Lanthanide Chemistry

Expanding the LnZ_3/Alkali-Metal Reduction System to Organometallic and Heteroleptic Precursors: Formation of Dinitrogen Derivatives of Lanthanum**

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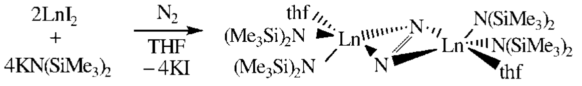
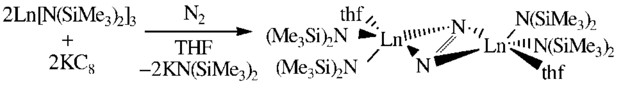
One of the recent advances in f-block-element reduction chemistry was the discovery that the simple combination of a trivalent lanthanide salt and potassium, that is, LnZ_3/K, could mimic the dinitrogen reduction reactivity of the highly reducing divalent ions Tm^{II} and Dy^{II}.[1] Hence, the reduced dinitrogen complexes, $[\{(Me_3Si)_2N\}_2(thf)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$, originally made from divalent TmI_2 and DyI_2 in the presence of $KN(SiMe_3)_2$[2] [Eq. (1)], could be obtained from KC_8 and the trivalent lanthanide amide salts $Ln^{III}[N(SiMe_3)_2]_3$ known for decades [Eq. (2)].[3]



(1)



(2)

Not only was the $Ln[N(SiMe_3)_2]_3$/K reduction system shown in Equation (2) successful for Ln = Tm and Dy, which have accessible divalent states in soluble molecular complexes,[4,5] but it also provided $(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)^{2-}$ complexes of Ho, Y, and Lu.[1] Molecular divalent chemistry has not been reported for these elements to date.[6] Reduction of lanthanide salts by alkali metals dates back to Wöhler,[7] but has generally been used only to make elemental metals or the common divalent lanthanides, Eu^{II}, Yb^{II}, and Sm^{II}.[8] The other alkali-metal reductions of trivalent lanthanide ions involving dinitrogen and arene substrates have also been interpreted in terms of divalent states.[9–14]

Herein we address the question of the generality of the $LnZ_3/K/N_2$ reduction system as a function of the monoanionic ligand, Z: specifically, is this reaction limited to some special feature of $N(SiMe_3)_2$ as the Z ligand? This ligand engages in agostic interactions with lanthanides that could lead to special reactivity.[15–20]

The $[(C_5Me_4H)_3Ln]$ complexes were chosen as desirable starting materials for LnZ_3/K chemistry since, like the $Ln[N(SiMe_3)_2]_3$ series, they are readily available, for the entire lanthanide series, from $LnCl_3$ and an alkali-metal salt.[21,22] The C_5Me_4H ligand was chosen since a variety of substituted cyclopentadienyl lanthanide dinitrogen complexes were known for Sm,[23] Tm,[24] and Dy.[25]

Lanthanum was one of the metals chosen for this study since no lanthanum dinitrogen complexes had yet been discovered and this would provide a diamagnetic complex of the largest lanthanide. Along with the diamagnetic Y and Lu complexes isolated from the reaction in Equation (2),[1] this would allow metal-size comparisons to be made with $[Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ complexes of both the largest and smallest diamagnetic ions in the lanthanide series.

$[(C_5Me_4H)_3La]$ reacts immediately with KC_8 in THF under dinitrogen, [Eq. (3)], in a reaction similar to that in Equation (2).[1] Since the KC_5Me_4H by-product has slight solubility in THF, the reaction solvent was removed in vacuo and the dinitrogen product extracted with toluene. The ^1H and ^{13}C NMR spectra of the lanthanum product showed resonance signals typical for C_5Me_4H and THF ligands. Similar results were obtained with $[(C_5Me_4H)_3Nd]$.

Crystal structure analysis of the Nd and La products showed that the dinitrogen complexes $[\{(C_5Me_4H)_2(thf)Ln\}_2(N_2)]$ (Ln = La (**1**); Nd (**2**)) had formed. Each had the $Ln(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ structure observed for other lanthanide complexes, Figure 1.[23] The overall structure was similar to that of the $[\{[(Me_3Si)_2N]_2(thf)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ complexes,[1] except that C_5Me_4H groups had replaced $N(SiMe_3)_2$ ligands. Considerable disorder occurred in these structures, particularly with the position of the ring carbon atom substituted with hydrogen in the C_5Me_4H ligands. Some refinements produced models which appeared to have a C_5Me_5 ring present. However, this disorder could be successfully modeled and the absence of C_5Me_5 rings was consistent with hydrolysis reactions which gave only $C_5Me_4H_2$ by GCMS.

To make a C_5Me_5 analogue for comparison with **1** and **2**, reactions of $[(C_5Me_5)_3Ln]$ complexes[26] with KC_8 could be considered. However, the $[(C_5Me_5)_3Ln]$ complexes react with the solvent, THF, to make $[(C_5Me_5)_2Ln\{O(CH_2)_4C_5Me_5\}]$ compounds.[26,27] To circumvent this problem, the precursor to $[(C_5Me_5)_3Ln]$, namely $[\{(C_5Me_5)_2Ln\}\{(\mu\text{-}Ph)_2BPh_2\}]$,[28] was examined as a starting material. This reaction was the first test of the use of a heteroleptic LnZ_2Z' precursor in the LnZ_3/K reduction system.

$[\{(C_5Me_5)_2La\}\{(\mu\text{-}Ph)_2BPh_2\}]$ reacts immediately with KC_8 in THF under dinitrogen to produce a red-orange complex, $[\{(C_5Me_5)_2(thf)La\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ (**3**; Equation (4)). Isolation was accomplished as for the reaction in Equation (3) and the yield was again high, >90%.

The ^1H NMR spectrum of $[\{(C_5Me_5)_2(thf)La\}_2(N_2)]$ was distinct from that of $[\{(C_5Me_4H)_2(thf)La\}_2(N_2)]$ and consistent with the presence of C_5Me_5 and THF ligands. In contrast to the C_5Me_4H complexes **1** and **2**, high quality X-ray data were obtained for the C_5Me_5 complex (Figure 1). The 1.233(5) Å

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[**] We thank the National Science Foundation for support of this research.

DOI: 10.1002/ange.200461170

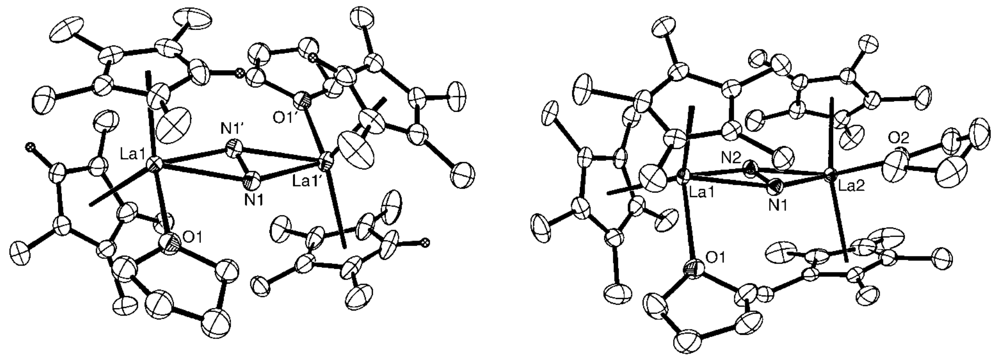
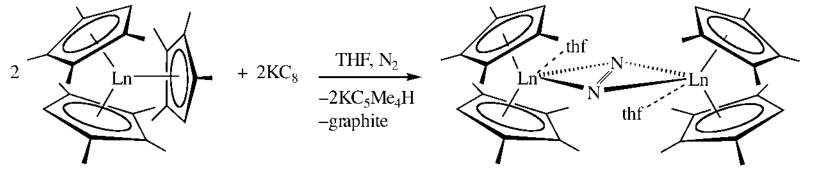
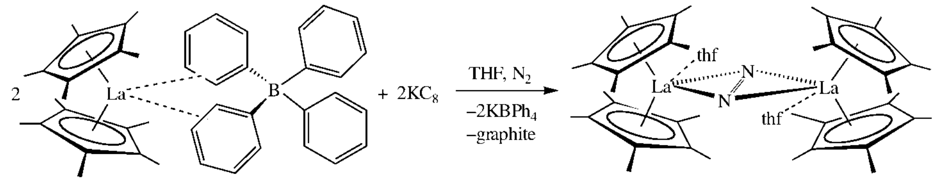


Figure 1. Ortep diagrams of **1** and **3** (thermal ellipsoids set at 50% probability).



(3)

Ln = La, Nd



(4)

nitrogen–nitrogen separation is consistent with the reduction of dinitrogen to $[N{=}N]^{2-}$.

^{15}N NMR spectroscopy was informative with diamagnetic **1** and **3** displaying resonance signals at $\delta = 495$ and 569 ppm, respectively (with respect to $MeNO_2$ referenced at $\delta = 0$ ppm). These chemical shifts are similar to those observed for the $[N{=}N]^{2-}$ ligands in the diamagnetic $[\{[(Me_3Si)_2N]_2(thf)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ complexes, $\delta = 513$ (Ln = Y) and 557 (Ln = Lu) ppm.[1]

In conclusion, these results provide not only the first lanthanum dinitrogen complexes, but also a high yield synthesis of $[Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ complexes. The yields of these reactions are the best yet obtained for $LnZ_3/KC_8/N_2$ reductions. For example, yields in the $Ln[N(SiMe_3)_2]_3/KC_8/N_2$ reactions [Eq. (2)], do not exceed 50%, a factor that has hindered the development of their chemistry. The low yields of the $[\{[(Me_3Si)_2N]_2(thf)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ syntheses indicate that additional reaction chemistry is occurring in these systems. We suspect that this complicating chemistry arises from interactions of the soluble by-product of Equation (2), $KN(SiMe_3)_2$, with both the starting material and perhaps the initially formed dinitrogen reduction product. In the reactions in Equations (3) and (4), this problem is avoided, since neither KC_5Me_4H nor $KBPh_4$ are very soluble in THF. Hence in the design of future applications of the LnZ_3/KC_8 reduction reaction, formation of an insoluble KZ by-product may be useful in obtaining high yields.

More generally, these results show that the LnZ_3/K dinitrogen reduction system is successful not only with $Ln[N(SiMe_3)_2]_3$ precursors, but also with organometallic $[(C_5Me_4H)_3Ln]$ complexes and with heteroleptic $[(C_5Me_5)_2La(thf)_2][BPh_4]$ precursors. These reactions demonstrate that dinitrogen can be reduced to form lanthanide $[N{=}N]^{2-}$ complexes with a variety of ligands in coordinating solvents such as THF and that high-yield routes to diamagnetic compounds are available. The synthetic utility of this LnZ_3/K/substrate reaction should be extensive.

Experimental Section

1: In a nitrogen filled glovebox, a pale yellow solution of $[(C_5Me_4H)_3La]$ (0.113 g, 0.22 mmol) in THF (10 mL) was added to a vial containing KC_8 (0.046 g, 0.34 mmol) and a stir bar. The mixture immediately became dark and was allowed to stir for 2 h. The mixture was centrifuged to remove black and white insoluble material (consistent with the formation of graphite and KC_5Me_4H) and evaporation of the supernatant yielded a light yellow powder. Extraction with toluene (10 mL) and removal of solvent gave a light yellow powder (0.075 g, 72%). A concentrated toluene sample of **1** at −35 °C produced pale yellow crystals over 2–3 days. ^1H NMR (500 MHz, C_6D_6): $\delta = 1.55$ (s, 2H, THF), 1.98 (s, 6H, Me), 2.22 (s, 6H, Me), 4.24 (s, 2H, THF), 5.55 ppm (s, 1H, H); ^{13}C NMR (125.8 MHz, C_6D_6): $\delta = 12.0$ ($C_5\mathit{Me}_4H$), 13.3 ($C_5\mathit{Me}_4H$), 26.0 (THF), 71.8 (THF), 112.7 (C_5Me_4H), 117.5 (C_5Me_4H), 118.6 ppm (C_5Me_4H); $^{15}N\{^1H\}$ NMR (50.7 MHz, C_6D_6) referenced to $MeNO_2$ at 0 ppm: $\delta = 495.0$ ppm. IR (thin film from THF): $\tilde{\nu} = 2961$ s, 2922 s, 2856 s, 2721 w, 1444 m, 1378 w, 1328 w, 1262 s, 1069 s, 1023 s, 872 m, 799 s, 756 s, 699 w cm^{-1}; elemental analysis (%) calcd for $C_{44}H_{68}N_2O_2La_2$: C 56.53, H 7.33, N 3.00, La 29.72; found: C 57.35, H 7.26, N 3.01, La 29.10. M.p. 120 °C (decomp).

2: Complex **2** was prepared similarly to **1** from $[(C_5Me_4H)_3Nd]$ (0.057 g, 0.112 mmol) and KC_8 (0.0228 g, 0.168 mmol) to give a green powder (0.050 g, 94%). ^1H NMR (500 MHz, C_6D_6): $\delta = -0.33$, 1.78, 4.74 ppm; elemental analysis (%) calcd for $C_{44}H_{68}N_2O_2Nd_2$: C 55.89, H 7.25, N 2.96, Nd 30.51; found: C 55.80, H 7.13, N 3.05, Nd 31.15.

3: An orange powder (0.119 g, 93%) was obtained similarly as for **1** and **2** from pale yellow $[(C_5Me_5)_2La(thf)_2][BPh_4]$ (0.225 g, 0.26 mmol). ^1H NMR (500 MHz, C_6D_6): $\delta = 2.07$ (s, 15H, Me), 1.47 (s, 1H, THF), 3.92 ppm (s, 1H, THF); ^{13}C NMR (125.8 MHz, C_6D_6): $\delta = 12.2$ ($C_5\mathit{Me}_5$), 25.8 (THF), 70.8(THF), 117.8 ppm (C_5Me_5); $^{15}N\{^1H\}$ NMR (50.7 MHz, C_6D_6) referenced to $MeNO_2$ at 0 ppm: $\delta = 569.1$ ppm. IR (thin film from THF): $\tilde{\nu} = 2961$ s, 2910 s, 2856 s, 2721 s, 1567 w, 1444 m, 1378 w, 1262 s, 1069 s, 1027 s, 872 m, 799 s, 683 w, 663 w cm^{-1}; elemental analysis (%) calcd for $C_{48}H_{76}N_2O_2La_2$: La 28.04; found: La 28.2. M.p. 120 °C (decomp).

Compound **1** crystallizes in the space group $C2/c$ with $a = 15.305(3)$, $b = 14.221(2)$, $c = 25.794(4)$ Å, $\alpha = 90$, $\beta = 103.959(3)$, $\chi = 90°$, $V = 5448.4(15)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.364\ \text{Mg}\,\text{m}^{-3}$, $R1 = 0.0271$ [$I > 2\sigma(I)$], $wR2 = 0.0709$, GOF = 1.043. Compound **2** crystallizes in the space group $C2/c$ with $a = 15.286(3)$, $b = 14.085(3)$, $c = 25.744(5)$ Å, $\alpha = 90$, $\beta = 104.266(3)$, $\chi = 90°$, $V = 5371.6(19)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.397\ \text{Mg}\,\text{m}^{-3}$, $R1 = 0.0279$ [$I > 2\sigma(I)$], $wR2 = 0.0741$, GOF = 1.174. Compound **3** crystallizes in the space group $P2_1/c$ with $a = 11.086(2)$, $b = 14.627(3)$, $c = 32.882(7)$ Å, $\alpha = 90$, $\beta = 95.740(4)$, $\chi = 90°$, $V = 5305.2(18)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.356\ \text{Mg}\,\text{m}^{-3}$, $R1 = 0.0468$ [$I > 2\sigma(I)$], $wR2 = 0.1040$, GOF = 1.067. CCDC-242602 (**1**), CCDC-242600 (**2**), CCDC-242601 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: July 3, 2004

Keywords: alkali metals · cyclopentadienyl ligands · lanthanides · nitrogen fixation · reduction

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