{BPh}_4]$  do not form **7** even at  $70^\circ\text{C}$  for 24 h. The  $(\text{N}_2)^{2-}$  complex, **1**, does not react with  $[\text{HNET}_3][\text{BPh}_4]$  and the  $(\text{N}_2)^{3-}$  complex, **2**, reacts with  $[\text{HNET}_3][\text{BPh}_4]$  via reductive disproportionation to form the doubly protonated  $(\text{N}_2\text{H}_2)^{2-}$  complex,  $[(\text{R}_2\text{N})_2(\text{THF})\text{Y}]_2(\mu-\eta^2-\eta^2-\text{N}_2\text{H}_2)$ .<sup>5</sup> However, the reaction of the  $(\text{N}=\text{N})^{2-}$  complex, **1**, with 2 equiv of  $\text{AgBPh}_4$  in

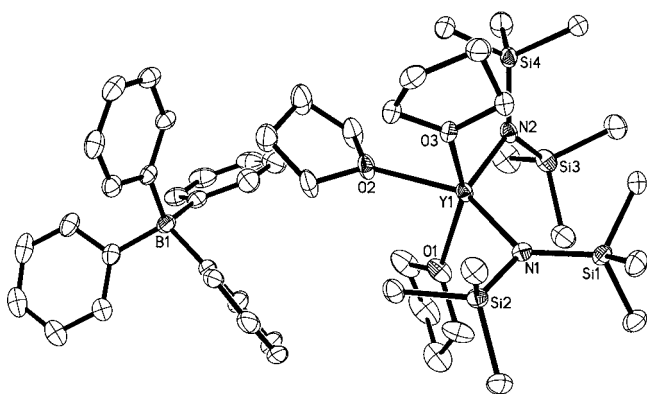
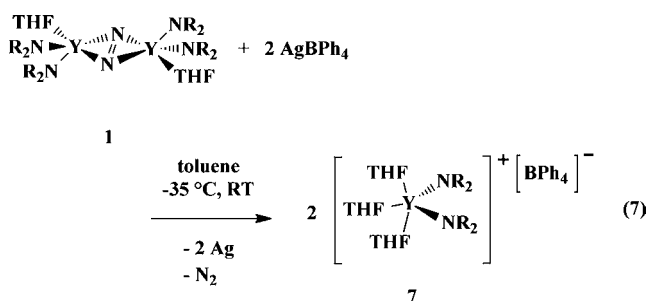


Figure 5. Thermal ellipsoid plot of  $[(R_2N)_2(THF)_3Y][BPh_4]$ , **7**, drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

toluene did yield complex **7** as an analytically pure material in a modest yield, eq 7. The reaction was also run in THF, the only



solvent in which **7** displays good solubility, but multiple products were obtained, even when the reaction was maintained at low temperature.

**Structure of  $[(R_2N)_2(THF)_3Y][BPh_4]$ , **7**.** Complex **7** crystallizes from THF with the cations and anions separated in the lattice beyond bonding distance. Three molecules of THF are coordinated to yttrium to give a five coordinate metal center. The  $[(R_2N)_2(THF)_3Y]^+$  cation adopts a slightly distorted trigonal bipyramidal geometry with the amide ligands in equatorial positions. The  $O(THF)-Y-O(THF)$  angles of  $79.94(7)^\circ$ ,  $84.97(7)^\circ$  and  $155.79(7)^\circ$  demonstrate the distortion from idealized trigonal bipyramidal symmetry. The  $2.218(2)$  and  $2.227(2)$  Å  $Y-N$ (amide) distances are similar to the  $2.224(6)$  Å  $Y-N$ (amide) distance in the parent complex,  $Y[N(SiMe_3)_2]_3$ ,<sup>45</sup> which is formally three coordinate, but has additional silylmethyl–yttrium interactions. The  $Y-O(THF)$  distances in **7** are typical for five coordinate yttrium.<sup>46,29c</sup>

**(TEMPO)<sup>-</sup> Complex,  $(R_2N)_2(THF)Y(\eta^2-ON-C_5H_6Me_4)$ , **8**.** Given the propensity of the  $[(R_2N)_2Y]^+$  system to stabilize radicals like  $(N_2)^{3-}$  and  $(NO)^{2-}$ , the reaction of the  $(N_2)^{2-}$  complex, **1**, with the radical (2,2,6,6-tetramethylpiperidin-1-yl)-oxyl, TEMPO, was examined. This did not generate a new radical product, but instead reduced TEMPO with loss of dinitrogen to form the  $(TEMPO)^-$  anion in the complex  $(R_2N)_2(THF)Y(\eta^2-ONC_5H_6Me_4)$ , **8**, eq 8, Figure 6.

Complex **8** is synthesized in a straightforward manner from the addition of 2 equiv of the TEMPO radical to a solution of complex **1** in toluene, and can be isolated from the same solvent as colorless crystals in high yield with a THF of solvation and a molecule of either toluene or THF in the crystal lattice. The complex has diamagnetic NMR spectra consistent with the structure.

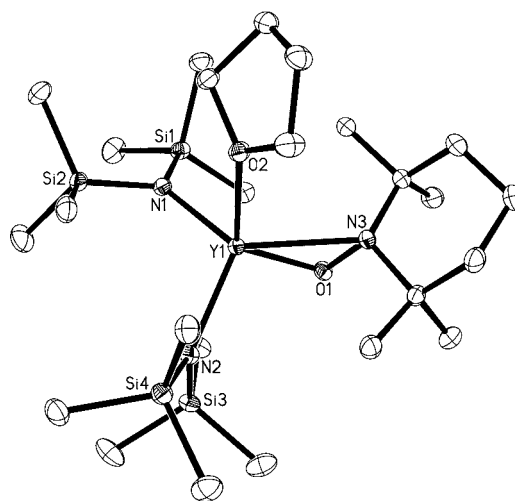
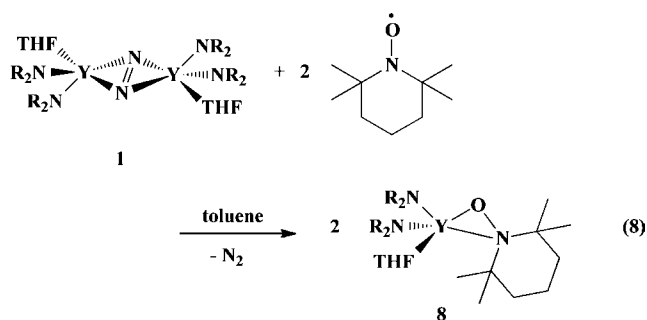


Figure 6. Thermal ellipsoid plot of  $(R_2N)_2(THF)Y(\eta^2-ONC_5H_6Me_4)$ , **8**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

**Structure of  $(R_2N)_2(THF)Y(\eta^2-ONC_5H_6Me_4)$ , **8**.** Complex **8** crystallizes from toluene with a THF of solvation and the  $(TEMPO)^-$  anion bound to yttrium in an  $\eta^2$ -fashion. This coordination is like that in  $[(C_5Me_5)(\eta^2-ONC_5H_6Me_4)SmCl]_2$ . Since the structural data on the latter complex provided connectivity only, comparisons will be made with  $[(\eta^1-ONC_5H_6Me_4)_2Sm(\mu-\eta^1:\eta^2-ONC_5H_6Me_4)]_2$ , **10**.<sup>12</sup> There are relatively few examples of TEMPO complexes of the transition metals, but the  $\eta^2$ -binding mode is the most commonly observed.<sup>47</sup>

The  $2.274(1)$  and  $2.269(1)$  Å  $Y-N$ (amide) distances and the  $2.3987(9)$  Å  $Y-O(THF)$  distance are comparable to those seen in complexes **1** and **4**. The  $1.452(1)$  Å  $O1-N3$  distance in **8** is equivalent within error limits to the  $1.427(8)$ – $1.434(7)$  Å  $N-O$  distances in **10** and is consistent with reduction of the TEMPO radical, which has a  $1.283(9)$  Å  $N-O$  distance.<sup>48</sup> Since the  $(TEMPO)^-$  ligand is bound  $\eta^2$  in **8** but is  $\eta^1:\eta^2$  and  $\eta^1$  in **10**,  $Ln-TEMPO$  distance comparisons are not so direct, but the numbers seem reasonable. The  $Y-O1(TEMPO)$  distance of  $2.116(1)$  Å in **8** is shorter than the bridging  $Sm-O(TEMPO)$  distances in **10**,  $2.295(4)$  and  $2.354(4)$  Å, but longer than the terminal  $Sm-O(TEMPO)$  distances of  $2.110(5)$  and  $2.124(5)$  Å, when the  $0.058$  Å difference in ionic radii is considered.<sup>28</sup> The  $Ln-N(TEMPO)$  distances of  $2.516(1)$  Å for  $Y-N3$  and  $2.537(6)$  Å for  $Sm-N$  are comparable.

The  $Y-TEMPO$  distances in **8** are also comparable to the  $2.172(2)$  Å  $Y-O$  and  $2.437(2)$  Å  $Y-N$  distances observed in the hydroxylamino complex  $\{Cp_2Y[ON(C_2H_4-o-py)_2]\}$ .<sup>49</sup> In contrast,  $[C(CN)_2NO]^-$  dicyanonitrosomethanide lanthanide complexes, that also have  $\eta^2-ON$  binding, show variable binding



dependent on the steric constraints of the complex: in some cases the Ln-O and Ln-N bonds are the same length and in other cases they are asymmetric like those in **8**.<sup>50</sup>

## DISCUSSION

Although oxide and tetraphenylborate complexes of the  $[(R_2N)_2Y]^+$  cation have been identified crystallographically in this study, their direct synthesis has proven challenging. This is consistent with the fact that  $Y[N(SiMe_3)_2]_3$  has been known since 1973<sup>1</sup> and these common types of bis(ligand) rare earth complexes are only now being identified. It is surprising that the  $[(R_2N)_2Y]^+$  moiety that has been so successful in stabilizing unusual anions like  $(N_2)^{3-}$  and  $(NO)^{2-}$  has not previously provided simple oxide and tetraphenylborate complexes with the common  $(O)^{2-}$  and  $(BPh_4)^-$  ligands.

The formation of the oxides  $[(R_2N)_2(THF)Y]_2(\mu-O)$ , **4**, and  $\{[(R_2N)_2Y]_2(\mu-O)_2K_2(\mu-C_7H_8)\}_n$ , **5**, from NO and  $N_2O$  is consistent with the fact that these nitrogen oxides can be oxide delivery agents. Isolation of **4** now allows it to be identified by NMR spectroscopy when it is formed as a byproduct. The synthesis of  $[(R_2N)_2(THF)_3Y][BPh_4]$ , **7**, in eq 7 does show that  $Ag^+$  can oxidize the  $(N_2)^{2-}$  complex, but the reaction is not synthetically useful and precludes using **7** as an alternative synthetic precursor in bis(amide) yttrium chemistry. The oxidation of **1** by TEMPO similarly provides a new heteroleptic amide complex,  $(R_2N)_2(THF)Y(\eta^2-ONC_5H_6Me_4)$ , **8**. The yield of that reaction is sufficient for **8** to be used as a precursor into mixed ligand yttrium chemistry.

Neither  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-N_2)$ , **1**, nor  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-O_2)$ , **6**, reacted with  $AgBPh_4$  to form  $Y_2E_2$  complexes containing an  $(E_2)^-$  monoanion. It will be interesting to see if a monoanion can form a bridge that connects two  $[(R_2N)_2Y]^+$  cations. Recently it has been found that  $(CO)^-$  and  $(CO_2)^-$  will bridge  $Y(NR_2)_3$  units,<sup>51</sup> but even simple  $[(R_2N)_2-Ln-X-Ln(NR_2)_2]^+$  moieties are unknown when X = monoanion and Ln = Y. In contrast, monoanionic bridges are common in rare earth metallocene chemistry.<sup>52</sup>

The direct formation of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-O_2)$ , **6**, from **1** and  $O_2$  in eq 6 at ambient temperatures as well as the stability of **6** toward excess  $O_2$  and NO is very unusual in rare earth chemistry. Syntheses of rare earth peroxides such as  $\{[(L)_nCe]_2(\mu-\eta^2:\eta^2-O_2)_2\}^{m-}$  [ $(L)_n = (CO_3)_3$ ,  $m = 8$  or EDTA],  $m = 4$ ,<sup>53</sup>  $[Ln_4(\mu_3-\eta^2:\eta^2:\eta^2-O_2)_2(Cl)_8(py)_{10}]$  (Ln = Sm, Eu, Gd),<sup>54</sup>  $\{[Ln(Cl)(L)]_2(\mu-\eta^2:\eta^2-O_2)\}[ClO_4]_2$  [Ln = Yb, Lu; L = 2,14-dimethyl-3,6,10,13,19-pentaazabicyclo[13.3.1]nonadecan-1(19),2,13,15,17-pentaene],<sup>55</sup>  $Ln_2(NR_2)_4(O_2)(OPPh_3)_2$  [Ln = La, Pr, Sm, Eu, Lu],<sup>13</sup> and  $[Yb(\eta^5-\{C_5H_4(cyclo-C_5H_9)\})_2(THF)_2-Yb]_2(\mu-\eta^2:\eta^2-O_2)$ <sup>56</sup> generally require low temperature and controlled conditions and these compounds have been either isolated adventitiously or in low yield. The synthesis of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-O_2)$ , which can be isolated in a good yield, is an exception, but the reaction is done at  $-60^\circ C$  and from  $Yb^{2+}$ .

The isolation of  $[(R_2N)_2(THF)Y]_2(\mu-\eta^2:\eta^2-O_2)$ , **6**, specifically is valuable for comparison with **1–3**. When **1–3** were initially isolated, there was some concern that the diatomic ligand between the two metals was dioxygen since it is difficult to differentiate N from O by X-ray crystallography in such complexes. Isolation of **6** with a 1.535(3) Å O–O distance and a  $\nu_{O-O}$  767  $cm^{-1}$  Raman resonance clearly excludes the presence of peroxide in complexes **1–3**.

## CONCLUSION

The reaction chemistry of  $(N_2)^{2-}$ ,  $(N_2)^{3-}$ , and  $(NO)^{2-}$  complexes of  $[(R_2N)_2Y]^+$  has led to the first examples of oxide, peroxide, and tetraphenylborate complexes of this yttrium bis(amide) cation. The high yield conversion of the  $Y_2(\mu-\eta^2:\eta^2-N_2)$  complex, **1**, to the  $Y_2(\mu-\eta^2:\eta^2-O_2)$  complex, **6**, is another example of a  $Ln_2(\mu-\eta^2:\eta^2-E_2)$  complex reacting with a diatomic molecule,  $E'_2$ , to make an  $Ln_2(\mu-\eta^2:\eta^2-E'_2)$  product and  $E_2$ . This was previously observed in the conversion of the  $(N_2)^{3-}$  complex **2** to the  $(NO)^{2-}$  complex, **3**. These reactions are unusual in that a well-protected, diatomic, reduced dianionic ligand is replaced by another diatomic molecule, which enters the reaction as the free diatomic species.

## ASSOCIATED CONTENT

### Supporting Information

Crystallographic data collection, structure solution, and refinement (PDF) and X-ray diffraction details of compounds **8**, **5**, **7**, **4**, and **6** (CIF, CCDC No. 883505–883508 and 894283). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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