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Synthesis of the $(N_2)^{3-}$ Radical from Y^{2+} and Its Protonolysis Reactivity To Form $(N_2H_2)^{2-}$ via the $Y[N(SiMe_3)_2]_3/KC_8$ Reduction System

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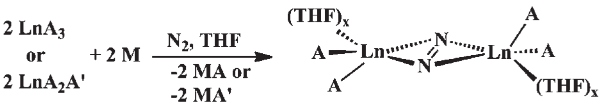
Supporting Information

ABSTRACT: Examination of the $Y[N(SiMe_3)_2]_3/KC_8$ reduction system that allowed isolation of the $(N_2)^{3-}$ radical has led to the first evidence of Y^{2+} in solution. The deep-blue solutions obtained from $Y[N(SiMe_3)_2]_3$ and KC_8 in THF at −35 °C under argon have EPR spectra containing a doublet at $g_{iso} = 1.976$ with a 110 G hyperfine coupling constant. The solutions react with N_2 to generate $(N_2)^{2-}$ and $(N_2)^{3-}$ complexes $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**1**) and $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)[K(THF)_6]$ (**2**), respectively, and demonstrate that the $Y[N(SiMe_3)_2]_3/KC_8$ reaction can proceed through an Y^{2+} intermediate. The reactivity of $(N_2)^{3-}$ radical with proton sources was probed for the first time for comparison with the $(N_2)^{2-}$ and $(N_2)^{4-}$ chemistry. Complex **2** reacts with $[Et_3NH][BPh_4]$ to form $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}N_2H_2)$, the first lanthanide $(N_2H_2)^{2-}$ complex derived from dinitrogen, as well as **1** as a byproduct, consistent with radical disproportionation reactivity.

The recent discovery of the $(N_2)^{3-}$ ion via the reaction of $Y[N(SiMe_3)_2]_3$ with KC_8 under N_2[1] demonstrated that new dinitrogen chemistry is accessible via the combination of a trivalent metal complex, LnA_3 or LnA_2A' (Ln = Sc, Y, or a lanthanide; A = amide, cyclopentadienyl; A′ = BPh_4, I), with an alkali metal (M = K, KC_8, Na).[2−8] These LnA_3/M and LnA_2A'/M combinations[9] have previously been shown to generate divalent "LnA_2" type reactivity and lead to an extensive series of $(N_2)^{2-}$ complexes of general formula $[A_2(THF)_xLn]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$:[2−8]



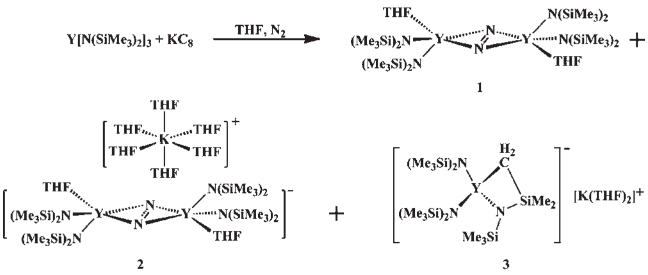
(1)

Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Y, Ho, Er, Tm, Lu, Sc
A = $N(SiMe_3)_2$, $OC_6H_3{}^tBu_2$-2,6, C_5Me_5, $C_5H_4SiMe_3$, C_5Me_4H, $C_5H_2{}^tBu_3$
A' = BPh_4, I; M = K, KC_8, Na; x = 0-2

Although the reaction is broadly successful with scandium,[8] yttrium,[2] and the lanthanides,[3−7] the detailed mechanism of the reduction remains unknown.

Determining the mechanistic details of the reduction is challenging because it forms a distribution of diamagnetic and paramagnetic products having similar solubilities that is highly dependent on the mode of combining the reagents. The reported yields of any one product are typically low, since a yield is not claimed unless the complex can be crystallized in pure form. For example, the $Y[N(SiMe_3)_2]_3/KC_8/N_2$ system (Scheme 1) was found to generate the $(N_2)^{2-}$ and $(N_2)^{3-}$ complexes $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**1**)[2] and $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)[K(THF)_6]$ (**2**),[1] respectively, as well as the metallacyclic species $\{[(Me_3Si)_2N]_2Y[CH_2Si(Me_2)NSiMe_3]\}[K(THF)_2]$ (**3**).[12]

Scheme 1. Products of the LnA_3/M Reductive System with Ln = Y, A = $N(SiMe_3)_2$, and M = KC_8



Formally, the LnA_3/M reaction could go through Ln^{2+} intermediates, but the intense colors expected for Ln^{2+} species are not observed in these reactions. In addition, of the metals in eq 1 that have this reactivity, only La, Ce, Nd, Dy, Tm, and Sc have been shown to form isolable Ln^{2+} complexes in solution.[13−17] The fact that reduced dinitrogen complexes can be made from Nd^{2+}, Dy^{2+}, and Tm^{2+} starting materials[7,18−21] supports the idea that the LnA_3/M reductions can occur through Ln^{2+} species, but definitive evidence for 2+ intermediates with the other metals has, until now, not been obtainable. Yttrium was targeted in this study because both of its congeners, Sc and La, have been observed as 2+ ions in solution[13,17] and the 100%-abundant $I = {}^1/_2$ nuclear spin of yttrium should aid in identification. We now report evidence that Y^{2+} ion can be generated in solution and is a source of dinitrogen reduction reactivity.[22−26]

In addition, we describe the first examination of the reactivity of the $(N_2)^{3-}$ ion with a proton source, which allows a comparison with the reactivities of the isoelectronic $(O_2)^-$ ion and the previously studied $(N_2)^{2-}$ and $(N_2)^{4-}$ ions.[27−31] This was made possible by the isolation of yet another component in the LnA_3/M reaction system shown in Scheme 1, a $(N_2H_2)^{2-}$ complex originally detected via $^1H-^{15}N$ HMQC NMR. Although there are many examples of the formation of $(N_2H_2)^{2-}$ ligands from dinitrogen in transition-metal systems,[32−37] protonation or hydrogenation has not been observed with any of the over 20 examples of $(N_2)^{2-}$ complexes of Sc, Y, and the lanthanides shown in eq 1. A lanthanide

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complex of $(N_2H_2)^{2-}$ is known, $[(C_5Me_5)_2Sm]_2(N_2H_2)$, but it was synthesized from $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$ and hydrazine.[38]

The chemistry of the $(N_2)^{2-}$ complexes in eq 1 is dominated not by electrophilic derivatization reactions but rather by two-electron-reduction reactivity that releases N_2. Hence, the $[A_2(THF)_xLn]_2N_2$ complexes have not been a source of functionalizable nitrogen. Chirik has noted that high reactivity from reduced dinitrogen complexes generally occurs only when dinitrogen is reduced to the $(N_2)^{4-}$ level, whereas $(N_2)^{2-}$ species are less "activated".[29] The isolation of $(N_2H_2)^{2-}$ in this system provides the first opportunity to determine how $(N_2)^{3-}$ fits into the hierarchy of reactivity of $(N_2)^{x-}$ species.

Evidence for Y^{2+} was discovered via one of the several methods investigated for combining $Y[N(SiMe_3)_2]_3$ and KC_8. Specifically, forcing a THF solution of the yttrium amide complex through a pipet packed with freshly prepared KC_8 produced a blue solution inside the pipet in nitrogen-deficient regions. Attempts to isolate the blue solution under argon at room temperature led to quick disappearance of the blue color and formation of a yellow solution, in contrast to the pale-blue and orange colors found when **1** and **2**, respectively, are predominant. NMR studies revealed that three complexes are present after the disappearance of the blue color: the starting material, $Y[N(SiMe_3)_2]_3$, the metallacyclic product $\{[(Me_3Si)_2N]_2Y[CH_2Si(Me_2)NSiMe_3]\}[K(THF)_2]$ (**3**),[12,39] and one other species exhibiting resonances consistent with a THF ring-opened product (see the Supporting Information (SI)). However, when a THF solution of $Y[N(SiMe_3)_2]_3$ previously chilled to −35 °C was forced through a KC_8 column under argon, a deep-blue solution formed and was stable for several hours at −35 °C.

EPR spectroscopic studies of the blue THF solution at −78 °C showed a doublet centered at $g_{iso} = 1.976$ (Figure 1). The large hyperfine coupling of 110 G and the g value are similar to those found in the endohedral metallofullerene $Y_2C_{78}N$, which displayed a triplet at 1.9740 with a coupling constant of 81.23 G.[22] The g value and coupling constant of the blue solution are consistent with the presence of the Y^{2+} ion.[40]

Since the deep-blue solutions persisted nearly twice as long in 1:1 (v/v) THF/DME as in THF, the mixed solvent system was used for reactivity studies with dinitrogen. The intense blue color of a THF/DME solution of Y^{2+} quickly disappeared when N_2 was introduced at −45 °C. EPR studies of the resulting orange solution showed a spectrum identical to that of the $(N_2)^{3-}$ complex **2**.[1] NMR studies of the same solution showed the presence of the $(N_2)^{2-}$ complex **1** as well as the metallacyclic product **3**. The fact that the blue Y^{2+} species can reduce dinitrogen by two and three electrons is consistent with the presence of Y^{2+} as a reactive intermediate in the $Y[N(SiMe_3)_2]_3/KC_8$ dinitrogen reduction system. Since the EPR signal arises from the combination of only $Y[N(SiMe_3)_2]_3$ and potassium graphite in THF and since the solutions warm up to form primarily $Y[N(SiMe_3)_2]_3$, it is possible that the complex in solution was something like the $Ln[N(SiMe_3)_2]_3M(THF)_x$ complexes (M = Na, K) known for the lanthanides with more stable divalent states (i.e., Eu, Yb, and Sm).[39,41,42]

A $(N_2H_2)^{2-}$ product was initially isolated from a $Y[N(SiMe_3)_2]_3/KC_8$ reaction by recrystallization of the reaction mixture obtained by slow addition of KC_8 to $Y[N(SiMe_3)_2]_3$ in THF under dinitrogen. This generated an orange solution containing **2** (identified by EPR), whereas the NMR spectrum indicated the presence of **1** and two additional diamagnetic products. Crystallization of this mixture from THF at −35 °C afforded **2** cleanly in 20% yield. Removal of THF from the orange mother liquor and recrystallization from *toluene* at −35 °C formed pale-blue crystals of **1** as well as a small amount of colorless crystals identified as $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}N_2H_2)$ (**4**). Crystals of **4** were separated from **1** by the Pasteur method.

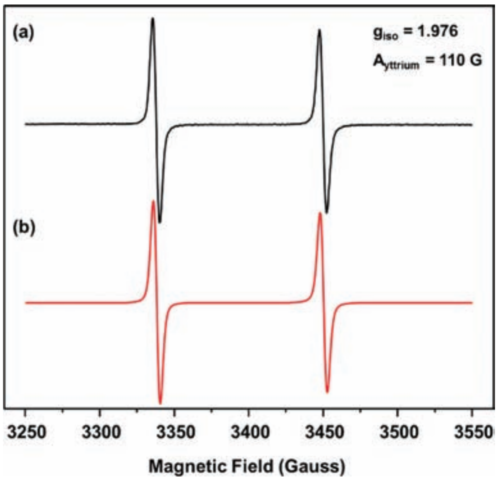


Figure 1. (a) EPR spectrum of a divalent Y^{2+} species generated by reduction of $Y[N(SiMe_3)_2]_3$ with KC_8 in THF. (b) Simulated spectrum.

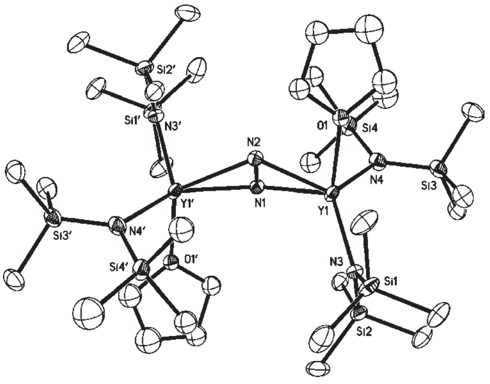
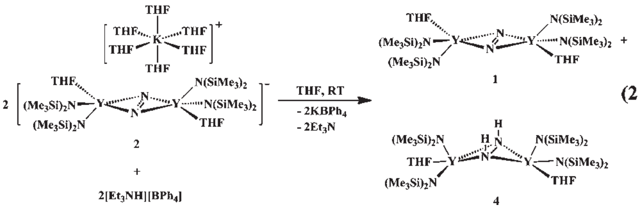


Figure 2. Thermal ellipsoid plot of a model of the data for $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}N_2H_2)$ (**4**) drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. The hydrogen atoms on N1 and N2 could not be located by the X-ray experiment because of disorder in the structure.

The X-ray data for **4** were significantly different from those for **1** and **2** and the complexes in eq 1, each of which has a well-defined planar arrangement of the central Y_2N_2 core. In **4**, the dinitrogen ligand is disordered between the two yttrium atoms. A model with the N_2 unit disordered above and below the Y···Y vector of the two $\{[(Me_3Si)_2N]_2(THF)Y\}^+$ moieties was used, but the disorder limited the ability to draw firm conclusions about the structure. Figure 2 shows a model for the data. The N−N distances in the models for data sets on two different crystals were 1.473(7) and 1.524(6) Å. These distances are significantly longer than the N−N distances of 1.268(3) and 1.401(6) Å in **1** and **2** that correspond to bond orders of 2 and 1.5, respectively. This suggested a bond order of 1 in **4**. In the literature, $(N_2)^{4-}$ complexes with a formal bond order of 1 have N−N distances in a broad range, 1.377(2)−1.635(5) Å.[32,35,43−48] Charge balance in **4** required that the central ligand in **4** be a dianion, a requirement that is met with a diprotonated $(N_2)^{4-}$ ion [i.e., $(N_2H_2)^{2-}$].

The N−N distance in **4** was in the range of N−N distances observed in $(N_2H_2)^{2-}$ complexes: 1.457(3), 1.467(4), 1.434(9), and 1.473(6) Å in $\{(C_5Me_4H)_2ZrH\}_2(N_2H_2)$,[32] $\{(C_5Me_4H)_2HfH\}_2(N_2H_2)$,[35] $\{[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]_2Zr_2\}(N_2H_2)(O)$,[36] and $[(C_5Me_5)_2Sm]_2(N_2H_2)$,[38] respectively.

Since X-ray crystallography was consistent with but not definitive for $(N_2H_2)^{2-}$, other spectroscopic methods were pursued. However, since the yield of **4** from the reaction above was low, an improved synthesis was first required. Specifically, the reactivity of the $(N_2)^{3-}$ complex, **2**, with protons was examined to see if it would form N−H bonds, in contrast to the reactions of $(N_2)^{2-}$ complexes in eq 1. As shown in eq 2, the reaction of **2** with 1 equiv of $[Et_3NH][BPh_4]$ generates **1** and **4** in a 1:1 ratio:



(2)

This is formally equivalent to disproportionation of the $(N_2)^{3-}$ radical to $(N_2)^{2-}$ and $(N_2)^{4-}$ followed by double protonation of the latter species. Radical disproportionation is quite reasonable for the $(N_2)^{3-}$ radical, since the isoelectronic superoxide anion, $(O_2)^-$, is known to disproportionate to O_2 and H_2O_2 in the important biological reaction catalyzed by superoxide dismutases.[49,50] The disproportionation in eq 2 is not efficient in $(N_2)^{3-}$ for the production of **4** since half of the nitrogen goes into byproduct **1**, but **1** can be quantitatively recycled back to **2** by addition of KC_8 to this reaction mixture.[12] Repetition of this protonation and reduction process four additional times in the same reaction vessel generates pure **4** in 73% yield.

With significant quantities of **4** in hand, the complex could be more definitively characterized by NMR spectroscopy (see SI). The $^{15}N\{^1H\}$ NMR spectrum of **4-^{15}N** showed a triplet at −242.3 ppm with a 7 Hz yttrium coupling constant. $^1H-^{15}N$ HMQC NMR studies with **4-^{15}N** showed that the proton at 3.06 ppm was coupled to the ^{15}N nucleus at −242.3 ppm (Figure S5, SI). The −242.3 ppm ^{15}N NMR shift for **4-^{15}N** is shifted significantly upfield compared to the 468−569 ppm values[2−5,51] observed for yttrium and lanthanide $(N_2)^{2-}$ complexes. This is consistent with the trend observed for the group IV transition metal dinitrogen complexes upon hydrogenation of the dinitrogen unit.[52]

The IR spectrum of **4** showed an absorption at 3129 cm^{-1} that was assigned as the N−H stretch (Figure S6, SI). In comparison, free hydrazine has N−H absorptions at 3329 and 3398 cm^{-1}, and absorptions at 3453 and 3238 cm^{-1} have been observed for $[(\eta^5\text{-}C_5Me_4H)_2Zr(C{\equiv}C^nBu)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2H_2)$ and $\{(\eta^5\text{-}C_9H_5\text{-}1\text{-}^iPr\text{-}3\text{-}Me)_2ZrH\}(N_2H_2)$, respectively.[34,37,53] The 3129 cm^{-1} absorption was diminished in the IR spectrum of **4-D** made from 2 and $[Et_3ND][BPh_4]$ that showed a new absorption at 2386 cm^{-1}. This is similar to those for $(N_2D_2)^{2-}$ complexes in the literature, e.g., 2441 cm^{-1} for $[(\eta^5\text{-}C_5Me_4H)_2Zr(C{\equiv}C^nBu)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2D_2)$[34] and 2403 cm^{-1} for $\{(\eta^5\text{-}C_9H_5\text{-}1\text{-}^iPr\text{-}3\text{-}Me)_2ZrH\}(N_2D_2)$,[37] but does not match the 2278 cm^{-1} value calculated from a simple ν_D/ν_H formula. This suggests strong coupling between the two localized N−H stretching modes. Density functional theory (DFT) was used to evaluate the IR data. The values calculated by DFT, 3165 and 2434 cm^{-1} for the symmetric N−H and N−D stretches, respectively, are consistent with the experimental values.

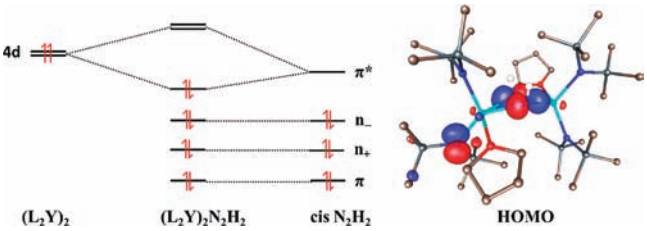


Figure 3. Simplified molecular orbital scheme of **4** with eight electrons shown in red. The highest occupied molecular orbital (HOMO) shows a two-electron, four-center Y(dπ)−N(π^*) bond.

Comparison of the NMR spectrum of **4** with NMR spectra of other $Y[N(SiMe_3)_2]_3/KC_8/N_2$ reaction mixtures showed that **4** is always formed as a byproduct. In these reactions, the $(N_2)^{3-}$ radical evidently reacts with other proton sources such as $HN(SiMe_3)_2$, the product of inadvertent protonation of the $[N(SiMe_3)_2]^-$ anion. This type of reactivity has been independently confirmed: the less solvated analogue of **2**, i.e., $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}N_2)K$ (**2a**),[1] reacts with $HN(SiMe_3)_2$ in C_6D_6 to form **4** and **1**. Nevertheless, radical abstraction of hydrogen atoms from the solvents could also happen concurrently to afford the $(N_2H_2)^{2-}$ species.[54]

X-ray crystallographic evidence for a gadolinium analogue of **4** suggested these yttrium results are extendable to the lanthanides. $\{[(Me_3Si)_2N]_2(THF)Gd\}_2(\mu\text{-}N_2H_2)$ (**5**) was isolated in 46% crystalline yield from reaction of $\{[(Me_3Si)_2N]_2(THF)Gd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)^3$ with KC_8 and $[Et_3NH][BPh_4]$. X-ray crystallography showed that the N−N distance in **5**, 1.497(7) Å, is similar to that of **4**, is in the 1.377(2)−1.635(5) Å range for $(N_2)^{4-}$ complexes in the literature, and is longer than typical N−N distances in $(N_2)^{2-}$ and $(N_2)^{3-}$ lanthanide complexes.[1,3]

The structure of **4** was optimized using the Tao−Perdew−Staroverov−Scuseria hybrid functional at the SV(P) level previously used for **1** and **2**.[1] The optimized computed structure shows the N_2H_2 unit above the Y···Y vector with a nonplanar butterfly arrangement of Y_2N_2, consistent with the model used for the X-ray data. In contrast to free N_2H_2, the cis form of N_2H_2 appears to be preferred to the trans form in **4**. The calculated N−N bond length of 1.506 Å is similar to the experimental values, 1.473(7) and 1.524(6) Å, and longer than the 1.446 Å N−N distance in hydrazine.[55] The N−H distance for the bridging atoms is also similar to, but longer by ~0.02 Å than that in hydrazine (1.016 Å). The computed vibrational frequency (811 cm^{-1}) supports an N−N bond order of 1, as this mode is significantly lower in frequency than the free diimide value of 1529 cm^{-1} and similar to that of hydrazine (966 cm^{-1}).[56]

The π^* orbital formerly unoccupied in **1** is now occupied through a dπ−π^* back-bond, fixing the bridge between the yttrium atoms (Figure 3). This interaction is favorable due to the high energy of the yttrium 4d orbital and the highly nodal structure of the (N_2H_2) π^* orbital. (See Table S4 in the SI for comparison of bond distances.)

In summary, the Y^{2+} ion has been observed for the first time in the $Y[N(SiMe_3)_2]_3/K$ system, and it has been shown to reduce dinitrogen to make both $(N_2)^{2-}$ and $(N_2)^{3-}$ ions. The $(N_2)^{3-}$ radical anion has been found to react with protons to form an $(N_2H_2)^{2-}$ complex with an $(N_2)^{2-}$ byproduct. This reaction suggests that $(N_2)^{3-}$ may disproportionate into $(N_2)^{4-}$ and $(N_2)^{2-}$ when reactive proton sources are present. This could be a reason that the $(N_2)^{3-}$ ion has not been isolated in past studies of dinitrogen reduction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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