Synthesis, Structure, and \(^{15}\text{N} \) NMR Studies of Paramagnetic Lanthanide Complexes Obtained by Reduction of Dinitrogen

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The recently discovered LnZ\textsubscript{2}/M and LnZ\textsubscript{2}Z’/M methods of reduction (Ln = lanthanide; M = alkali metal; Z, Z’ = monooanmonic ligands that allow these combinants to generate “LnZ\textsubscript{2}” reactivity) have been applied to provide the first crystallographically characterized dinitrogen complexes of cerium, \([\text{C}_{5}\text{Me}_{5}]_{2}\text{(THF)Ce}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\] and \([\text{C}_{5}\text{Me}_{5}]_{2}\text{(THF)Ce}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\] so that the utility of \(^{15}\text{N} \) NMR spectroscopy with paramagnetic lanthanides could be determined. \([\text{C}_{5}\text{Me}_{5}]_{2}\text{(THF)Pr}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\] and \([\text{C}_{5}\text{Me}_{5}]_{2}\text{(THF)Pr}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\] were also synthesized, crystallographically characterized, and studied by \(^{15}\text{N} \) NMR methods. The data were compared to those of \([\text{C}_{5}\text{Me}_{5}]_{2}\text{Sm}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\] and \([\text{C}_{5}\text{Me}_{5}]_{2}\text{(THF)Ce}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\] and \([\text{C}_{5}\text{Me}_{5}]_{2}\text{(THF)Pr}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\] are unlike their \((\text{C}_{5}\text{Me}_{5})_{2}\text{H}^{+}\) analogs in that the solvating THF molecules are cis rather than trans. Structural information on precursors, \((\text{C}_{5}\text{Me}_{5})_{2}\text{Ce}, (\text{C}_{5}\text{Me}_{5})_{2}\text{Pr}, and the oxidation product \([\text{C}_{5}\text{Me}_{5}]_{2}\text{Ce}_{2}(\mu-\text{O})\] is also presented.

Introduction

Although \(^{15}\text{N} \) NMR spectroscopy is used extensively to study dinitrogen reduction in diamagnetic metal systems,\(^ {1-7}\) no spectra have been reported, to our knowledge, on any of the dinitrogen complexes of the paramagnetic lanthanides.\(^ {1-8}\) Since most of the lanthanide ions are paramagnetic and numerous paramagnetic lanthanide dinitrogen complexes have been synthesized, it was of interest to determine if \(^{15}\text{N} \) NMR spectroscopy could be used to characterize these complexes.

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The paramagnetic Ln\textsuperscript{3+} ions most desirable for initial study are those with the smallest magnetic moments, namely the elements at the beginning of the series, Ce–Sm, where orbital and spin angular momentum are in opposition. Sm\textsuperscript{3+} (\(\mu = 0.84 \mu_B\)) has the lowest magnetic susceptibility of these ions, but analysis of the dinitrogen complex of this ion, \([\text{C}_{5}\text{Me}_{5}]_{2}\text{Sm}_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\].\(^ {10}\) 1, is complicated because the complex forms an equilibrium with its Sm\textsuperscript{2+} precursor, eq 1. The ions with the next lowest moments are 4f\textsuperscript{1} Ce\textsuperscript{3+} (\(\mu = 2.54 \mu_B\)) and 4f\textsuperscript{2} Pm\textsuperscript{3+} (\(\mu = 2.68 \mu_B\)).\(^ {9}\) Since the latter is radioactive, cerium was the best target for study. Unfortunately, Ce\textsuperscript{3+} was one of the ions that did not give crystallizable dinitrogen complexes in the earlier study of LnZ\textsubscript{2}/K reactions in which \(Z = [\text{Ni(SiMe}_{3})_{2}]^{2+}\), eq 2.

To obtain cerium dinitrogen complexes for \(^{15}\text{N} \) NMR studies and to demonstrate that crystallographically characterizable dinitrogen complexes could be isolated for cerium,
Studies of Paramagnetic Lanthanide Complexes


The LnZ/K and LnZ/Z/K reduction methods3–7 were applied to cerium using Z = (C(Me3)2)3− and (C(Me3)2H)4− and Z′ = (BPh4)−. This method also was applied to the praseodymium analogs to obtain another pair of paramagnetic dinitrogen complexes with low magnetic moments (4p6 Pr3+, \( \mu = 3.58 \mu_0 \)). With these data in hand for comparison, variable-temperature 15N studies were conducted on the equilibrium in eq 1.

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. [(C(Me3)2)3Ce([\( \mu\)-Pr]-BPPh3)] (Ln = Ce, Pr),11 (C(Me3)2)3Sm,12 and KC513 were made according to the literature. 13N2 was purchased from Cambridge Isotope Laboratories and used as received. Hydridated lanthanide trichlorides were desolvated with NH2Cl.14 CeMe5H was dried over molecular sieves and degassed prior to use. CeMe4H2 was distilled onto molecular sieves and degassed prior to use. KC5Me4H and KC5Me5 were prepared by adding C5Me5H and C5Me4H2, respectively, to excess K or excess Na. 1H NMR (C7D8) of CeMe4H2 could not be located. 13C NMR (C7D8) resonances could not be located. 13C NMR (C7D8) of KC5Me5H2 was removed from the supernatant in vacuo to give dark red solids. Anal. Calcd for CeMe4H2: Ce, 27.81. Found: Ce, 27.93. Anal. Calcd for C27H39Ce: Ce, 27.81. Found: Ce, 27.8.

Synthesis of [((C(Me3)2)3Ce)//Ce((\( \mu\)-Pr)-BPPh3)]2, 2. In a glovebox, [(C(Me3)2)3Ce][(\( \mu\)-Pr)-BPPh3] (136 mg, 0.16 mmol) was added to KC5 (37 mg, 0.27 mmol) in 10 mL of THF, and the mixture was stirred for 2 h. The solution was centrifuged to remove white and black solids, and the solvent was removed in vacuo. Toluene extraction followed by centrifugation and removal of solvent from the supernatant in vacuo left a dark red oil. Recrystallization from toluene gave dark red needles of 2 (60 mg, 74%). 2M0288 was 1459 × 10−6 (cgs); \( \mu_{\text{eff}} \) = 1.9 \( \mu_0 \). 1H NMR (C5D5) \( \delta = -0.46 \) (8H, THF), −0.03 (8H, THF), 1.17 (60H, CeMe5). 13C NMR (C5D5) \( \delta = 4.3 \) (CeMe5), 22.0 (THF), 53.8 (THF), 159.4 (CeMe5). 15N NMR (C5D5) \( \delta = 671 \) (fwhh 22 Hz). Anal. Calcd for C34H36N2O2Ce: Ce, 26.81. Found: Ce, 27.7. IR (C6D6) 3675w, 3640w, 3560w, 3034w, 2957s, 2907s, 2856v, 2725v, 2362w, 2342w, 1552v, 1494v, 1404v, 1378s, 1258w, 1189m, 1058m, 1023s, 973m, 872w, 803m, 730m, 710m, 676vs, 587cm−1.

Synthesis of [(C(Me3)2)3Ce][Pr((\( \mu\)-H)-Pr)]2, 3. Following the procedure for 2, [(C(Me3)2)3Ce][((\( \mu\)-H)-Pr)-BPPh3] (202 mg, 0.24 mmol) was added to KC5 (43 mg, 0.31 mmol) in 10 mL of THF. Recrystallization from toluene gave dark orange needles of 3 (18 mg, 0.13 mmol) in 10 mL of THF. 13C NMR (C7D8) of 3 (2362w, 2343w, 1552v, 1494v, 1404v, 1378s, 1312s, 1298v, 1239w, 1208s, 1104m, 1069vs, 1031s, 988w, 911s, 733w, 714w, 664w cm−1). 15N NMR (C7D8) of 3 (2362w, 2343w, 1552v, 1494v, 1404v, 1378s, 1312s, 1298v, 1239w, 1208s, 1104m, 1069vs, 1031s, 988w, 911s, 733w, 714w, 664w cm−1). Synthesis of (C5Me4H)3Ce, 4. Similar to the method of Schumann, et al.,21,22 CeCl3 (280 mg, 1.14 mmol) and KC5Me4H (548 mg, 3.42 mmol) were combined in 100 mL of THF and allowed to stir overnight. The solution was filtered, and the solvent was removed from the solution in vacuo. Toluene extraction followed by filtering and removal of the solvent in vacuo left a green powder (448 mg, 85%). 1H NMR (C5D5) \( \delta = 10.88 \) (18H, CeMe6H), 7.82 (18H, CeMe6H), 33.56 (3H, CeMe4H). 13C NMR (C5D5) \( \delta = 11.6 \) (CeMe5H), 15.9 (CeMe5H), 176.8 (CeMe4H). 15N NMR (C5D5) of 4, 198.4 (CeMe5H). Anal. Calcd for C7H59Ce: Ce, 27.81. Found: Ce, 27.4.

Synthesis of (C5Me4H)3Ce, 5. Following the procedure for 4, PrCl3 (402 mg, 1.63 mmol) and KC5Me4H (766 mg, 4.84 mmol) gave a yellow powder. (0.640 g, 78%). 1H NMR (C5D5) \( \delta = -30.5 \) (18H, CeMe6H), 19.0 (18H, CeMe6H), 7.82 (3H, CeMe4H). 13C NMR (C5D5) of 5, −49.3 (CeMe5H), 15.8 (CeMe5H), 251.3 (CeMe3H), 280.4 (CeMe3H), 328.8 (CeMe3H). Anal. Calcd for C35H59Pr: Pr, 27.93. Found: Pr, 27.6.

Synthesis of [(C(Me3)2)3Ce]/(THF)/Ce[Ce((\( \mu\)-\( \eta\)-\( \eta\)-2N2)]2, 6. In a glovebox, complex 4 (68 mg, 0.13 mmol) was added to KC5 (20 mg, 0.15 mmol) in 10 mL of THF. The solution became red and was allowed to stir for 3 h. The solution was centrifuged, and the solvent was removed from the supernatant in vacuo to give dark red solids. Toluene extraction, followed by centrifugation and removal of solvent from the supernatant in vacuo, left a yellow-green oil. Yellow crystals were obtained from toluene at −35 °C (45 mg, 71%). Complex 6 was obtained similarly from reaction of 4 and either excess K or excess Na. 1H NMR (C5D5) \( \delta = -4.16, -0.31, 0.80, 1.63, 11.80 \). 13C NMR (C5D5) of 6, 0.9, 1.5, 14.2. 15N NMR of 6, 1404v, 1378s, 1312s, 1298v, 1239w, 1208s, 1104m, 1069vs, 1031s, 988w, 911s, 733w, 714w, 664w cm−1.

(20) Exponential line broadening at 10 Hz was used in the data processing.


(C\(_5\)Me\(_4\))\(_2\)Ce(C\(_7\)H\(_8\)).

\[
\begin{array}{cccccc}
\text{empirical formula} & C_{48}H_{76}Pr_2N_2O_2 & C_{44}H_{68}Pr_2N_2O_2 & C_{27}H_{39}Pr_2 & C_{27}H_{39}Ce_2 & C_{27}H_{39}Pr_2
\
fw & 1121.51 & 1121.09 & 837.12 & 1.376 & 1.383 & 1.484 & 1.293 & 1.383
\
T (K) & 163(2) & 163(2) & 163(2) & 1.702 & 1.826 & 2.426 & 1.702 & 1.826 & 2.426
\
\text{cryst syst} & monoclinic & monoclinic & monoclinic & 1.001 & 0.0366 & 1.0417 & 0.0366 & 1.0417 & 0.0366
\
\text{space group} & C2/c & C2/c & H2m & 1.001 & 0.0964 & 1.001 & 0.0964 & 1.001 & 0.0964
\end{array}
\]

Table 1. X-ray Data Collection Parameters for [(C\(_5\)Me\(_4\))\(_2\)THF]Ce\(_x\)(\(\mu\)-\(\eta^3\)-\(\eta^3\)-N\(_2\)) \(_2\), 2, [(C\(_5\)Me\(_4\))\(_2\)THF]Pr\(_x\)(\(\mu\)-\(\eta^3\)-\(\eta^3\)-N\(_2\)) \(_2\), 3, (C\(_5\)Me\(_4\))\(_2\)H\(_8\)Ce, 4, (C\(_5\)Me\(_4\))\(_2\)Pr, 5, [(C\(_5\)Me\(_4\))\(_2\)THF]Ce\(_x\)(\(\mu\)-\(\eta^3\)-\(\eta^3\)-N\(_2\)) \(_2\), 6, [(C\(_5\)Me\(_4\))\(_2\)THF]Pr\(_x\)(\(\mu\)-\(\eta^3\)-\(\eta^3\)-N\(_2\)) \(_2\), 7, and [(C\(_5\)Me\(_5\))\(_2\)Ce] \(_2\)(\(\mu\)-O). 8a

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the other was located about an inversion center. Both solvent molecules were disordered and included using multiple components, partial site-occupancy factors, and geometrical restraints. Hydrogen atoms associated with the solvent molecules were not included. At convergence, \( wR2 = 0.1318 \) and GOF = 1.041 for 295 variables refined against 5845 data (0.80 Å). As a comparison for refinement on \( F \), \( R1 = 0.0456 \) for those 4445 data with \( I > 2.0 \alpha(I) \).

\[ [(\text{C}_5\text{Me}_3)_2(\text{THF})\text{Pr}]_2(\mu-\eta^2-\eta^2-N_2)_2, \] 3. A yellow-orange crystal of approximate dimensions \( 0.08 \times 0.10 \times 0.20 \) mm\(^3\) was handled as described above. 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 structure was solved by direct methods and refined on \( F^2 \) by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. The molecule was located about a 2-fold rotation axis. Hydrogen atoms were included using a riding model. There were two molecules of toluene solvent present per formula unit. The solvent molecules were disordered and included using multiple components with partial site-occupancy factors. The tetramethylenepentadienyl ring defined by atoms C(10)--C(19) was also disordered. Atoms C(17A) and C(17B) were disordered over two positions. The site-occupancy factors of these two atoms were set to approximately 0.60 and 0.40, respectively, to account for the methyl carbon atom being disordered over the two positions. The ring-hydrogen atom associated with the disordered tetramethylenepentadienyl ligand could not be located and was not included in the refinement. At convergence, \( wR2 = 0.0964 \) and GOF = 1.136 for 155 variables refined against 6197 data (0.77 Å). As a comparison for refinement on \( F \), \( R1 = 0.0366 \) for those 5802 data with \( I > 2.0 \alpha(I) \). Refinement of the model using the TWIN command or the Flack parameter\(^{28} \) was inconclusive and yielded an absolute structure parameter of 0.50.

\[ [(\text{C}_5\text{Me}_3)_2\text{Ce}]_2(\mu-\text{O}), \] 8. Crystals of 8 were obtained from an attempted synthesis of 2. A green crystal of approximate dimensions \( 0.05 \times 0.20 \times 0.20 \) mm\(^3\) was handled as described above. The diffraction symmetry was \( 4/\text{mmm} \), and the systematic absences were consistent with the tetragonal space group \( I4_2m \), which was later determined to be correct. The structure was solved using the coordinates of an isomorphous lanthanum complex.\(^{29} \) Hydrogen atoms were included using a riding model. At convergence, \( wR2 = 0.0417 \) and GOF = 1.112 for 59 variables refined against 1247 data. As a comparison for refinement on \( F \), \( R1 = 0.0170 \) for those 1188 data with \( I > 2.0 \alpha(I) \). The structure was refined using the TWIN\(^{26} \) command (BASF = 0.39(2)).

**Results**

**Synthesis.** 2 and 3 were made using the method previously reported for the lanthanum analog, \( [(\text{C}_5\text{Me}_3)_2(\text{THF})\text{La}]_2(\mu-\eta^2-\eta^2-N_2)_2 \).\(^{9,5} \) eq 3. The LnZ\(_2\)Z/M (\( M = \text{K}, \text{Na} \)) method\(^{5} \)

\[ \text{Ln} + 2 \text{K} \text{C}_8 + \text{THF} \xrightarrow{2 \text{KPB}} \text{LnZ}_2\text{Z} \text{M} \]

with \( [(\text{C}_5\text{Me}_3)_2\text{Ln}]_2(\mu-\text{Pb})_2\text{BPh}_3 \) precursors was used to obtain these complexes instead of the LnZ\(_2\)Z/M approach\(^{3,4} \) with \( (\text{CsMe}_3)_2\text{Ln} \) complexes\(^{11} \) since the tetraphenylborate complexes are precursors to the \( (\text{CsMe}_3)_2\text{Ln} \) compounds.


Inorganic Chemistry, Vol. 45, No. 26, 2006   10793
Complexes 2 and 3 formed as dark red and yellow-orange thin needles, respectively, and were structurally characterized by X-ray crystallography, Figure 1.

6 and 7 were synthesized via the LnZ₃/M method, eq 4, and identified by X-ray crystallography, Figure 2. The LnZ₃/M method was used in these cases since the (C₅Me₄H)₃-Ln (Ln = Ce, Pr, Tb, Lu) precursors can be made directly from LnCl₃ and KC₅Me₄H, eq 5. La (10), Nd (11), Sm (12), Tb (13), and Lu (14) analogs of precursors 4 and 5 were previously reported, as were La (15), Nd (16), and Lu (17) analogs of the reduced dinitrogen complexes 6 and 7.

Figure 1. Thermal ellipsoid plot of [(C₅Me₅)(THF)Pr]₂(μ-η²:η²-N₂), 3, with thermal ellipsoids drawn at the 50% probability level. The cerium analog, 2, is isomorphous.

Figure 2. Thermal ellipsoid plot of [(C₅Me₄H)(THF)Ce]₂(μ-η²:η²-N₂), 6, with thermal ellipsoids drawn at the 50% probability level.

Figure 3. Thermal ellipsoid plot of (C₅Me₄H)₃Pr, 5, with thermal ellipsoids drawn at the 50% probability level. The cerium analog, 4, is isomorphous.

6 and 7 were obtainable from excess sodium or potassium, as well as KC₅. Hence, the more weakly reducing sodium can be used in this LnZ₃/M reaction in a manner analogous to the [(Me₃Si)₂N]₃Ln/M/N₂ reduction system. The colors of the (C₅Me₄H)¹⁻ complexes differ from those of the (C₅Me₅)¹⁻ complexes, 2 and 3. Complex 6 crystallizes as bright yellow crystals, while 7 crystallizes as dark green crystals.

¹⁵N NMR Spectra of Ce and Pr Complexes. ¹⁵N analogs of 2, 3, 6, and 7 were prepared from ¹⁵N₂. The ¹⁵N NMR spectra of 2-¹⁵N and 6-¹⁵N showed singlets with 20–25 Hz half-height line widths at 871 and 1001 ppm, respectively. To our knowledge, the only other reports of ¹⁵N NMR data on cerium complexes are those reported for solutions of Ce³⁺ in the presence of (¹⁵NO₃)⁻ and (¹⁵NCS)⁻ counter ions. In those studies, the ¹⁵NO₃⁻ ion exhibited a shift of between −40 and −120 ppm compared to the sodium salt, whereas the (¹⁵NCS)⁻ ion, which can bind directly via nitrogen to Ce³⁺, was shifted between 450 and 550 ppm from the resonances for the sodium salt. The 450–550 ppm upfield shift of the thiocyanates is comparable to the differences between the resonances of 2-¹⁵N and 6-¹⁵N and the diamagnetic lanthanide (N₂)²⁻ analogs reported to date,¹²–⁶ Table 2, which have resonances from 495 to 569 ppm.

The ¹⁵N NMR spectra of the two ¹⁵N-labeled praseodymium compounds, 3-¹⁵N and 7-¹⁵N, showed broad singlets

The presence of Sm_{3}ppm. 2,34 However, as the temperature was lowered to 263 of the dinitrogen complexes 2-15N (34) (a) Grinter, R.; Mason, J. Studies of Paramagnetic Lanthanide Complexes 2:15N NMR Shifts of [Z_{2}(THF)Ln]_{2} (a) Fratiello, A.; Kubo-Anderson, V.; Lee, R. A.; Patrick, M.; Perrigan, Mtunzi, S.; Richards, R. L. Structural Studies. (C_{5}Me_{5})_{2}(THF)Ln (Ln = Ce, Pr). In the course of preparing 6 and 7, the precursors 4 and 5 were characterized by X-ray crystallography. Since the NMR spectra of highly symmetric paramagnetic species of this type are not very definitive, crystallographic data are often obtained to ensure the identity of the complex. The structural data are presented here first for comparison with the dinitrogen complexes later. 5 and 6 are isomorphous with all of the previously characterized (C_{5}Me_{5})_{2}Ln complexes, Ln = La^{21} (10), Nd^{22} (11), Sm^{21} (12), Tb^{21} (13), and Lu^{t} (14). The three (C_{5}Me_{5})^{t} ring centroids in each of these complexes define a trigonal planar geometry around the metal with 120° (C_{5}Me_{5}H ring centroid) –Ln–(C_{5}Me_{5}H ring centroid) angles. There is only one crystallographically independent (C_{5}Me_{5})^{t} ring in the structures. The bond distances vary from structure to structure in a regular way depending on the size of the metal. Table 3 shows the comparison of the Ce and Pr complexes whose trivalent nine-coordinate radii differ by 0.017 Å. The five Ln–(Cring) distances vary in the following way, as illustrated with data for 4: the ring carbon sans methyl, C(5), is the closest (2.748- (2) Å), the adjacent ring carbons, C(1) and C(4), are next (2.795(2) and 2.794(2) Å, respectively), and the remaining ring carbons, C(2) and C(3), are further away, (2.886(2) and 2.881(2) Å, respectively). Table 3 shows the analogous distances in 5.

Structural Studies. (C_{5}Me_{5}H)_{2}Ln (Ln = Ce, Pr). In the course of preparing 6 and 7, the precursors 4 and 5 were characterized by X-ray crystallography. Since the NMR spectra of highly symmetric paramagnetic species of this type are not very definitive, crystallographic data are often obtained to ensure the identity of the complex. The structural data are presented here first for comparison with the dinitrogen complexes later. 5 and 6 are isomorphous with all of the previously characterized (C_{5}Me_{5})_{2}Ln complexes, Ln = La^{21} (10), Nd^{22} (11), Sm^{21} (12), Tb^{21} (13), and Lu^{t} (14). The three (C_{5}Me_{5})^{t} ring centroids in each of these complexes define a trigonal planar geometry around the metal with 120° (C_{5}Me_{5}H ring centroid) –Ln–(C_{5}Me_{5}H ring centroid) angles. There is only one crystallographically independent (C_{5}Me_{5})^{t} ring in the structures. The bond distances vary from structure to structure in a regular way depending on the size of the metal. Table 3 shows the comparison of the Ce and Pr complexes whose trivalent nine-coordinate radii differ by 0.017 Å. The five Ln–(Cring) distances vary in the following way, as illustrated with data for 4: the ring carbon sans methyl, C(5), is the closest (2.748- (2) Å), the adjacent ring carbons, C(1) and C(4), are next (2.795(2) and 2.794(2) Å, respectively), and the remaining ring carbons, C(2) and C(3), are further away, (2.886(2) and 2.881(2) Å, respectively). Table 3 shows the analogous distances in 5.

\[(C_{5}Me_{5}H)_{2}(THF)Ln\]_{2}(\mu-\eta^{2}:\eta^{2}-N_{2}) (Ln = Ce, 6; Pr, 7).

The structure of 6 will be discussed next, since the (C_{5}Me_{5}H)_{2}Ln complexes just discussed, is similar to the other (C_{5}Me_{5}H)_{1}– analogs that have been crystallographically characterized, Ln = La^{t} (15), Nd^{t} (16), and Lu^{t} (17). Each of these complexes has a planar Ln(\mu-\eta^{2}:\eta^{2}-N_{2}) arrangement involving a formally dianionic (N_{2})^{2–} ligand. This formerly rare mode of binding dinitrogen has become the signature structure of lanthanide dinitrogen complexes.7 Complex 6 has a N–N distance of 1.235(6) Å that is consistent with the reduction of dinitrogen to (N\equiv N)^{2–}.37 Table 4.

In contrast to the [(C_{5}Me_{5}H)_{2}(THF)Ln]_{2}(\mu-\eta^{2}:\eta^{2}-N_{2}) complexes discussed above, which all crystallize in the C2 space group, complex 7 crystallizes in the C2/c space group. This was found in two separate attempts to collect X-ray data. Although the data for 7 were sufficient to show that the atomic connectivity matched that of the other [(C_{5}Me_{5}H)_{2} (THF)Ln]_{2}(\mu-\eta^{2}:\eta^{2}-N_{2}) complexes, the data were not good enough to provide reliable metrical information. Although this variation in space group is not common for lanthanides, structurally analogous lanthanide complexes do sometimes crystallize in different space groups.38

\[(C_{5}Me_{5}H)_{2}(THF)Ln\]_{2}(\mu-\eta^{2}:\eta^{2}-N_{2}), (Ln = Ce, 2; Pr, 3). Complexes 2 and 3 are isomorphous and have a planar Ln_{2}(\mu-\eta^{2}:\eta^{2}-N_{2}) structure similar to other [(Z)_{2}(THF)Ln]_{2}(\mu-\eta^{2}:\eta^{2}-N_{2}) complexes.3–7 39 However, 2 and 3 both differ from

Table 2. 15N NMR Shifts of [Z_{2}(THF)Ln]_{2}(\mu-\eta^{2}:\eta^{2}-N_{2}) Complexes

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<td>{[C(Me_{5})]<em>{2}(THF)Ce}</em>{2}(\mu-\eta^{2}:\eta^{2}-N_{2})</td>
<td>1721</td>
<td>6</td>
</tr>
</tbody>
</table>

a All chemical shifts were measured using an external reference of 15N-formamide.
Another difference between the \([\text{C}_3\text{Me}_5\text{H}_2(\text{THF})\text{Ln}]_2(\mu-\eta^\#\eta^\#-\text{N}_2)\) complexes, 2, 3, and 9, and the other previously characterized \([\text{Z}_2(\text{THF})\text{Ln}]_2(\mu-\eta^\#\eta^\#-\text{N}_2)\) complexes \((\text{Z} = \text{C}_2\text{Me}_2\text{H}_2)^{5,6}\) is that the nitrogen atoms in the \((\text{N}_2)^2\) ligand in 2, 3, and 9 are not crystallographically equivalent. They are symmetry-related in the other structures. The \(\text{N}−\text{N}\) distances in 2, 3, and 9, 1.258(9), 1.242(9), and 1.233(5) Å, respectively, are consistent with the reduction of dinitrogen to \((\text{N}=\text{N})^2\) and are similar to those in the other complexes. However, the \(\text{Ln}−\text{N}\) distances in 2, 3, and 9 span a wider range than those found in the \((\text{N}_2)^2\) complexes with symmetry-equivalent nitrogen atoms. These \(\text{Ln}−\text{N}\) distances are 2.478(4) and 2.537(4) Å for 9, 2.455(2) and 2.524(2) Å for 2, and 2.446(1) and 2.512(2) Å for 3. In comparison, the \(\text{Ln}−\text{N}\) distances in \({\text{[(Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Ln}]_2(\mu-\eta^\#\eta^\#-\text{N}_2)}\) are at most 0.031 Å different in nine different examples. The angles are also disparate: \(\text{Ln}_1−\text{N}_1−\text{Ln}_1′−\text{N}_1′\) and \(\text{Ln}_1−\text{N}_2−\text{Ln}_1′−\text{N}_2′\) angles are, respectively, 157.3(2°) and 145.8(2°) in 9, 156.9(3)° and 144.7(3)° in 2, and 157.0(3)° and 145.1(3)° in 3. In contrast, the \(\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Ln}]_2(\mu-\eta^\#\eta^\#-\text{N}_2)\) complexes have a single \(\text{Ln}−\text{N}−\text{Ln}′\) angle and all fall in the range of 146.9(1)−149.4(1)°. As a result of the unsymmetrical \(\text{Ln}−\text{N}−\text{Ln}′\) angles in 2, 3, and 9, the \((\text{N}_2)^2\) ligand does not lie symmetrically between the lanthanide ions in the \(\text{Ln}_2\text{N}_2\) plane, Figure 5. It is located to one side of the plane, as shown in the top view in Figure 6 and this puts it closer to the THF molecules. This variation in structure reflects the flexibility in the coordination sphere of lanthanide complexes. It is likely that in solution these asymmetries are not maintained.

\[\text{[(C}_3\text{Me}_5\text{H}_2)_2\text{Ce}]_2(\mu-\eta^\#)\]

Crystals of 8, Figure 7, Table 6, were obtained in one synthesis of 2. The presence of oxide might indicate the relatively high reactivity of the dinitrogen species, but oxide products are known to arise despite attempts to rigorously exclude air and water.


Complex 8 is isomorphic with other unsolvated pentamethylcyclopentadienyl lanthanide oxides [(C₅Me₅)₂Ln]₂⁻(μ-O) (Ln = La²⁹ (18), Nd³⁺ (19), Sm¹⁵ (20), and Y⁶⁺ (21)). The Ce(1)−O(1)−Ce(1') angle is linear, and the metrical parameters of the metallocene unit are similar to the other analogs when the differences in ionic radii are taken into account.⁴⁰ For example, the 2.534 Å Ce−(C₅Me₅ ring centroid) distance is similar to the radius normalized values⁴⁰ in the other examples: 2.522 for 19, 2.564 for 20, and 2.520 Å in 21. There is also reasonably close agreement between the 2.1405(3) Å Ce−O distance and the radius normalized analogs: 2.127 Å for 18, 2.135 Å for 19, 2.158 Å for 20, and 2.177 Å in 21.


Table 6. Selected Bond Distances (Å) and Angles (deg) for 
\[[\text{C}_5\text{Me}_5\text{O}]_{2}\text{Ce}_{2}(\mu_{3}\text{-O}_{3})\], 8

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(1)–C(4)</td>
<td>2.534</td>
<td></td>
</tr>
<tr>
<td>Ce(1)–C(5)</td>
<td>2.783(3)</td>
<td>1.495(3)</td>
</tr>
<tr>
<td>Ce(1)–O(1)</td>
<td>2.793(2)</td>
<td></td>
</tr>
<tr>
<td>Cnt–Ce(1)–O(1)</td>
<td>110.3</td>
<td>Cnt–Ce(1)–Cnt</td>
</tr>
</tbody>
</table>

The structure of complex 8 differs significantly from that of the solvated \[[\text{C}_5\text{Me}_5\text{O}]_{3}\text{THF}]\text{Ce}_{2}(\mu_{3}\text{-O}_{3})\]. As expected for a higher-coordinate complex, the solvated complex has slightly longer Ce–(C5Me5 ring centroid) distances, 2.588–2.594 Å, and Ce–O(oxygen) lengths, 2.183(5) Å. In addition, it has a nonlinear Ce–O–Ce angle of 175.9(2)°.

Discussion

The successful use of the LnZ/M and LnZ′/Z/M reductive methods with the precursors \[[\text{C}_5\text{Me}_5\text{O}]_{2}\text{Ce}[(\mu-\text{Ph})_{2}\text{BPh}_{2}]\] and 4 via eqs 3 and 4, respectively, has provided the first crystallographically characterized reduced dinitrogen complexes of cerium. Similarly, using \[[\text{C}_5\text{Me}_5\text{O}]_{2}\text{Pr}[(\mu-\text{Ph})_{2}\text{BPh}_{2}]\] and 5 as precursors, examples of reduced dinitrogen complexes of praseodymium have been obtained. In contrast, attempts to accomplish dinitrogen reduction with Ce and Pr using the \[[\text{Me}_3\text{Si}]_{2}\text{N}]_{3}\text{Ln}/\text{M} \text{ reduction system did not generate crystallographically characteristic reduced dinitrogen complexes of cerium. Similarly, using \[[\text{C}_5\text{Me}_5\text{O}]_{2}\text{Ce}[(\mu-\text{Ph})_{2}\text{BPh}_{2}]\] and 4 as precursors, examples of reduced dinitrogen complexes of praseodymium have been obtained. In contrast, attempts to accomplish dinitrogen reduction with Ce and Pr using the \[[\text{Me}_3\text{Si}]_{2}\text{N}]_{3}\text{Ln}/\text{M} \text{ reduction system did not generate crystallographically characteristic reduced dinitrogen complexes of cerium. Similarly, using \[[\text{C}_5\text{Me}_5\text{O}]_{2}\text{Ce}[(\mu-\text{Ph})_{2}\text{BPh}_{2}]\] and 4 as precursors, examples of reduced dinitrogen complexes of praseodymium have been obtained.

With the synthesis of the new complexes discussed here, reduced dinitrogen complexes have been crystallographically characterized for all the lanthanides except for radioactive Pm and the two most readily reducible trivalent ions Eu3+ and Yb3+. The (N2)2− ligand is likely to be sufficiently reducing to convert Eu3+ and Yb3+ to their divalent ions and N2.

The 15N NMR studies of the Ce and Pr dinitrogen complexes show that 15N NMR data are obtainable on these paramagnetic systems. The shifts are substantial, however, even for these lanthanide ions that have relatively low magnetic moments. In fact, there was difficulty in initially finding the resonances. Given the challenges in collecting these data, this is clearly not a routine characterization technique. However, it does unequivocally show the presence of complexes of dinitrogen.

The temperature-dependent 15N data on 1 are consistent with the equilibrium observed earlier by 1H and 13C NMR spectroscopy. Due to the accessibility of the Sm2+ oxidation state, this dinitrogen reduction is reversible. In this sense, it is the crossover point between Eu2+ and Yb2+, which are too weak to reduce dinitrogen, and the other lanthanides that do not revert to Ln3+ complexes once the (Ln3+)2(N2)2− complex has formed.

The structural data obtained on 4, 5, 6, and 8 were conventional. These complexes had structures and metrical parameters as expected based on analogues in the literature. This is typical of lanthanide complexes since the 4f valence orbitals have a limited radial extension and the 4f6 electron configuration generally does not affect structure.

The structures of 2 and 3, however, show a new aspect of lanthanide dinitrogen chemistry and the planar Ln2(μ-η2:η2-N2) unit. In these complexes, the (N2)2− ligand is skewed to one side in the plane. Also asymmetric in these structures is the location of the THF molecules of solvation. This readily accessible variation in structure is also consistent with the fact that the valence orbitals of these ions are not heavily involved in generating the structures. Evidently, there is considerable flexibility in how the (N2)2− ion binds to two [Z2Ln(THF)]1+ moieties. As a compact, two-donor-atom, dianionic ligand, the (N2)2− ion constitutes a powerful ligation moiety for binding two lanthanide ions together. This ion apparently has an additional advantage in that it can bind asymmetrically, as well as symmetrically, to the two electropositive centers. The consequences of this structural variation in reactivity remain to be determined.

Conclusion

The synthetic results reported here demonstrate that the LnZ/M and LnZ′/M reduction systems apply to Ce and Pr, as well as the other lanthanides. Reduced dinitrogen complexes are now known for all of the nonradioactive lanthanides except the most easily reduced Eu and Yb. The structures of 2 and 3 demonstrate how a slight change in the ancillary ligand, Z, can change the solid-state structure of the [Z2Ln(THF)]1+ complexes. The first 15N NMR spectra of paramagnetic reduced dinitrogen lanthanide complexes have been obtained and demonstrate that 15N NMR spectroscopy can be used to characterize paramagnetic lanthanide dinitrogen complexes.

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Supporting Information Available: X-ray diffraction details (CIF) and X-ray data collection, structure solution, and refinement of compounds 2–8 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

Evans et al.